

2 CHARACTERIZING EMISSIONS, AIR QUALITY, DEPOSITION AND WATER QUALITY

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

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

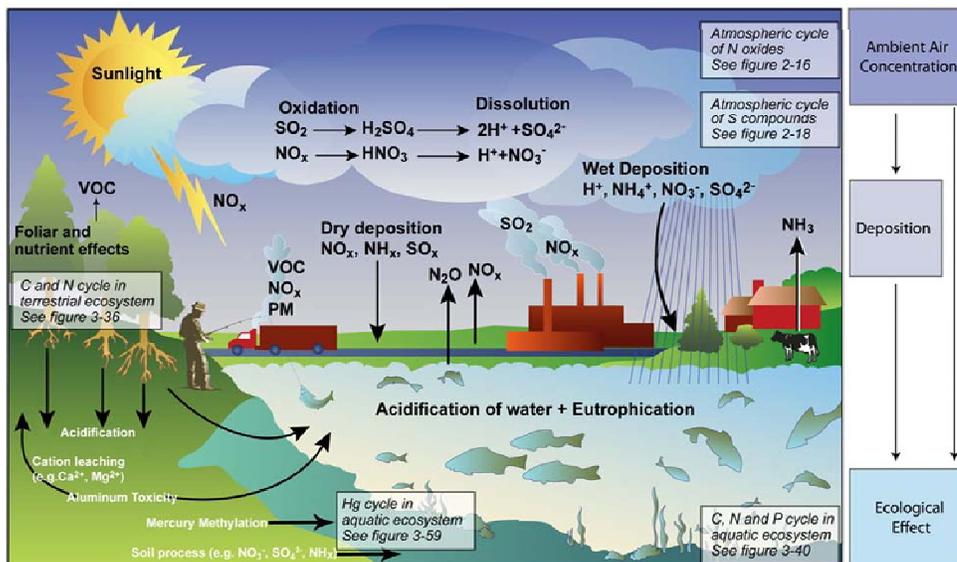


Figure 2-1. Overview of atmospheric, soil and aquatic processes relevant to acidification.

The multiple pollutant, multiple-media technical systems framework

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

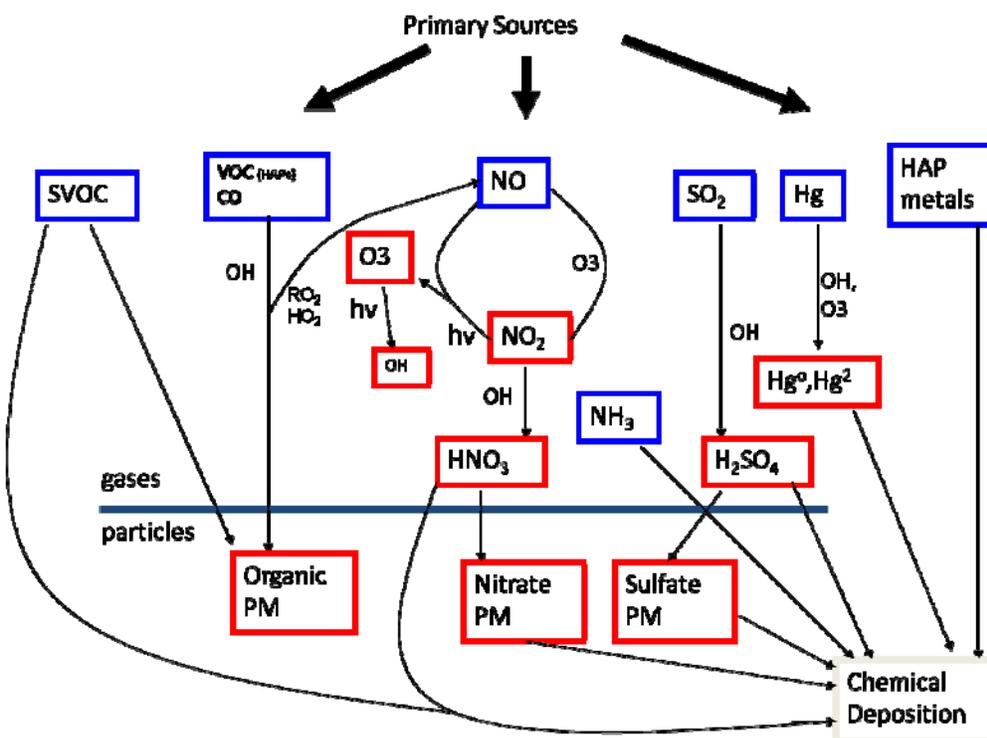


Figure 2-2 Diagram illustrating the multiple pollutant, multiple media linkages that are incorporated in air quality models like CMAQ. While this assessment focuses on the combined effects of oxides of nitrogen and sulfur, the technical basis for characterizing spatial and temporal patterns of N and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

Terminology, definitions and units.

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

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

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

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

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

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

Parameter	Units	Conversions to other unit conventions used in figures and calculations (multiply value in Units column by:	Explanation
Dep_i^{Total}	$meq/m^2\text{-yr}$		total (wet+dry) deposition
NO_y deposition ($SO_2 + SO_4$) NH_x Used in various conventions of: Dep_i	$meq/m^2\text{-yr}$ as N or S	$kg/ha\text{-yr} = (M_i/q)(10)^{-2} \cdot meq/m^2\text{-yr}$ where q = charge (1 for N, 2 for S)	
Ndep NO _y dep NH _x Sdep	$meq/m^2\text{-yr}$		Total (wet and dry) deposition; Ndep = NH _x + NO _y dep Sdep = SO _x =SO ₂ +SO ₄
v_i^{dry}	m/yr		dry deposition velocities
v_i^{wet}	m/yr		wet deposition velocities
Dep_i^{dry}	$meq/m^2\text{-yr}$		dry deposition fluxes
Dep_i^{Wet}	$meq/m^2\text{-yr}$		wet deposition fluxes
Dep_i^{total}	$meq/m^2\text{-yr}$		total (wet+dry) deposition
T_{SO_x} T_{NO_y}	m/yr	Calculated by dividing total ($SO_2 + SO_4$) or NO _y deposition (wet and dry) by the annual average ($SO_2 + SO_4$) or NO _y concentration.	the transfer ratio, which can be considered an aggregated, “effective” deposition velocity that relates total deposition of ($SO_2 + SO_4$) or NO _y to the total ambient concentration, and represents an average of the chemical species specific v_i^{Tot} (= $v_i^{Dry} + v_i^{Wet}$) values
Ecosystem variables			
ANC	$\mu eq/L$		measured ANC in surface water
ANC _{limit}	$\mu eq/L$		a “target” ANC level
CL _{anclim(i)} CL(N+S) CL(S)	$meq/m^2\text{-yr}$		Critical load that does not cause the catchment to exceed a given ANC _{lim} , where <i>i</i> indicates the pollutant of interest
Q	m/yr		Average surface water runoff rate for a water body
Q _r	m/yr		Median of the average runoff rates for water bodies in an ecoregion
N _{ECO}	$meq/m^2\text{-yr}$		Nitrogen uptake, retention and denitrification by terrestrial catchment
N _{leach}	$meq/m^2\text{-yr}$		N leaching based on observed surface water NO ₃
CL _r	$meq/m^2\text{-yr}$		Ecoregion representative critical load

2.1 SOURCES OF NITROGEN AND SULFUR

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

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

2.1.1 NO_x Emissions

The distribution of national total NO_x emissions across major source categories is provided in Table 2-1.1. Emissions summaries are also provided for the East² and West in Tables 2-1.2a and b, respectively, to reveal regional differences in source emissions profiles. In addition to anthropogenic sources, there are also natural sources of NO_x, including lightning, wildfires, and microbial activity in soils. Nationally, transportation-related sources (i.e., on-road, nonroad, and aircraft/locomotive/marine) account for ~60% of total anthropogenic emissions of NO_x, while stationary sources (e.g., electrical utilities and industrial boilers) account for most of the remainder (U.S. EPA, 2008, AX2, Table 2-1). Emissions from on-road vehicles represent the major component of mobile source NO_x emissions. Approximately half the mobile source emissions are contributed by diesel engines, and half are emitted by gasoline-fueled vehicles and other sources (U.S. EPA, 2008, AX2, Section 2.1.1 and Table 2-1-1). Nationwide, the nonroad,

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

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

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

Table 2-1.1. Annual National NO_x Emissions across Major Source Categories in 2002.

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

Table 2-1.2a. Annual NO_x Emissions across Major Source Categories in 2002 for the Eastern United States.

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

Table 2-1.2b. Annual NO_x Emissions across Major Source Categories in 2002 for the Western United States.

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

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

The spatial patterns of 2002 annual NO_x emissions across the United States are shown in Figure 2-1.1³. Emissions of NO_x are concentrated in and near urban and suburban areas and along major highways. Moderate or higher levels of NO_x emissions (>100,000 tons/yr)⁴ are also evident in some rural areas at locations (i.e., grid cells) containing major point sources. The amount of NO_x emissions in and near each of the case study areas can be seen from this map. All of the case study areas contain or are near locations with NO_x emissions in excess of 100,000 tons/yr.

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

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

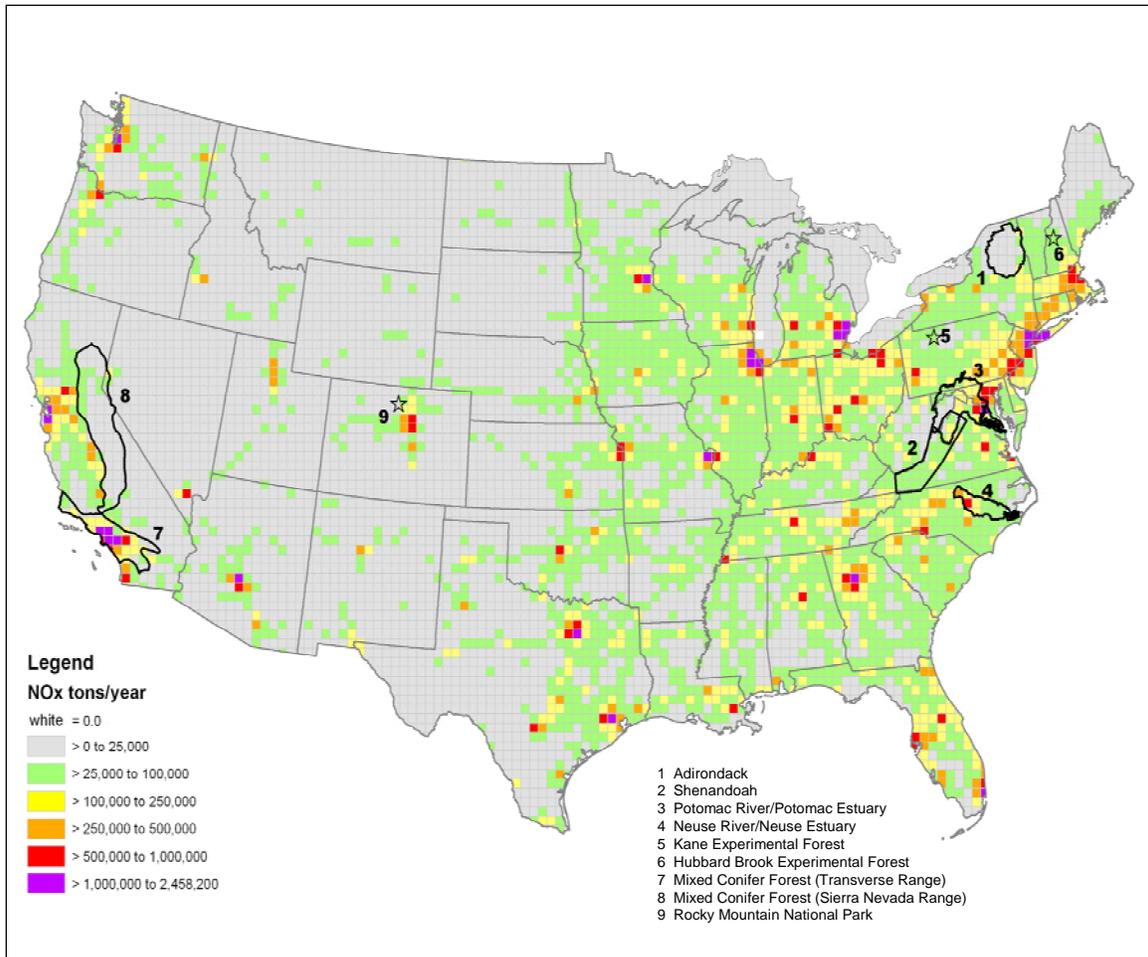


Figure 2-1.1. Spatial distribution of annual total NO_x emissions (tons/yr) for 2002.

2.1.2 NH₃ Emissions

The primary anthropogenic sources of NH₃ emissions are fertilized soils and livestock. Motor vehicles and stationary combustion are small emitters of NH₃. Some NH₃ is emitted as a byproduct of NO_x reduction in motor vehicle catalysts. The spatial patterns of 2002 annual NH₃ emissions are shown in Figure 2-1.2⁵. The highest emissions of NH₃ are generally found in areas of major livestock feeding and production facilities, many of which are in rural areas. In addition, NH₃ emissions exceeding 1,000 tons/yr are evident across broad areas that are likely associated with the application of fertilizer to crops. The patterns in NH₃ emissions are in contrast to the more urban-focused emissions of NO_x. The Potomac River/Potomac Estuary,

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

Neuse River/Neuse River Estuary, Shenandoah, and Mixed Conifer Forest (in the Sierra Nevada Range and the Transverse Range) case study areas all have sources with NH₃ emissions exceeding 5,000 tons/yr. Rocky Mountain National Park is adjacent to an area with relatively high NH₃ emissions exceeding 2,500 tons/yr. The Adirondack, Hubbard Brook Experimental Forest, and Kane Experimental Forest case study areas are more distant from sources of NH₃ of this magnitude.

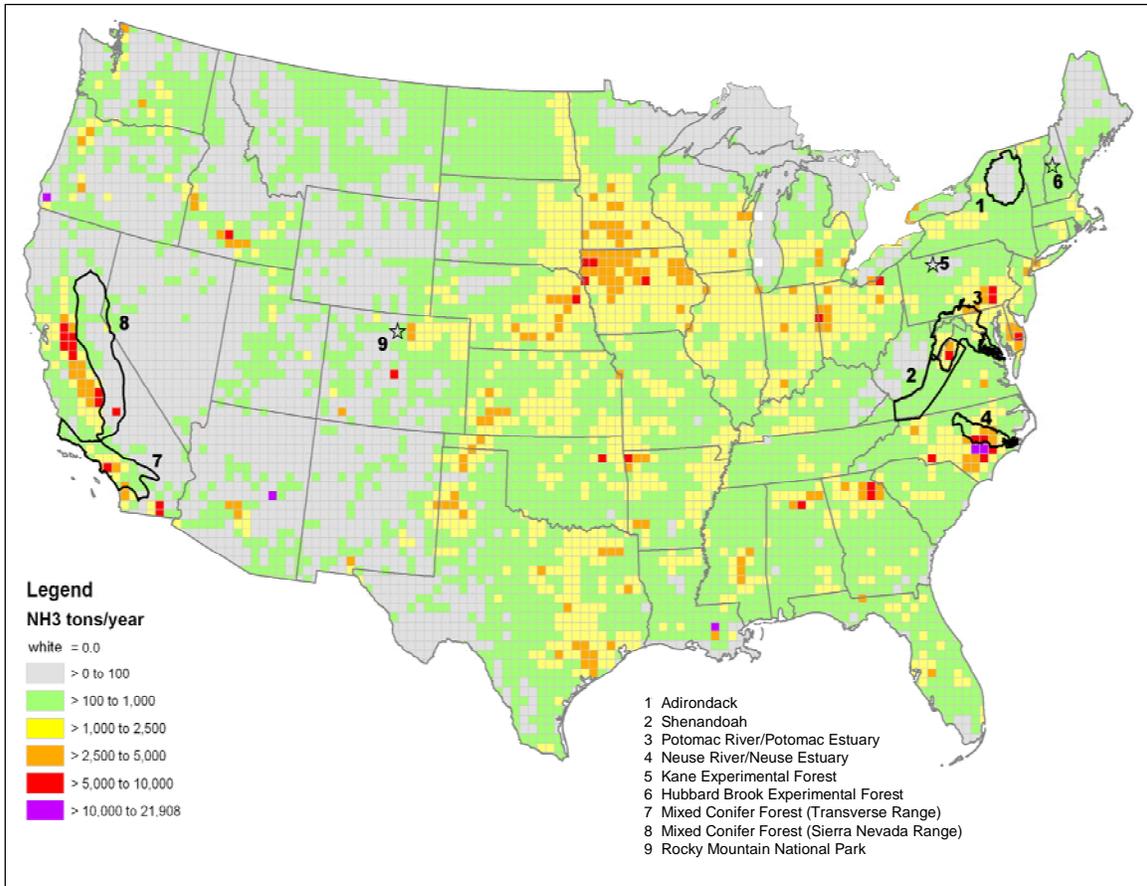


Figure 2-1.2. Spatial distribution of annual total NH₃ emissions (tons/yr) for 2002.

2.1.3 SO_x Emissions

The distributions of SO₂ emissions for major source categories nationally are provided in Table 2-1.3. Emissions of SO₂ for the East and West are presented in Tables 2-1.4a and b, respectively. Anthropogenic emissions of SO₂ in the United States are mainly due to combustion of fossil fuels by electrical generation units (70%) and industrial point sources (15%); transportation-related sources contribute minimally (7%). Thus, most SO₂ emissions originate

from point sources. Almost all the sulfur in fuel is released as volatile components (SO₂ or SO₃) during combustion. The higher sulfur content of coal compared to other types of fossil fuels results in higher SO₂ emissions from electrical utilities using coal as fuel.

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

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

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

Table 2-1.3. Annual National SO₂ Emissions across Major Source Categories in 2002.

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

Table 2-1.4a. Annual SO₂ Emissions across Major Source Categories in 2002 for the Eastern United States.

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

Table 2-1.4b. Annual SO₂ Emissions across Major Source Categories in 2002 for the Western United States.

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

The spatial patterns of 2002 annual SO₂ emissions are shown in Figure 2-1.3. High SO₂ emissions are scattered across the East, and there are large sources in both urban and rural locations. The greatest geographic concentration of SO₂ sources is in the Midwest, particularly along the Ohio River, where numerous electric generating units are located. As noted above, SO₂ emissions in the West are much lower than in the East, with sources concentrated in urban locations along with localized emissions in more rural areas associated with industrial sources (e.g., smelters) and gas-field operations.

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

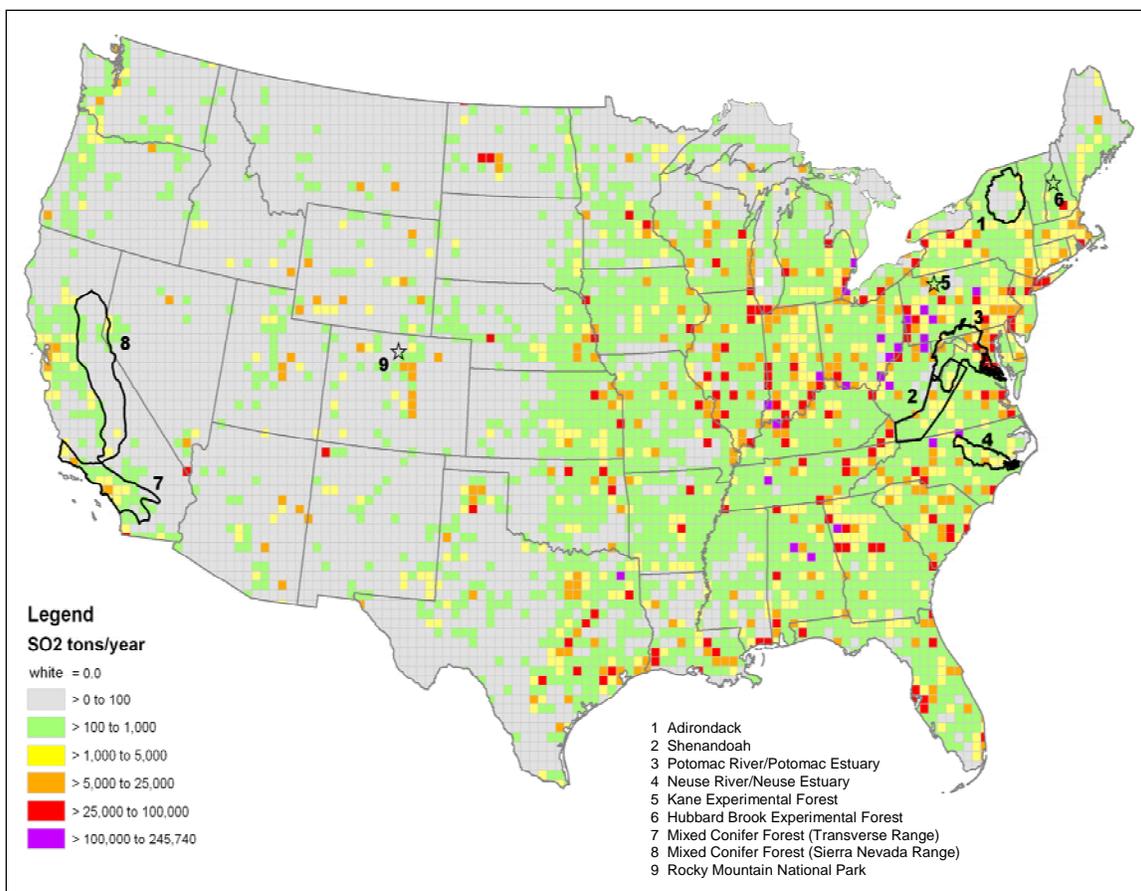


Figure 2-1.3. Spatial distribution of annual total SO₂ emissions (tons/yr) for 2002.

2.2 AMBIENT AIR CHARACTERIZATION

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

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

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

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

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

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

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

2.2.1 Air monitoring networks

There are over 1000 ground level monitoring platforms (Figures 2-2.1 and 2-2.2 and Table 2-2.1) that provide measurements of some form of atmospheric nitrogen or sulfur.

Table 2-2.1. Summary of Monitoring Networks.

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

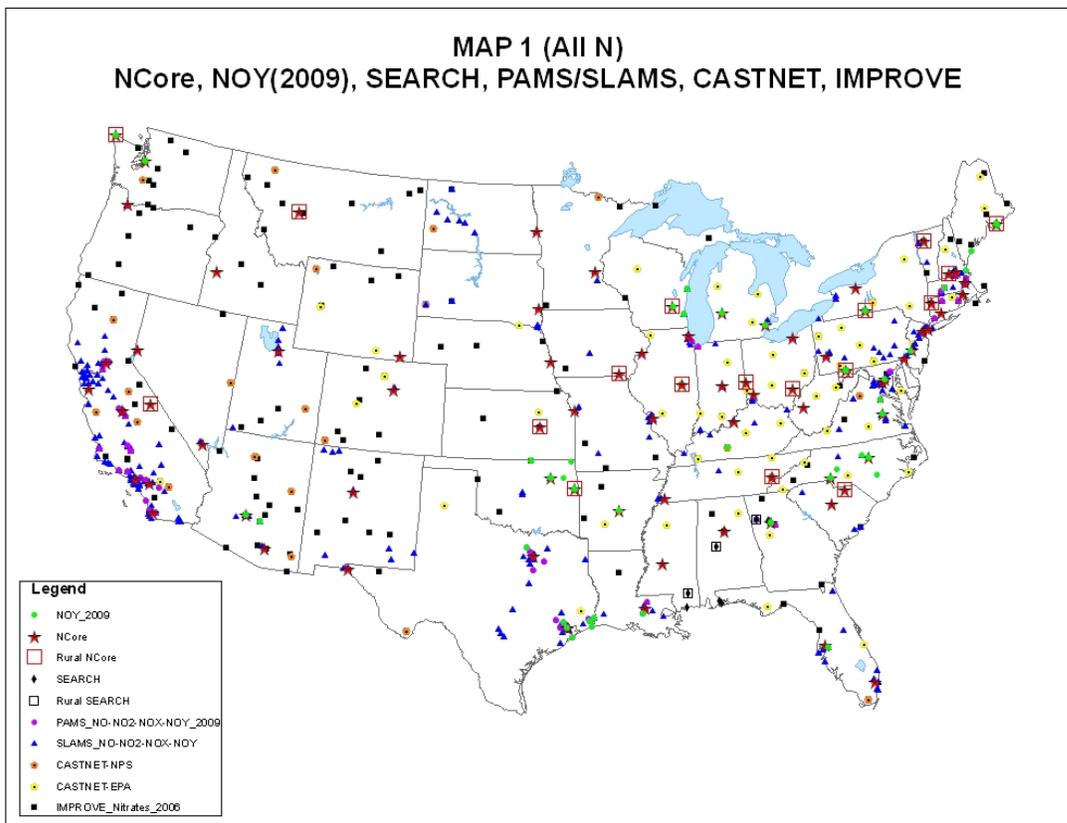


Figure 2-2.1 Routinely operating surface monitoring stations measuring forms of atmospheric nitrogen.

