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

First Draft, Chapters 7-8

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

FIRST DRAFT, CHAPTERS 7-8

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7. SYNTHESIS AND INTEGRATION OF CASE STUDY RESULTS

The final version of this chapter will synthesize the results of the current conditions assessments for each of the targeted ecosystem effect areas (i.e., aquatic acidification, terrestrial acidification, aquatic nutrient enrichment, and terrestrial nutrient enrichment). Further, we will use these summaries of ecological effects and their associated ecological indicators to characterize the relationship between levels of an ecological indicator and the associated degree of ecologically adverse effects. This characterization of adversity can then be used to inform policy judgments on public welfare. Once analyses are completed, the next draft of this chapter will describe the range of effects associated with the current deposition of nitrogen and sulfur and demonstrate the links between adverse ecological effects and the level of associated ecological indicators. These relationships will then be used to inform alternative standards by translating adverse effects levels into levels of ecological indicators that can be linked through atmospheric deposition to ambient air concentrations of NO_x and SO_x.

Conducting a joint risk assessment for two criteria pollutants that impact multiple (and in some cases overlapping) ecological processes means that disparities exist in the level of information available for the targeted ecosystem effect areas highlighted in this review. This is reflected in the nature of the science, data, models, and time available for the case study analyses. However, a concise synthesis of the information from the case studies, including an assessment of the similarities and differences in the level of scientific data available to support the risk assessments for each effect area, will be useful to inform the standard setting process. The case study synthesis is intended to provide an integrated, weight-of-evidence approach that will consider the combined information from both evidence-based (i.e., relying primarily on reference to the ISA review of published literature on the effects of the deposition of NO_x and SO_x) and empirical approaches (based on results of applications of data, models, and information from the published literature), and their associated uncertainties, to explain how the risk and exposure assessment can inform decision makers about what levels of protection might be appropriate to protect public welfare from adverse impacts on ecosystems. This synthesis will look at the ecological indicators selected for each of the targeted effect area and examine the commonalities and differences among them. This information can then be used to inform a policy judgment on a known or anticipated adverse public welfare effect.

This chapter summarizes the current progress of the case studies (Section 7.1), begins to discuss how the results of the case studies can be used to inform potential levels of protection against ecosystem effects (Section 7.2), and preliminarily points to how this might be used in designing a meaningful secondary standard or standards for ambient concentrations of NO_x and SO_x (Section 7.3). In this draft, we focus on the ecological effects of aquatic acidification, using surface water ANC as an ecological indicator. As our analyses progress, we will include additional ecological indicators and explain how they may be used to characterize adverse ecological effects.

7.1 SUMMARY OF CASE STUDY ANALYSES

Table 7.1-1 summarizes the ecosystem characteristics, ecological indicators, ecological effects, and ecosystem services evaluated in the case study analyses presented in Chapters 4 and 5. *Note: currently these results reflect the present status of the first draft risk and exposure assessment and will be updated for the second draft as the analyses progress.*

7.1.1 Aquatic Acidification

Acidic deposition has altered major biogeochemical processes in the United States by increasing the sulfur and nitrogen content of soils. This increase accelerates SO_4^{2-} and NO_3^- leaching from soil to drainage water, depletes base cations (namely Ca^{2+} and Mg^{2+}) from soils, and increases the mobility of toxic aluminum (Al) (see ISA Section 3.2) (U.S. EPA, 2008). Some ecosystems and some areas of the United States are more sensitive than others to the effects of acidic nitrogen and sulfur deposition, particularly streams and lakes with naturally low ANC. The impact of acidic deposition on aquatic systems is controlled by several environmental factors, such as geology, surface water flow, soil depth, and weathering rates, all of which contribute to the ability of an ecosystem to neutralize the additional acidic deposition and prevent the lowering of ANC. The Adirondack Mountains of New York and the Blue Ridge Mountains in the Shenandoah National Park of Virginia were selected for the evaluation of impacts from acidic deposition of nitrogen and sulfur. These regions receive relatively high levels of acidic deposition and are known to be predisposed to acidification, and extensive research, data, and models exist for these areas. In addition, the results will likely be relevant in characterizing risks to larger areas of the Appalachian Mountains and the Northeast.

ANC is a key indicator of acidification with relevance to terrestrial and aquatic ecosystems. ANC is useful because it integrates the overall acid-base status of a lake or stream and reflects how aquatic ecosystems respond to acidic deposition over time. There is also a relationship between ANC and the surface water constituents that directly contribute to or ameliorate acidity-related stress, in particular, concentrations of hydrogen ion (as pH), Ca^{2+}, and aluminum. Moreover, low pH surface waters leach aluminum from soils, which is quite lethal to fish and other aquatic organisms. In aquatic systems, there is a direct relationship between ANC and fish and phyto-zooplankton diversity and abundance (see Section 7.3). These relationships also impact several ecosystem services, such as fishing, recreation, food, natural habitat, and tourism.

7.1.2 Terrestrial Acidification

Terrestrial acidification occurs where inorganic and mineral acids are added to the soil. This occurs as a result of both natural biogeochemical processes and acidic deposition of nitrogen and sulfur. Biological effects of acidification on terrestrial ecosystems are generally attributable to aluminum toxicity and decreased ability of plant roots to take up base cations. Acidic deposition increases concentrations of sulfur and nitrogen in soil, which accelerates leaching of SO_4^{2-} and NO_3^- from soil to drainage water. In the absence of anthropogenic sulfur and nitrogen deposition, the limited mobility of anions in the soil controls the rate of base cation leaching. Atmospheric deposition of sulfur and nitrogen provides anions that are more mobile in the soil environment than naturally occurring anions in the soil; these mineral acid anions can accelerate natural rates of base-cation leaching, particularly Ca^{2+} and Mg^{2+}, leading to mobilization of inorganic aluminum, which is toxic to tree roots. Acidic deposition can also affect terrestrial ecosystems by causing direct impacts on plant foliage.

The regions considered to be most sensitive to terrestrial acidification effects due to acidic deposition are forested ecosystems of the Adirondack Mountains of New York, Green Mountains of Vermont, White Mountains of New Hampshire, Allegheny Plateau of Pennsylvania, and high-elevation forests in the southern Appalachians. The Kane Forest in the Allegheny Plateau of Pennsylvania and the Hubbard Brook Experimental Forest in the White Mountains of New Hampshire were selected to evaluate the effects of acidic deposition on the sugar maple and red spruce due to known sensitivity of these species in these areas and the availability of data. The ecosystem services affected include food, natural habitat, and tourism.

For our case study areas, we anticipate that sugar maple and red spruce abundance and growth (i.e., crown vigor, biomass, and geographic extent) will be quantitatively linked to acidification symptoms (specifically the calcium to aluminum ratio in the soil) through U.S. Forest Service Forest Inventory and Analysis (FIA) database analyses and the analysis of estimated sales of maple sugar products for the second draft risk and exposure assessment.[1]

7.1.3 Aquatic Nutrient Enrichment

Nitrogen is an essential nutrient for estuarine and marine ecosystem fertility and is often the limiting nutrient in aquatic ecosystems. Excessive nitrogen contributions can cause habitat degradation, algal blooms, toxicity, hypoxia (i.e., reduced dissolved oxygen), anoxia (i.e., absence of dissolved oxygen), fish kills, and decreases in biodiversity. A recent national assessment of estuary trophic conditions used five biological indicators to assess nutrient enrichment: chlorophyll *a*, macroalgae, dissolved oxygen, nuisance/toxic algal blooms, and SAV. This assessment is discussed in detail in Attachment 5.

The Chesapeake Bay and Pamlico Sound were chosen as case study areas based on the availability of atmospheric deposition data, water quality modeling data that accounted for atmospheric deposition, a large main stem river, and scalability. Because the Chesapeake Bay and Pamlico Sound are fed by multiple river systems, the case study areas were scaled to one main stem river for each system: the Potomac River Basin for the Chesapeake Bay and the Neuse River Basin for the Pamlico Sound. A eutrophication index, developed by National Oceanic and Atmospheric Administration's (NOAA's)) National Estuarine Eutrophication Assessment (NEEA) was used in this analysis, which estimates the likelihood that the estuary is experiencing eutrophication or will experience eutrophication in the future. The endpoints of interest are fish populations; water quality; and habitat quality and their related ecosystem services, including fisheries (e.g., closings, decreased species richness), recreation, and tourism.

7.1.4 Terrestrial Nutrient Enrichment

Terrestrial ecosystems typically respond to total reactive nitrogen loading and, with few exceptions, have limited differential responses to the specific chemical species of deposited nitrogen. Nitrogen compounds that are contained in atmospheric deposition, and that influence

[1] The FIA can be found at http://fia.fs.fed.us/.

nutrient dynamics, include multiple oxidized and reduced forms of inorganic nitrogen. Excess nitrogen in ecosystems causes inadvertent fertilization of trees and grasslands, creating unnatural growth rates in some species and changing competitive interactions among species, and nutrient imbalances. These impacts ultimately decrease ecosystem health and biodiversity. Forest growth enhancement can potentially exacerbate other nutrient deficiencies, such as Ca, Mg, or K, thereby causing problems with forest health. Enhanced growth generally occurs above ground level. This can cause changes in the shoot-to-root ratio, causing decreased resistance to environmental stressors, such as drought. In conifer forests, multiple long-term experiments (see Attachment 6) have demonstrated transient growth increases (generally at deposition rates lower than 10 kg N/ha/yr) followed by increased mortality, especially at higher rates of fertilization. In the western United States, atmospheric nitrogen deposition has been shown to cause increased litter accumulation and carbon storage in aboveground woody biomass, which, in turn, may lead to increased susceptibility to more severe fires. Grassland communities that are adapted to low nutrient supply can exhibit substantial sensitivity to nutrient enrichment effects of nitrogen deposition.

Two of the primary indicators of nitrogen enrichment in forested watersheds are the leaching of NO_3^- in soil drainage waters and the export of NO_3^- in stream water, especially during the growing season. Low C:N ratios in soils are also commonly related to increased nitrification, potential increases in soil acidity, and releases of nitrate to receiving waters; however, these measurements are not always widely available.

California's CSS and mixed conifer forest communities were selected for an initial case study analysis. These areas were selected based on the availability of atmospheric ambient and deposition data; the availability of digitized datasets of biotic communities; fire-prone areas; sensitive, rare species; their representativeness of western United States ecosystems potentially impacted by nitrogen deposition; and their scalability and generalization potential.

California's CSS and mixed conifer forests on the slopes of the San Bernardino and Sierra Nevada Mountains have important recreational value, protect water resources, and provide habitats for many other species. In the mixed conifer forest, lichen communities and nitrogen saturation can provide a means to identify the effects of nitrogen loadings. Both habitats provide a number of ecological services, including biodiversity, water quality, recreation, timber, and fire hazard mitigation. Linkage methods from endpoint to services may include measurement of

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

7.1.5 Sulfur and Mercury Methylation

The biogeochemical cycle of mercury, a well-known neurotoxin, is closely tied to the sulfur cycle. Mercury is taken up by living organisms in the methylated form, which is easily bioaccumulated in the food web. Sulfate-reducing bacteria in wetland and lake sediments play a key role in mercury methylation. Changes in sulfate[2] deposition have resulted in changes in both the rate of mercury methylation and the corresponding mercury concentrations in fish.

Although sulfur deposition is important to mercury methylation, several other interrelated factors seem to also be related to mercury uptake, including low lake water pH, dissolved organic carbon, suspended particulate matter concentrations in the water column, temperature, and dissolved oxygen. In addition, the proportion of upland to wetland land area within a watershed, as well as wetland type and annual water yield, appear to be important.