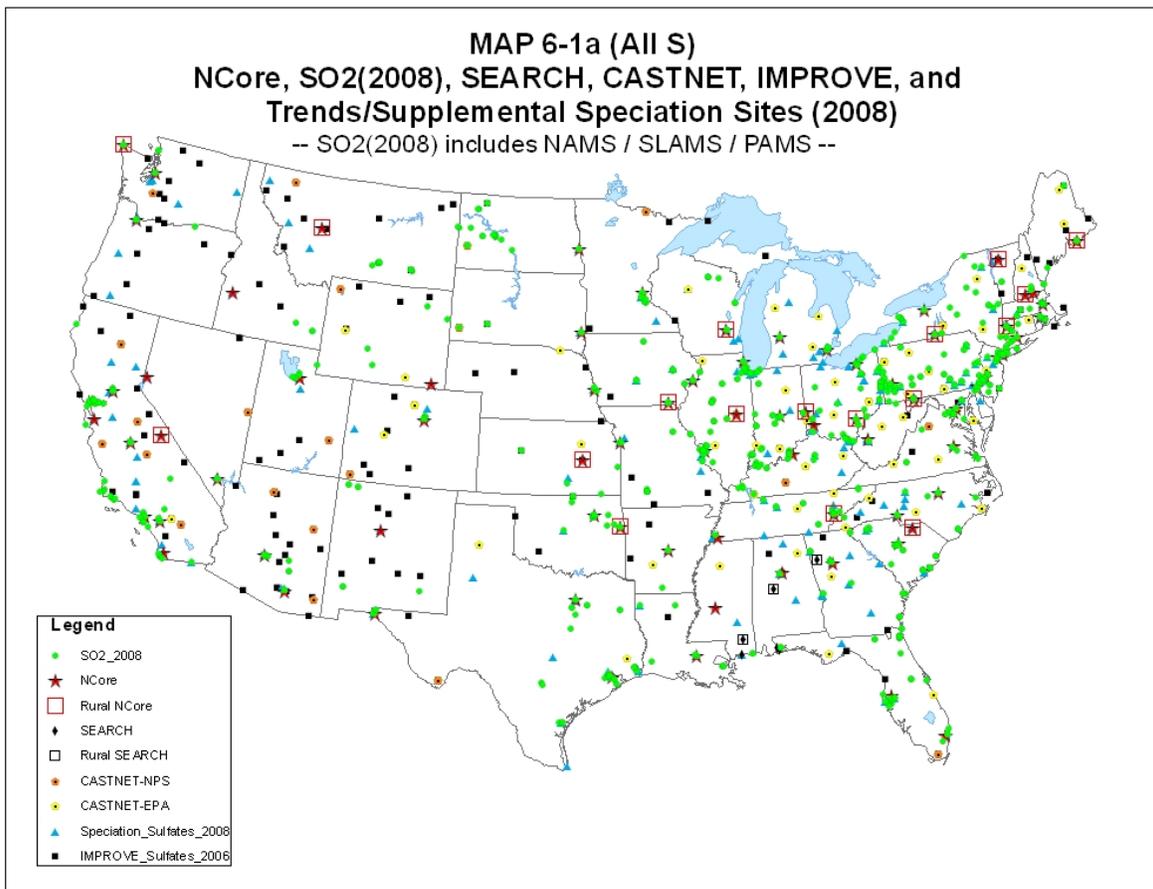


Figure 2-2.2 Routinely operating surface monitoring stations measuring forms of atmospheric sulfur. All site locations measure both SO₂ and sulfate except for the green SO₂ only sites.

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

The principal monitoring networks include the regulatory based State and Local Air Monitoring Stations (SLAMS) providing mostly urban-based SO₂, NO and NO_x, the PM_{2.5} chemical speciation networks Interagency Monitoring of Protected Visual Environments (IMPROVE) and EPA's Chemical Speciation Network (CSN) providing particle bound sulfate and nitrate, and the Clean Air Status and Trends Network (CASTNET) providing weekly averaged values of SO₂, nitric acid, and particle bound sulfate, nitrate and ammonium. The private sector supported South Eastern Aerosol Research and Characterization (SEARCH) Study network of 4-8 sites in the Southeast provides the only routinely operating source of true continuous NO₂, ammonia, and nitric acid measurements. SEARCH also provides PM_{2.5} size fractions of nitrate and sulfate. Collectively, the SLAMS, Photochemical Assessment Measurement Stations (PAMS), SEARCH and NCore networks will provide over 100 sites measuring NO_y (Figure 2-2.3). The NCore network (Scheffe et al., 2009) is a multiple pollutant network with co-located measurements of key trace gases (CO, SO₂, O₃, NO and NO_y), PM_{2.5} and PM_(10-2.5) mass and PM_{2.5} chemical speciation. Additional air pollutants, particularly volatile organic compounds (VOCs), will be measured at those sites that are part of the existing PAMS and National Air Toxics Trends (NATTS) platforms. The NATTS (EPA, 2008) include 27 stations across the U.S. that monitor for a variety of hazardous air pollutants and are intended to remain in place to provide a long-term record. Additional measurements of ammonia and possibly true NO₂ are under consideration. True NO₂ is noted to differentiate from the NO₂ determined through routine regulatory networks that have known variable positive bias for NO₂.

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

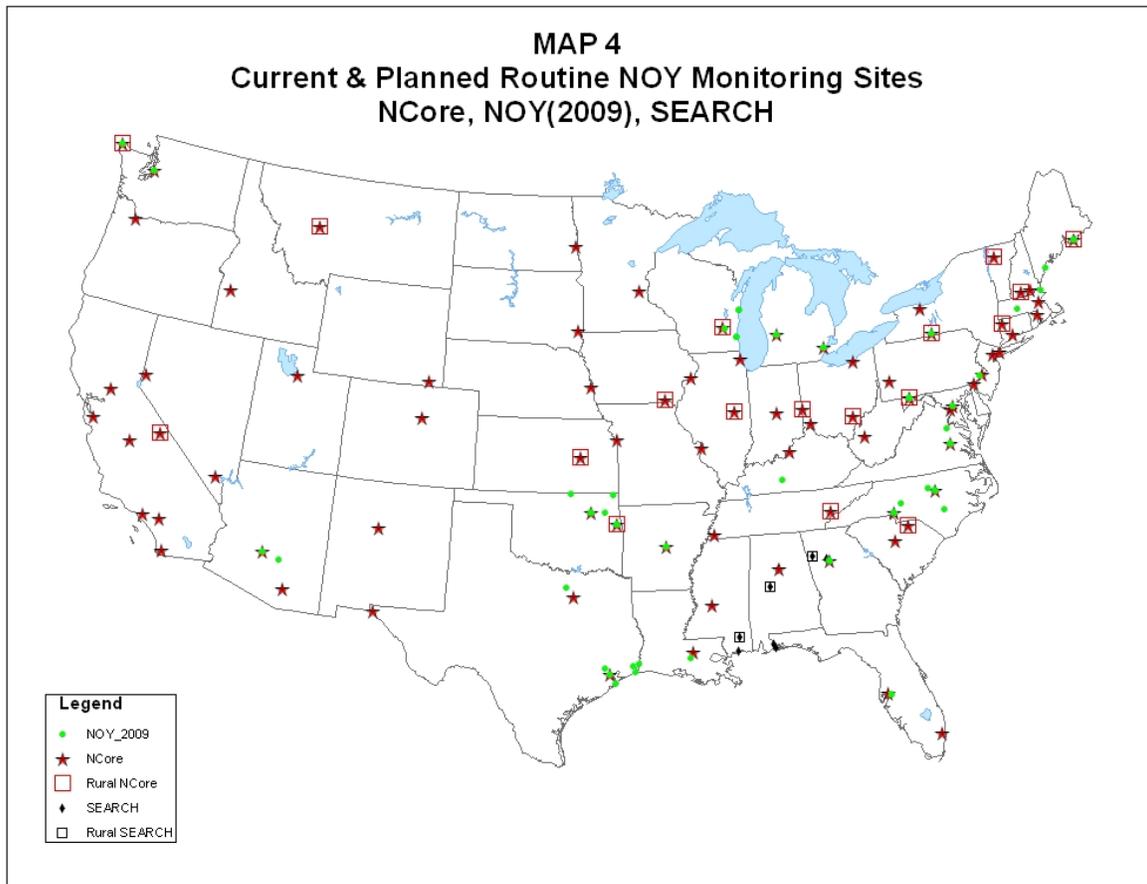


Figure 2-2.3. Anticipated network of surface based NO_y stations based on 2009 network design plans. The NCore stations are scheduled to be operating by January, 2011.

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

exception of the SEARCH network in the Southeast, there have been virtually no routine networks that measure ammonia until the recent addition of the AMON passive ammonia sampling network (Figure 2-2.4) as part of the NADP. EPA is considering adopting the AMON passive sampling techniques and other ammonia sampling options in the NCORE network. Ammonium is reported in EPA chemical speciation networks, although the values are believed to be biased low due to ammonia volatilization.

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

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

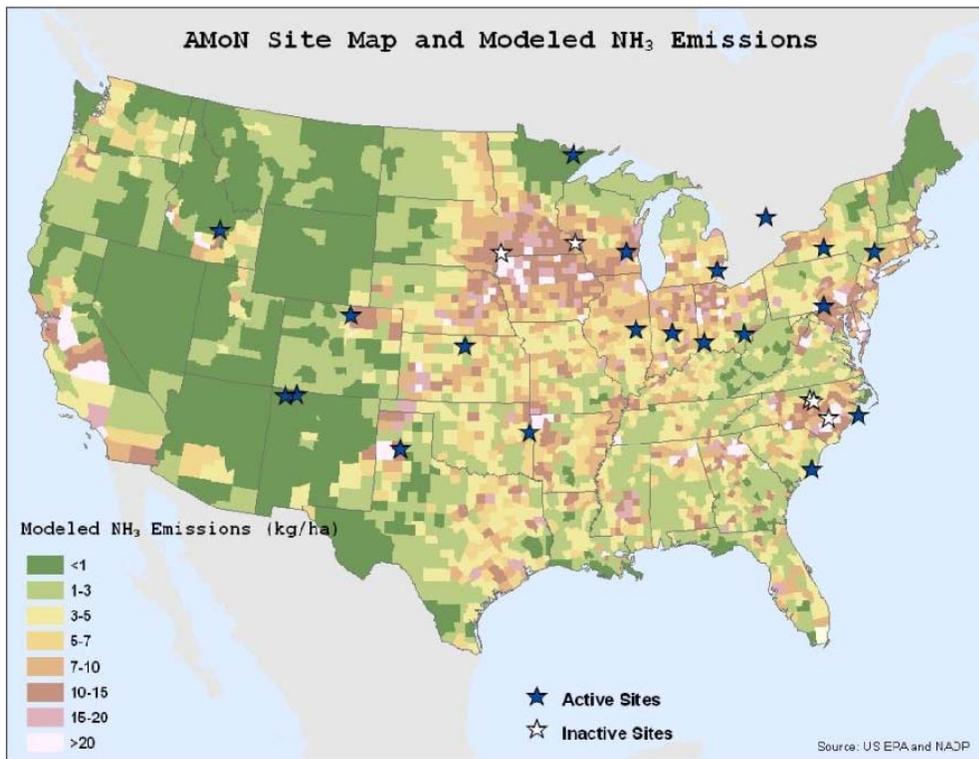


Figure 2-2.4. Location of NADP passive ammonia sampling locations for the AMON network (<http://nadp.sws.uiuc.edu/nh3net/>).

Of the currently operating monitoring networks, precipitation based sulfate, ammonium and nitrate measurements provided by the NADP are the most relevant measurements that would support the secondary standard as they provide atmospheric deposition inputs that drive ecosystem models, and NADP site locations generally include acid sensitive areas. However, there are significant gaps in ambient air (aerosols and gases) monitoring networks for the measurement of the likely ambient indicators of NO_y, SO₂, and SO₄. CASTNET filter packs provide the most relevant source of ambient sulfate (SO₄) measurements as the open inlet of the filter packs incorporates the full range of particle sizes that contribute to deposition. The SO₂ measurements from CASTNET represent about 10% of all SO₂ sites nationally, but are especially relevant based on their locations in rural and regional settings, although CASTNET is not as spatially extensive (breadth and resolution) as the NADP network of precipitation sites. Although CASTNET does provide measurements of total ambient nitrate, other oxidized nitrogen species constituting a more complete NO_y budget are not captured. In their current configuration, the State and local monitoring networks offer virtually no support for a secondary

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

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

2.2.2 Overview of CMAQ

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

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

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

The CMAQ model is a comprehensive, peer-reviewed (Aiyyer et al., 2007), three-dimensional grid-based Eulerian air quality model designed to simulate the formation and fate of gaseous and particle (i.e., particulate matter or PM) species, including ozone, oxidant precursors, and primary and secondary PM concentrations and sulfur and nitrogen deposition over urban, regional, and larger spatial scales (Dennis et al., 1996; U.S. EPA, 1999; Byun and Schere, 2006). CMAQ is run for user-defined input sets of meteorological conditions and emissions.

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

Model domain and grid resolution.

CMAQ modeling analyses were performed for a domain covering the continental United States, as shown in Figure 2-2.5 and Table 2-2.2. This domain has a parent horizontal grid of 36 km with two finer-scale 12 km grids over portions of the eastern and western U.S. The model extends vertically from the surface to 100 millibars (approximately 15 km) using a sigma-pressure coordinate system. Air quality conditions at the outer boundary of the 36 km domain were taken from a global model and did not change over the simulations. In turn, the 36 km grid was only used to establish the incoming air quality concentrations along the boundaries of the 12 km grids. Table 2-2.2 provides some basic geographic information regarding the CMAQ domains.

Table 2-2.2. Geographic elements of domains used in RFS2 modeling.

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

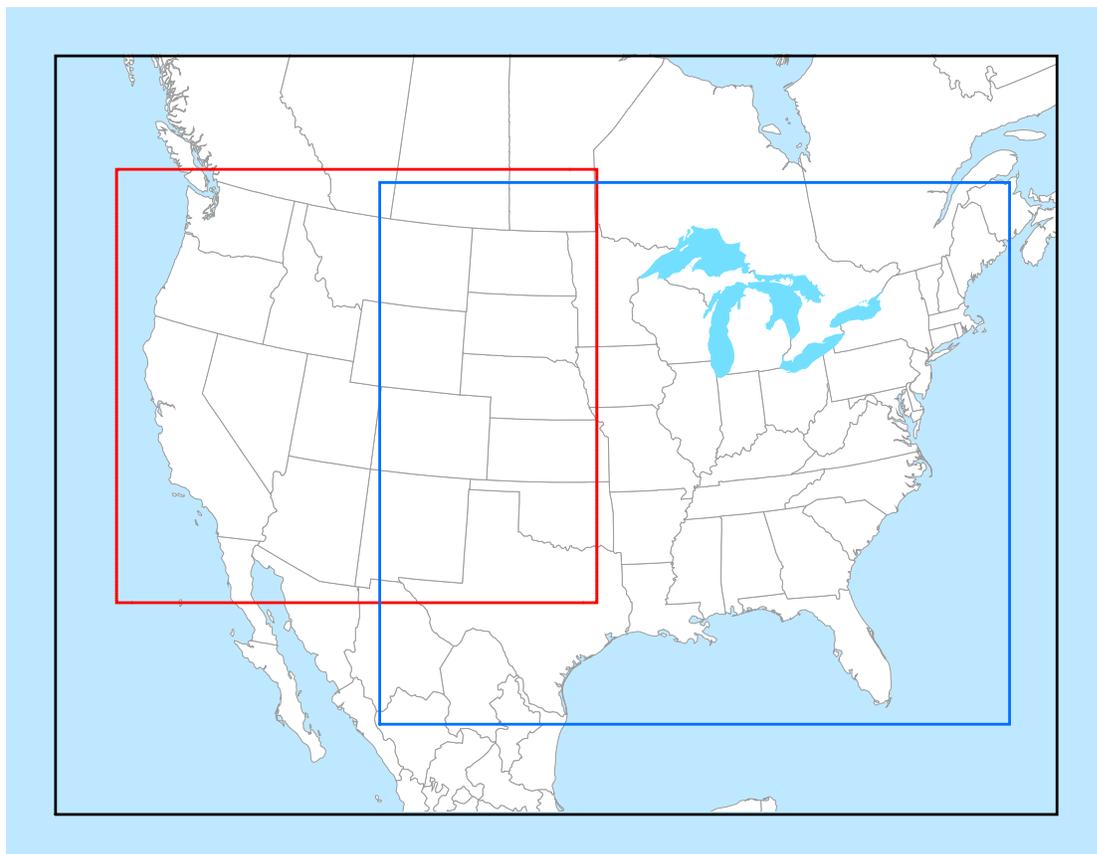


Figure 2-2.5. Map of the CMAQ modeling domain. The black outer box denotes the 36 km national modeling domain; the red inner box is the 12 km western U.S. fine grid; and the blue inner box is the 12 km eastern U.S. fine grid.

2.2.3 Overview of air quality using modeled and observed data

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

Nationwide maps of CMAQ-predicted 2005 annual average NO_Y , NH_X (NH_3 and NH_4), NH_3 , NH_4 , SO_X , SO_4 , and SO_2 are provided in Figures 2-2.6 through 2-2.12 respectively. Given the considerable gaps in air quality observation networks as discussed in the REA and ISA (EPA, 2008), modeled concentration patterns are used here to illustrate national representations

of current air quality conditions for nitrogen and sulfur. The 2005 model year reflects the most recent available simulation for inclusion in this policy assessment. In addition, Figures 2-13 and 2-14 provide maps of 2005 annual average SO_2 and SO_4 , respectively based on CASTNET observations. Site specific annual average 2005 NO_Y measured concentrations at SLAMS (Figure 2-2.15) are typically are less than 40 ppb. The spatial patterns for the 2005 modeled and observed NO_Y , NH_x , and SO_2 concentrations are similar to the 2002 CMAQ-based maps provided in the REA, largely capturing the influence of major emissions patterns (Figures 2-2 – 2-4) throughout the nation. The NO_Y patterns (Figure 2-2.6) reflect the distribution of NO_x emissions power generation and widely dispersed transportation sources with a spreading into more rural locations associated with transformation of NO_x to more aged NO_Y species such as PAN and nitric acid, discussed in more detail in section 2-3. Ammonia and ammonium concentration patterns (Figures 2-9 – 2-11) are influenced strongly by the ammonia emissions distribution, with marginal spreading associated with the formation of NH_4 . The NH_x fields are more strongly influenced by source location, relative to sulfur, based on the fast removal of atmospheric ammonia through deposition. However, recent incorporation of ammonia bi-directional flux treatment (Appendix F) does reduce NH_3 spatial gradients. A spreading of the oxidized sulfur fields (Figures 2-13 and 2-14), relative to SO_2 , is consistent with sulfate transformation and associated air mass aging and transport. Note that SO_2 is the dominant contributing species in the mix of SO_2 and particulate SO_4 with the most elevated levels in proximity to the Ohio River valley.

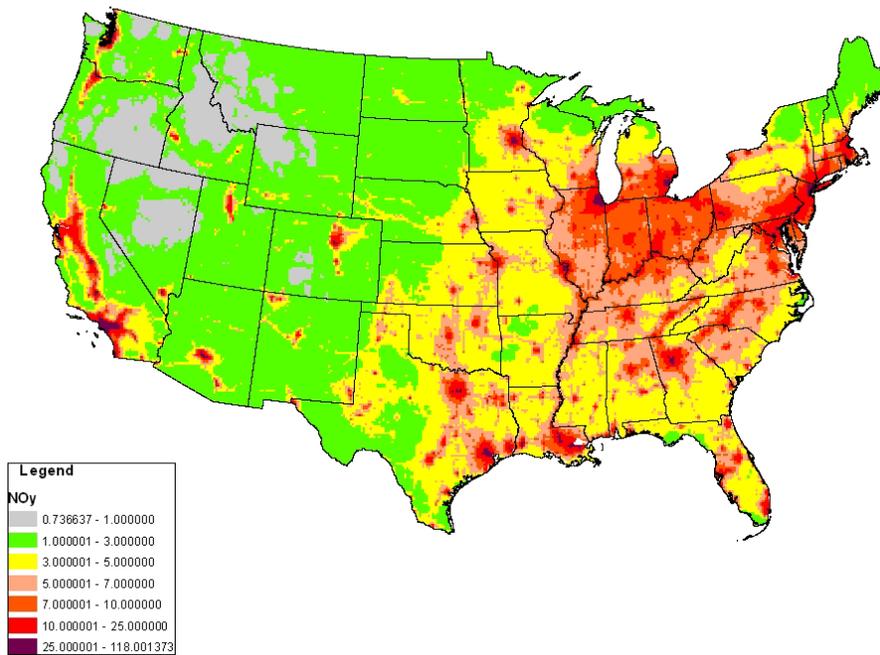


Figure 2-2.6. 2005 CMAQ modeled annual average NO_y (ppb; see Table 2-1 for unit conversions).

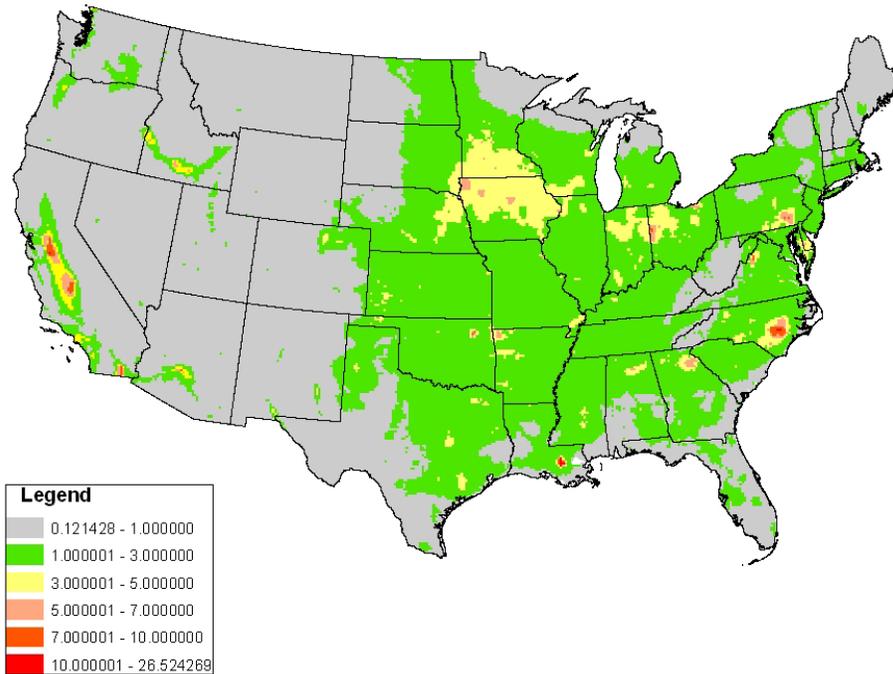


Figure 2-2.7. 2005 CMAQ modeled annual average total reduced nitrogen (NH_x) (as ug/m³ nitrogen – see Table 2-1 for unit conversions)

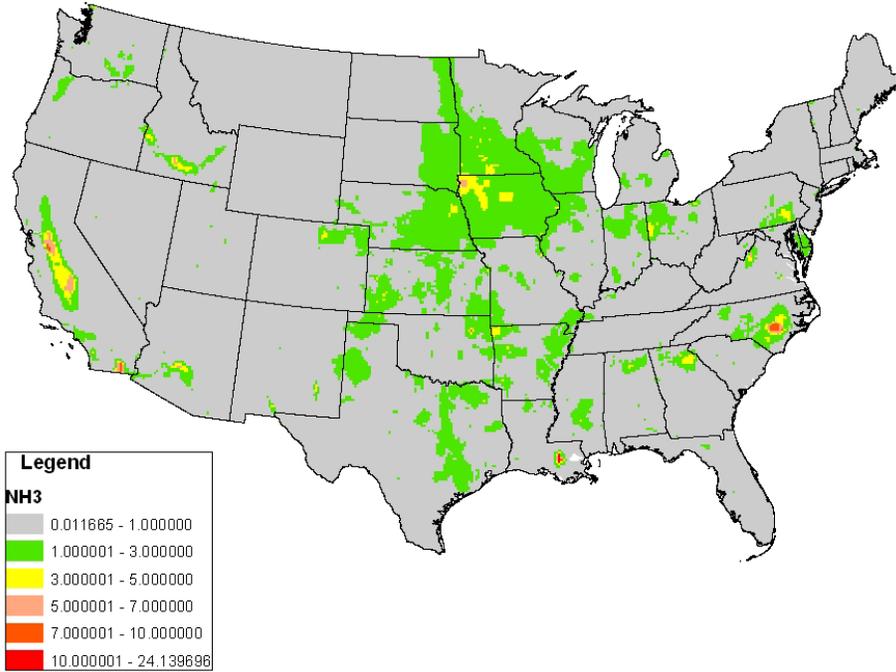


Figure 2-2.8. 2005 CMAQ modeled annual average total reduced nitrogen (NH₃) (as ug/m³ nitrogen – see Table 2-1 for unit conversions).

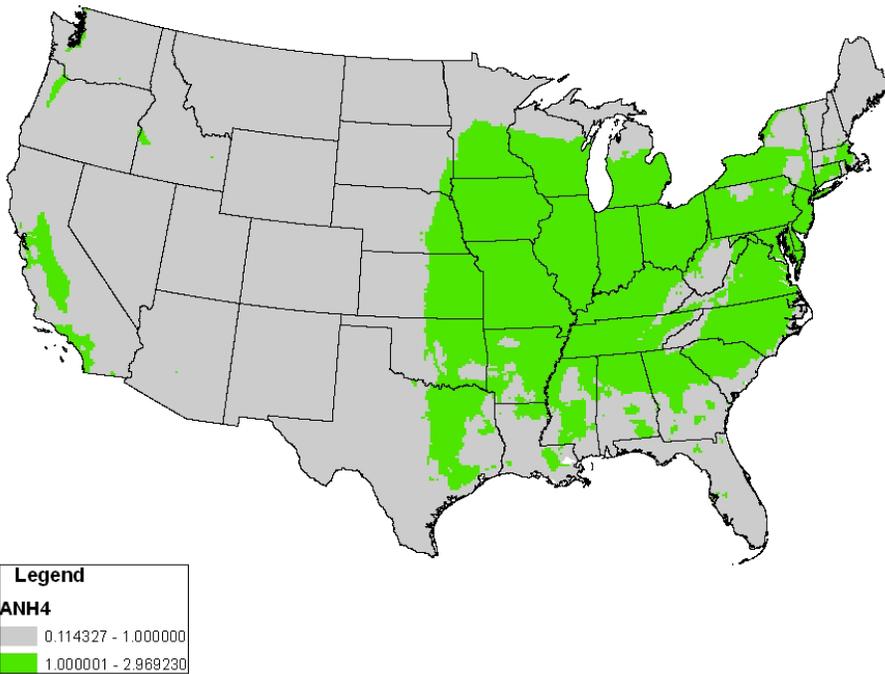


Figure 2-2.9. 2005 CMAQ modeled annual average ammonium, NH₄, (as ug/m³ N; see Table 2-1 for unit conversions)

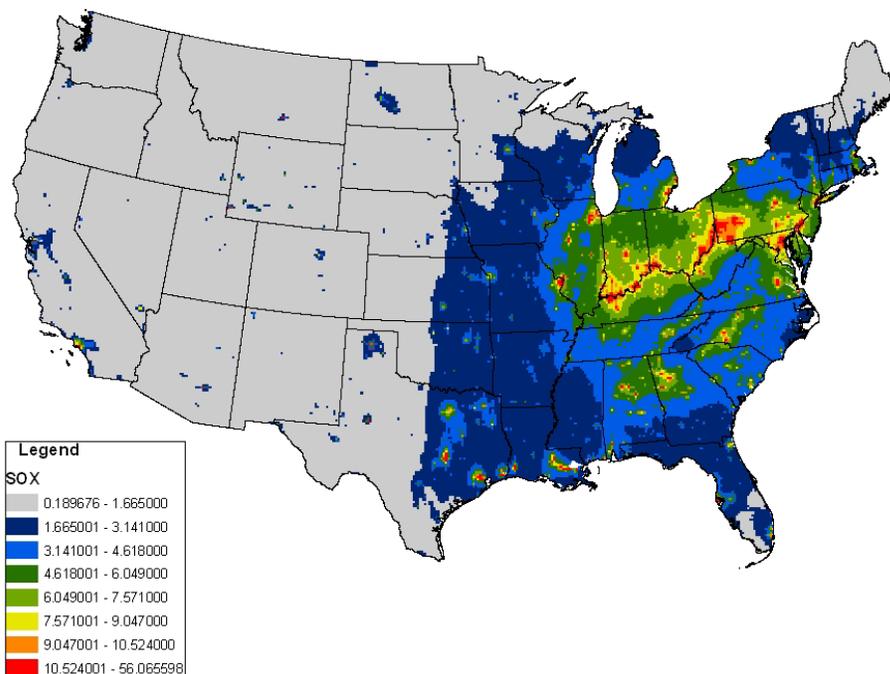


Figure 2-2.10. 2005 CMAQ modeled annual average SO_x, (as ug/m³ S from SO₂ and SO₄; see Table 2-1 for unit conversions).

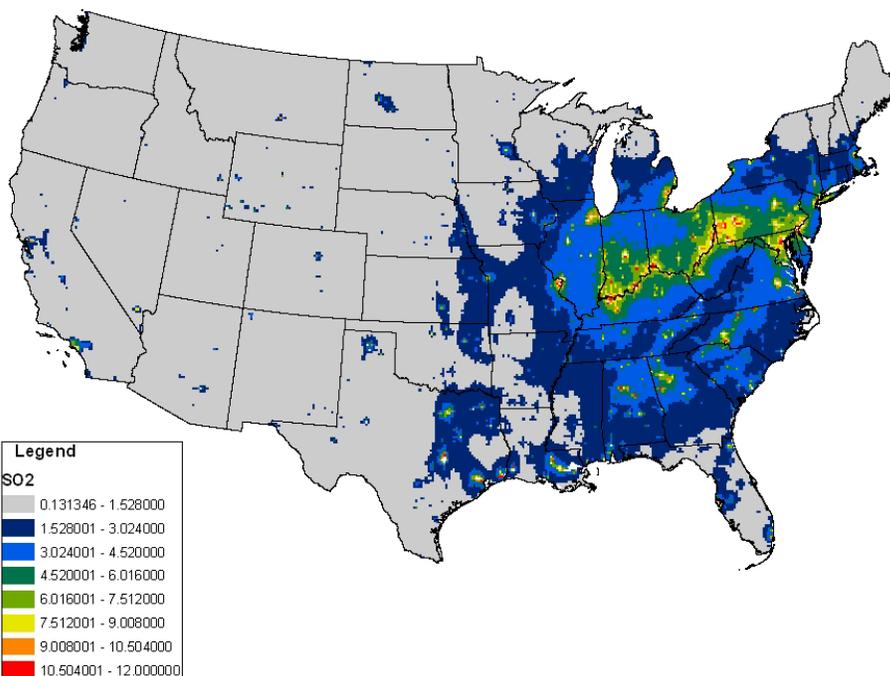


Figure 2-2.11. 2005 CMAQ modeled annual average SO₂ (as ug/m³ S; see Table 2-1 for unit conversions).

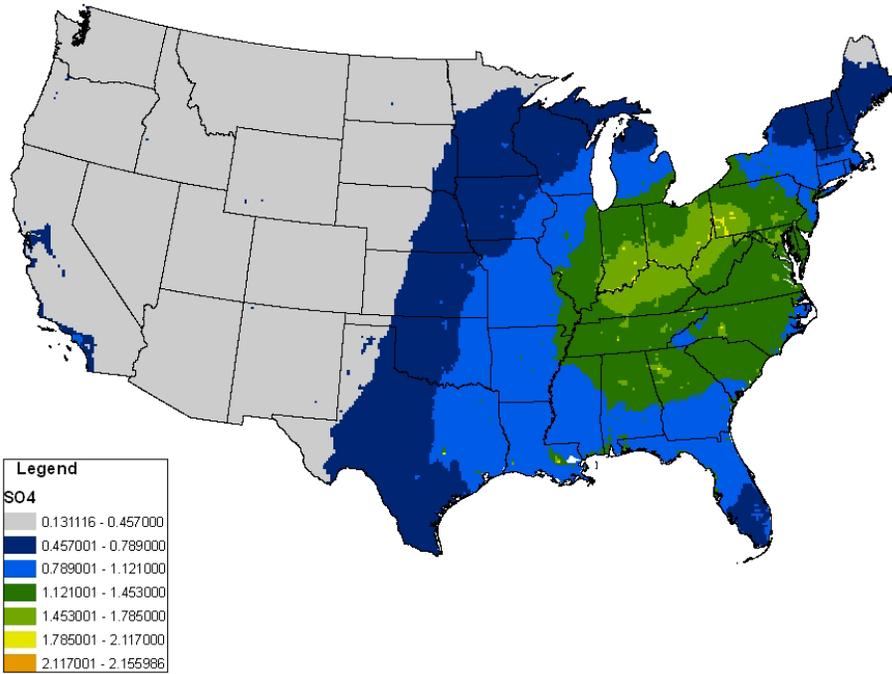


Figure 2-2.12. 2005 CMAQ modeled annual average SO₄ (as ug/m³ S; see Table 2-1 for unit conversions).

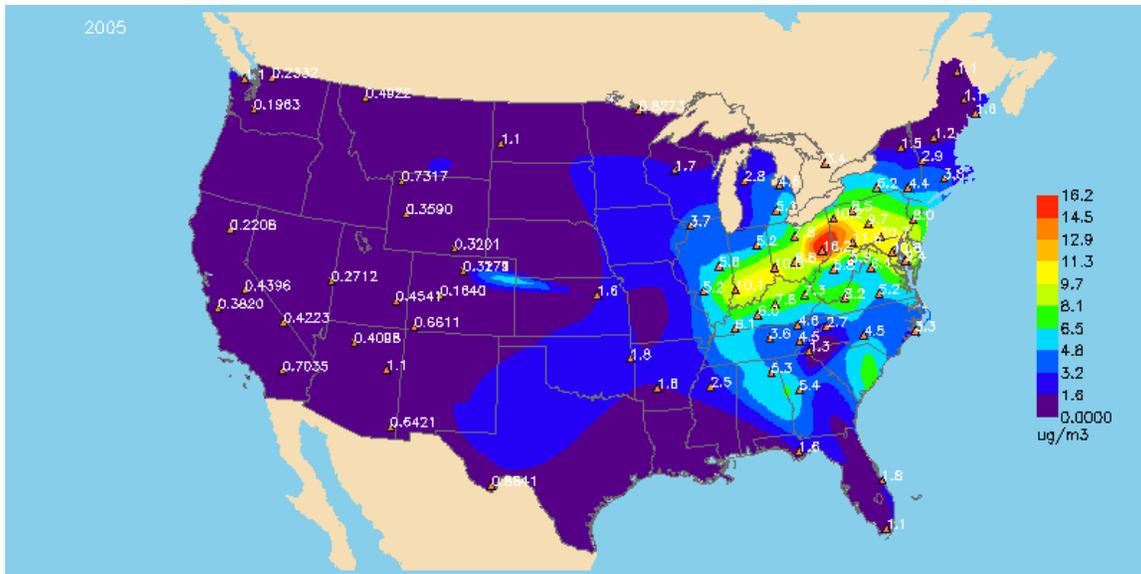


Figure 2-2.13. 2005 annual average sulfur dioxide concentrations (total mass) based on CASTNET generated by the Visibility Information Exchange Web System (VIEWS) (see Table 2-1 for unit conversions).

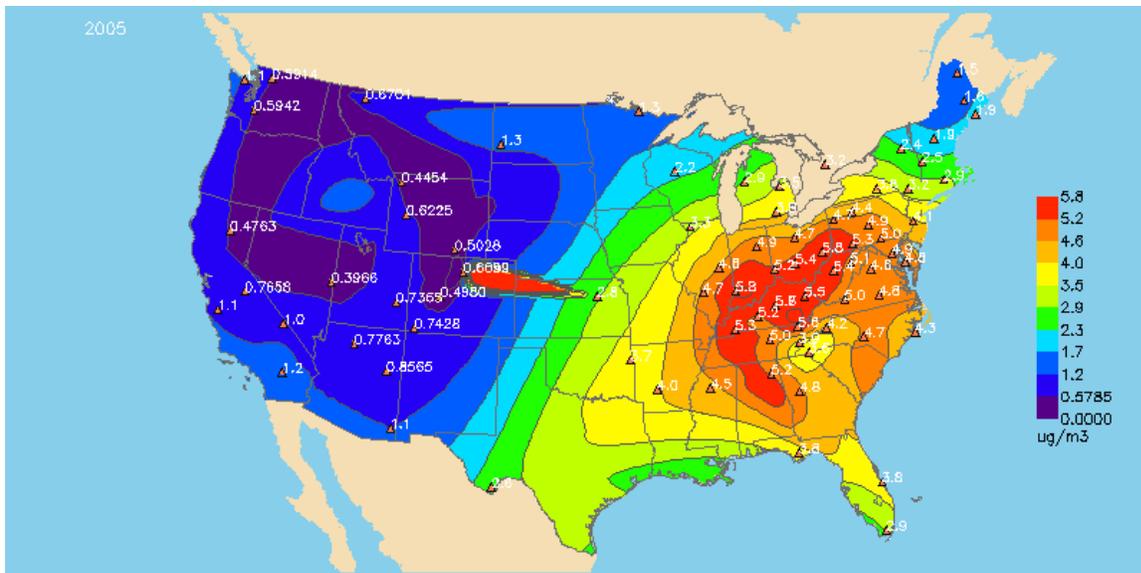


Figure 2-2.14. 2005 annual average sulfate concentrations (total mass) based on CASTNET generated by the Visibility Information Exchange Web System (VIEWS). [interpolating relative sparse data can produce unrealistic concentration plumes as demonstrated in the central U.S.] (see Table 2-1 for unit conversions).

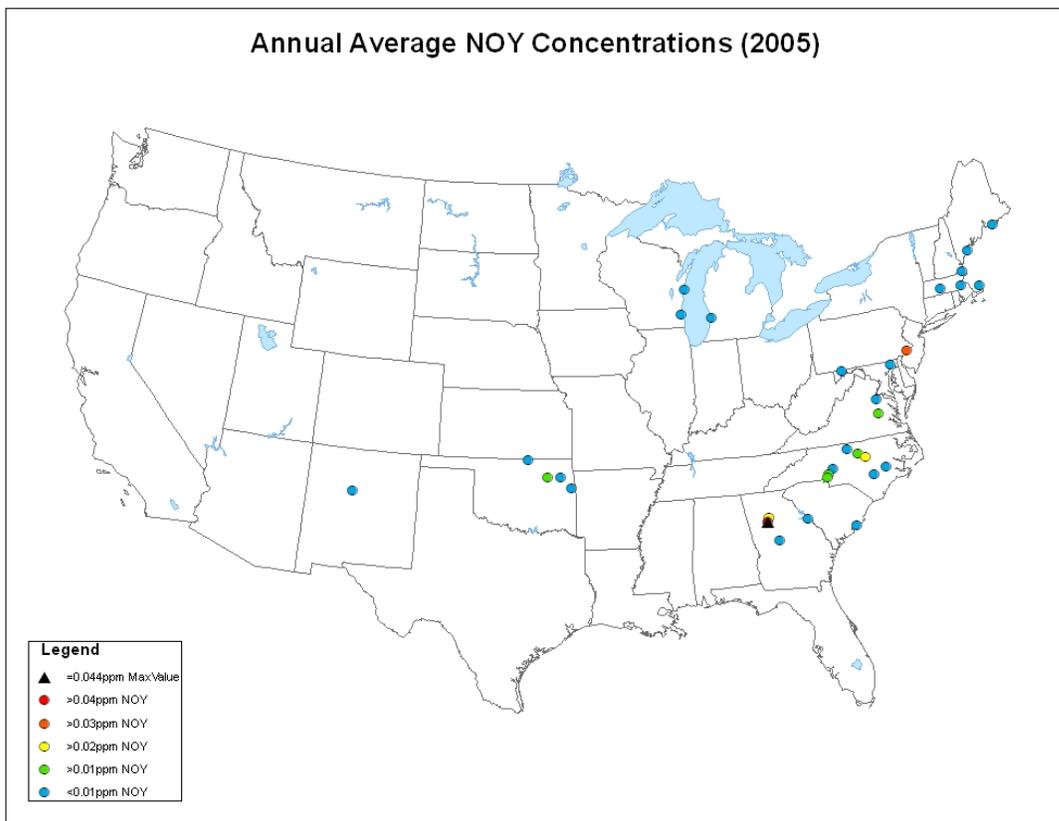


Figure 2-2.15. Annual average 2005 NO_y concentrations from reporting stations in the Air Quality System (AQS). (see Table 2-1 for unit conversions).

2.3 Characterizing deposition through monitoring and models

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

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

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

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

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

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

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

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

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

2.3.1 Current patterns of dry and wet deposition

The National Atmospheric Deposition Program (NADP) includes approximately 250 sites (Figure 2-3.1) across the U.S. providing annual total wet deposition based on weekly averaged measures of wet deposition of nitrate, ammonium, sulfate and other ions based on the concentrations of these ions in precipitation samples. Meteorological models have difficulty in capturing the correct spatial and temporal features of precipitation events, raising the importance of the NADP as a principal source of precipitation chemistry. The NADP has enabled several organizations to participate in a measurement program with a centralized laboratory affording measurement and analysis protocol consistency nationwide. Virtually every CASTNET site is located at an NADP site and the combined NADP/CASTNET infrastructure is a starting point for discussions addressing future NO_x and SO_x monitoring needs. Analysis of organic bound nitrogen recently has been added to the NADP suite of parameters. Consideration might be given to adding NADP sites in locations where ambient air monitoring is conducted to assess compliance with a secondary NO_x / SO_x standard. For consistency, we use CMAQ developed national maps of total deposition. Additional NADP maps of wet deposition are available at <http://nadp.sws.uiuc.edu/>.

Ammonium ion wet deposition, 2005

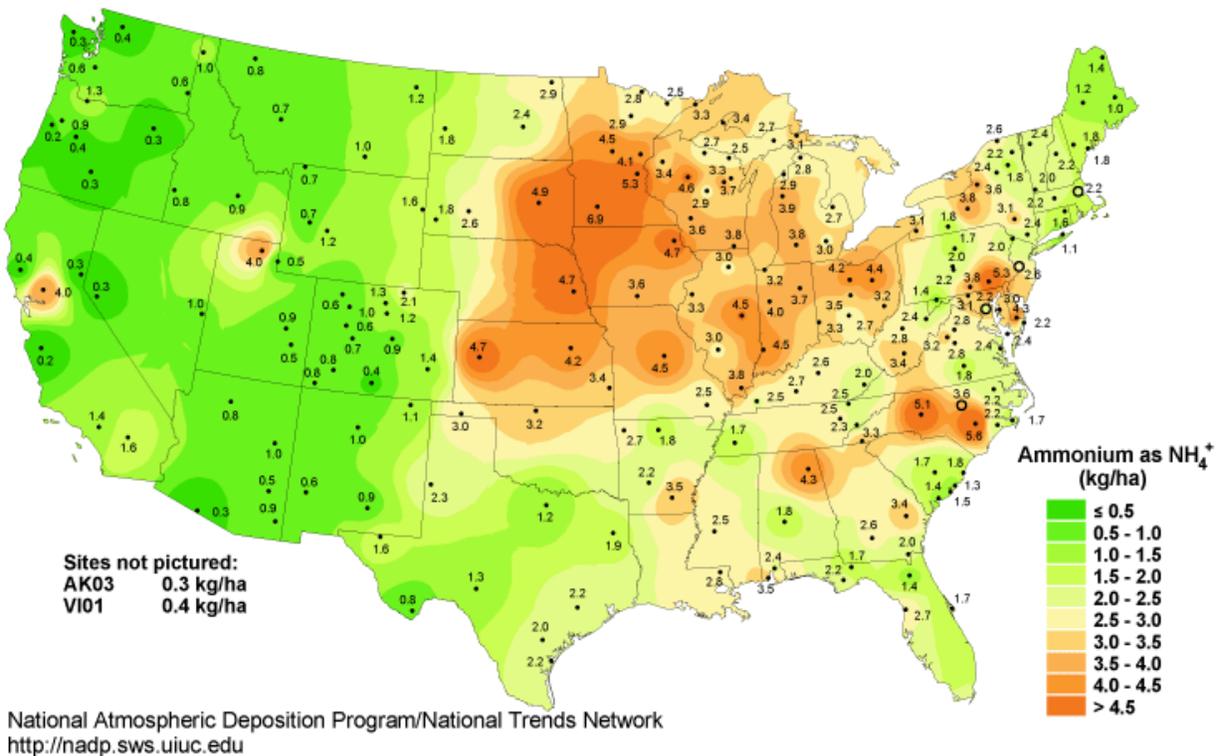


Figure 2-3.1. Location of approximately 250 National Atmospheric Deposition Monitoring (NADP) National Trends Network (NTN) sites illustrating annual ammonium deposition for 2005. Weekly values of precipitation based nitrate, sulfate and ammonium are provided by NADP.

2.3.2 Characterizing deposition through CMAQ

Total deposition for nitrogen, reduced nitrogen, the ratio of reduced to total nitrogen and sulfur (Figures 2-3.2 and 2-3.5) basically follow the patterns of ambient air concentrations described earlier. The contribution of reduced nitrogen to total nitrogen deposition (Figure 2-3.4) illustrates the strong influence of agricultural based ammonia emissions, particularly in upper midwest and eastern North Carolina. These maps represent the deposition values used in the calculations of areas likely not meeting alternative standards in section 7.5.

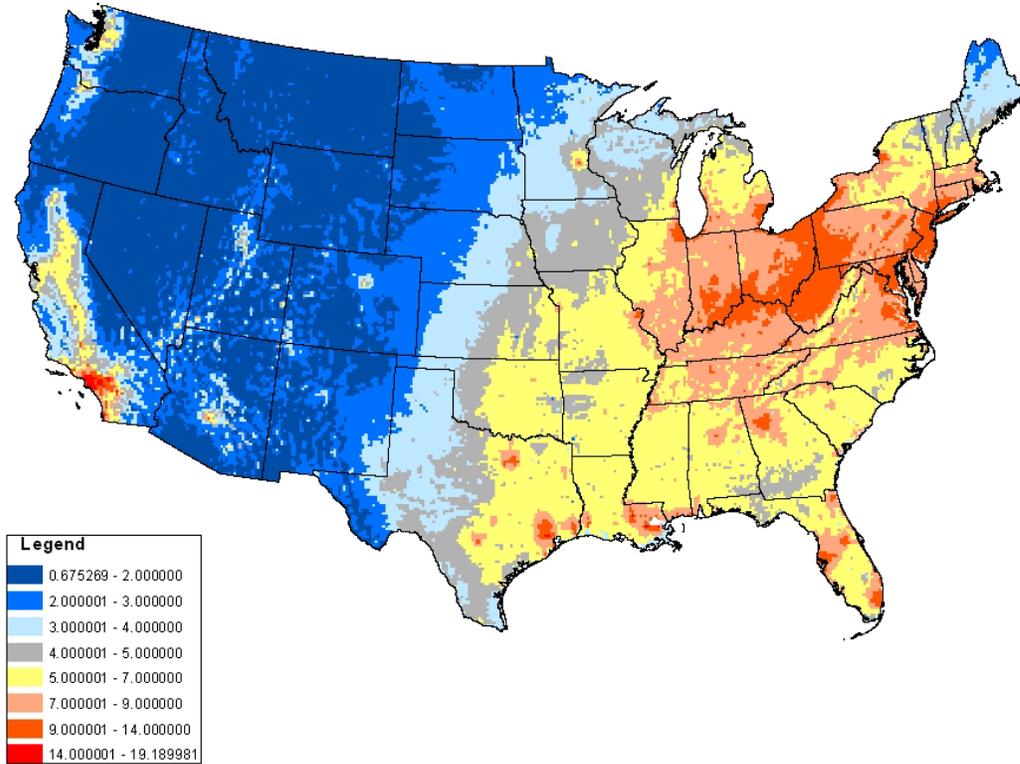


Figure 2-3.2. 2005 CMAQ modeled oxidized nitrogen deposition (kgN/ha-yr). (see Table 2-1 for unit conversions).