The major ecosystem services potentially impacted by sulfur-mediated mercury methylation are provisioning and cultural services. Fishing and shellfishing can involve both commercial operations and sports fishing, which provide food for human populations. For some socioeconomic groups (especially groups with low incomes), fishing is a subsistence activity that makes a very significant contribution to household food intake. Sport fishing often involves important recreational services, and for many groups (e.g., Native Americans, Alaska native villagers), fishing and consuming local fish or shellfish is of cultural and spiritual significance.

[2] EPA notes that in its review of the primary NAAQS for sulfur oxides, it has made the decision to examine all sulfate health effects as part of the review of the PM NAAQS (sulfates being one of the chief types of secondary PM). EPA believes it appropriate; however, to consider secondary sulfate effects as part of this review, rather than in the PM NAAQS review, because the effect at issue is related specifically to chemical composition. The fact that sulfate is deposited as a particle is not relevant to its contribution to mercury methylation.

Table 7.1-1. Summary of Characteristics, Ecological Indicators, Effects, and Ecosystem Services Impacted for Each Case Study Evaluated in This Review

Targeted Effect Area	**Characteristics of Sensitivity (Variable Ecological Factors)**	**Biological/Chemical Characteristic**	**Ecological Indicator**	**Ecological Effects**	**Ecosystem Services Impacted**	**Case Study Locations**	**Deposition Levels (NO_x and/or SO_x) Associated with Observed Effects (from ISA)**
Aquatic Acidification	Geology, surface water flow, soil depth, weathering rates	[Al] pH ANC	Species richness, abundance, composition ANC	Species losses of fish, phytoplankton, zooplankton; changed community composition, ecosystem structure, and function	Fisheries, recreation, tourism	Adirondack Mountains, NY Blue Ridge Mountains, Shenandoah National Park, VA	15 kg SO_4^{-2}/ha yr 10 kg NO_3^-/ha yr
Terrestrial Acidification	Geology, surface water flow, soil depth, weathering rates	Soil base saturation [Al] [Ca] C:N ratio Ca:Al ratio	Tree health Red spruce, sugar maple ANC Ca:Al ratio	Decreased tree growth Increased susceptibility to stress, episodic dieback; changed community composition, ecosystem structure, and function	Food, natural habitat, tourism	Kane Forest (Allegheny Plateau, PA) Hubbard Brook Experimental Forest (White Mountains, NH)	
Aquatic Nutrient Enrichment	N-limited systems, presence of nitrogen in surface water, eutrophication status, nutrient criteria	Chlorophyll *a*, macroalgae, dissolved oxygen, nuisance/toxic algal blooms, submerged aquatic vegetation (SAV)	Eutrophication Index (EI)	Habitat degradation, algal blooms, toxicity, hypoxia, anoxia, fish kills, decreases in biodiversity	Fish populations, water quality, habitat quality	Potomac River Basin, Chesapeake Bay Neuse River Basin, Pamlico Sound	

Targeted Effect Area	**Characteristics of Sensitivity (Variable Ecological Factors)**	**Biological/Chemical Characteristic**	**Ecological Indicator**	**Ecological Effects**	**Ecosystem Services Impacted**	**Case Study Locations**	**Deposition Levels (NO_x and/or SO_x) Associated with Observed Effects (from ISA)**
Terrestrial Nutrient Enrichment	Presence of acidophytic lichens, anthropogenic land cover	Cation Exchange Capacity, C:N ratios, Ca:Al ratios, NO_3^- leaching and export	Species composition	Species changes, nitrogen enrichment of soil, changes in fire regime, changes in nutrient cycling	Loss of habitat, loss of biodiversity, recreation, water quality	Coastal sage scrub and mixed conifer forest (San Bernardino and Sierra Nevada Mountain Ranges, CA)	10–15 kg N/ha yr 3–8 kg/ha yr for lichen effects
Sulfur and Mercury Methylation Potential	Wetland type, presence of sulfate-reducing bacteria, water pH, dissolved organic carbon, suspended particulate matter	Interaction among dissolved organic carbon, temperature, anoxia, and sulfide Land cover, precipitation response, and limnography	MeHg concentra-tions in fish and shellfish	Neurotoxic effects in fish and throughout food web	Fishing, shellfishing, sports fishing, food, recreation, biodiversity	Little Rock Lake, WI (ISA case study)	

7.2 INTEGRATING CASE STUDY RESULTS

The ISA and case study analyses have shown that, in certain ecosystems, welfare effects are occurring under current ambient concentrations of NO_x and SO_x, even though nationwide (with only a few exceptions) we are in attainment of the current primary and secondary NO_2 and SO_2 NAAQS. The next step in the risk and exposure assessment process is to determine what alternative levels of ambient NO_x and SO_x might allow (1) various degrees of recovery of impacted systems, (2) acceleration of recovery of impacted systems, and (3) protection against further damage, recognizing the variability in ecosystem sensitivities to nitrogen and sulfur deposition. At this point in the risk and exposure assessment, we have begun to address many of the policy-relevant questions guiding this review. Our initial case study analyses have begun to show the variability associated with these responses and the degree to which ecological indicators are suited to address a particular type of effect (i.e., acidification or nutrient enrichment in terrestrial or aquatic ecosystems).

There are many factors that determine whether or not an ecological effect occurs in response to ambient concentrations of NO_x and SO_x. These "variable factors" may refer to either ecological factors or atmospheric factors, both of which influence deposition or exposure and the associated ecological effects (i.e., acidification or nutrient enrichment). The degree to which any given level of atmospheric deposition of nitrogen and sulfur impacts ecosystems depends in large part on a suite of variable ecological factors at the point of deposition, including geology, surface water flow, soil depth, and weathering rates. The levels of these ecological factors in a given location determine the ecological conditions governing sensitivity to atmospheric deposition of nitrogen and sulfur. The linkages between a given ecological indicator and deposition, as influenced by the variable ecological factors, are discussed in Chapter 8.

In the next draft of the risk and exposure assessment, we will look across the results of the case studies to identify ecological indicators that provide the most comprehensive coverage across sensitive ecosystems. These indicators will form the basis for assessing links between adverse effects and potential levels of an ecological indicator to protect against those effects. At this point, the Aquatic Acidification Case Study analysis is the furthest along and will be used to illustrate how an ecological indicator of acidification (i.e., ANC) and the levels of ecological

effects associated with changes in that indicator can be used to characterize adversity to public welfare.

7.3 LINKAGES BETWEEN ECOLOGICAL INDICATORS AND ADVERSE EFFECTS

Within the limitations of currently available data and models, our case study analyses indicate the degree, if any, to which adverse ecological effects are already occurring in specific sensitive ecosystems at current levels of ambient nitrogen and sulfur deposition. Note that ecological recovery may not immediately result from decreases in atmospheric deposition, but may lag behind changes in atmospheric deposition. Since current ecological conditions reflect past deposition and responses to it, it is possible that an ecological indicator such as ANC may improve over time (years) under current deposition levels. However, the recovery rate may be affected by current levels of deposition, with lower levels of deposition leading to a more rapid recovery compared to current levels.

7.3.1 ANC: The Critical Chemical Parameter

Ambient air concentrations are linked to adverse ecological effects via the process of atmospheric deposition. For our purposes, it is necessary to identify a suitably generalized ecological indicator for these effects because linking individual ecological endpoints directly to atmospheric deposition is difficult. The relationship between ecological effects associated with nitrogen and sulfur deposition and a commonly measured and well understood ecological indicator, ANC, is described below. In addition, we conceptually describe linking ecological effects with potential measures of adversity to public welfare by characterizing impacts on ecosystem services. This information can then help to inform judgments about the extent to which different levels of a particular ecological indicator might affect public welfare.

The susceptibility of a catchment to terrestrial or aquatic acidification by nitrogen and sulfur deposition is controlled by the ability of the watershed to neutralize the addition of nonmarine acid anion concentrations of SO_4^{2-} or NO_3^- to the catchment. The neutralizing ability of a catchment is a function of the acid-base balance; the balance between the sum of base cations (i.e., Ca* + Mg* + K* + Na*) inputs minus the sum of acid anions (i.e., SO_4^{2-} or NO_3^-) inputs. In general, catchments with positive acid-base balance have base cations inputs that

exceed acid anions inputs which "buffer" the watershed from becoming acidic. The ability of a catchment to buffer acid anion deposition is known as the "buffering capacity," which is controlled by a host of environmental factors within the watershed. Such factors include base cation leaching rate, base cation weathering rates, base saturation, uptake by vegetation, rate of surface water flow, soil depth, bedrock, etc. The buffering capacity of a catchment is controlled by the flux of base cations, which act to balance acid anion inputs. The effect of acid anion deposition is to lower this acid-base balance, causing a decline in the ecological system's composition, structure, and the biological fitness of its organisms over time.

The ANC of surface waters is widely used as a chemical indicator of acidic conditions because it has been found in many studies to be the best single indicator of the biological response and health of aquatic communities in acid-sensitive systems (Lien et al., 1992; Sullivan et al., 2006). Logistic regression of species presence/absence data against ANC provides a quantitative dose-response function, which indicates the probability of occurrence of an organism for a given value of ANC. For example, the number of fish species present in a waterbody has been shown to be positively correlated with the ANC level in the water, with higher values supporting a greater richness and diversity of fish species (**Figure 7.3-1**). The diversity and distribution of phyto-zooplankton communities are also positively correlated with ANC.

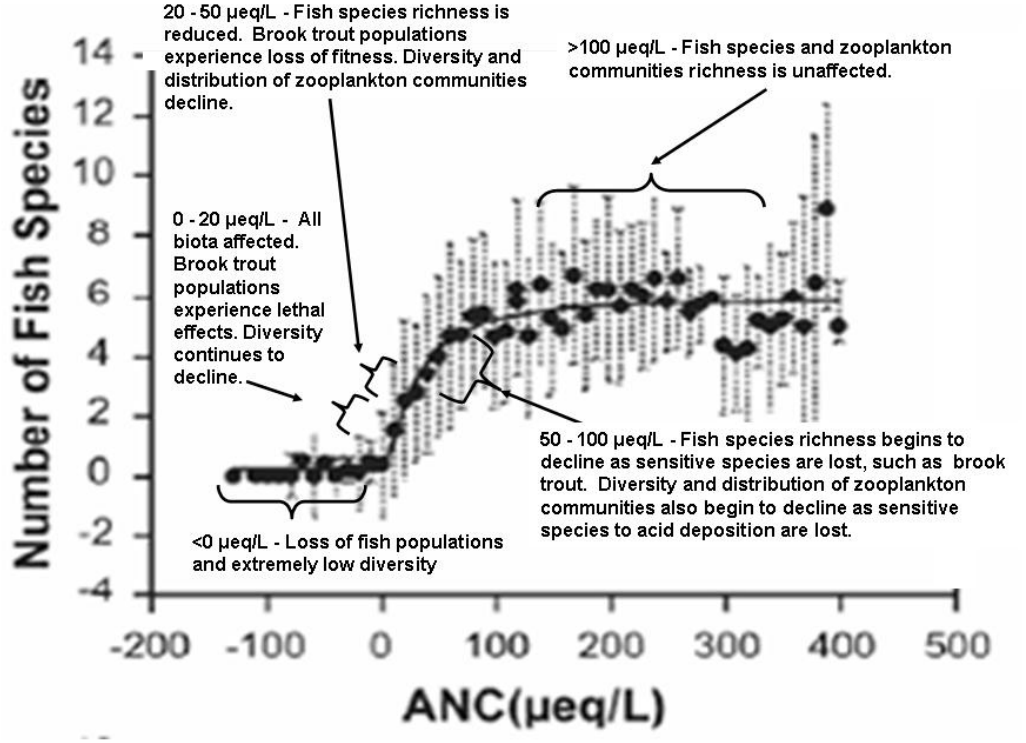

Figure 7.3-1. Number of fish species per lake or stream versus acidity status, expressed as ANC in lakes in the Adirondacks of New York (Sullivan et al., 2006). Five classes: <0, 0–20, 20–50, 50–100 µeq/L, and >100 µeq/L describe the biological effects at a range of ANC concentrations. See Table 7.3-1 for more details.