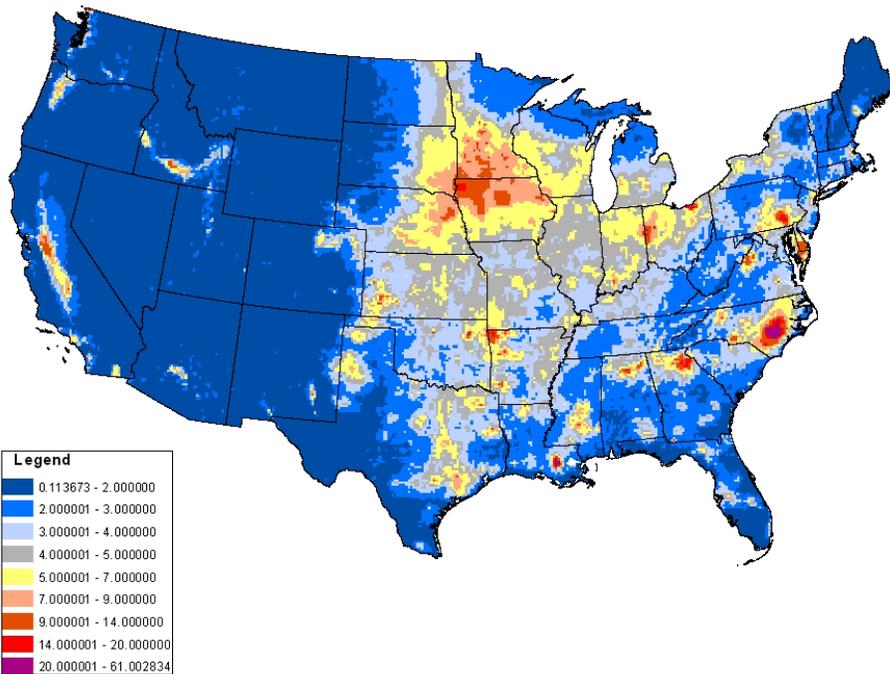


Figure 2-3.3. 2005 CMAQ modeled reduced nitrogen deposition (kgN/ha-yr). (see Table 2-1 for unit conversions).

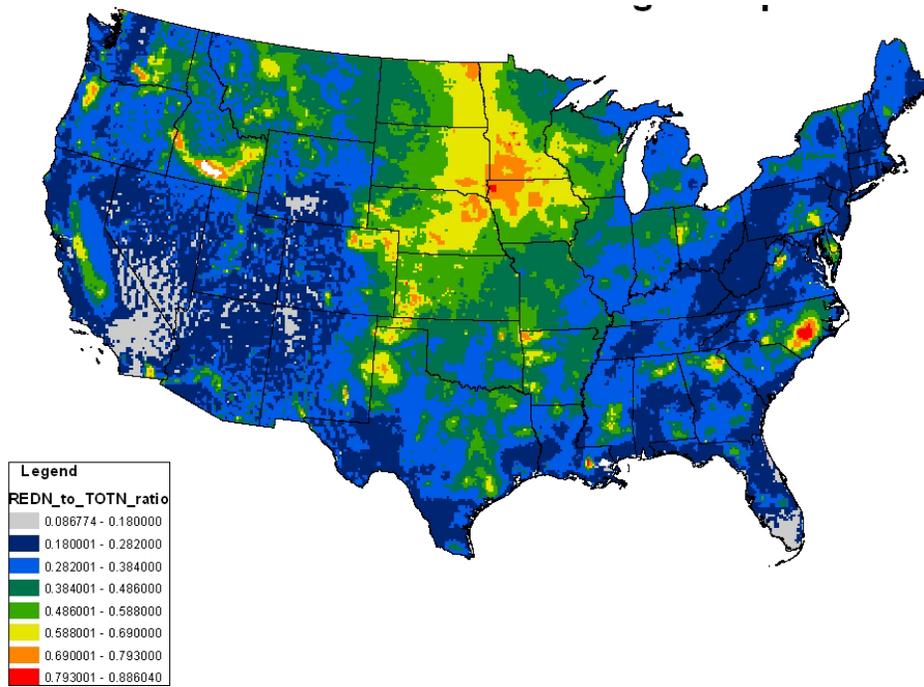


Figure 2-3.4. 2005 CMAQ modeled ratio of reduced to total nitrogen deposition.

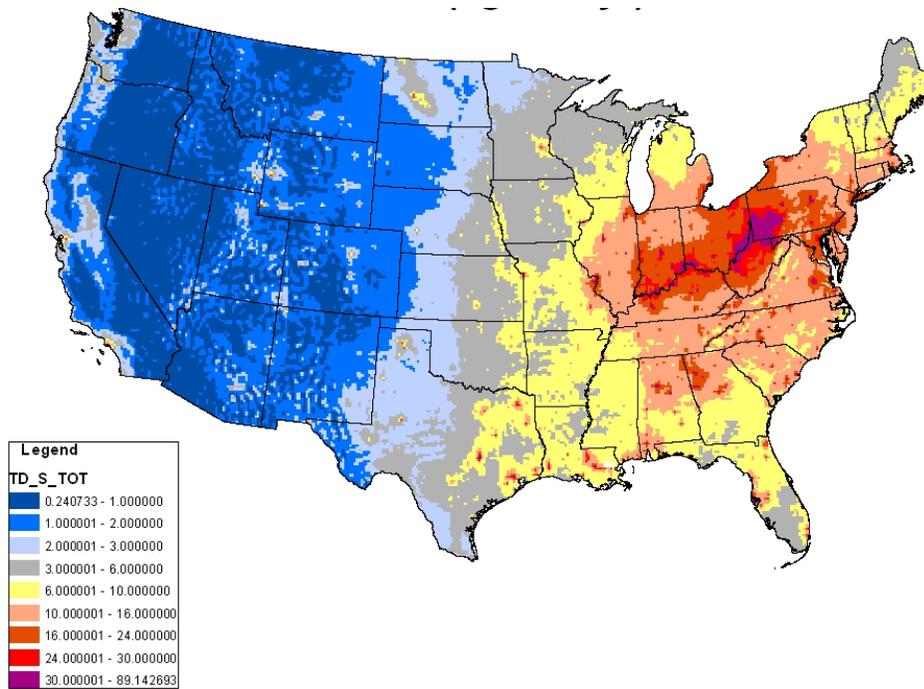


Figure 2-3.5. 2005 CMAQ modeled oxidized sulfur deposition (kgS/ha-yr). (see Table 2-1 for unit conversions).

2.3.3 Relationships between patterns of ambient concentrations and deposition

The development of an aquatic acidification standard relies on relationships between air concentrations and deposition. Consequently, it is informative to understand some of the basic patterns and relationships between concentrations and deposition of SO_x and NO_y species. While there are the obvious first order associations that we see between concentration patterns (Figures 2-2.6 to 2-2.12) and deposition (Figures 2-3.2 to 2-3.5), as well between emissions and concentrations, there exist marked differences between concentration and deposition at the individual species level. While the differences between emissions and air concentrations can generally be attributed to a plethora of atmospheric chemistry and transport mechanisms that change the nature and location of emitted species, the differences between concentration and deposition are all about the inherent characteristics of each species and how various meteorological and surface attributes (meaning landtypes, water systems, vegetation, suspended cloud and rain droplets) influence the transfer of a species to a (or through and within) a surface. This section describes these relationships and provides background for the discussion on the selection of ambient air indicators (section 7.1).

NO_y species

Air quality models and deposition models that use direct observations calculate deposition on a species by species basis to account for differences in deposition velocities. Consequently, the relative fractional contributions of individual NO_y or SO_x species to deposition or concentration is influenced by the differences in species deposition velocities. For example, nitric acid with a high deposition velocity, would exhibit a larger relative contribution to overall deposition compared to ambient concentrations in a particular area (Figures 2-3.6 and 2-3.7). The dominant ambient air NO_y species are NO, NO₂, HNO₃, P-NO₃ and PAN. Near source urban environments typically have a relatively higher fraction of NO_x (NO and NO₂) compared to the products of NO_x reactions, nitrates and PAN, which are relatively more dominant in rural locations (Figures 2-3.7 – 2-3.10).

Sulfur Species

The use of SO₂ and SO₄ does reflect the use of individual where it is practical to measure each species independently. Although sulfur dioxide and particulate sulfate contribute approximately 60 and 40 %, respectively, to ambient SO_x concentrations, sulfur dioxide is the dominant contributor to SO_x deposition (Figure 2-3.11), which is consistent with CASTNET

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

2.3.4 Monitoring Considerations

The differences in the relative patterns between ambient air and deposition on a species-by-species basis illustrate a number of challenges and considerations in developing a monitoring strategy. It is clear in the Adirondacks and Shenandoah areas, for example, that nitric acid is the most dominant contributing species from a deposition perspective (Figure 2-3.6), with significant contributions from particulate nitrate, PAN and NO₂. The original source of emissions (NO accounts for 90-95% of all emitted NO_x) ultimately is transformed in the atmosphere and provides very small fraction of oxidized nitrogen in ambient air and deposition in rural environments. The combination of nitric acid and particulate nitrate consistently contribute greater than 50% of the oxidized nitrogen dry deposition load, whereas PAN and NO₂ contribute roughly 15-25% of the deposition load.

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

of the deposited NO_Y is accounted for by total nitrate combined with the availability of reliable total nitrate measurements (the sum of nitric acid and particulate nitrate) through CASTNET, a total nitrate measurement may be adequate for deposition based assessments.

These patterns suggest the possibility of using total nitrate as a key indicator for acidifying deposition contributions associated with oxides of nitrogen. However, a nitrate observation alone would miss a considerable fraction of the ambient NO_Y burden reflected in significant levels of NO_2 and PAN. Characterization of NO_2 deposition is an area requiring further refinement especially considering that NO_2 is a significant component of total oxidized nitrogen. Zhang et al. (2005) suggest that NO_2 contributes up to 36% of dry NO_Y deposition in rural Eastern Canadian locations, and suggest, based on observational evidence (Figure 2-3.7), that in some locations NO_2 deposition may be similar to nitric acid contributions.

Another way of addressing the relative benefit of using part of the NO_Y mix relative to total NO_Y in regard to deposition is to probe the dynamic response of changes in oxidized nitrogen deposition to changes in ambient concentrations NO_Y and nitric acid. Dynamic response refers to sensitivity of the ambient to deposition response with respect to changes in NO_X emissions, which is relevant to air quality management as ambient indicators are used to assess if an area meets or exceeds a target value in current and future time frames. While such a response to emission changes may be linear or non-linear, the details of which are encoded in chemical transport air quality models like CMAQ, typically there is a directional relationship between the change in the precursor emissions and the target species of interest. By extension, one would expect that a significant change in emissions of NO_X would lead to a change both in the ambient and deposition fields of NO_Y species, recognizing that NO_Y species all evolve from NO_X emissions, which is dominated by nitrogen oxide, NO . We can apply this reasoning to the consideration of using HNO_3 as a more narrowly defined indicator, relative to NO_Y . A 2005 base case and projected 2030 CMAQ simulation, with roughly 50% NO_X and SO_X reductions, respectively, are used to illustrate the relationship of HNO_3 and NO_Y concentration changes to changes in NO_Y deposition (wet and dry) which address the question: Does the indicator respond in a manner directionally similar to deposition over periods of significant emissions reductions? Based on this paired set of current and future projection scenarios, ambient NO_Y more closely captures the change in NO_Y deposition, compared to using ambient HNO_3 as an indicator (figure 2-3.12).

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

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

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

As discussed earlier, two - five locations nationally, in airsheds with different atmospheric chemistries, that sample not only for the NAAQS indicator NO_y but for the suite of major NO_y species as well; HNO₃, p-NO₃, PAN, NO₂, and NO as discussed earlier. Not only is this important from a modeling and process diagnosis perspective, but it is especially useful in the introduction of new measurements that have a limited track record to provide insight into

instrument performance. In the case of NO_Y , it is even more relevant since there effectively are no standards that explicitly challenge instrument accuracy given the highly variable nature of NO_Y species distribution and the instability associated with mixing NO_Y gases. This quality assurance issue is analogous to $\text{PM}_{2.5}$ where aerosol standards are not available and measurement accuracy is judged against periodic challenges relative to a “gold standard” instrument. Reduced nitrogen measurements of ammonia and ammonium ion are recommended at all locations with FRM/FEM instruments based on the need to support the AAPI as discussed above.

Sampling frequencies

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

present challenges in that they are not routinely sampled and analyzed for, and the combined quantity, NH_x is of interest. Because NH_x is of interest, some of the problems of volatile ammonia loss from filters may be mitigated. However, for model diagnostic purposes, delineation of both species at the highest temporal resolution is preferred.

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

Spatial scales

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

Critical load models applied for the purposes of this standard would be based on annual averages, which would effectively serve to dampen much of the spatial variability. Furthermore, the development of an area-wide depositional load tradeoff curve implies focus on region wide characterization. Toward that end, CMAQ concentration fields will provide insight into the likely spatial representativeness of monitors leading to efficient application of monitoring resources. For example, the CMAQ based spatial coefficient of variation (standard deviation/mean) of oxidized nitrogen in the Adirondacks was 1.46%. Improved dry deposition estimates will result from enhancements of ambient monitoring addressing the N/S secondary

standards as each additional location could serve a similar role that existing CASTNET sites provide in estimating dry deposition.

Candidate monitoring methods

Ambient NO_y, SO₂ and particulate sulfate (SO₄) concentrations are likely candidates for ambient air indicators (section 7.1). All of these indicators are measured in different places within the current routine monitoring networks. Traditionally, Federal Reference or Equivalency Method (FRM/FEM) status of measurement techniques is used for estimating air concentrations for NAAQS comparisons. A FRM for SO₂ exists, but not for NO_y or SO₄. Only recently have NO_y measurements, which historically were viewed as research venue measurements, been incorporated as “routine” observations, partly as a result of the NCore program. Particulate SO₄ is measured at over 500 sites nationally, and there is a general consensus that methods available are reliable and provide consistent data.

Particulate-SO₄. Particulate sulfate (p-SO₄) has been measured for several years in the IMPROVE, CASTNET and EPA CSN networks. The nation has over 500 24-hour average, every third day sulfate measurements produced by the PM_{2.5} speciation networks (IMPROVE and EPA CSN) and nearly 80 CASTNET sites that provide continuous weekly average samples of sulfate with an open inlet accommodating all particle sizes. As discussed above, particle size diameters increase beyond 2.5 μ should be accounted for in deposition based assessments, perhaps ruling out the use of PM_{2.5} data serving as indicators for a NO_x/SO_x secondary standard.

The routinely operating methodology for p-SO₄ is based on an integrated (i.e., time averaged over several hours or days) sample collection on a Teflon filter followed by ion chromatography (IC) detection in the laboratory. Two major variations of this approach are applied in the PM_{2.5} speciation (exclusion of particles larger than 2.5 μ and 24-hour collection typically every third day) and CASTNET (weekly average integrated sampling all year with an open inlet to include all size fractions). There are additional variations related to inlet design and flow characteristics of PM_{2.5} speciation samplers in which two designs are prevalent in the networks: (IMPROVE and EPA CSN SASS samplers). These variations are considered minor as sulfate species (dominated by ammonium sulfate) typically are not subject to major sampling artifacts associated with volatilization or condensation. The difference in inlets (open vs. 2.5 μ) is perceived by some as not an issue of concern as 80 - 90 % of the PM sulfate mass is distributed

in size fractions less than 2.5 μ . However, the higher deposition velocities associated with larger diameter particles argue for including all size fractions as discussed above. Continuously operating in-situ sulfate instruments that allow for hourly, or less, data reporting are available. However, the limited deployment (less than 20 sites nationally) of these instruments combined with the 2.5 μ inlet cutoff configuration preclude consideration at this time.

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

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

NO_y. In principle, measured NO_y is based on catalytic conversion of all oxidized species to NO followed by chemiluminescence NO detection. While there are caveats associated with instrument conversion efficiency and possible inlet losses, the technique is considered adequate and routinely operational. Approximately 25 sites (out of a planned 75) in EPA's NCore network are operating NO_y instruments, and additional sites are operated in SEARCH,

CASTNET and other programs. NO_Y measurements are nearly continuous, reporting at hourly intervals providing far greater temporal information compared to filter or denuder based methods.

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

One of the challenges associated with specifying performance attributes for p-SO_4 and NO_Y is the lack of specific challenge standards. For example, instruments measuring discrete gases such as ozone or nitrogen oxide can be challenged by comparing an instrument's reading when measuring known concentrations of gases which are readily provided for single gas concentrations. Particle standards are not available. NO_Y performance typically is challenged by known mixtures of NO_2 , and occasionally with N-propyl nitrate, which only addresses part of the spectrum of nitrogen species in an NO_Y mix. Consequently, instrument performance in EPA's national networks for aerosol mass is quantified in terms of bias and precision relative to a co-located "performance evaluation" instrument. There is no comparable program in place for p-SO_4 or NO_Y .

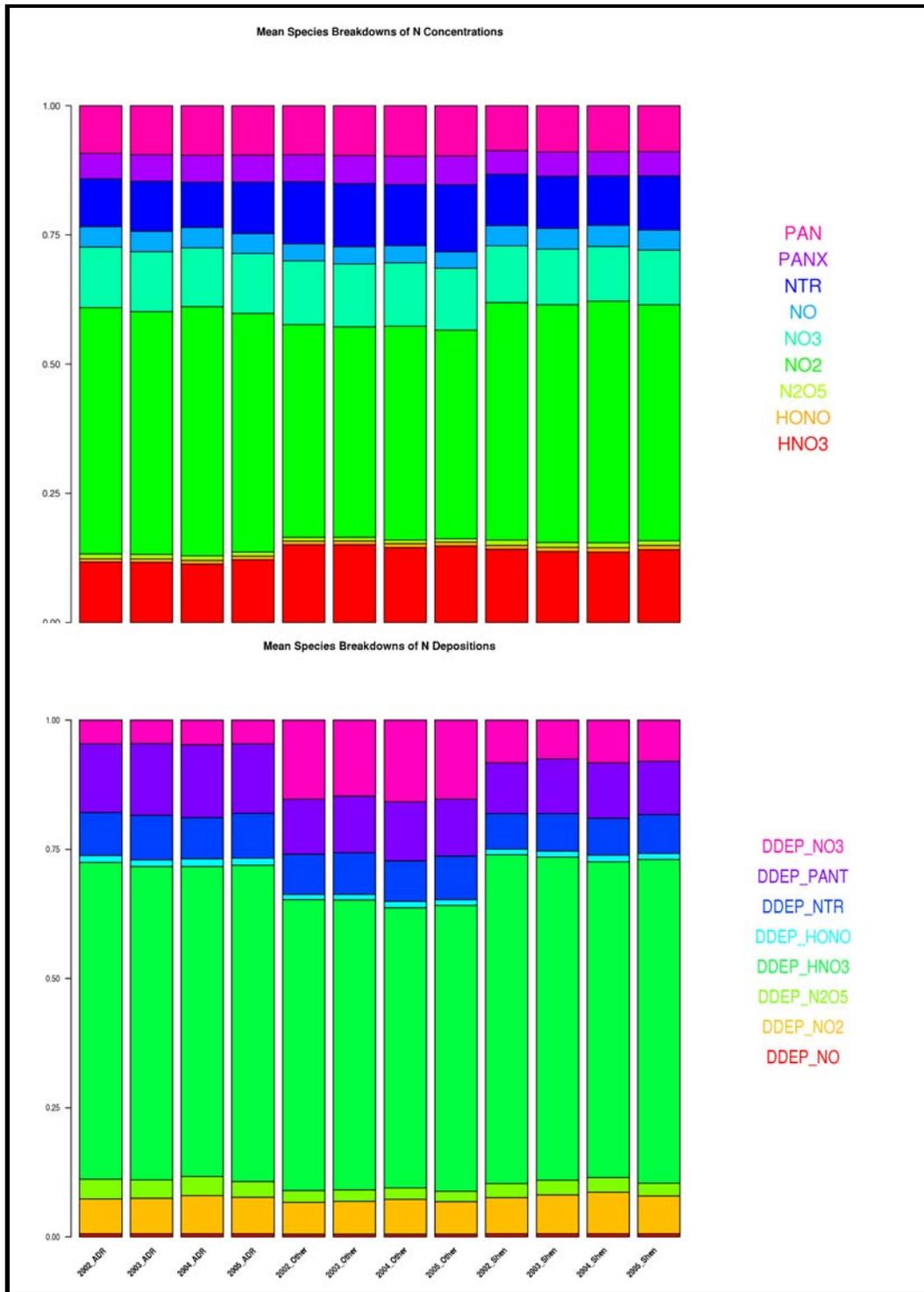


Figure 2-3.6. Annual 2002 – 2004 CMAQ derived annual average fraction of ambient concentrations (above) and deposition (below) of individual NO_y species delineated by the Adirondack and Shenandoah case study areas and the remainder of the Eastern U.S. domain. NTR refers to non-PAN organic nitrates. PANX refers to aggregation of PAN type compounds, other than PAN, specifically.

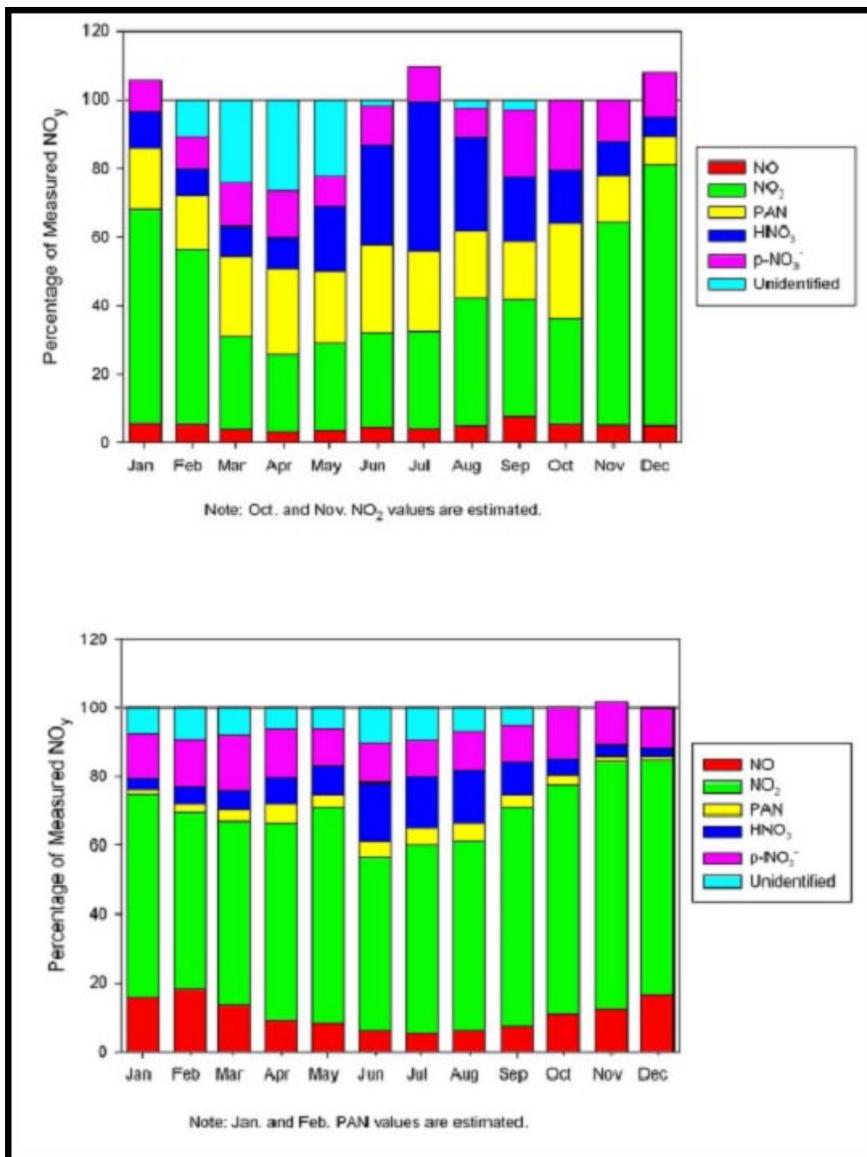


Figure 2-3.7. Examples of the Relative Abundance of Several NO_y Species Measured at Two Rural Southeastern Canadian Sites as a Fraction of the Total Measured NO_y Concentration -- Kejimikujik, NS, (top) and Egbert, ON, (bottom) during 2003. Although both sites are in rural locations, the Kejimikujik, NS site represents more aged air masses as it lies considerably further downwind from major sources of NO_x relative to the Egbert site. (*Source: NARSTO, 2010*)

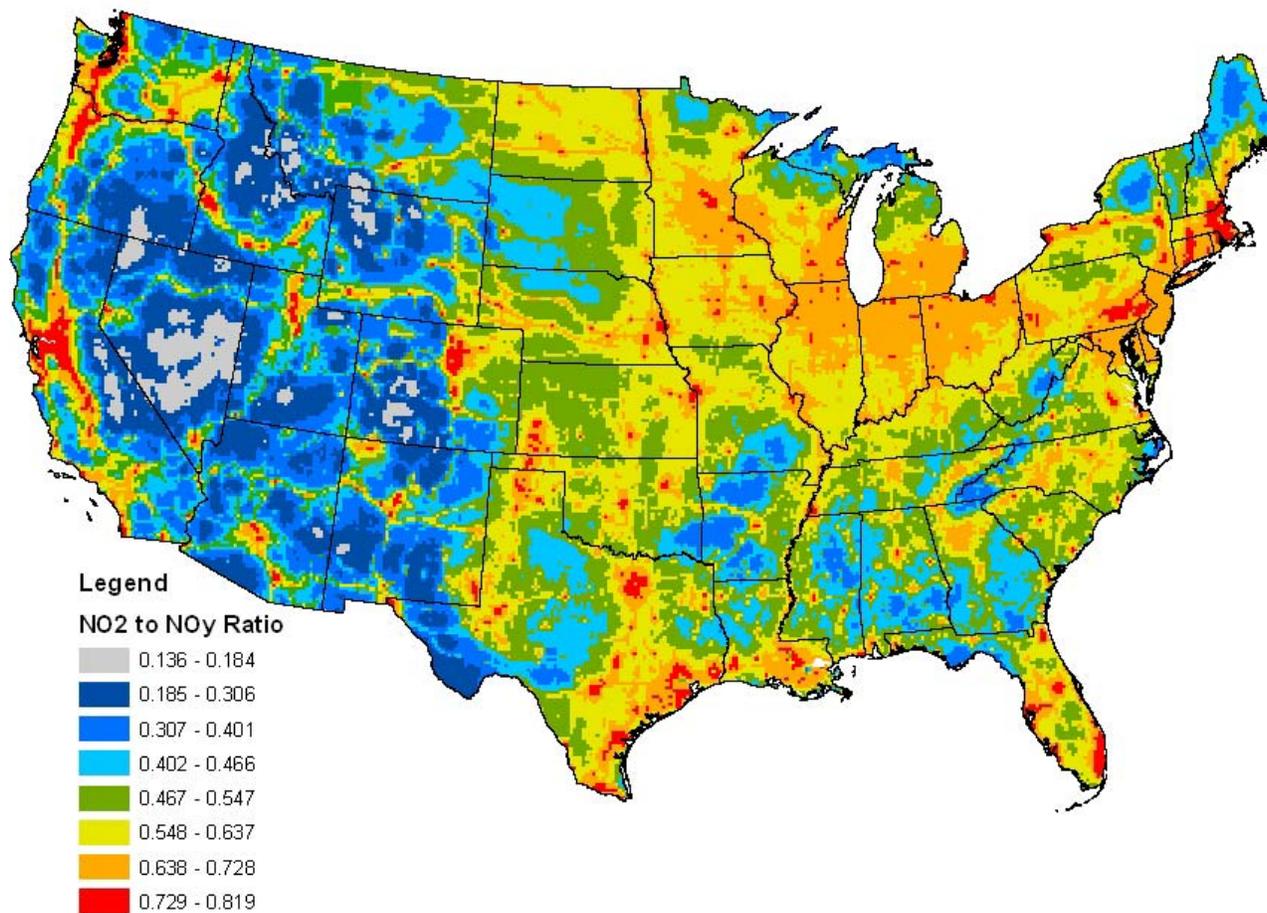


Figure 2-3.8 Annual average fraction of NO_y ambient air contributed by NO₂ based on 2005 CMAQ Eastern U.S. simulation at 12 km grid cell resolution.

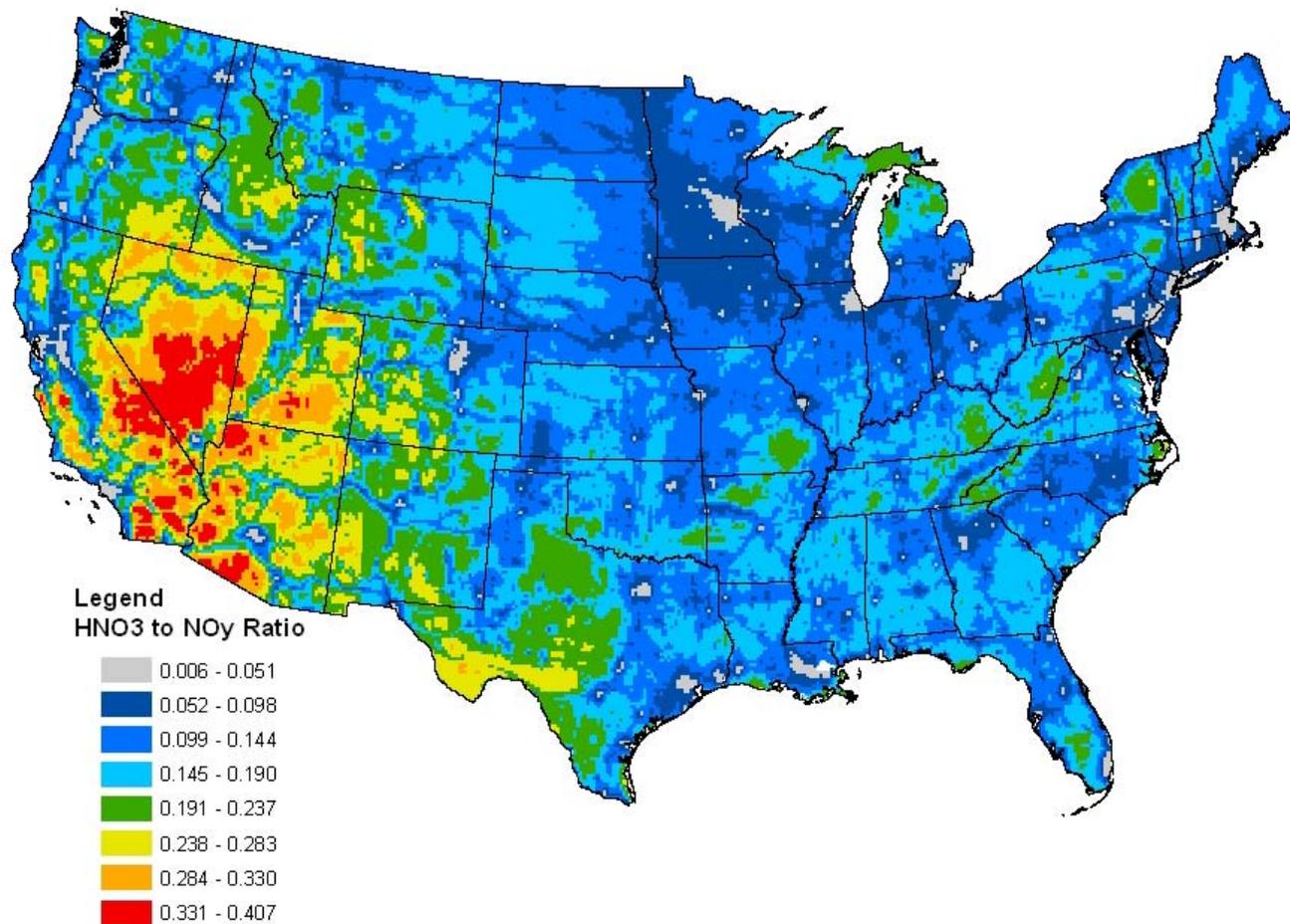


Figure 2-3.9 Annual average fraction of NO_y ambient air contributed by HNO₃ based on 2005 CMAQ Eastern U.S. simulation at 12 km grid cell resolution.

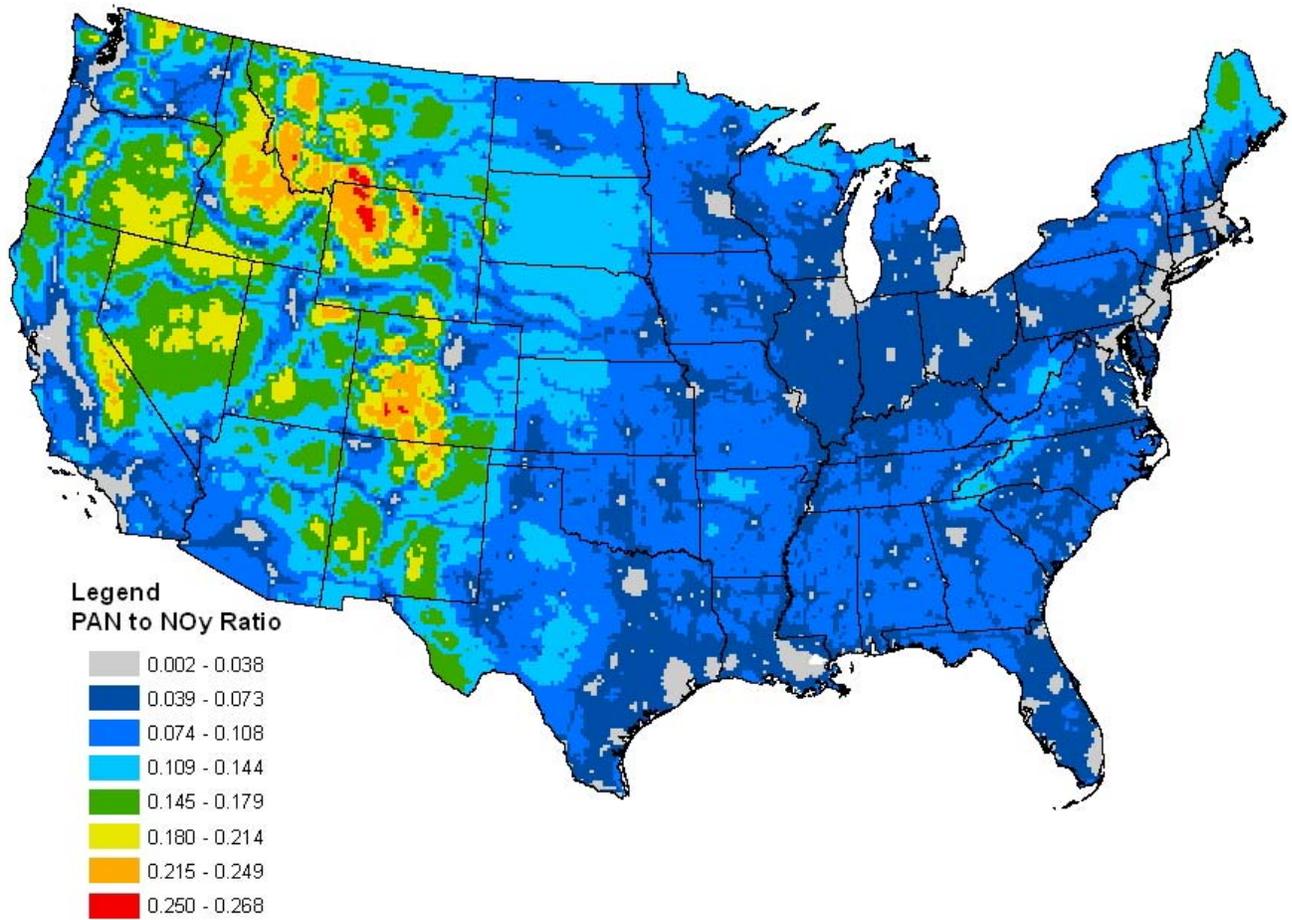


Figure 2-3.10 Annual average fraction of NO_y ambient air contributed by PAN based on 2005 CMAQ Eastern U.S. simulation at 12 km grid cell resolution.

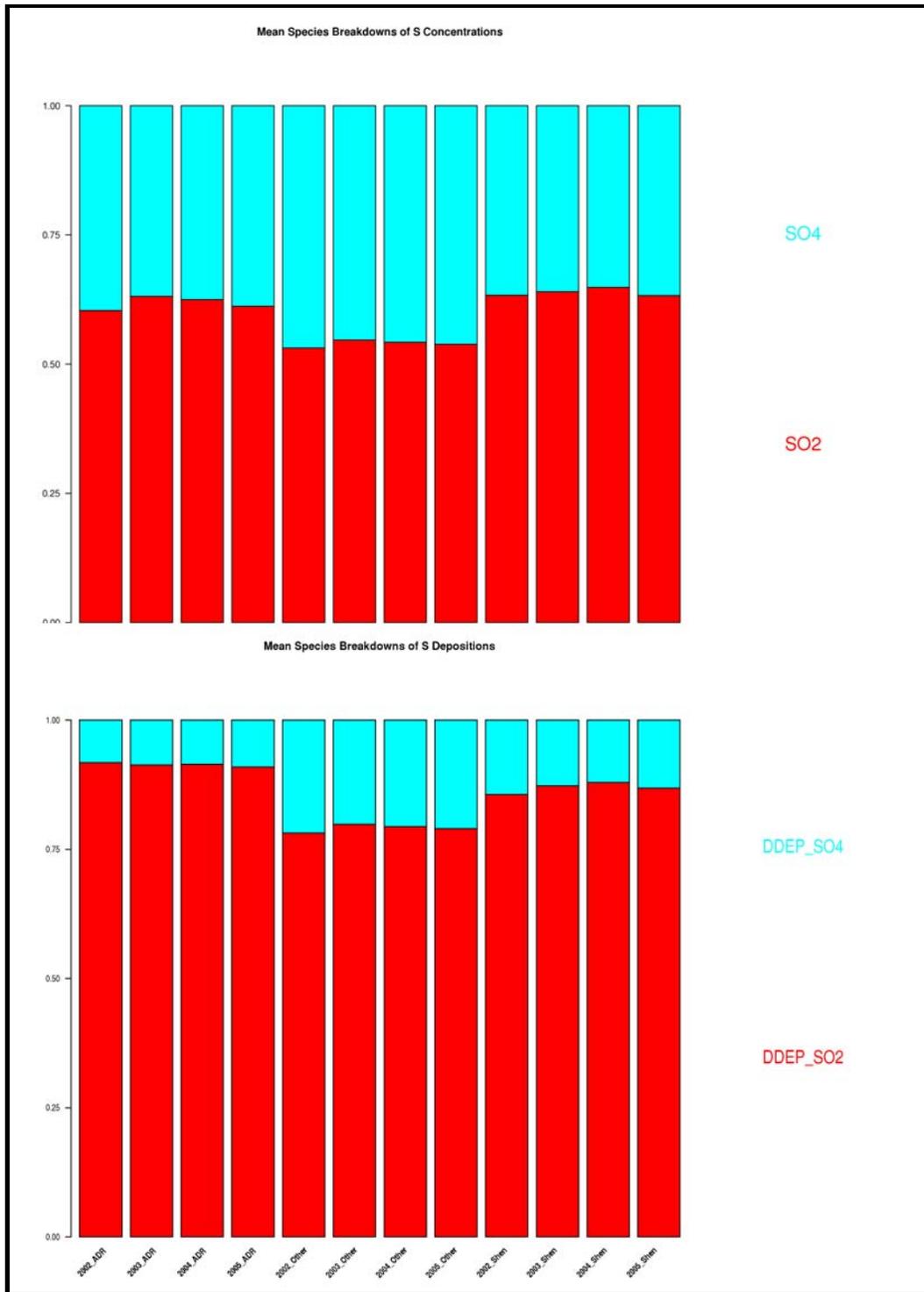


Figure 2-3.11. Annual 2002 – 2004 CMAQ derived annual average fraction of ambient concentrations (above) and deposition (below) of individual SO_x species delineated by the Adirondack and Shenandoah case study areas and the remainder of the Eastern U.S. domain.

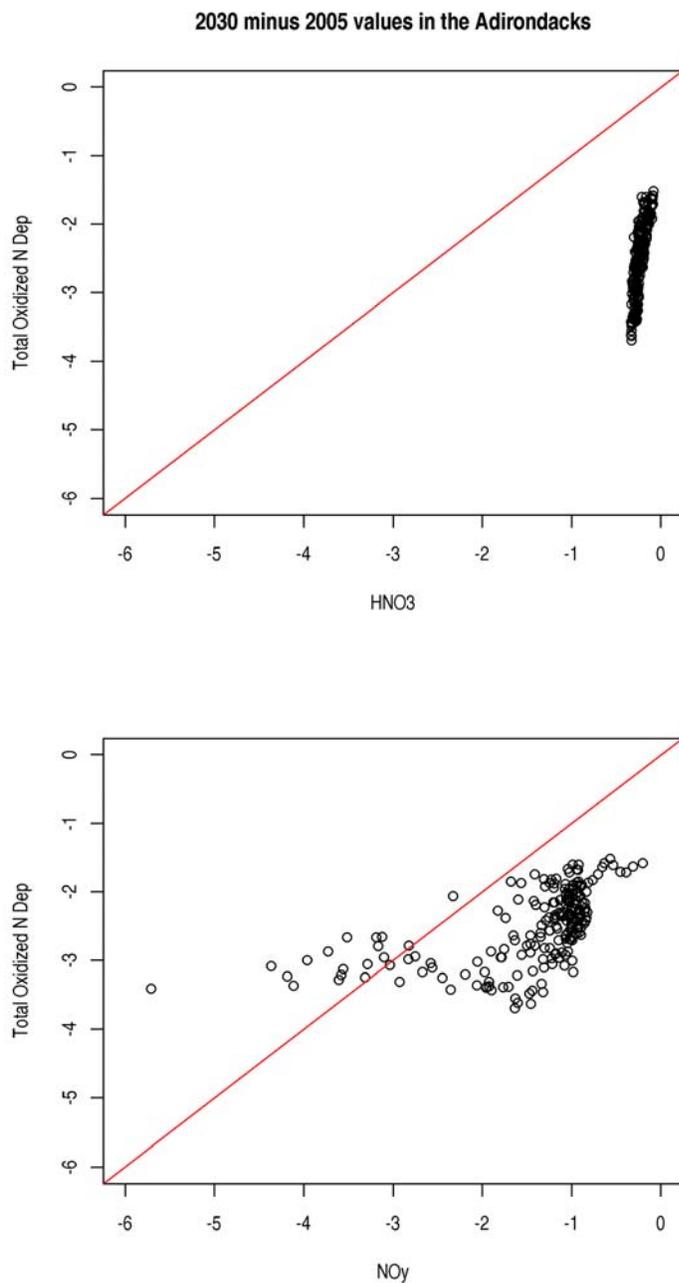


Figure 2-3.12. Relationship of the change in total oxidized nitrogen deposition to change in ambient nitric acid (top) and ambient NO_y (bottom) based on changes in concentration and deposition fields associated with current (2005) and reduced emission CMAQ simulations. The values are based on the changes imparted for each 12 km grid cell within the Adirondack region. The NO_x and SO_x emissions reflect reductions of 50% and 42%, respectively, across the entire Eastern U.S.

2.4 Characterizing freshwater aquatic system chemistry using models and measurements

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

2.4.1 Water chemistry basics

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

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

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

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

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

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

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

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

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

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

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

$$[OH^-][H^+] = 10^{-14}; \quad (2-1)$$

And Cl mass also must be retained:

$$[HCl] + [Cl^-] = [HCl]_t \quad (2-4)$$

Consequently, for a known amount of HCl_t added to pure water, equations 2-1 to 2-4 are easily solved as there are four equations and four unknowns, $[HCl]$, $[OH^-]$, $[H^+]$ and $[Cl^-]$. Because the addition of HCl, which is a strong acid, results in the addition of strong anions, Cl^- ,

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

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

$$K_b = [\text{Na}^+][\text{OH}^-]/[\text{NaOH}] \quad (2-5)$$

Electroneutrality is met by:

$$[\text{Na}^+] + [\text{H}^+] = [\text{OH}^-], \quad (2-6)$$

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

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

$$[\text{H}^+] = [\text{OH}^-] + 2[\text{CO}_3^{-2}] + [\text{HCO}_3^-]; \quad (2-7)$$

To the extent carbonic acid dissociates (Figure 2-4.1), it adds negatively charged anions that can only be balanced by hydrogen ion, consequently lowering the pH of a system of pure water exposed to atmospheric CO₂. This example explains why natural water often has a pH lower than 7 of approximately 5.7.

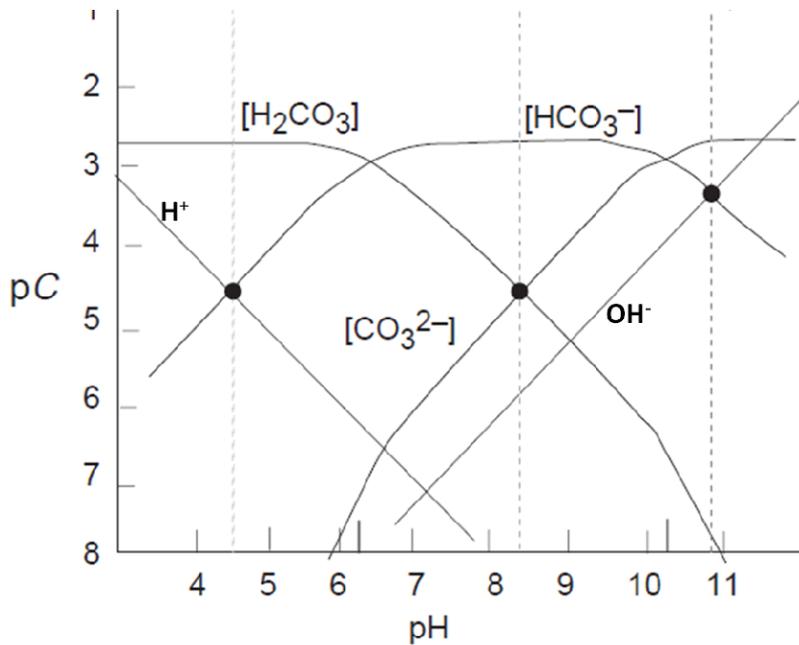


Figure 2-4.1. Equilibrium diagram illustrating distribution of carbonate species as a function of pH which is closed to atmospheric CO_2 exchange and therefore has a constant fixed amount of dissolved carbonate. The intersection where H^+ equals HCO_3^- is the common equivalence point, approximately a pH of 4.5, used when titrating a solution with strong acid to determine ANC. The amount of strong acid that it would take to reach that equivalent point is a measure of ANC or alkalinity. Adopted from Stumm and Morgan, 1981.