For freshwater systems, ANC levels can be grouped into five major classes: <0, 0–20, 20–50, 50–100 µeq/L, and >100 µeq/L with each range representing a probability of ecological damage to the community (see Attachment 3). ANC values above 100 µeq/L are generally not harmful (Figure 7.3-1) to biota. Below 100 µeq/L, it has been shown that fish fitness and community diversity begin to decline, but the overall health of the community remains high as long as ANC concentrations do not go below 50 µeq/L. ANC concentrations below 50 µeq/L result in negative effects on sensitive biota. From 50 to 20 µeq/L, it has been shown that fish diversity and the overall fitness (i.e., health and reproduction) of most aquatic organisms in the waterbody are reduced. Below 20 µeq/L, all biota exhibit some level of negative effects, particularly because surface waters at this level are susceptible to episodic acidification and their associated harmful effects. Fish and plankton diversity and the structure of the communities continue to decline sharply to levels where acidophilic species begin to outnumber all other

species. Below an ANC of 0 μeq/L, complete loss of fish populations and extremely low diversity of planktonic communities occur. At these low levels, only acidophilic species are present, but even their population and community structure are sharply reduced. The five categories of ANC and expected ecological effects are described in **Table 7.3-1** and are supported by a large body of research completed throughout the eastern United States (Sullivan et al., 2006). The connection between the ecological effects described in Table 7.3-1 and ecosystem services that can be indicative of adverse impacts to public welfare will be explored in the second draft risk and exposure assessment. However, examples of these ecosystem services include recreational and subsistence fishing, recreational lake use, natural habitat provision, and tourism. Potential values of these ecosystem services related to alternative levels of ANC will be assessed in the second draft risk and exposure assessment.

Table 7.3-1. Aquatic Status Categories

Category Label	**ANC Levels**	**Expected Ecological Effects**
Acute Concern	<0 micro equivalent per Liter (μeq/L)	Complete loss of fish populations is expected. Planktonic communities have extremely low diversity and are dominated by acidophilic forms. The numbers of individuals in plankton species that are present are greatly reduced.
Severe Concern	0–20 μeq/L	Highly sensitive to episodic acidification. During episodes of high acidic deposition, brook trout populations may experience lethal effects. Diversity and distribution of zooplankton communities decline sharply.
Elevated Concern	20–50 μeq/L	Fish species richness is greatly reduced (i.e., more than half of expected species are missing). On average, brook trout populations experience sub-lethal effects, including loss of health and reproduction (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 sub-lethal effects. Diversity and distribution of zooplankton communities begin to decline as species that are sensitive to acidic 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.

Whether the biological community of a waterbody is at risk from current deposition loads depends on the ability of the watershed to neutralize the incoming acid anion deposition and

maintain an acid-base balance or ANC level that protects the biological community. This linkage between deposition and biological processes is derived from a series of empirical relationships, that relate the sustainable buffering capacity (preindustrial) of a catchment to the maximum flux of acidic deposition which will maintain a particular level of ANC concentration in the surface water. ANC is operationally defined as the sum of base cations minus the sum of acid anions, with the proportion of ions deriving from neutral sea-spray removed:

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

where $[BC]_t^*$ is the current, measured sum of nonmarine base cation equivalent concentrations (i.e., $Ca^* + Mg^* + K^* + Na^*$) and $[AA]_t^*$ is the sum of nonmarine acid anion equivalent concentrations (i.e., $SO_4^* + NO_3^*$). It is assumed that all chloride is derived from marine sources. The * denotes the nonmarine component, whereby the marine contribution of each ion is subtracted as a proportion of measured chloride concentration from the known ratio of these ions in seawater. The equation defining ANC forms the basis of the linkage between deposition and surface water ANC concentrations. This linkage is explored in greater detail in Chapter 8.

7.4 REFERENCES

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

The previous chapters have provided an understanding of the risks associated with current deposition of nitrogen and sulfur associated with ambient atmospheric concentrations of NO_x and SO_x. Given that information, the next step is to provide a framework for developing standards for NO_x and SO_x that provide the appropriate level of protection against those risks. The purposes of this chapter are 1) to propose one possible framework for a NO_x and SO_x secondary standard(s), based on the linkages that exist between ambient atmospheric concentrations of NO_x and SO_x, atmospheric deposition of N and S, ecological effects and the related ecological indicators and 2) to illustrate how such a standard might be expressed for aquatic acidity using data from lakes in the Adirondacks case study area. The framework is designed to both meet statutory and legal requirements, and to reflect the complex nature of atmospheric and ecological systems.

In this chapter, we discuss constructing a standard based on achieving a uniform level of ecosystem protection. We explore a framework by which ambient atmospheric concentrations of NOx and SOx can be translated into a measure of ecosystem effects, using the transformation functions described below. To facilitate a more concrete understanding of this framework, we illustrate how the atmospheric concentration standards can be calculated using the Adirondacks case study example.

The remainder of this chapter is organized as follows. In Section 8.1, we discuss a possible structure for a secondary NAAQS for NO_x and SO_x, building on the conceptual model introduced in Chapter 1. In section 8.2, we present a discussion of the statutory and legal considerations that affect the design of an ecologically relevant ambient air quality standard for NO_x and SO_x. Section 8.3 discusses the framework for structuring a standard which links atmospheric concentrations of NO_x and SO_x to a specific ecological indicator of effects (i.e., ANC) through the deposition process, taking atmospheric and ecological factors into account. It also builds upon the current conditions risk and exposure assessment presented in Chapters 3 through 6 as well as the linkages presented in Chapter 7 to discuss the nature of a meaningful standard in light of the wide range of ecological effects resulting from deposition of NO_x and SO_x. In so doing, Section 8.3 expands on the standards framework through which the linkages

between ambient atmospheric concentrations of NOx and SOx, deposition of N and S, and ecological indicators can be described. Section 8.4, which is being developed for inclusion in the next draft, will describe an illustrative example of how ambient atmospheric concentrations for NOx and SOx can be compared to a desired level of ecological protection, as expressed using the ecological indicator ANC. This example will also show how observed (or modeled) ambient atmospheric concentrations of NOx and SOx can be transformed into ANC values for comparison against the level of a standard defined in terms of a value of the ecological indicator. This example will also provide step-by-step calculations to show how different combinations of atmospheric concentrations of NO_x and SO_x can achieve the same level of ANC, based on the deposition transformation functions and ecological effect functions that are described in Section 8.3. In each case, the example calculations will show clearly how the standards framework can incorporate 1) the influence of atmospheric factors that affect deposition, 2) the influence of ecological factors that affect ANC, and 3) the influence of reduced forms of nitrogen (ammonia and ammonium).

8.1 POSSIBLE STRUCTURE OF A SECONDARY NAAQS

Throughout this assessment, we have recognized there are important linkages between ambient nitrogen and sulfur and their depositional effects on the environment. Our approach to this joint, multi-pollutant review of two secondary standards has been to evaluate the science driving welfare effects and consider what is needed to develop a secondary standard or suite of standards that appropriately protects public welfare. The structure of the current secondary standards for NOx and SOx is based on the ambient concentration of a single indicator that is specified as a nitrogen- or sulfur-containing compound (i.e., NO_2 and SO_2, respectively) where the level of the indicator does not necessarily correlate well with the ecological effects of concern (USEPA, 2008). As discussed in Chapter 7, we recognize that the scientific basis that forms our understanding of the relationship between the criteria air pollutants, NOx and SOx and their associated public welfare effects supports the use of a more complex structure for the secondary standard(s). The inherently complex and variable linkages between ambient concentrations of NOx and SOx, their deposited forms of nitrogen and sulfur, and the ecological

responses that are associated with public welfare effects call for a more complex standard design that reflects these linkages.

A critical difference between the current risk and exposure assessment and those from previous reviews is that in the current assessment, exposures and ecological effects are related to current levels of nitrogen and sulfur deposition in selected case study locations, rather than just the ambient concentrations of NO_x and SO_x in those locations. Based on the recognized linkages between ambient concentrations of NO_x and SO_x and deposition of nitrogen and sulfur (see Chapter 3), as well as the linkages between deposition and ecosystem effects, a specified level of ecosystem effect will require limits on ambient concentrations of NO_x and SO_x, all other factors being held constant. A standard that is expressed in terms of atmospheric concentrations of NO_x and SO_x will require a process to translate ambient concentrations through the deposition process into ecological effects, to determine if the specified level of ecosystem effect is achieved This atmospheric concentration-based standard will explicitly identify the role of modifying factors in affecting the levels of NO_x and SO_x concentrations that would be necessary to achieve the standard.

A possible structure for such standards is shown below in Figure 8.1-1, which builds upon the conceptual model presented in Chapter 1. Figure 8.1-1 represents the pathway from atmospheric concentrations of NOx and SOx to an ecological effect (aquatic acidification) as represented by an ecological indicator (ANC), through the processes of deposition, with each of the steps along the pathway expanded to reflect the example of aquatic acidification using the ecological indicator ANC. Suites of variable factors reflecting both ecological and atmospheric complexity modify the pathways. Critical to developing an ecologically appropriate secondary standard for NO_x and SO_x is understanding that the different levels of the ecological indicator can be associated with different levels of protection against adverse public welfare effects. The ambient standard is then specified as the level(s) of ambient NO_x and SO_x such that the calculated ecological indicator meets the level of protection of public welfare set by the Administrator. Thus, the standard is expressed in terms of the relationship between ambient NO_x and SO_x and the ecological indicator, linked through the deposition of N and S.

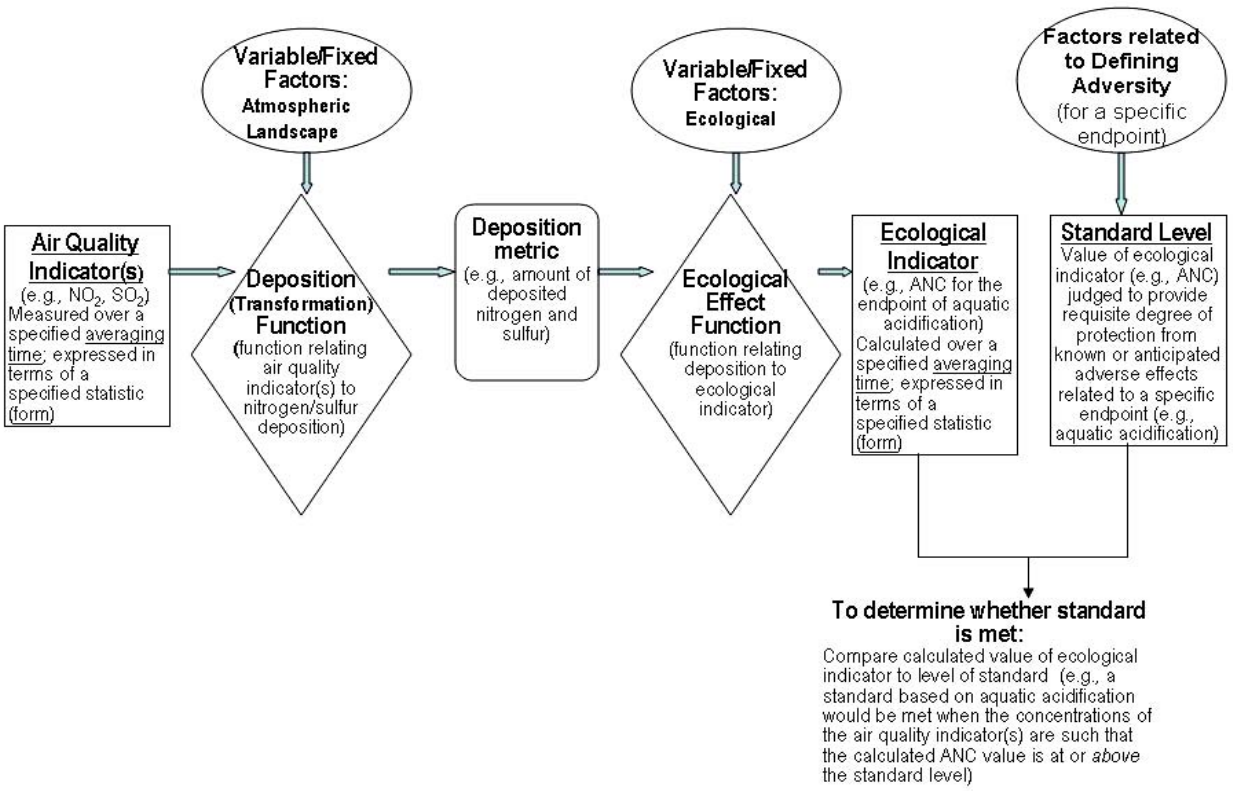

Figure 8.1-1. Possible structure of a secondary NAAQS for NOx and SOx based on the ecological indicator ANC for the effect of acidification.