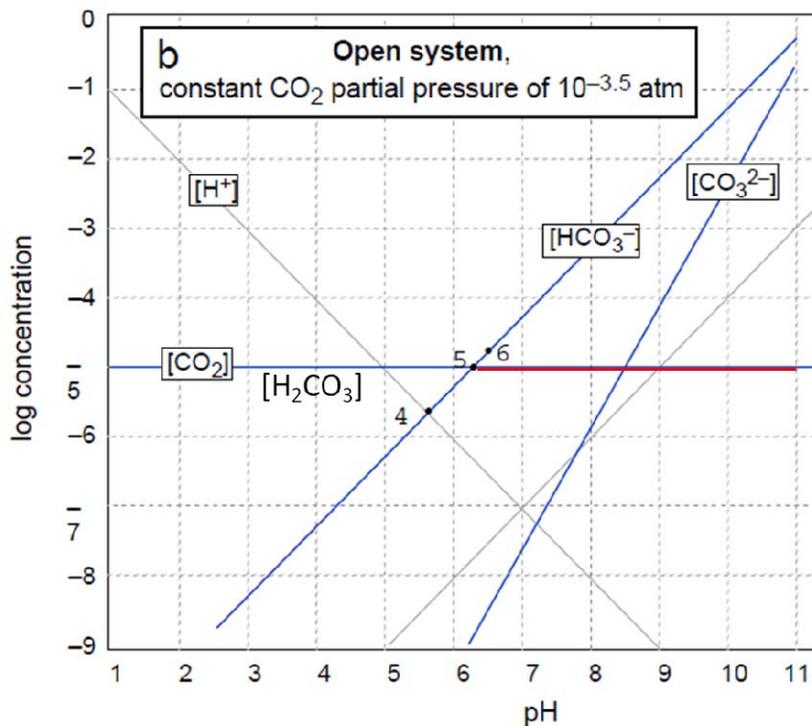


Figure 2-4.2. The same system open to atmospheric CO_2 exchange where the amount of dissolved carbon is determined by the partial pressure of atmospheric CO_2 and pH. Note that a pH of about 5.7 reflects a pH of pure water exposed just to atmospheric CO_2 .

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

$$C_B + [H^+] = [OH^-] + 2[CO_3^{2-}] + [HCO_3^-] + C_A; \quad (2-8)$$

Therefore:

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

Defining ANC. The right side of equation represents the capacity of the system to neutralize available excess protons, H^+ , and conceptually represents acid neutralizing capacity, ANC. The actual definition of ANC is more specific and is based on how much strong acid it takes to titrate a solution to a defined reference or equivalence point. In effect, the equivalence point is synonymous with the point where there no longer is a deficit of protons. This definition of ANC reflecting the difference between major cations and anions ($C_B - C_A$) is operational defined by equation 2-9 and is incorporated in many ecosystem models and this policy assessment:

$$ANC = 2([Ca^{2+}] + [Mg^{2+}]) + [K^+] + [NH_4^+] - (2[SO_4^{2-}] + [NO_3^-] + [Cl^-]) \quad (2-9)$$

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

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

pH and ANC relationships. ANC is a conserved property. This means that ANC can be tracked in a mass balance sense as the level of ANC in a system (e.g., a lake or stream) is calculated by adding how much ANC initially exists with how much flows in and is deposited, balanced how much flows out. The term “mass balance” underlies the basic formulation of any physical modeling construct, and refers to the accounting of the flow of mass into a system, the transformation to other forms, and the loss due to flow out of a system and other removal processes. Hydrogen ion is not a conserved property as its concentration in a system is not related to the inflow and outflow of hydrogen ion, but influenced by several factors such as temperature, atmospheric pressure, mixing conditions of a water body and the levels of several chemical species in the system which all exist, or at least move towards, a state of equilibrium. The conservative nature of ANC also can be explained by Equation 2-9 in which the quantities of strong cations and anions are directly attributable to inputs to and outputs from a system. Strong cations (Mg^+ , Ca^{+2} , K^+ , Na^+) and strong anions (NO_3 , SO_4 , Cl) are always completely dissociated in surface waters, that is why they are referred to as strong ions. Consequently, they can be accounted for in basic modeling approaches. Hydrogen ion, on the other hand, is dependent on the balance of all ions in meeting electroneutrality conditions, as are other “weak” ions associated with dissolved inorganic (DIC) and organic (DOC) carbon.

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

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

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

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

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

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

Dissolved Aluminum. Aluminum species in natural systems is commonly based on the equilibrium relationships among solid Gibbsite and its dissolved ions (figure 2-4.3). Dissolved aluminum affects the charge relationships in aquatic systems and the distribution of dissolved Al species is a function of pH. The prevalence of relatively toxic AL^{+3} at low pH levels is perhaps the most direct causative chemical species with regard to adverse biological effects. From a chemical characterization perspective, aluminum solubility is treated like other weak acid base systems, DIC and ANC, and therefore knowledge of 4 of the 5 variables among total dissolved aluminum, DIC, DOC, ANC and pH uniquely determine the fifth variable. Collectively, these principles of mass conservation, equilibrium and electroneutrality are adhered to in water chemistry models used to estimate key water quality variables as a system responds to acidification inputs.

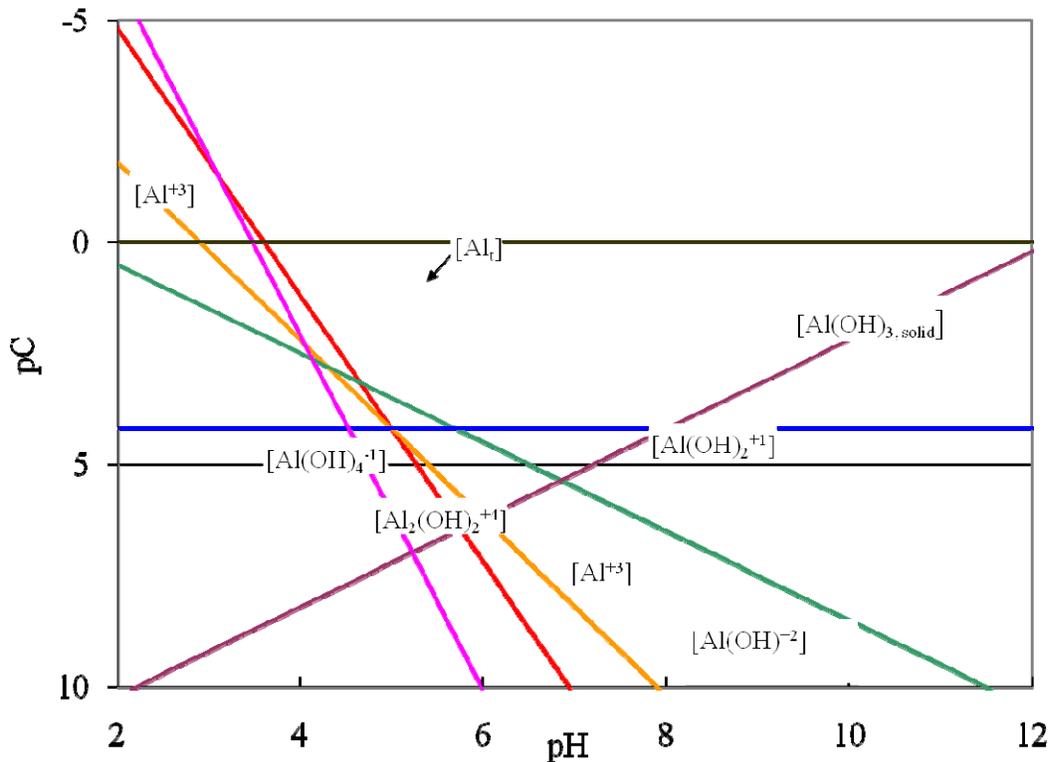


Figure 2-4.3. Equilibrium diagram of the log of aluminum species concentrations as a function of pH. At lower pH there is far greater proportion of dissolved Al species relative to solid gibbsite (solid aluminum hydroxide, $Al(OH)_3$). The most toxic form of Al, free trivalent aluminum, Al^{3+} levels rapidly increase with lower pH values.

2.4.2 Bedrock, soil and vegetation processes relevant aquatic acidification.

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

plant uptake of nitrogen as a nutrient and general immobilization through adsorption in soil and vegetation layers.

Soil physical/chemical processes and acidification

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

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

Sulfur deposition can be adsorbed to soil particles, a process that removes SO_4^{-2} from soil solution, and therefore prevents leaching of cations and further acidification. The degree to which SO_4^{-2} adsorbs on soil is dependent on soil characteristics, in particular the content of clay minerals. Soils in the United States that most effectively adsorb SO_4^{-2} occur south of the maximum extent of glaciation that occurred during the most recent ice age (Rochelle and Church, 1987). Sulfate adsorption is strongly pH dependent, and a decrease in soil pH resulting from acidic deposition can enhance the ability of soil to adsorb SO_4^{-2} . The adsorbed SO_4^{-2} acts to delay the soil and surface water from acidifying. However, this potentially reversible process results in an accumulation of S in the soil, which can contribute to soil acidification if, and when, that SO_4^{-2} is eventually released back into solution.

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

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

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

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

Therefore, neutralization of drainage water is accomplished at the expense of soil base cations. The ability of a soil to exchange base cations between drainage waters is known as the cation exchange capacity (CEC) and is determined by many factors. Soils north of the maximum

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

Conceptualized Model of Acidification

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

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

other programs has provided empirical evidence of stages II and III and that base cation deposition in soils has occurred as a consequence of chronic acidification from atmospheric deposition (Norton et al. 1999). Moreover, many long-term monitoring programs, such as LTM and TIME with 20 years or more of data, show a slowing of the recovery of ANC in surface waters despite continued reductions acid anions from acid deposition (http://www.epa.gov/airmarkets/progress/ARP09_3.html). While this pattern of slowing surface water recovery follows Galloway's model, it is uncertain what is driving the slowing recovery of ANC because of limited soil data. Currently, no study has shown an increase in soil base saturation as a result of decreasing in acid deposition. Most soil studies continue to show declining base saturations in areas impacted by acidic deposition (Warby et al 2009).

2.4.3 Biogeochemical ecosystem models used to estimate water quality

Biogeochemical acidification ecosystem models which incorporate the basic chemical principles discussed above are important tools to evaluate how multiple environmental factors alter the relationship between ANC and atmospheric deposition. Acidification models are capable of estimating how much acidifying deposition a watershed can accommodate to maintain a desired ANC, referred to as a critical load (Figure 2-4.4). The most commonly used models of acidification are presented in Table 2-4.1 These models are designed to be applied at the spatial scale of the watershed, with the exception of the SMART model.

Basic approach of steady-state vs. dynamic acidification models

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

Table 2-4.1 Summary several commonly used acidification models (See ISA Annex A for a more comprehensive list and discussion of acidification models)

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

Table 2-4.1 Summary several commonly used acidification models (See ISA Annex A for a more comprehensive list and discussion of acidification models)

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

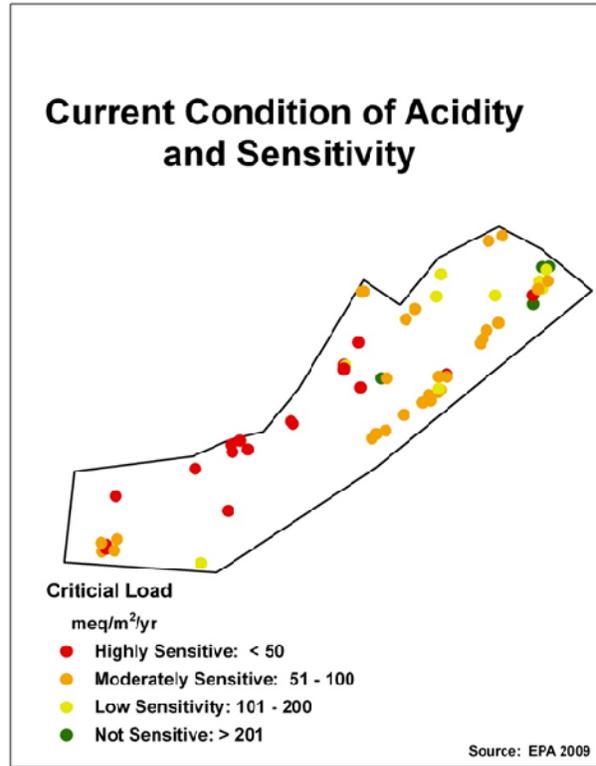
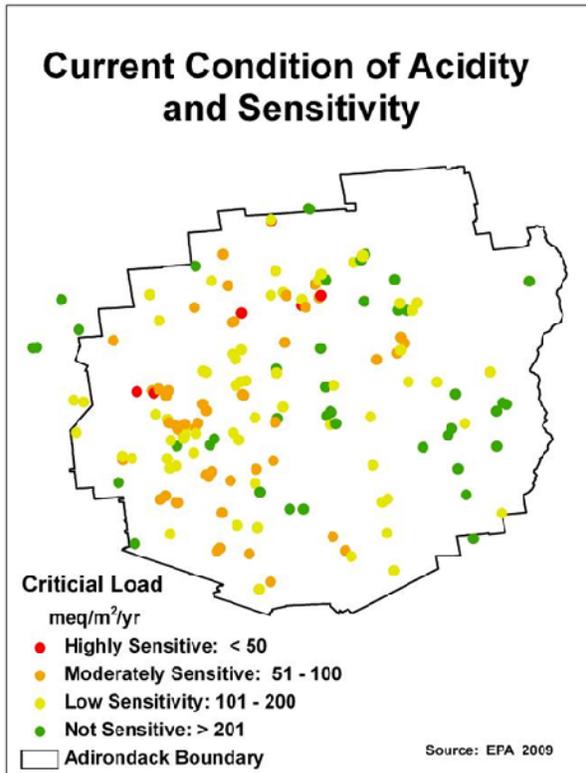


Figure 2-4.4. Critical loads of acidifying deposition based on MAGIC modeling that each surface water location can receive in the Adirondack and Shenandoah Case Study Areas while maintaining or exceeding an ANC concentration of 50 $\mu\text{eq/L}$ based on 2002 data. Watersheds with critical load values $<100 \text{ meq/m}^2/\text{yr}$ (red and orange circles) are most sensitive to surface water acidification, whereas watersheds with values $>100 \text{ meq/m}^2/\text{yr}$ (yellow and green circles) are less sensitive sites.

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

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

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

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

Data Requirements of steady-state vs. dynamic acidification models

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

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

Comparison of two steady-state models: FAB and SSWC

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

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

In contrast to the SSWC approach, the FAB model includes more explicit modeling of N processes including soil immobilization, denitrification, and wood removal, in-lake retention of N and S, as well as lake size. Although N cycling is more detailed in the FAB model, there is greater uncertainty in the input data needed to characterize the components of the N cycle. The FAB model yields a deposition load function for a specified level of an endpoint. This function is characterized by three nodes that are illustrated on Figure 2-4.1, 1. the maximum of amount of N deposition when S deposition equals zero ($DL_{max}(N)$); 2. the amount of N deposition that will be captured by the ecosystem before it leaches ($DL_{min}(N)$); and 3. the maximum amount of S deposition considering the N captured by the ecosystem ($DL_{max}(S)$). The function represents many unique pairs of N and S deposition that will equal the critical load for acidifying deposition.

The three models, MAGIC, SSWC and FAB, discussed above were widely used in the REA and this PA. MAGIC enabled the construction of time series estimates of water quality change and provided a more scientifically rigorous model to conduct comparisons with certain parameterizations used in steady state models. As will be described in Section 7, attributes of SSWC and FAB modeling, several of which are illustrated in Figure 2-4.5, were incorporated in constructing the form of the standard.

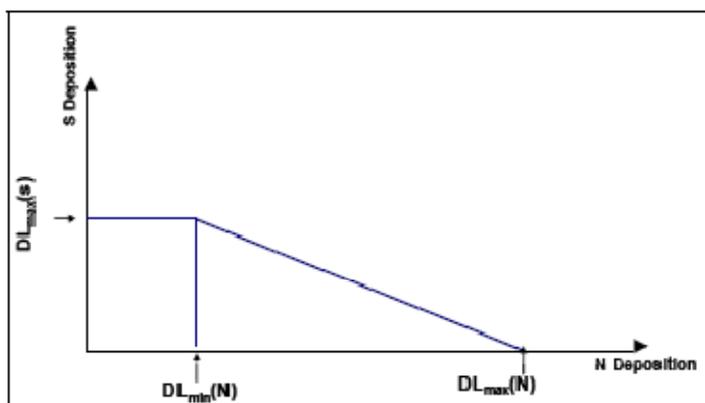


Figure 2-4.5 Illustration of a generalized N + S deposition tradeoff curve that is calculated by using the FAB approach.

2.4.4 Water Quality Networks

An overview of surface water chemistry monitoring programs is incorporated in EPA's ISA (EPA, 2008) and is the basis for much of this discussion. The TIME/LTM program is described immediately below. A summary of the water quality data bases used in the PA are provided in Table 2-4.3. National alkalinity and ANC maps, which help support development of acid sensitive and less sensitive categories which are considered in developing the standard (see section 7.2.5), are included at the end of this sub-section (figures 2-4.7, 2-4.8). Appendix D provides data summaries of water chemistry variables (SO_4 , natural base cation supply, DOC, ANC) delineated by Omernik Ecoregion Level III categories.

TIME/LTM Program descriptions

The Temporally Integrated Monitoring of Ecosystems (TIME) and the long-Term Monitoring (LTM) programs (Table 2-4.3; Figure 2-4.6) are complementary EPA surface water monitoring networks that provide information on a variety of indicators necessary for tracking temporal and spatial trends in environmental response to changes in regional air quality and acid deposition in ecosystems sensitive to acid rain in the eastern United States. Some of these indicators include, but are not limited to: acid neutralizing capacity (ANC), sulfate (SO_4^{2-}), and nitrate (NO_3^-). Both programs are operated cooperatively with numerous collaborators in state agencies, academic institutions, and other federal agencies.

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

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

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

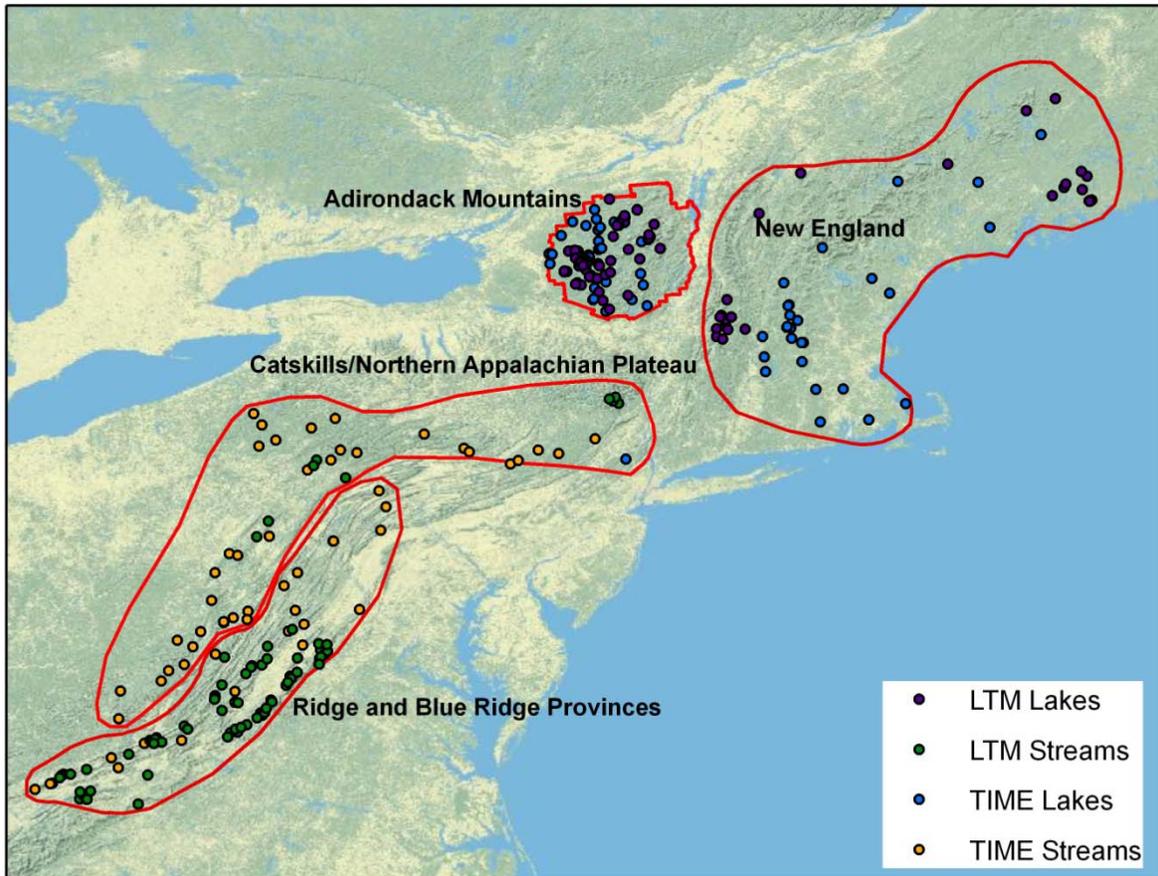


Figure 2-4.6 Active TIME/LTM sampling locations.

Table 2-4.2. Characteristics of TIME/LTM Sites

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

* Samples are collected once per specified season/interval

** All TIME sites are monitored annually

± Stream flow data are collected from these sites

Table 2-4.3. Summary of data sources considered for the evaluation of national ANC.		
Program	Dates of observations	Reference
EPA Long Term Monitoring Vermont (LTM_VT)	1983-2007	EPA/903/R-00/015
EPA Eastern Lakes Survey (ELS)	1984	EPA/620/R-93/009
Adirondack Lake Survey (ALS)	1984-1987	Stoddard.et.al.WRR.1996
EPA Western Lake Survey (WLS)	1985	EPA 620-R-05-005
EPA National Stream Survey (NSS)	1986	Stoddard.et.al.WRR.1996
VT SSS	1987 & 2000	EPA 841-B-06-002
EPA Long Term Monitoring_Colorado sites (LTM_CO)	1990-1994	Stoddard.et.al.WRR.1996
EPA Long Term Monitoring_Midwest Sites (LTM_MW)	1990-2000	Stoddard.et.al.WRR.1996
VT SSS LTM	1990-2007	Stoddard.et.al.WRR.1996
EPA Long Term Monitoring_Pennsylvania sites(LTM_PA)	1990-2007	Stoddard.et.al.WRR.1996
EPA Long Term Monitoring_Catskill sites (LTM_CAT)	1990-2007	EPA 905-R-92-001
EPA Long Term Monitoring: Annual average from 1992-2007	1990-2007	EPA/600/4-88/032
EPA EMAP Northeast Lake Survey	1991-1994	Stoddard.et.al.WRR.1996
EPA Long Term Monitoring_Maine sites (LTM_ME)	1992-2007	reg1_qa.pdf
Regional Environmental Monitoring Program_Maine sites (REMAP_ME)	1993	Stoddard.et.al.WRR.1996
EPA EMAP_Mid Atlantic streams (EPA EMAP_MAIA)	1993-1996	EPA/R-06/XX
EPA EMAP_Mid Atlantic streams (EPA EMAP_MAIA)	1997-1998	EPA-600-388-021a
EPA EMAP_Western Stream and River Survey (EMAP WEST)	2000-2004	EPA/600/3-86/054b
EPA National Lakes Survey (NLS)	2010	EPA 841-F-09-007.
USGS NAWQA Program		http://water.usgs.gov/nawqa/
EPA Storet Program		http://www.epa.gov/storet/

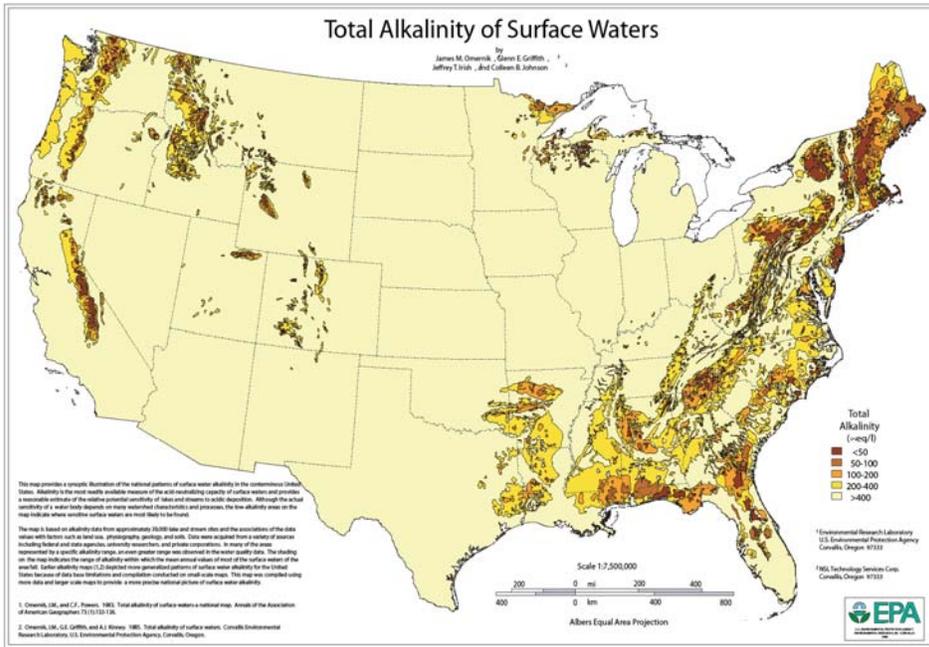


Figure 2-4.7. **Surface water alkalinity in the conterminous U.S.** Shading indicates the range of alkalinity within which the mean annual values of most of the surface waters of the area fall (Omernik and Powers), 1983.