The variable atmospheric factors which influence atmospheric conditions affecting the transformation, transport and deposition of ambient concentrations of NO_x and SO_x include relative humidity, precipitation, wind conditions, and chemical reactivity. Deposition is also affected by seasonally dependent landscape factors such as leaf surface area. Since deposition is the driver for many of the associated ecological effects due to NO_x and SO_x, such understanding of the factors that link atmospheric concentrations with deposition is critical. In addition, the relative contribution of NO_x to total deposition of nitrogen is affected by the ambient concentrations of ammonia and ammonium. The linkages between atmospheric concentrations and deposition as influenced by the variable atmospheric and landscape factors are discussed in Section 8.3.1.

The degree to which any given level of deposition of nitrogen and sulfur containing species impacts ecosystems depends in large part on a suite of variable ecological factors at the point of deposition, including soil base saturation, soil thickness, runoff rate, land use conditions, nutrient cycling, and non-atmospheric loadings of sulfur and nitrogen. The particular levels of these factors that occur at any location form the ecological baseline against which ecological effects from deposition are evaluated. The linkages between deposition and ecological effect as influenced by the variable ecological factors are discussed in Section 8.3.2.

The relationships illustrated in Figure 8.1-1 in concept can be operated in either direction, from known or assumed ambient atmospheric concentrations to the resulting ecological effects, or from desired ecological conditions in an area of interest to ambient concentrations that would achieve them. In either approach, there may not be a unique combination of ambient NOx and SOx that achieves a specified level of ecological protection, because of the multiple combinations of NO_x and SO_x concentrations that can yield the same level of ecological indicator. This is particularly true for the case of aquatic acidity, but may not hold true for other ecological endpoints. Whether precipitation occurs or not also greatly affects the relationship between ambient atmospheric concentrations of NO_x and SO_x and deposition of N and S, so knowledge or an assumption of precipitation is needed to complete the quantitative trail from ambient concentrations to ecological effects, or the reverse. Finally, concentrations and deposition of reduced nitrogen species influence ecological conditions, but these species are not currently encompassed by the listed criteria pollutant NO_x. While reduced species of nitrogen do contribute to the overall loadings of N, as will be demonstrated in a future version of Section 8.4, it may be possible to focus solely on NO_x contributions to loadings while recognizing that there are impacts from reduced forms of nitrogen that must be taken into account.

8.2 STATUTORY AND LEGAL CONSIDERATIONS IN THE STRUCTURE OF THE STANDARD

Inherent in the approach described above are various legal considerations as to the requirements of the CAA and EPA's ability to implement various types of standards under the Act. This section will begin to discuss the legal framework for considering appropriate air quality indicator(s), averaging time(s), form(s), and level(s) of standard(s) to protect against known or anticipated adverse impacts on public welfare. As noted above, the structure of such a

standard would likely be complex, reflecting the variable factors defining the atmospheric and environmental conditions that affect deposition of NO_x and SO_x, and those variable ecological factors that affect ecosystem responses.

In setting NAAQS to protect public health and welfare, EPA has historically established standards which require the comparison of locally monitored ambient concentrations of an air pollutant indicator against a specified numerical level of atmospheric concentration of a pollutant, using a specified averaging time and statistical form. For example, the current secondary standard for NO_x uses ambient concentrations of NO2 as the indicator, and attainment is determined by comparing the annual arithmetic mean of measured ambient concentrations, for a calendar year, against the level of 0.053 ppm. As more is learned about the effects of pollutants such as NOx and SOx on the environment, such a relatively simple framework may not be the most appropriate way to protect sensitive ecosystems from effects associated with ambient concentrations of the air pollutants. EPA is considering in this review of the secondary standard for NO_x and SO_x a conceptual framework for evaluating the environmental effect of ambient concentrations of NO_x and SO_x that takes into account variable factors, such as atmospheric and ecosystem conditions that modify the amounts and effects of deposited N and S on ecosystems. EPA is also considering whether the secondary standard can and should be structured to better take this framework into account, as a way to appropriately protect the public welfare from the effects associated with the presence of these pollutants in the ambient air.

As discussed previously, this could involve a standard with an ecological indicator which can be linked to ambient concentrations of SO_x and NO_x. The standard could include a nationally uniform level for a particular ecological indicator, for example a specified level of ANC that would be determined by the Administrator to represent the appropriate level of protection. This framework would also take into account other variables, both atmospheric and ecological that may modify the ecological effects. Compliance would be determined by measuring NO_x and SO_x concentrations, using these measurements and the various transformation functions to calculate an ANC level, and comparing the calculated level of ANC to the level of ANC set by the Administrator, including averaging time and form. Since the effect of a certain ambient concentration of SO_x and NO_x on ANC could vary depending on the other variable factors, whether a certain ambient concentration of SO_x and NO_x would attain the standard would depend in part on these other variables, which could vary geographically and temporally.

One important issue in evaluating such an approach is EPA's authority to structure a NAAQS in such a way. EPA's review of a NAAQS starts with its review of the air quality criteria for the pollutant. Under Section 109(d)(1) of the CAA, EPA must undertake a thorough review of the air quality criteria for the pollutant at issue as part of reviewing a secondary NAAQS to determine whether a current standard is requisite to protect the public welfare. Under Section 108, 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 as relevant, the review of air quality criteria should encompass a broad analysis of "any" anticipated adverse effects, as well as the ways in which variable conditions such as atmospheric conditions or ecological conditions may influence 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:

The criteria for an air pollutant to the extent practicable shall include information on the following:

1. 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;
2. 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
3. Any known or anticipated adverse effects on welfare.

Taking into account 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. The secondary standard is to "specify a level of air quality which, in the judgment of the Administrator, *based on such criteria*, 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) (emphasis added). "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). As with the description of the air quality criteria in Section 108, the CAA uses expansive language in describing the range of effects that EPA should take into account in setting a standard that is requisite to protect public welfare.

Thus, Section 108 and the definition of welfare require that EPA analyze and evaluate scientific information on the interaction between ambient concentrations of a pollutant and other variable factors, atmospheric and ecological, that affect the air pollutants impact on the environment. Section 109(b) makes it clear that EPA must base the standard on this scientific information but does not specify how EPA is to incorporate this information into the structure of the standard beyond the requirement that any secondary NAAQS be a level of air quality that is requisite to protect public welfare. Accordingly, while Sections 108 and 109(b) make it clear that EPA must take this kind of information into account when setting the NAAQS, specific directions are not provided on how to accomplish this.

It is also important to keep in mind the meaning of the term "requisite," as interpreted by EPA and the Courts. 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). In addition, while Section 109(b) requires that EPA establish "national" standards, it does not define this requirement in any greater detail than described above.

While EPA has most often made decision based on the results of direct exposure to an air pollutant in the ambient air in assessing effects on public health and welfare in establishing NAAQS, such as the health effects on humans when breathing in an air pollutant or the effects on vegetation through the uptake of air pollutants through leaves, EPA has also considered, where appropriate, the effects of exposure to air pollutants through more indirect mechanisms. For example, in 1978, EPA established a NAAQS for lead that included non-respirable particles based on the conclusion that these particles contribute to blood lead levels once they are deposited on the ground and then become a source of human lead exposure through the ingestion of lead-contaminated food or, particularly in children, the placing of hands and other contaminated objects in the mouth. *Lead Industries v. EPA*, 647 F.2d 1130 (DC Cir. 1980). In addition, EPA has previously considered acidification and nutrient enrichment concerns associated with ambient concentrations of NO_2 and other nitrogen compounds, but determined that the scientific and technical evidence that was available at the time did not provide an adequate basis to set a separate secondary standard to address such effects. 61 FR 52852, 52855 (October 8, 1996). The deposition of ambient NO_x and SO_x to terrestrial and aquatic

environments can affect ecosystems through direct and indirect mechanisms, as discussed in previous chapters. 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) (emphasis added), 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 SO_x and NO_x, as described in previous chapters.

The relationships between the impacts of ambient air concentrations on ecological effects such as acidification and nutrient enrichment, however, are extremely complex. To take these effects into account, including the variability in effects resulting from the same ambient concentrations of SO_x and NO_x, EPA is developing a biologically relevant framework in this risk assessment that relates ambient concentrations of an air pollutant to an ecological indicator, taking into account relevant atmospheric and ecological variables. In that context it is useful to explore whether a standard structured to take these elements into account is an appropriate way to provide protection that is sufficient but not more than necessary, as compared to a standard that treats ambient concentrations the same irrespective of these other biologically relevant variables. The CAA, which requires EPA to establish "national" standards, does not specifically address whether EPA can establish standards which could allow for varying levels of SO_x and NO_x in different areas. However, such an approach may be necessary if EPA is to establish a secondary standard that provides sufficient but not more than necessary to protect the public welfare. Given the lack of specificity in Section 109(b), EPA believes it is appropriate to explore the approach described in this chapter, with an aim of setting a national standard that provides sufficient but not more than necessary protection throughout the United States by taking into account the recognized variation of biologically relevant factors.

8.3 LINKAGES FOR STRUCTURING ECOLOGICALLY RELEVANT STANDARDS

Consistent with the framework depicted in Figure 8.1-1, the following sections provide a discussion of both the linkages between ambient air concentrations and resulting deposition metrics, and between the deposition metric and the ecological indicator of concern. These linkages are discussed conceptually in Section 8.3.1. Following that discussion, Section 8.3.2

describes the deposition transformation function that relates atmospheric concentrations of NOx and SOx to nitrogen and sulfur deposition metrics, while Section 8.3.3 describes the ecological effect function that transforms the deposition metric into the ecological indicator. 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 are also discussed more fully.

8.3.1 A Conceptual Model of the Pathway from Ambient Atmospheric Concentrations of NOx and SOx to Ecological Effects

For this first draft risk and exposure assessment, we have focused on developing an air quality indicator for protection against the adverse effects of aquatic acidification. Figure 7.3-1 demonstrates the various levels of protection of fish populations associated with varying ANC levels. Differing levels of an ecological indicator such as ANC will be associated with differing levels of protection of ecosystem functions (e.g. fish populations, biological diversity, fish population health). Different ecological indicators may be necessary for protection against the adverse effects of terrestrial acidification and aquatic and terrestrial nutrient enrichment. Indicators for other welfare effects categories of concern will be explored in future drafts of this risk and exposure assessment.