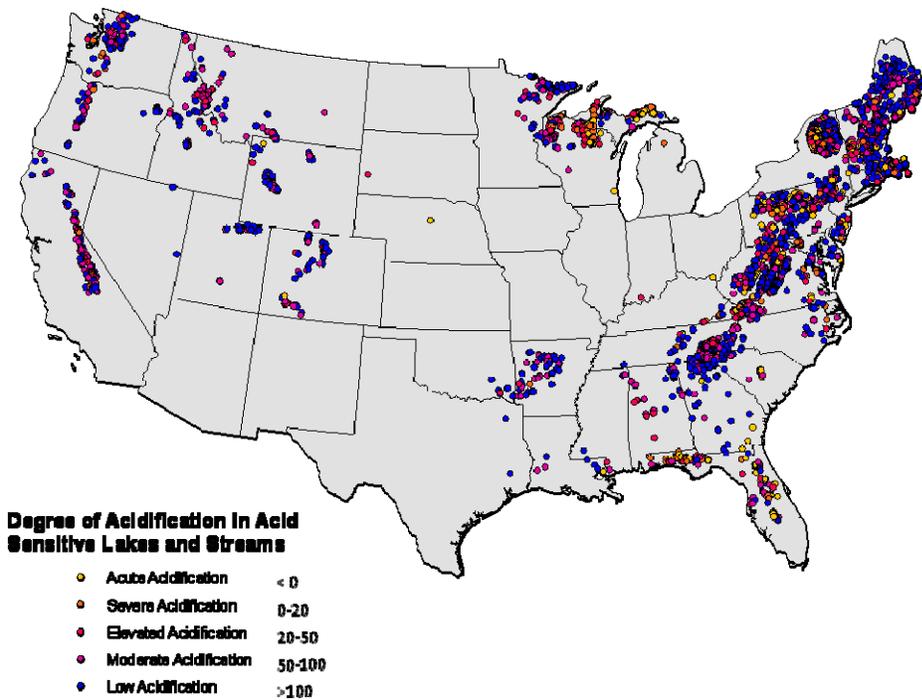


Figure 2-4.8. National map of ANC data ($\mu\text{eq/L}$) based on historical and contemporary data sorted by ANC classes.

2.5 TRENDS

This section provides summaries of time series trends of emissions, air quality, deposition and water quality relevant to oxides of nitrogen and sulfur and aquatic acidification. The value of this summary is in bringing the four components in the source-to-effects continuum (Figure 2-5.1) together in one place to provide general trends information but also to develop, at least conceptually, a retrospective view of how the basic components which underlie the form of the standard (section 7.2) respond together. Extensive use is made of EPA's own annual reports on progress associated with the Acid Rain Program (EPA, 2010). This information is a response to suggestions that the form of the standard be studied in a "hindcast" manner. Unfortunately, historical data and modeling results are not available to adequately support calculation of the standard as described in chapter 7. Consequently, these combined time series examples are used to demonstrate in an associative manner that the basic tenets of the conceptual model of the standard are valid for the standard being developed in this assessment, which relies on similar directional changes in the source to effects continuum. One could identify the acid rain emissions limits as part of Title IV as a marker to assess progress that is specific to the mission component at the beginning of the source-to-effects continuum. Similarly, the standard developed in this assessment might be thought of as providing an atmospheric marker upon which future progress can be judged.

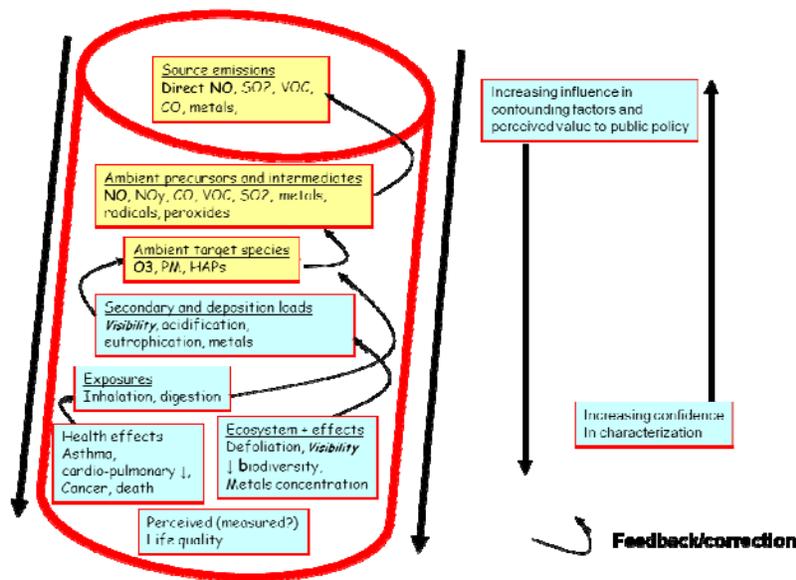


Figure 2-5.1. Conceptual source to effects pipeline diagram illustrating basic accountability concepts as one proceeds from source emissions through the air and eventually to effects.

2.5.1 Emissions

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

The recent declines from 2005 to 2009 in NO_x and SO_x emissions (Figures 2-5.2 – 2-5.4) are attributed to continued implementation of NO_x SIP CALL and transportation sector rules, as well efforts to implement controls associated with the Clean Air Interstate Rule (CAIR). Annual reports explaining the rules and programs addressing EGUs and the relationships between emission reductions and air quality and deposition changes is provided by EPA's Clean Air Market Division at <http://www.epa.gov/airmarkets/progress/progress-reports.htm>. Major reductions in EGU SO_x and NO_x emissions are associated with market trading of emissions which was a tool in implementing emissions reduction targets in Title IV and other rules.

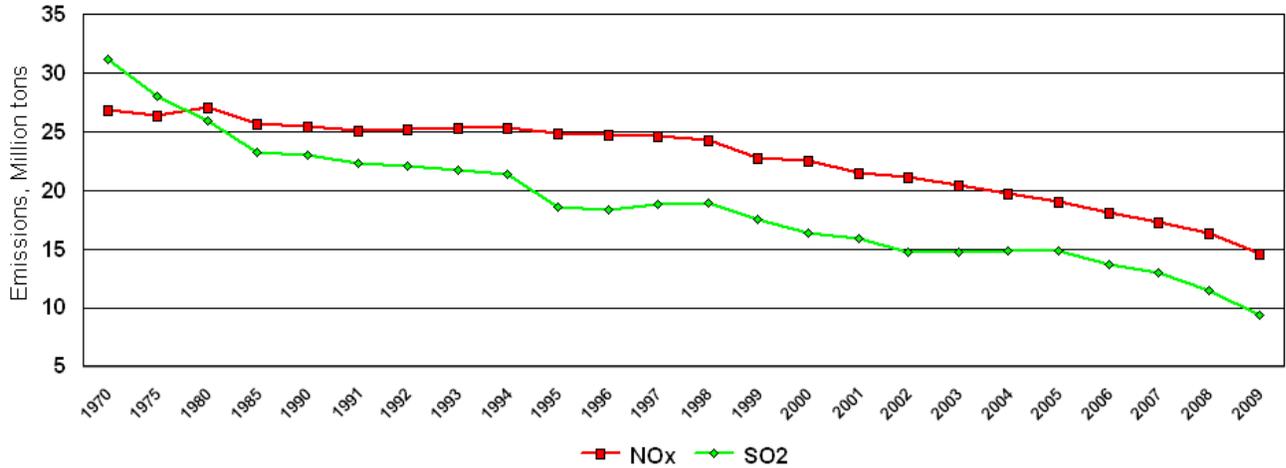


Figure 2-5.2 Time series trends of all anthropogenic NOx and SOx emissions based on EPA’s National Emissions Inventory (NEI).

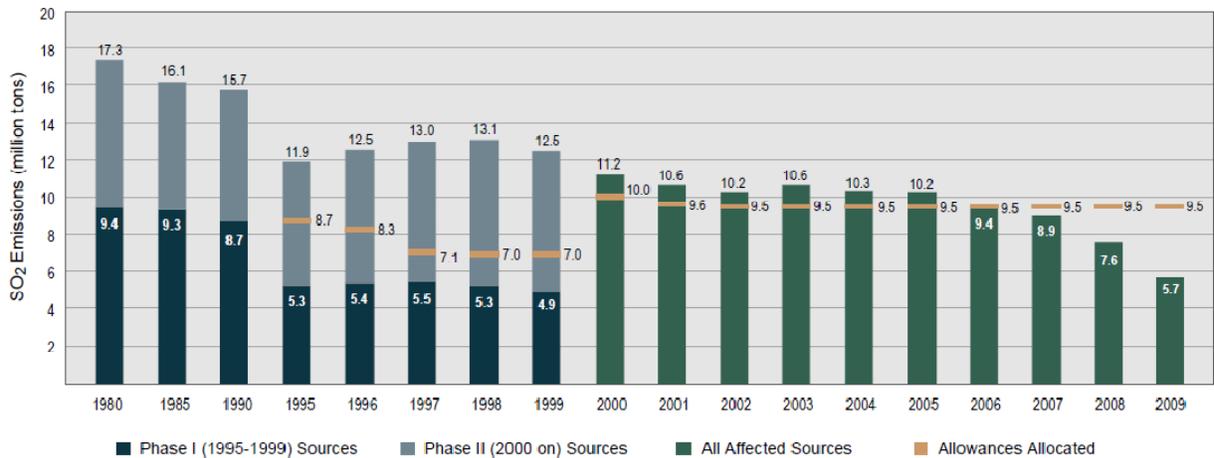
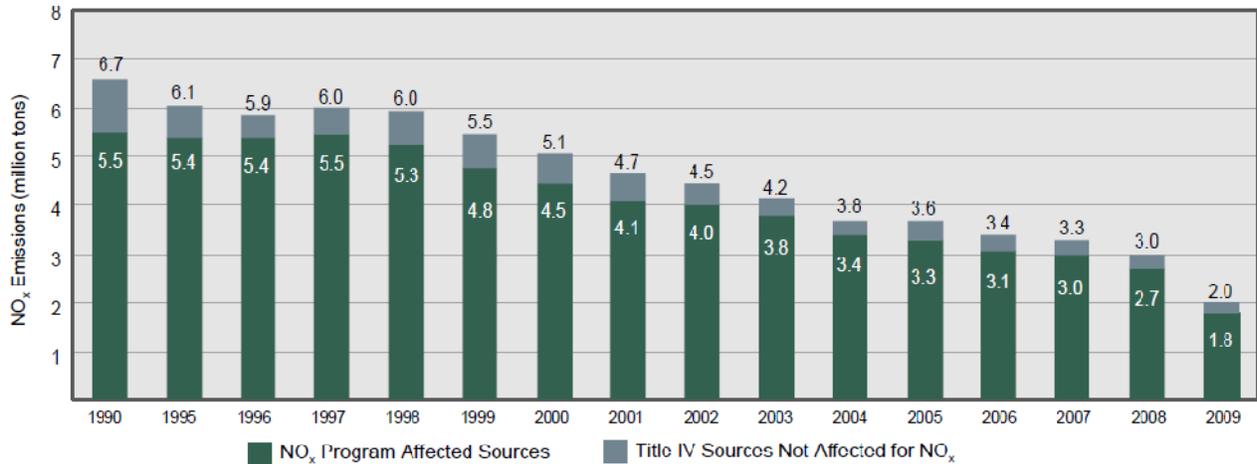


Figure 2-5.3. Trends of NOx (above) and SOx (below) reductions associated with EPA’s Acid Rain Program (ARP) which established market trade units for NOx and SOx emissions associated with EGUs (EPA, 2010). Trends of SO2 reductions associated with EPA’s Acid Rain Program (ARP) which established market trade units for NOx and SOx emissions associated with EGUs. ARP units have reduced annual SO2 emissions by 67 percent compared with 1980 levels and 64 percent compared with 1990 levels (EPA, 2010).

2.5.2 Air quality and deposition

Significant reductions in ambient air concentrations in the Eastern U.S. of SO₂, SO₄ and NO₃ over the last two decades (figures 2-5.4 – 2.5.6) are consistent with emission trends for NO_x and SO_x over the same period. Trends of observed wet deposition have been provided as a feature product by the NADP; sulfate and nitrate wet deposition patterns (fig 2-5.5) generally exhibit the same features of the analogous air quality patterns (fig 2-5.4). Dry deposition patterns can be assumed to exhibit identical patterns of air quality concentrations, given the direct dependence of dry deposition on concentration. Sickles and Chadwick (2007) provide quantitative estimates linking changes in emissions, concentrations and deposition patterns from 1990 to 2004. Their findings (Table 2-5.1) broken down by pollutant and three subregions across the Eastern U.S. demonstrate similar patterns of reductions through emission, concentrations and deposition. However, stronger correlations between emissions changes and total oxidized nitrogen and sulfur in concentration and deposition fields relative to relationships between emissions and a single species.

Table 2-5.1 Period 1 Emissions Density and Period 1-to-Period 3 Relative Changes (%) in Oxidized Sulfur and Nitrogen Emissions, Atmospheric Concentration, and Dry, Wet, and Total Deposition (from Sickles and Chadwick, 2007).

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

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

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

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

Trends in reduced nitrogen are based only on ammonium ion observations, given the very limited availability of ammonia gas monitoring. Patterns of reduced nitrogen (figure 2-5.6) based on ammonium ion are difficult to interpret with respect to trends of precursor ammonia emissions, which are not presented in this section. Ambient ammonium levels have decreased

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

Kim et al (2006) quantified changes in NO_x emission reductions and NO₂ concentrations for New York and Ohio, using satellite column NO₂ observations to capture region wide NO₂ patterns (Figure 2-5.7). The use of satellite data to capture region wide NO₂ patterns is indicative of the shortage of available NO₂ data in rural locations, as described earlier in section 2.2.

Before describing water quality trends, it is informative to note changes in pH over the last two decades. In this context, pH serves simply as an indicator and does not reflect that concurrent reductions in emissions of acid generating gases, NO_x and SO_x, clearly have resulted in significant reductions in rain water hydrogen ion levels (figure 2-5.8). The pH patterns continue to reflect a sulfur dominated air regime in the Eastern U.S., relative to the rest of the contiguous U.S.

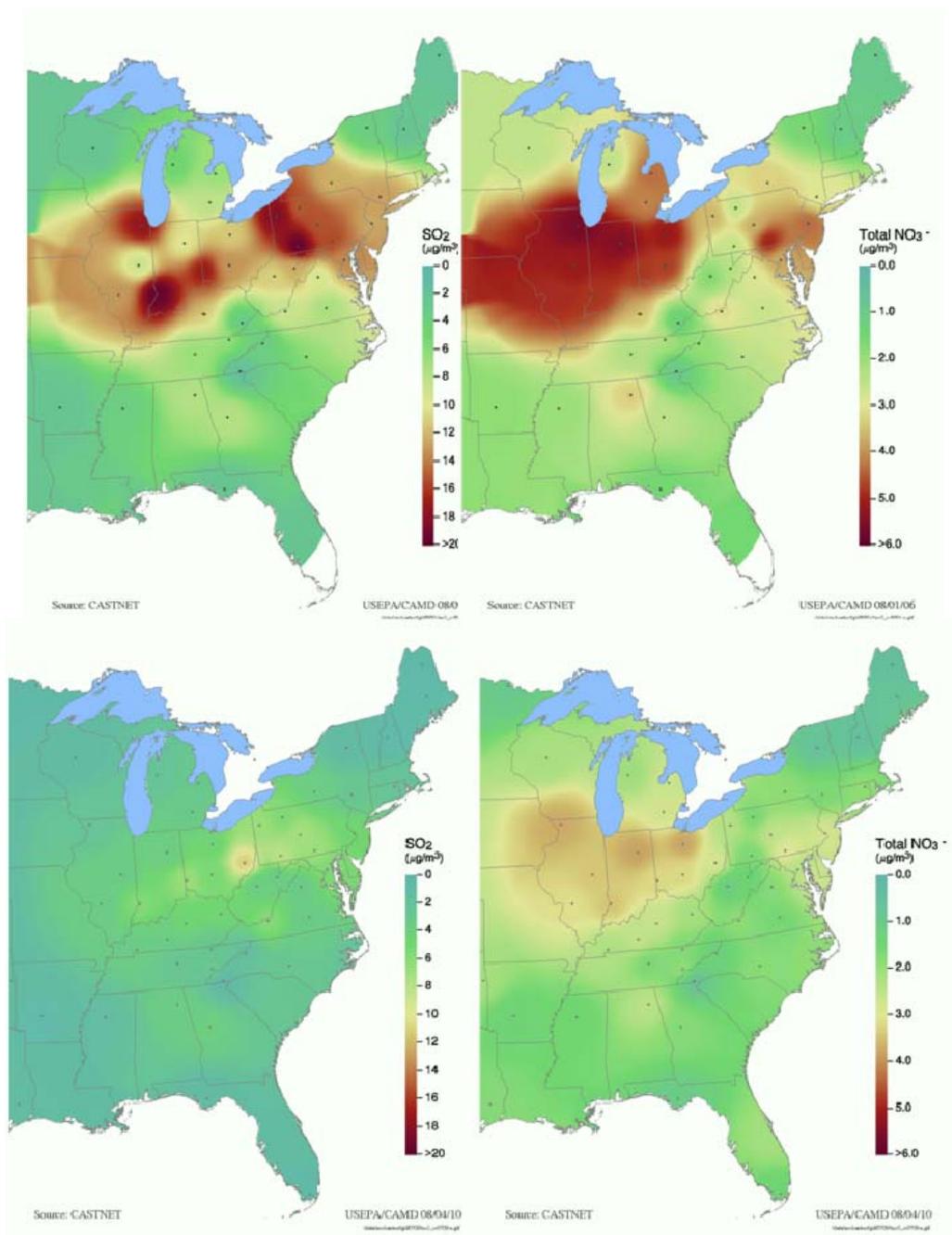


Figure 2-5.4. Eastern U.S. annual average spatial distribution of SO₂ (left) and total nitrate (right) concentrations averaged over 1989 -1991 (top) and 2007 – 2009 (bottom). Data are based on EPA’s CASTNET program.

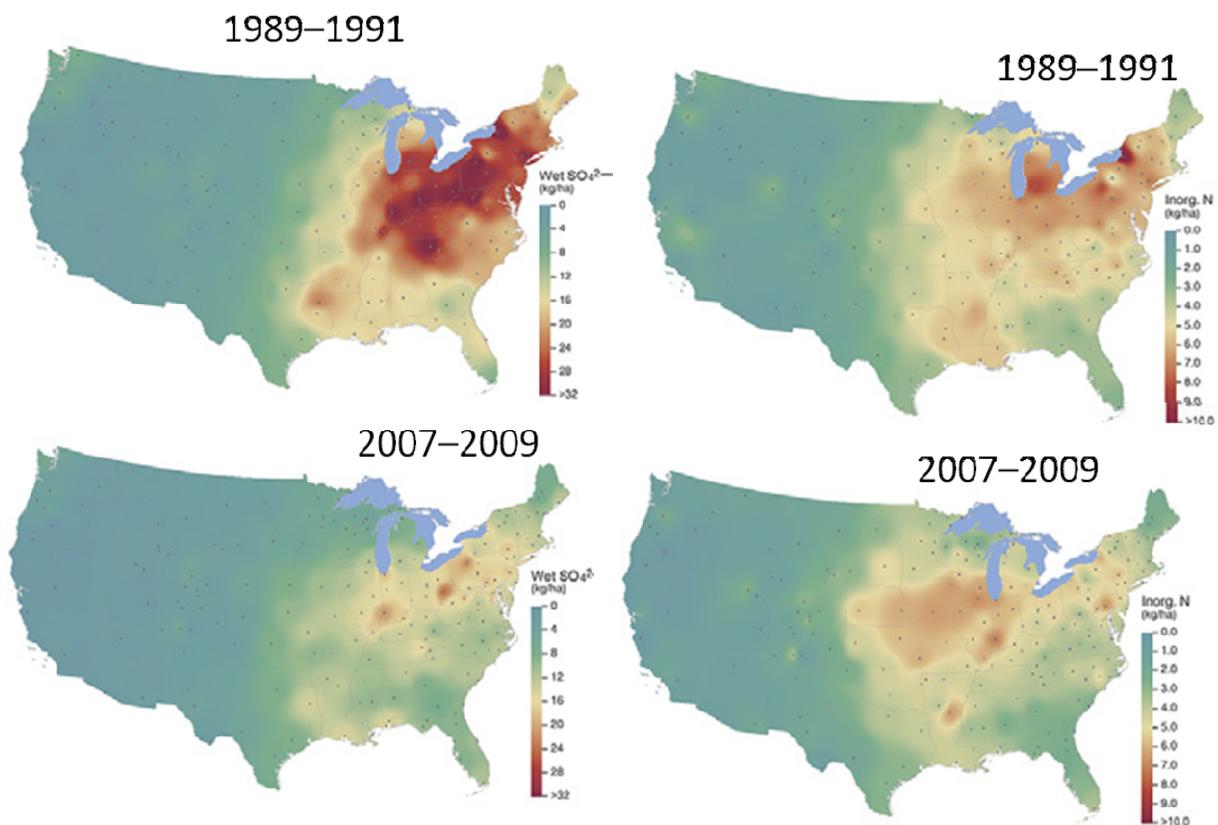


Figure 2-5.5. U.S. annual average spatial distribution of wet sulfate (left) and nitrate (right) deposition averaged over 1989 -1991 (top) and 2007 – 2009 (bottom) based on the NADP.