We have created a system of linked functions that translate an atmospheric indicator (concentrations of NO_x and SO_x) into an ecological indicator that expresses the potential for deposition of nitrogen and sulfur to acidify an ecosystem (Figure 8.1-1). The first part of this system is the deposition transformation function, which transforms ambient atmospheric concentrations (the atmospheric indicators) into a deposition metric. In this particular example, the deposition metric referred to in Figure 8.1-1. is the sum of atmospherically deposited oxidized nitrogen and sulfur, weighted by their molar ratio. The second part of this system of functions is an ecological effect function which converts the deposition metric to an ecological indicator (ANC) by adjusting for levels of other ecological factors that contribute to ANC. When the amounts of NOx and SOx in the ambient atmosphere can be used to derive a deposition metric (via the deposition transformation function) that can then be used to derive a level of ANC (through the ecological effect function) which falls within the range defined as acceptable by the standard, then those levels of NOx and SOx will be considered to meet that

standard of protection. 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 degradation of ANC. This latter amount is referred to as the maximum deposition load and is the amount that solves a mass-balance equation for that particular level of ANC. Mass-balance relationships developed in the scientific literature provide the basis for established equations that link levels of ANC to levels of nitrogen and sulfur deposition (given levels of other, non-deposition related parameters such as weathering rates, base cation uptake rates). Quantitative examples of these relationships will be provided in Section 8.4 of this chapter in the next draft of this document.

The value of the deposition metric can be calculated in terms of measured (or modeled) ambient NO_x and SO_x concentrations by using established relationships between ambient concentrations of NO_x and SO_x and nitrogen and sulfur deposition. As will be described in Section 8.4, these relationships are derived from the physical processes that govern transport and deposition; they are species dependent; they vary by particle mass, meteorology, compensation point, terrain and land use type.

It is important to note for this type of air quality indicator that the same level of protection from acidification can be obtained with different combinations of ambient NO_x and SO_x concentrations and their associated levels of nitrogen and sulfur deposition. As a result, the ambient air quality standard for NO_x and SO_x may be expressed jointly, and the air quality standard may be met by various combinations of NO_x and SO_x.

Determining the level of the air quality indicator that is associated with a particular level of protection against adverse effects of acidification may include consideration of factors that could potentially alter the depositional relationship of nitrogen or sulfur to ANC. In addition, the specific concentrations of ambient NO_x and SO_x that will result in a particular deposition metric can vary based on factors that affect the relationship between ambient concentrations and deposition. These two considerations imply that the levels of ambient NO_x and SO_x that would be consistent with a particular level of ANC may differ according to the specific levels of modifying factors in different locations and whether the ecosystem is nitrogen and/or sulfur limited or saturated. While the standard is set to achieve the same level of protection (ANC) nationwide, the atmospheric concentrations of NOx and SOx and the related amounts of deposition that can occur and still meet the standard may differ. For example, because of the

differences in maximum depositional loads between watersheds with high proportions of grasslands and those with high proportions of evergreen forest ecosystems, for the same level of ANC, there may be differences in the ambient concentrations of NOx and SOx that would meet that ANC level. The response variable associated with these examples will vary across effects categories, and might be based on soil base saturation or aluminum concentrations in soil water or biodiversity impacts, rather than ANC. Specific modifying factors for the ambient concentration to deposition relationship are discussed in Section 8.3.2 of this chapter. Specific modifying factors for the deposition to acidification relationship will be discussed in Section 8.3.3. The overall transformation function of the standard will be national in scope as will be the ecological indicator level, although specific modifying factors within the transformation function and maximum depositional load may vary by location. Therefore, while the Administrator may choose the level of protection that is desired by specifying a particular limiting value of ANC (ANC_{limit}), there are a series of transformations that link that level of protection to ambient concentrations of NO_x and SO_x. As a conceptual example, to express the previous discussion in mathematical terms, consider the following:

$$I = ANC_{limit} = g(\cdot) - DL(S) - DL(N) \quad (1)$$

where I is an indicator, $g(\cdot)$ is a series of non-atmospheric, non-depositional environmental factors (e.g., runoff, weathering rates, geology, etc.), ANC_{limit} is a critical limit for ANC necessary to provide a particular level of protections for biota in an ecosystem, DL(S) is the implied maximum depositional load of S associated with that ANC limit, and DL(N) is the implied maximum depositional load of N associated with that ANC limit. Note that DL(S) and DL(N) are jointly determined by the equation $g(\cdot) - ANC_{limit} = DL(S) + DL(N)$, and that there is no unique solution for either one unless the other is fixed. Further, we can express the deposition of NOx and SOx through the following relationships:

$$S_D = f_S(NO_x, SO_x \mid Z) \text{ and } N_D = f_N(NO_x, SO_x \mid Z) \quad (2)$$

where S_D is sulfur deposition, N_D is nitrogen deposition, Z is a series of parameters affecting deposition of ambient SO_x and NO_x (including NH_3), f_S is a function relating S_D to ambient concentrations of NO_x and SO_x, given Z, and f_N is a function relating N_D to ambient concentrations of NO_x and SO_x, given Z.

It is clear that the indicator of NO_x and SO_x effects (I) is a function of deposition. However, by substituting in the ambient to deposition conversion functions in (2), the indicator I can be made into an ambient indicator:

$$I= g(\cdot)-S_D(f_S(NO_x, SO_x\ |Z)-N_D(f_N(NO_x, SO_x\ |Z). \quad (3)$$

Not all values of S_D and N_D cause adverse welfare effects. The point where the levels of deposition associated with the ambient NOx and SOx lead to an ANC that does not achieve the specified ANC limit are when S_D and N_D are equal to or greater then the DL(S) and DL(N) for a particular location.

$$I= g(\cdot)-DL(f_S(NO_x, SO_x\ |Z)-DL(f_N(NO_x, SO_x\ |Z). \quad (4)$$

Clearly, the establishment of the functional forms for $g(\cdot)$, f_S, and f_N, as well as for the values of the parameter series Z, will be critical. Note that variable factors in $g(\cdot)$ and Z can be in many forms, some continuous, e.g. precipitation, and some discrete, e.g. type of bedrock. However, continuous variables can be converted to discrete categories, which may be easier to implement in the form of a standard. For example, precipitation could be expressed as inches per year, or precipitation could be categorized as high, medium, and low, possibly based on percentiles of the observed distributions of precipitation values.

8.3.2 Linkages between Ambient Concentrations and Deposition

Defining the linkages between ambient concentrations of NO_x and SO_x and deposition of N and S is a crucial piece of the framework as described in Section 8.1. Atmospheric deposition of nitrogen from ambient concentrations of NO_x (N_{NOx}) and atmospheric deposition of sulfur from ambient concentrations of SO_x (S_{SOx}) to a surface is a complex function of numerous meteorological parameters and surface properties. A transformation function that incorporates the nationwide variability of the important meteorological and surface parameters is expected to be a useful approach to describing the deposition process. The derivation of this transformation function, which converts ambient concentrations of NO_x and SO_x to their associated depositions, is described below. The derivation takes algorithms from the U.S. EPA-developed Community Multi-scale Air Quality (CMAQ) modeling system (U.S. EPA, 1999) into consideration, and CMAQ output is used to calculate key parameters in the resulting function. The use of CMAQ

data is intended to be illustrative of the process. Specific models, data sets and methods appropriate to use in other locations or on different spatial/temporal scales may differ.

8.3.2.1 Data and Tools

8.3.2.1.1 Physics and Chemistry of Atmospheric Deposition

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). The magnitude of each deposition process is related to the ambient concentration through the time-, location-, process- and species-specific *deposition velocity* (Seinfeld and Pandis, 1998):

$$Dep_i^{Dry} = v_i^{Dry} \cdot C_i^{Amb} \quad (19)$$

$$Dep_i^{Wet} = v_i^{Wet} \cdot C_i^{Amb} \quad (20)$$

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

$$Dep_i^{Tot} = Dep_i^{Dry} + Dep_i^{Wet} \quad (21)$$

Substituting Equations 19 and 20 into 21 yields

$$Dep_i^{Tot} = v_i^{Dry} \cdot C_i^{Amb} + v_i^{Wet} \cdot C_i^{Amb} \quad (22)$$

The total deposition of sulfur and nitrogen would therefore be:

$$Dep_{S+N}^{Tot} = \sum_i (v_i^{Dry} + v_i^{Wet}) \cdot m_i \cdot C_i^{Amb} \quad (23)$$

where m_i is the molar ratio of the atom (sulfur or nitrogen) of interest to the *i*th pollutant. Ambient sulfur- and nitrogen-containing pollutants include gases such as sulfur dioxide (SO_2), ammonia (NH_3), various nitrogen oxides (NO, NO_2, N_2O_5), nitric acid (HNO_3), and peroxyacetyl nitrate (PAN); and particulate species such as sulfate (SO_4^{2-}), nitrate (NO_3^-), and ammonium (NH_4^+). Oxides of nitrogen and oxides of sulfur are currently regulated by the NAAQS as defined in

the CAA. These compounds include the sulfur-containing species above as well as the above oxidized forms of nitrogen (referred to here as NO_x); ammonia and ammonium, which are reduced forms of nitrogen, are not currently included as regulated pollutants.

For this section, Equation 5 is termed the *deposition transformation function*, and it provides the functional form of the relationship between instantaneous atmospheric pollutant concentrations and deposition fluxes of sulfur and nitrogen. Equation 5 can also be thought to represent the relationship between cumulative or average values of the variables over time and/or space, but doing so raises issues of exactly how integration/averaging over time and/or space is to be done. To some extent, the degree of temporal and spatial averaging needed will depend on the ability to measure or model concentrations at particular spatial (e.g. at specific water bodies) and temporal (e.g. hourly or daily) scales. However, the need for temporal or spatially aggregated values may also be driven by the form of the ecological indicator, which may be annual or seasonal, and may reflect local ecological attributes. The remainder of Section 8.3.2 discusses this and other policy-relevant scientific and mathematical issues and proposes methods for determining parameter values (i.e. v_i^{dry} and v_i^{wet}) for input to Equation 23; results of example calculations will be shown in Section 8.4.

8.3.2.1.2 Air Quality Simulation Models

Deposition velocities necessary for employing the deposition transformation function can be obtained either through models or direct measurements, although the logistics of accurate measurements are currently prohibitive to deploying a measurement network. For purposes of the current discussion and accompanying future example calculations (Section 8.4), deposition velocities will be obtained from CMAQ output, and research will be conducted to assess if this is the optimal source of these parameters for future regulatory analyses.

CMAQ determines the deposition fluxes of the suite of modeled air pollutants at each time step and location in the user-specified spatial grid. Deposition velocities can be found in CMAQ output in the following ways:

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. Equation 20 is not directly expressed in CMAQ source code: the cloud processing module of CMAQ 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. Explicit v^{wet} values can and will be calculated in a post-processing step by applying Equation 20 to the wet depositions and ambient concentrations output by the model.

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 development work that has been based on peer-reviewed literature from the past two decades (U.S. 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 should be considered if v_i^{wet} values are applied to ambient measurements (this will be discussed in Section 8.4). 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 first choice for exploring inputs to Equation 23. Gaseous v^{dry} values are directly output by MCIP, whereas aerosol v^{dry} values and all species' v^{wet} values currently need to be calculated from standard CMAQ output. In all cases, data aggregation issues need to be carefully considered: while MCIP and CMAQ give hourly output values, the particular averaging time relevant for ecological processes for NO_x and/or SO_x is likely to be the same as the time resolution of the ecological indicator of choice (which is likely to be seasonal or annual). As such, values of v^{dry} and v^{wet} for each species should either be representative of the desired averaging period, or aggregation of resulting depositions after applying hourly deposition velocities to concentrations will need to be performed. It is proposed that the spatial scale of the deposition velocities used here reflect that of future analyses, e.g. be relevant at scales that may range from individual water bodies up to regional or national scales, as discussed in Chapters 4 and 5. Specific methods for performing calculations are discussed below.

8.3.2.2 Analytical Techniques

8.3.2.2.1 Hourly Deposition Velocities

As stated above, hourly v^{dry} values of gaseous species are complex functions of meteorology and land surface properties that are directly available in the outputs of MCIP. Deposition velocities of aerosol species were calculated by applying Equation 19 to CMAQ grids of aerosol C_i^{Amb} and Dep_i^{Dry} values to calculate hourly grids of v_i^{Dry} values for the example in a future Section 8.4. Plans are underway to obtain the size-specific aerosol deposition velocities from future CMAQ model runs. This will provide v_i^{Dry} for fine as well as coarse mode aerosols.