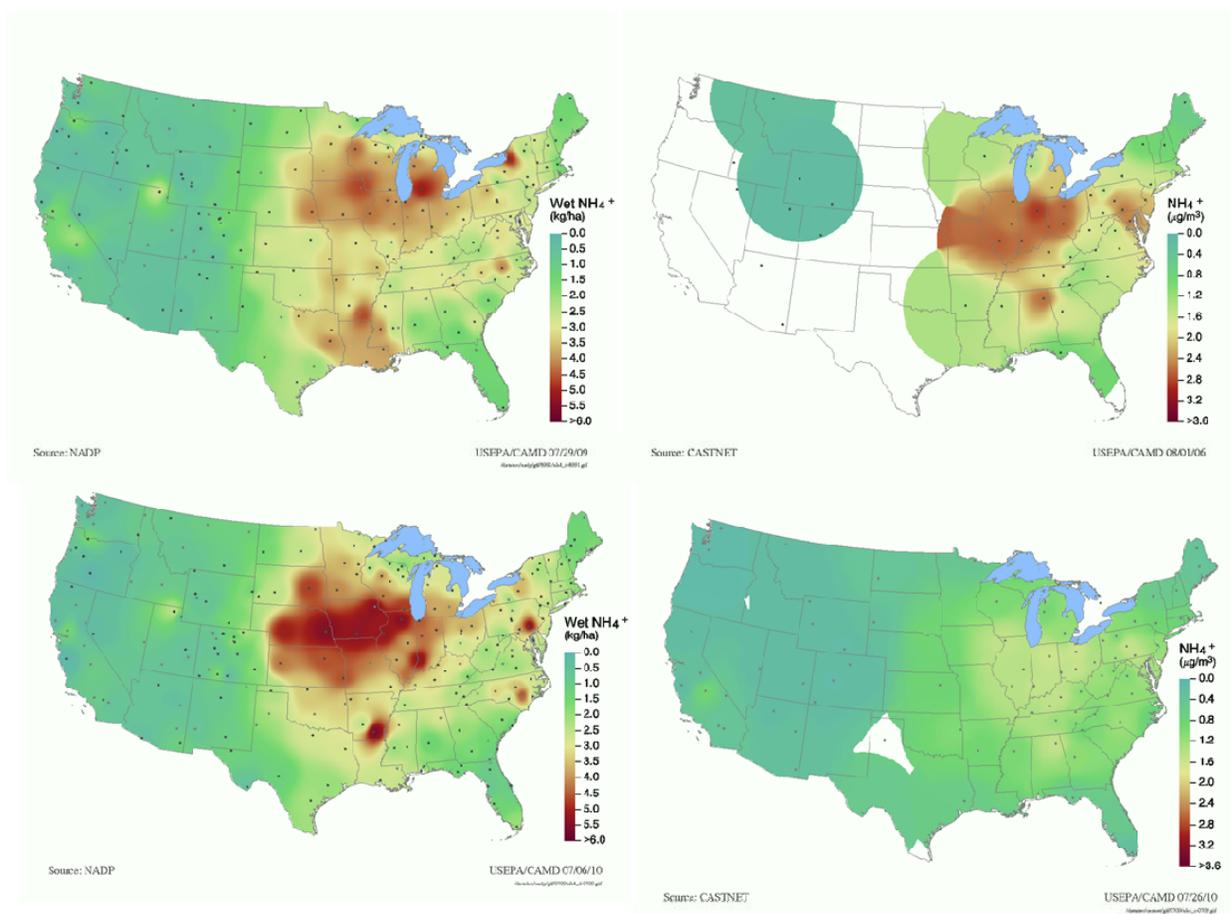


Figure 2-5.6. U.S. annual average spatial distribution of wet ammonium sulfate deposition (left) and ambient air ammonium concentrations (right) averaged over 1989 -1991 (top) and 2007 – 2009 (bottom) based on CASTNET and NADP.

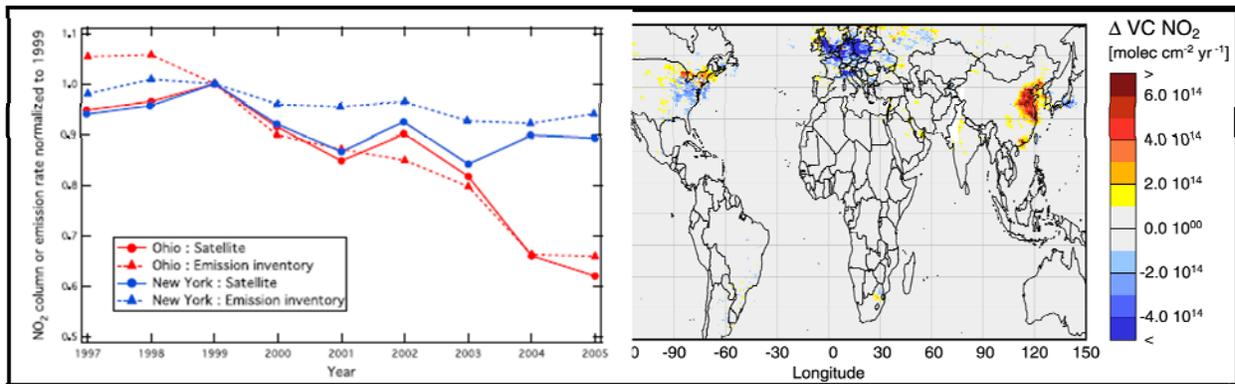


Figure 2-5.7. Left - superimposed Eastern U.S. emission and combined GOME and SCIAMACHY NO₂ 1997-2002 trends (Kim et al., 2006); right - GOME NO₂ trends from 1995 – 2002 (after Richter, 2005). Clear evidence of reductions in midwest U.S. and European NO_x emissions, and increased NO_x generated in Eastern Asia

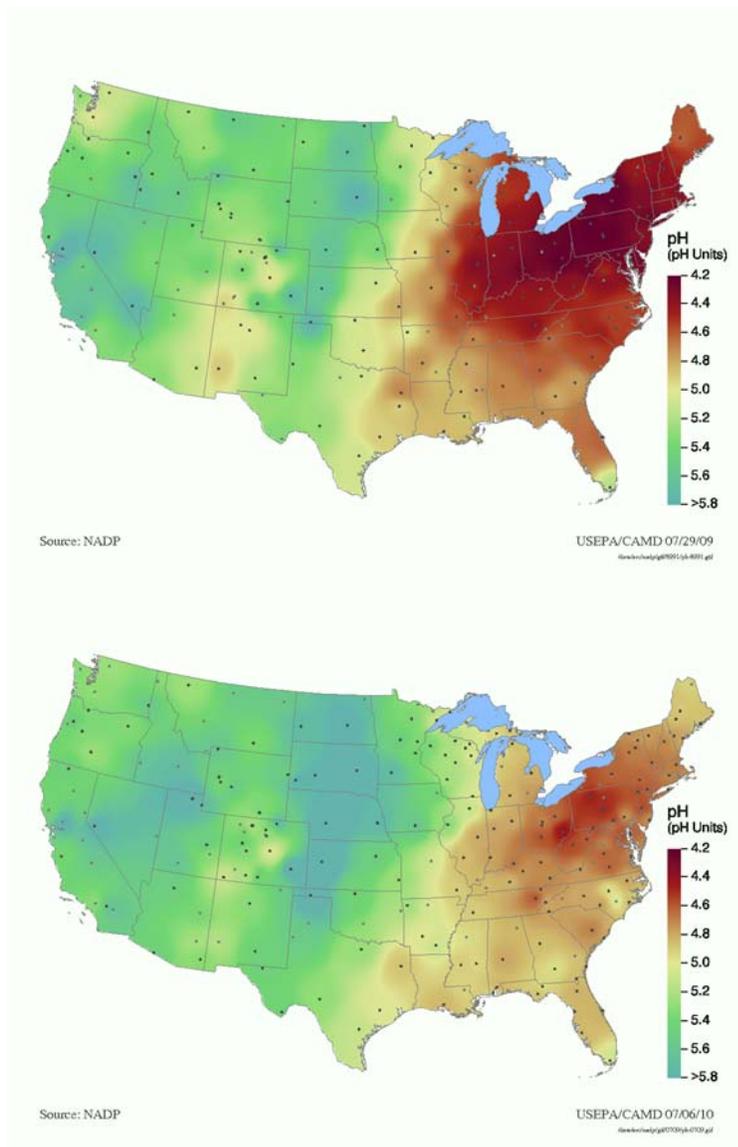


Figure 2-5.8. U.S. annual average spatial distribution of hydrogen ion concentration in rain water as pH averaged over 1989 -1991 (top) and 2007 – 2009 (bottom) based on the NADP.

2.5.3 Water quality

General patterns in the trends of major anions directionally track emission changes over the last two decades (EPA, 2010; Figures 2-5.9 - 2-5.11). Summaries of water quality trends prior to 2000 (Driscoll et al, 2003; Stoddard, 2003; Figure 2-5.10-2-5.11) illustrate the initial period of declining SO_x emissions with evidence of decreasing anions and increasing ANC. Several studies have illustrated the general trend of decreasing water column levels of strong

ions and increasing ANC with reductions in SO_x and NO_x deposition are synthesized in EPA's ISA.

However, as one proceeds through the source to effects continuum, strong direct relationships gradually diminish at each step as there are a myriad of confounding factors that start to affect each stage. This is particularly true in moving from deposition to water quality, where a variety of ecosystem processes moderate nitrogen and sulfur deposition both in terms of chemical transformations and delivery rates associated with soils and vegetation processes discussed above. For example, there are directionally different responses of water column sulfate (e.g., increase in southern Appalachians, decreases in Adirondacks) to declining levels of sulfate deposition (Figure 2-5-9). The inherent lag in recovering from acidification largely associated with soil adsorption and exchange processes implies that several decades of information may be required to sort out long term responses in water column chemistry relative to changes in emissions, air and deposition but the relative degree of responsiveness will be influenced strongly by watershed soil and vegetation characteristics. A recognition of the inherent lag in ecosystem response to changes in atmospheric variables is necessary to conceptualize the linking of air quality to water quality that rely on steady state models ecosystem models which provide the long term sustained response of water chemistry to atmospheric conditions. This understanding underlies the basic difference between the air quality water indices of acidification, both of which are incorporated in the form of the standard (section 7.2). An air quality acidification index reflects the eventual steady state conditions in aquatic systems that would be achieved assuming atmospheric a given atmospheric state of air quality conditions. The time lag in those conditions between aquatic and atmospheric media can range from near real time to decadal differences.

For example, the analyses of the Adirondack and Shenandoah Case Study Areas indicated that although wet deposition rates for SO₂ and NO_x have been reduced since the mid-1990s, current concentrations are still well above simulated pre-acidification (1860) conditions (figure 2-5.12 – 2-5.15). Modeling predicts NO₃⁻ and SO₄²⁻ are 17- and 5-fold higher, respectively, in 2006 than under simulated pre-acidification conditions. Based on the 2006 Model of Acidification of Groundwater in Catchment (MAGIC) simulations, the estimated average ANC across the 44 lakes in the Adirondack Case Study Area is 62.1 µeq/L (± 15.7

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

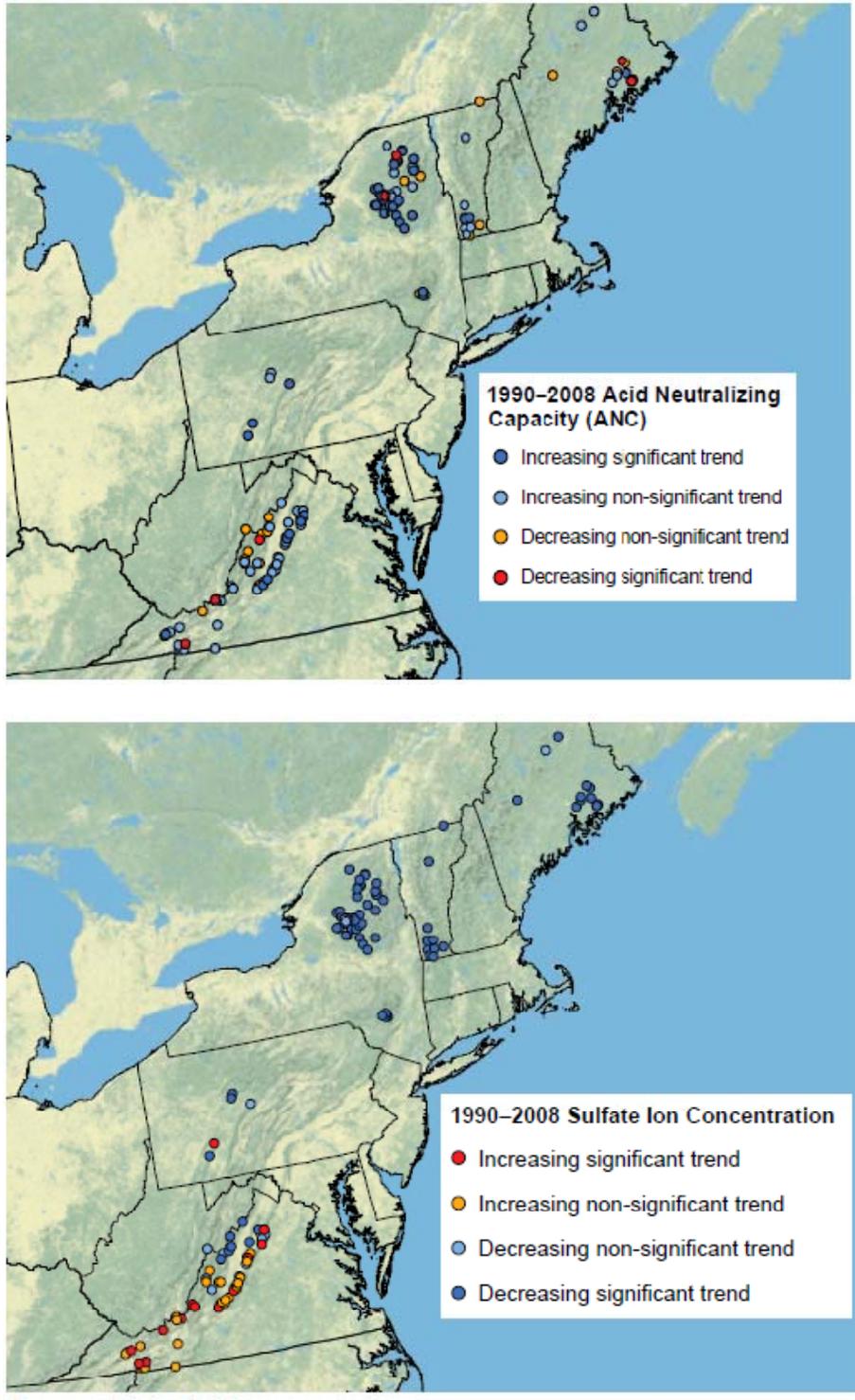
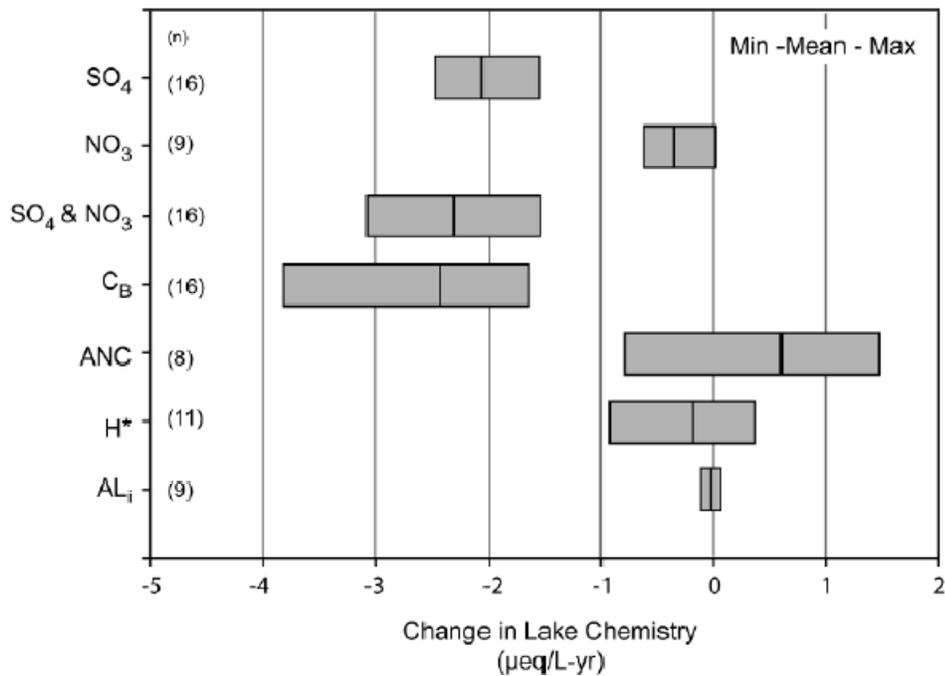


Figure 2-5.9. Generalized trends in water quality variables ANC (above) and sulfate ion (below) – EPA, 2010.



Source: Driscoll et al. (2003b)

Figure 2-5.10 Mean rates of change in solute concentration in 16 lakes of the Adirondack Long-Term Monitoring (ALTM) program from 1982 to 2000. Minimum, mean, and maximum changes in concentrations and number of lakes showing significant trends are shown. All values are in $\mu\text{eq/L/yr}$, except for concentrations of inorganic monomeric aluminum (Al_i), which are expressed in $\mu\text{M/yr}$.

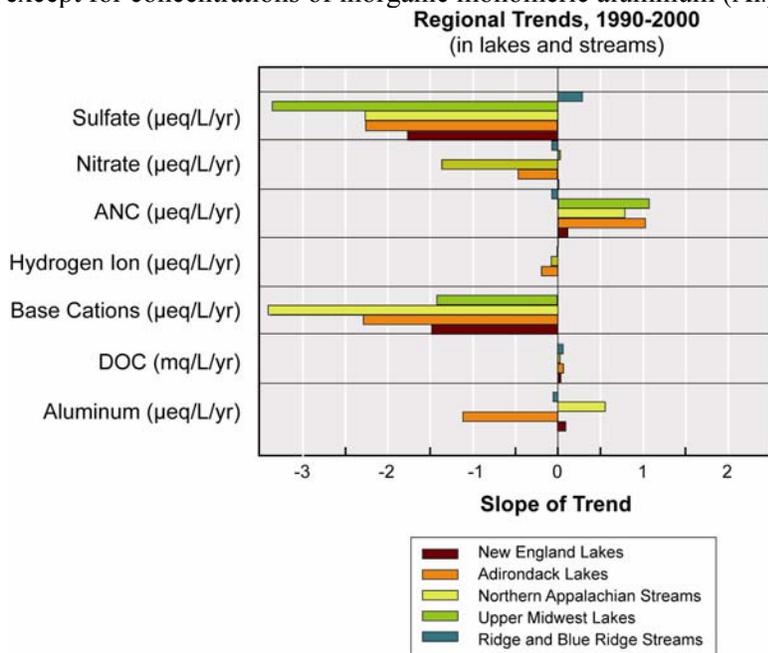


Figure 2-5.11 Summary of regional trends in surface water chemistry from 1990 to 2000 in regions covered by the Stoddard et al. (2003).

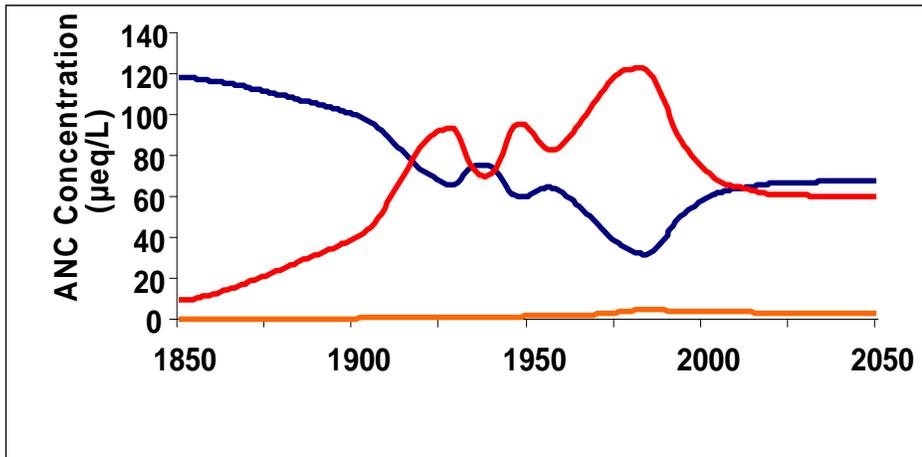


Figure 2-5.12. Average NO₃⁻ concentrations (orange), SO₄²⁻ concentrations (red), and ANC (blue) across the 44 lakes in the Adirondack Case Study Area modeled using MAGIC for the period 1850 to 2050.

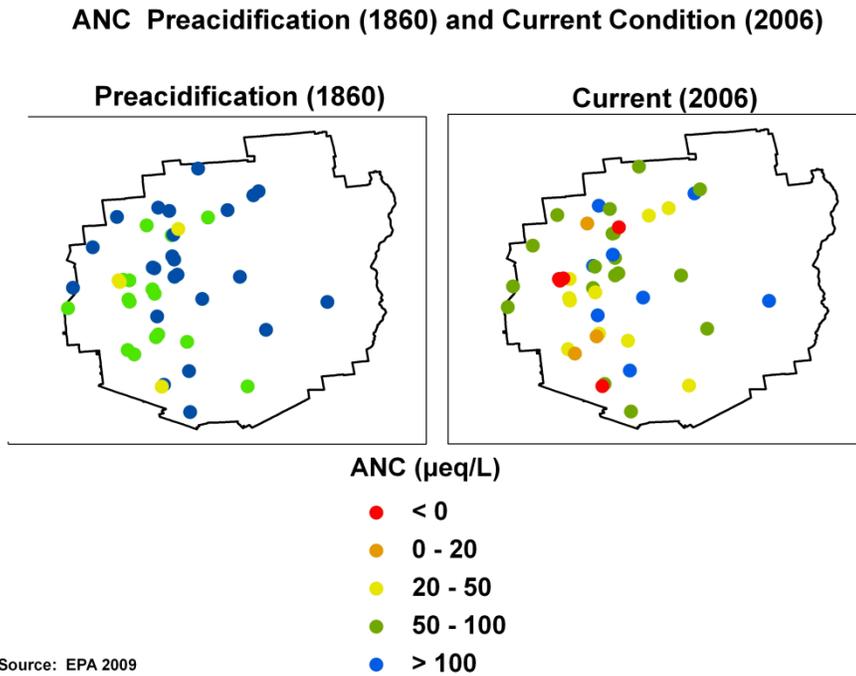


Figure 2-5.13. ANC concentrations of preacidification (1860) and 2006 conditions based on hindcasts of 44 lakes in the Adirondack Case Study Area modeled using MAGIC.

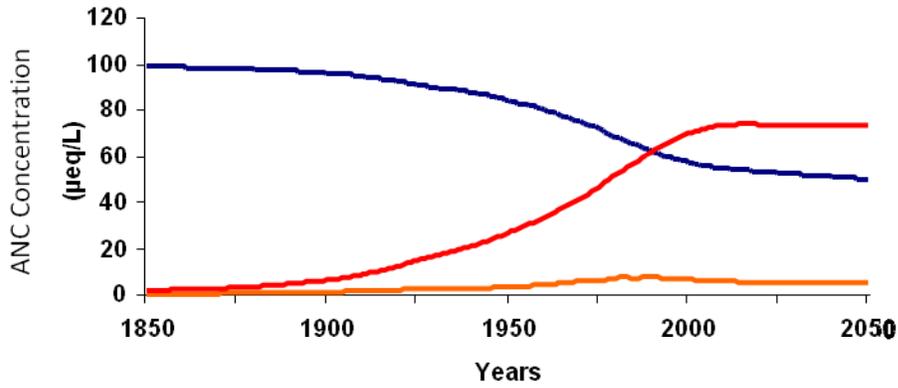


Figure 2-5.14. Average NO₃⁻ concentrations (orange), SO₄²⁻ concentrations (red), and ANC (blue) levels for the 60 streams in the Shenandoah Case Study Area modeled using MAGIC for the

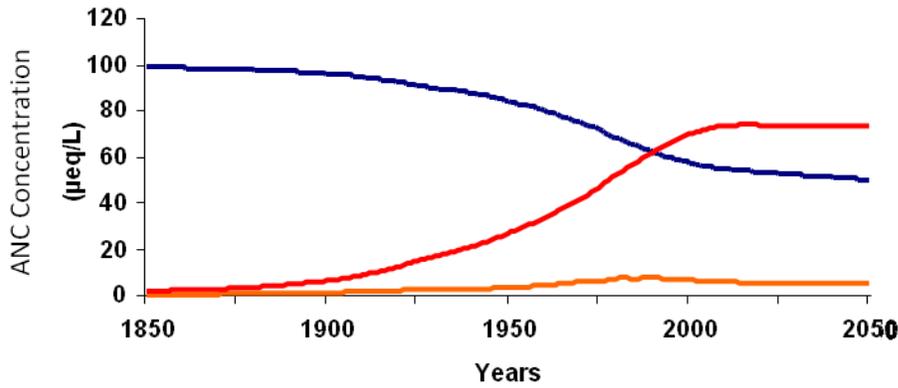


Figure 2-6.15. ANC levels of 1860 (preacidification) and 2006 (current) conditions based on hindcasts of 60 streams in the Shenandoah Case Study Area modeled using MAGIC

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