Unlike dry deposition velocity, the wet deposition velocity is independent of land surface properties and can be effectively expressed in a simple form (Seinfeld and Pandis, 1998):

$$v_i^{Wet} = w_i^r \cdot p^0 \tag{24}$$

$$w_i^r = \frac{C_i^{Aq}}{C_i^{Amb}} \tag{25}$$

where w^r is the washout ratio, C_i^{Aq} is the concentration of species i in the rainwater, and p^0 is the precipitation intensity.

If Equation 25 is substituted into 24, and Equation 24 is substituted into Equation 20, the ambient concentration cancels out and wet deposition can be expressed as a function of only rainwater concentration and precipitation (both of which are routinely measured by the NADP network). However, deposition can be expressed in terms of ambient concentrations since the atmospheric indicators for the framework discussed above are ambient air concentrations of NO_x and SO_x. Calculating the transformation function will therefore use values of w^r derived from CMAQ output for input into Equation 24 (which is then input to Equation 5). Solving for v_i^{wet} in Equations 2 and 6, equating them and rearranging these equations yields:

$$w_i^r = \frac{Dep_i^{wet}}{p^0 \cdot C_i^{Amb}} \tag{26}$$

which expresses the washout ratio in terms of CMAQ outputs. As mentioned above, simulated precipitation is a source of error in CMAQ's wet deposition simulations. The washout ratio offers a method of dealing with this error: CMAQ output can be used to calculate w_i^r values and

precipitation measurements (e.g. from NADP) can be used to obtain p^0 values for input to Equation 24 to obtain measurement-corrected wet deposition velocities.

8.3.2.2.2 Aggregation Issues

The deposition velocities and washout ratio are dynamic quantities that depend on numerous conditions that are highly variable with both space and time. However, an ecologically relevant standard is likely to be based on an averaging time greater than hourly, which might require temporal aggregation of deposition velocities. Use of deposition velocities that reflect a spatial scale consistent with this review might also require some level of spatial aggregation of deposition velocities. The v^{dry}, v^{wet}, and w_i^r parameters are all expressible as ratios of other quantities, which allow for multiple possible methods of calculating aggregate values, including the following:

1. Average ratio: Averaging hourly values of the deposition velocities and the washout ratio is equivalent to find the average ratios of their component quantities.
2. Weighted Average Ratio: Same as above but weight the hour-specific ratios by either concentration or deposition during the averaging process.
3. Ratio of averages: Instead of working with hourly deposition velocities and w_i^r values, concentrations and depositions can be aggregated (concentrations are averaged, depositions and precipitation are summed) over space and/or time and the ratios of the resulting aggregate values can be computed. This method removes the outlier effect of unrealistically large ratios resulting from small denominators (this seems most likely to be an issue in calculations of w_i^r when precipitation is very small but non-zero).
4. Conservatism: Single hourly values from the pool of available data can be chosen that provide a more conservative calculation of depositions, such as predicting the largest possible depositions from a given concentration (i.e., choose the annual and spatial maximum values of v_i^{dry} and/or w_i^r for each species and region).

Temporal aggregation is known to produce substantial biases in dry depositions when correlation exists between v^{dry} and C_i^{Amb} (Clarke et al., 1997), and it is presumed that this bias needs consideration when performing spatial aggregation as well. Some exploration of the conservative method of finding v^{dry} values has been performed, and it was found that this produced unrealistically high annually representative values. For purposes of the example calculations that will be presented in Section 8.4, the Ratio of Averages method will be employed to obtain all annual deposition velocities, but the best method of obtaining such values remains an open research question.

8.3.2.3 Results and Findings

Potential applications of the transformation function to the standard setting and implementation processes will be presented in Section 8.4. In this section, the variability of the deposition velocities resulting from CMAQ output is explored to 1) highlight the complexity of the process of converting between ambient concentrations and depositions and 2) illustrate some possible visualization techniques

Fields of dry deposition velocities of SO_2 output by MCIP are shown in **Figure 8.3-2**. The figure shows maps of mean and standard deviation of hourly dry deposition velocities over 24 hours during four seasonally distinct days across the eastern U.S. output by MCIP. The plots show that v^{dry} values vary by at least two orders of magnitude over the spatial domain, and that there appears to be some spatial correlation between the magnitude of v^{dry} values (mean plots) and the hourly variability (standard deviation plots). These maps highlight the difficulty of choosing a single nationally representative v^{dry} value.

Therefore, v^{dry} values could also be studied at smaller spatial scales. **Figures 8.3-3** and **8.3-4** show distributions of v^{dry} values from a Case Study Area (Pamlico Sound, NC) of the same four days used for Figure 8.3-2. v^{dry} values in Figure 8.3-3 show an increasing trend in the January 1 plot, a decreasing trend on April 1, and relatively stable trends on July 1 and October 1, but with much greater spatial variability in the July 1 plot. Figure 8.3-4 shows maps of the diurnal distributions of the same data, and reveals that a substantial portion of the spatial variability might be explained by differences in the dominant land use of the grid cells (see **Appendix A** for the full list of land use categories in the model), especially when distinguishing between water and land surfaces. This suggests that v^{dry} values specific to at least the land use type, if not the grid cell, should be considered when using the transformation function.

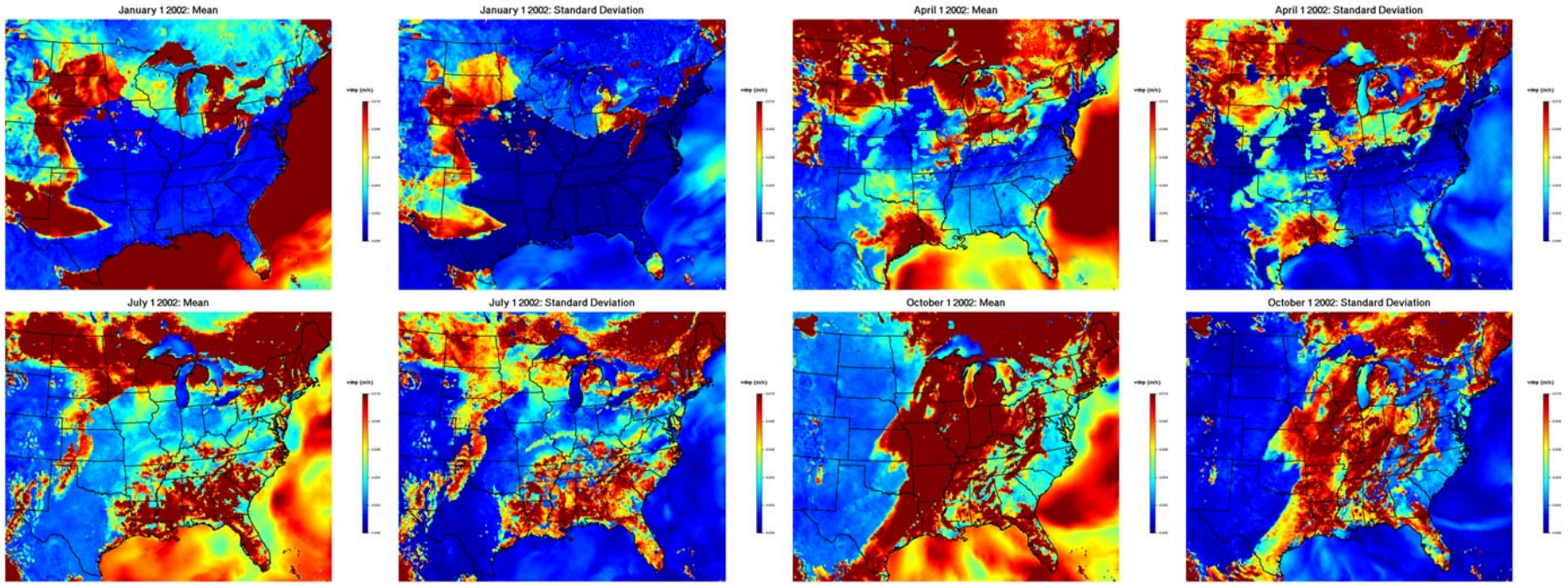

Figure 8.3-2: Mean and standard deviations of SO_2 v^{dry} values across the CMAQ eastern United States modeling domain for the first day of four seasonally distinct months. Note that the high value of the legend represents the maximum of the scale, not of the data.

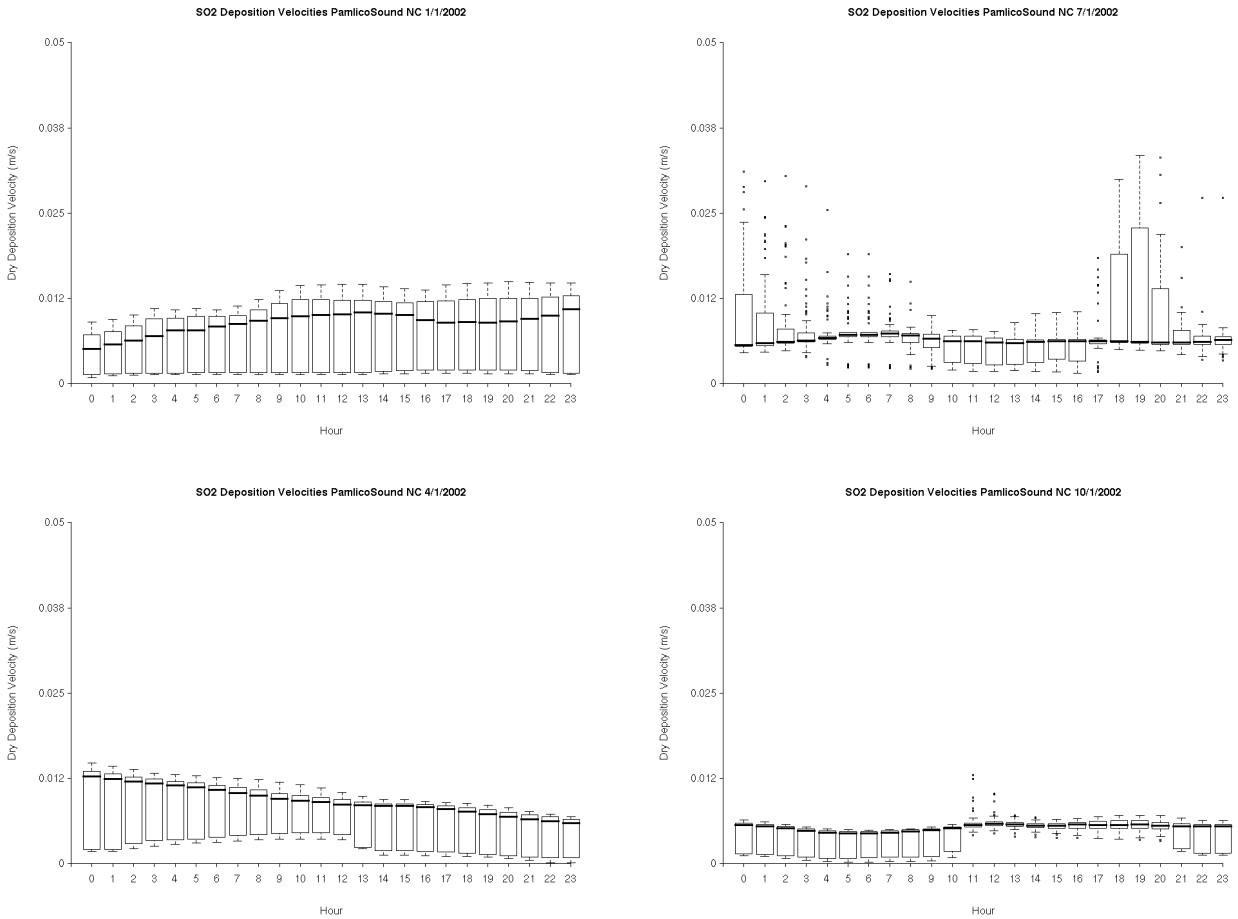

Figure 8.3-3: Hourly distributions of SO_2 v^{dry} values for one HUC (#3020105: Pamlico Sound, NC) over the first day of four seasonally distinct months.

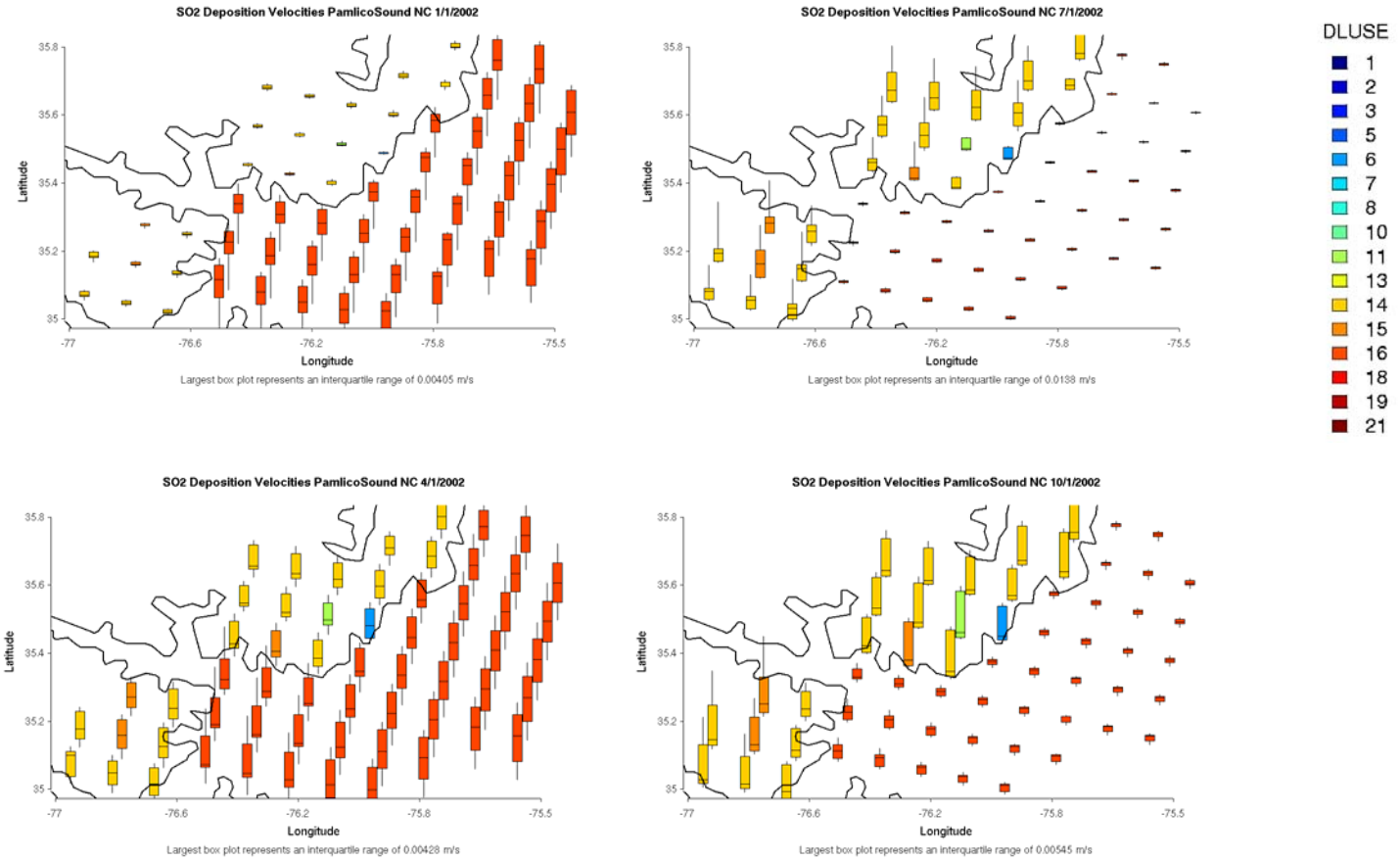

Figure 8.3-4: Distributions of SO_2 v^{dry} in each gridcell of one HUC (#3020105: Pamlico Sound, NC) over the first day of four seasonally distinct months. Colors indicate the dominant land use category (DLUSE) of the gridcell; see **Appendix A** for a description of each categorical value.

Figure 8.3-5 shows domain-wide SO_2 washout ratios values for the same four seasonally distinct days as above, calculated using the Average Ratio and the Ratio of Averages methods. These plots illustrate that the potential for unrealistically extreme values is far greater using the Average Ratio method. Exploration of the numbers in these calculations showed that, despite excluding times when p^0 was 0, very low ambient concentration values could also cause extreme values such as those shown in Figure 8.3-5. These results thus suggest that the Ratio of Averages might be a better choice for calculations of w_i^r rather than the Average ratio method to help mitigate the use of unrealistically large outlier values.

8.3.2.4 Uncertainties

The most prominent uncertainty in the process of converting between concentrations and depositions is the known lack of accuracy of the deposition velocities that are input to Equation 23. The CASTNET and NADP networks measure concurrent weekly values of wet deposition and ambient concentrations of select species; these data might be used to estimate the bias present in calculations of v_i^{Wet}. Such data explorations are also expected to aid in understanding the stability of w_i^r values, which might be low due to the dependence of cloud chemistry dynamics on meteorology of the upper atmosphere. Estimates of deposition velocities might be improved over CMAQ predictions by packaging the relevant portions of the MCIP and CMAQ source code into a stand-alone tool that generates values using local meteorological *measurements* (as opposed to the simulated values that are used during model runs). Further discussions of uncertainty will be included in future drafts of this document.

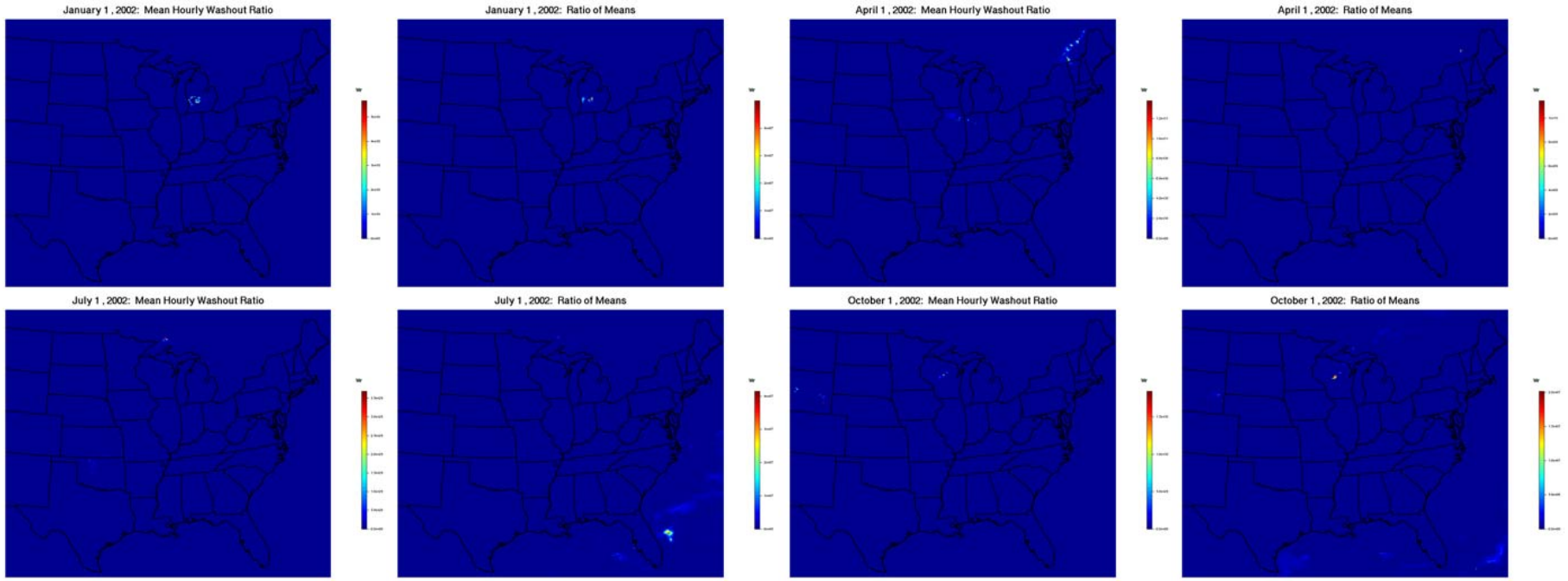

Figure 8.3-5: **Daily average washout ratios of SO_2 across the CMAQ eastern United States modeling domain for the first day of four seasonally distinct months (calculated using two different aggregation methods).**

8.3.3 Linkages between Deposition and Ecological Indicators

The equation defining ANC forms the basis of the linkage between deposition and surface water acidic condition and the modeling approach used. In the discussion below, the functions are framed in terms of a maximum depositional load given a specified ANC limit, for ease of discussion. However the maximum depositional load is not the deposition metric employed in Fig 8.1. The deposition metric is the deposition associated with a certain measured or assumed level of atmospheric concentration of NOx and SOx, and under Fig 8.1 the deposition metric is used to calculate an ANC level associated with that atmospheric level. The next draft will also frame the functions in terms of calculating an ANC level from a specific deposition metric, whether it is above or below the depositional load.

Given an ANC concentration ($[ANC_{level}]$), the corresponding depositional load (DL) is simply the input flux of acid anions from atmospheric deposition, which gives the $[ANC_{level}]$ when subtracted from the sustainable acidity or charge balance, defined as the uptake (N_{upt}), immobilization (N_{imm}), and denitrification (N_{den}) of NO_x deposition, the in-lake retention of NO_x deposition (N_{re}) and SO_x deposition (S_{ret}), and the acid anion leaching from the catchment as a function of the pre-industrial flux of base cations $[BC]_0^*$ from weathering, a described in Equation 5:

$$DL(N_{NOx}) + DL(S_{SOx}) = \{fN_{upt} + (1 - r)(N_{imm} + N_{den}) + r(N_{ret} + S_{ret})\} + ([BC]_0^* - [ANC_{level}])Q \quad (5)$$

where f and r are dimensionless parameters that define the fraction of forest cover in the catchment and the lake/catchment ratio, respectively. The right hand side of equation (5) is equivalent to the g(·) function discussed in Section 8.3.1. To convert into fluxes, concentrations ([x] = X/Q) are simply multiplied by runoff (Q) (in m/yr) from the site. The charge balance equates the deposition inputs of acid anions with the sum of processes which control their long term storage, removal and leaching exports. Several major assumptions are made: 1) steady-state conditions, 2) the effect of nutrient cycling between plants and soil is ignored 3) there are no significant N inputs from sources other than atmospheric deposition, 4) ammonium leaching is negligible because any inputs are either taken up by biota, adsorbed onto soils or nitrate compounds, and 5) long-term sinks of sulfate in the catchment soils are negligible.

Using equation 5 to derive the terms for internal catchment processes, the charge balance provides those combinations of N_{NOx} and S_{SOx} deposition that defines the DL function given by:

$$DL_{max}(S_{SOx}) = ((\,[BC]_0^{*} - [ANC_{level}])Q)/\,(1- p_s) \quad (6)$$

$$DL_{min}(S_{SOx}) = 0 \quad (7)$$

$$DL_{max}(N_{NOx}) = fN_{upt} + (1\text{-}r)(\,N_{imm} + N_{den}) + [(\,[BC]_0^{*} - [ANC_{level}])Q]/\,(1-p_n) \quad (8)$$

$$DL_{min}(N_{NOx}) = fN_{upt} + (1\text{-}r)(\,N_{imm} + N_{den}) \quad (9)$$

where p_s and p_n define the fraction of in-lake retention of N_{ret} and $S_{ret,}$ which is similarly proportional to the net input of N_{NOx} and S_{SOx} to the lake. It is not possible to define a single value of maximal loading of total acidity, since the acid anions sulfate and nitrate behave differently in the way they are transported with hydrogen ions; one unit of deposition of S will not have the same net effect on surface water ANC as an equivalent unit of N deposition. Equations 2 and 4 define the deposition loads for N_{NOx} and S_{SOx} individually. $DLmax(S_{SOx})$ defines the loading for sulfur when total N_{NOx} deposition is less then $DLmin(N_{NOx})$. $DLmin(N_{NOx})$ defines the deposition of N_{NOx} at which terrestrial catchment processes effectively remove N_{NOx}, so that deposition loads lower then $DLmin(N_{NOx})$ result in no leaching of nitrate. $DLmax(N_{NOx})$ defines the load for total N_{NOx} deposition when S deposition is zero. In reality, neither N_{NOx} and S_{SOx} deposition will ever be zero, so the DL for the deposition of one is fixed by the deposition of the other, according to the line defining in **Figure 8.3-1**. It is our intention to construct a similar line for N deposition originating from NO_x only for the second draft of this risk assessment.

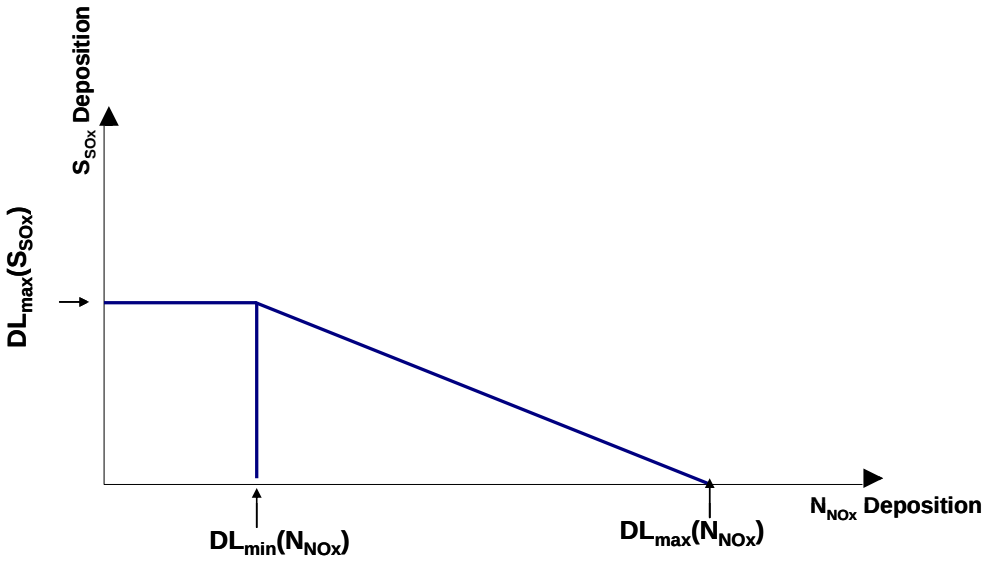

Figure 8.3-1. The deposition load function defined by the model.

The thick lines indicate all possible pairs of DL of N_{NOx} and S_{SOx} acidity. Note that in the above formulation individual DL of N_{NOx} and S_{SOx} are not specified; each pair of depositions (N_{NOx} and S_{SOx}) fulfilling equations 2-5.

Given a $[ANC_{level}]$ for a desired level of protection, the modeling has to provide the calculations of the N_{NOx} and S_{SOx} sinks (N_{upt}, N_{imm}, N_{den}, N_{ret}, S_{ret}), landscape characteristics (f and r) and critical leaching of acid anions (($[BC]_0^*$ - $[ANC_{level}]$)Q), which are described below.

Given a maximum deposition load, ANC concentration at a site can be provided by the difference between future base cation and acid anion concentrations, which is equal to the predicted, steady-state sulfate (S_{leach}) and nitrate (N_{leach}) leaching fluxes:

$$[ANC] = [BC]_0^* - (S_{leach} + N_{leach})/Q \quad (10)$$

where S_{leach} and N_{leach} are:

$$S_{leach} = (1 - p_s)S_{dep} \quad (11)$$

$$N_{leach} = (1- p_n)(N_{dep} - fN_{upt} - (1 - r)(N_{imm} + N_{den})) \quad (12)$$

8.3.3.1 Parameters

Net growth uptake of N_{NOx} in forest (N_{upt})

At steady-state or over long timescales, the only permanent sink for N (from any source) in the terrestrial system occurs when there is removal of biomass from the catchment. Short term, seasonal cycling of N does not affect the mean annual budget over these timescales. The main removal of N from the catchment is through the harvesting of the forest or grazing. There are various ways for estimating this N loss from the catchment, which take into account the N content of various tree species and the time periods of harvesting cycle. For forests without harvesting, like the Adirondack region of New York, N_{upt} is zero.

Immobilization (N_{imm}) and denitrification (N_{den}) of N_{NOx} in catchment soils

For long-term immobilization of N is forest soils, a constant value of 2 kg N / ha/ yr is used. This value represents the lower end of the range suggested from studies (Downing et al 1993). Thus, the amount of N removed for a given N_{NOx} depositional load is simply propositional to its total N_{tot} load (N_{NOx}/N_{tot})

It is assumed that the denitrification is related to the net input of N_{NOx} loading into the soil system after accounting for the removal of N_{NOx} by immobilization and uptake as follows:

$$N_{den} = f\text{de}(N_{nox} - N_{imm} - N_{upt}) \quad (13)$$

where *f*de is the denitrification faction (value between 0 and 1), ascribed to the catchment soil. Denitrification is an anaerobic process and therefore a function of soil moisture content, with higher rates in peat soils. A typical upland soils denitrify N at a rate of 10% of N input while peat soils work at a rate of 70 to 80 %. Therefore, the average denitrification fraction for a catchment is approximated by the following linear relationship:

$$f\text{de} = 0.1 + 0.7f\text{peat} \quad (14)$$

where *f*peat is the proportion of peat soils within the catchment.

In-lake retention of N_{NOx} and S_{SOx}

The in-lake retention of acid anions is assumed to be a linear function of net input of acidity. It is sequentially the final sink of acidity encountered by inputs that move through the catchment.

The in-lake retention fractions for N_{NOx} (p_n) and S_{SOx} (p_s) are calculated from a kinetic equation accounting for water retention time (Kelly et al 1987; Posch et al 1997).

$$p_n = (s_n / s_n + Q/r) \text{ and } Ps = (s_s / s_s + Q/r) \quad (15)$$

where Q is the runoff and s_n and s_s are the net mass transfer coefficient for N_{NOx} and S_{SOx}. Due to a lack of data, the net mass transfer coefficient for sulfate (s_s) was taken from a retention model calibration to mass balance data of 11 lakes located in North America and northern Europe (Baker and Brezonik 1988). The mean value of s_s for these lakes, 0.5 m/yr, was used for the maximum depositional load calculations. The value for s_n, 5 m/yr, was obtained from a similar study of 12, mostly Canadian, lakes (Dillon and Molot 1990).

Pre-Industrial Base Cation Concentration

The pre-industrial concentration of base cations $[BC]_0^*$ effectively set the long term capacity of the catchment to neutralize acidic deposition, because it represents the only source of base cation input that is sustainable over the long-term. Input of cations from weathering is assumed to be a relatively constant process driven largely by the reaction of CO_2 with primary minerals in the soils and bedrock. Base cations are removed by leaching from the soil solution through surface water runoff. At a steady-state, the leaching rate of base cation occurs at lesser or greater rates than the weathering supply. However, base cation leaching is not at steady-state today because anthropogenic acid deposition actually increases the leaching of base cations through ion-exchange within catchment soils. Soils contain a store of adsorbed base cations, as measured as base saturation, which are derived from weathering, but have accumulated in the soil over millennia, until eventually a steady-state is achieved, whereby the supply of base cations from weathering was in approximate equilibrium with the removal of base cations by rainwater, itself in equilibrium with the atmosphere. For this reason, $[BC]_0^*$ cannot be derived from measured data in runoff, but derived from a empirical relationships (i.e., pre-industrial base cation concentration).

The pre-industrial base cation concentration is the sum of weathering ($[BC^*_w]$) supply plus base cation deposition ($[BC^*_{dep}]$), if it is assumed that base cation deposition has not

significantly changed since pre-industrial times, minus long-term average uptake of base cations in the biomass (i.e., the annual average removal of base cations due to harvesting):

$$[BC]_0^* = [BC_w] + [BC^*_{dep}] - [BC_u]. \quad (16)$$

The first step is to quantify the proportion of measured base cation leaching which is derived from transient ion-exchange processes (BC_{ex}) and is proportional to the load of acid anions. This proposition is represented by the term 'F', calculated according to the methodology of Brakke and colleagues (1990):

$$F = \sin (\pi/2 \cdot [BC^*]_t/[S] \quad (17)$$

where $[BC^*]_t$ is the measured non-marine base cation concentration and S is a constant which varies regionally according to geology, but from empirical studies is taken as 400 μeq/L (Harriman and Christie, 1995). This constant determines the measured non-marine base cation concentration which represents a catchment likely to be unaffected by acid deposition; $[BC^*]_t$ = S, F =1 and base cation leaching is increased by exactly the value of the acid anion load, resulting in no change in the ANC of runoff. For values of $[BC^*]_t$ greater then S, F is 1.

This F value is then used to calculate the pre-industrial base cation concentration according to the following equation:

$$[BC^*]_0^* = [BC^*]_t - F([AA]_t^* - [AA]_0^*) \quad (18)$$

where $[AA]_0^*$ is the pre-acidification concentration of non-marine acid anions from weathering and natural atmospheric sources and the measured leaching rate of non-marine base cations $[BC^*]_t$ represent the sum of weathering, non-marine deposition and leaching sources. We assumed the steady-state concentration of nitrate ($[AA]_0$) was zero ($[AA]_0^* = 0$). Since $[BC^*]_0^*$ is now known, the maximum depositional load can be defined by Equation 9.

Catchment Parameters (r, f, and Q)

Lake and catchment areas can be estimated from topographical maps (1:50,000) and from the EMAP lake survey. The annual runoff can be obtained by interpolation from a national runoff map (Krug et al., 1990) for water years 1951-80. The fraction of forest in the catchment can be estimated from 2001 National Land Cover Data (NLCD).

8.4 EXAMPLE APPLICATIONS OF SECONDARY NAAQS STRUCTURE

This section is intended to provide an illustrative example applying actual data sets for the Adirondacks to the above derivations and linkage calculations. It is our intent that this section will be developed in the second draft of this document.

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APPENDIX A

Land Use Categories in MCIP (from USGS).

1. Urban Land
2. Dryland Cropland and Pasture
3. Irrigated Cropland and Pasture
4. Mixed Dryland and Irrigated Cropland
5. Cropland/Grassland Mosaic
6. Cropland/Woodland Mosaic
7. Grassland
8. Shrubland
9. Mixed Shrubland/Grassland
10. Savannah
11. Deciduous Broadleaf Forest
12. Deciduous Needleleaf Forest
13. Evergreen Broadleaf Forest
14. Evergreen Needleleaf Forest
15. Mixed Forest
16. Water
17. Herbaceous Wetland
18. Wooded Wetland
19. Barren or Sparsely Vegetated
20. Herbaceous Tundra
21. Wooded Tundra
22. Mixed Tundra
23. Bare Ground Tundra
24. Snow or Ice

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