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7 Policy Assessment for the Review of the
8 Secondary National Ambient Air Quality
9 Standards for NO_x and SO_x

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12 First External Review Draft

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**Policy Assessment for the Review of the
Secondary National Ambient Air Quality Standards
for NO_x and SO_x:**

First External Review Draft

U.S. Environmental Protection Agency
Office of Air and Radiation
Office of Air Quality Planning and Standards
Health and Environmental Impacts Division
Research Triangle Park, North Carolina 27711

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LIST OF ACRONYMS AND ABBREVIATIONS

1		
2	AAPI	Atmospheric Acidification Potential Index
3	ADR	Adirondack Mountains of New York
4	Al ³⁺	aluminum
5	ANC	acid neutralizing capacity
6	AQCD	Air Quality Criteria Document
7	AQRV	air quality related values
8	ASSETS EI	Assessment of Estuarine Trophic Status eutrophication index
9	Bc/Al	Base cation to aluminum ratio, also Bc:Al
10	C	carbon
11	Ca/Al	calcium to aluminum ratio
12	Ca ²⁺	calcium
13	CAA	Clean Air Act
14	CASAC	Clean Air Scientific Advisory Committee
15	CASTNet	Clean Air Status and Trends Network
16	CCS	coastal sage scrub
17	Chl <i>a</i>	chlorophyll <i>a</i>
18	CLE	critical load exceedance
19	CMAQ	Community Multiscale Air Quality model
20	CSS	coastal sage scrub
21	CWA	Clean Water Act
22	DIN	dissolved inorganic nitrogen
23	DO	dissolved oxygen
24	DOI	U.S. Department of Interior
25	EMAP	Environmental Monitoring and Assessment Program
26	EPA	U.S. Environmental Protection Agency
27	FHWAR	fishing, hunting and wildlife associated recreation survey
28	FIA	Forest Inventory and Analysis National Program
29	FWS	Fish and Wildlife Service
30	GIS	geographic information systems
31	GPP	gross primary productivity
32	H ⁺	hydrogen ion
33	H ₂ O	water vapor
34	H ₂ SO ₄	sulfuric acid
35	ha	hectare
36	HAB	harmful algal bloom
37	HFC	hydrofluorocarbon
38	Hg ⁺²	reactive mercury
39	Hg ⁰	elemental mercury
40	HNO ₃	nitric acid
41	HONO	nitrous acid
42	HUC	hydrologic unit code
43	IMPROVE	Interagency Monitoring of Protected Visual Environments
44	ISA	Integrated Science Assessment
45	K ⁺	potassium

1	kg/ha/yr	kilograms per hectare per year
2	km	kilometer
3	LRMP	Land and Resource Management Plan
4	ILTER	Long Term Ecological Monitoring and Research
5	LTM	Long-Term Monitoring
6	MAGIC	Model of Acidification of Groundwater in Catchments
7	MCF	Mixed Conifer Forest
8	MEA	Millennium Ecosystem Assessment
9	Mg ²⁺	magnesium
10	N	nitrogen
11	N ₂	gaseous nitrogen
12	N ₂ O	nitrous oxide
13	N ₂ O ₃	nitrogen trioxide
14	N ₂ O ₄	nitrogen tetroxide
15	N ₂ O ₅	dinitrogen pentoxide
16	Na ⁺	sodium
17	NAAQS	National Ambient Air Quality Standards
18	NADP	National Atmospheric Deposition Program
19	NAPAP	National Acid Precipitation Assessment Program
20	NAWQA	National Water Quality Assessment
21	NEEA	National Estuarine Eutrophication Assessment
22	NEP	net ecosystem productivity
23	NH ₃	ammonia gas
24	NH ₄ ⁺	ammonium ion
25	(NH ₄) ₂ SO ₄	ammonium sulfate
26	NH _x	category label for NH ₃ plus NH ₄ ⁺
27	NO	nitric oxide
28	NO ₂	nitrogen dioxide
29	NO ₂ ⁻	reduced nitrite
30	NO ₃ ⁻	reduced nitrate
31	NOAA	National Oceanic and Atmospheric Administration
32	NO _x	nitrogen oxides
33	NO _y	total oxidized nitrogen
34	NPP	net primary productivity
35	NPS	National Park Service
36	NRC	National Research Council
37	NSWS	National Surface Water Survey
38	NTN	National Trends Network
39	NTR	organic nitrate
40	O ₃	ozone
41	OAQPS	Office of Air Quality Planning and Standards
42	OW	Office of Water
43	PAN	peroxyacyl nitrates
44	PFC	perfluorocarbons
45	pH	relative acidity
46	ppb	parts per billion
47	ppm	parts per million

1	ppt	parts per trillion
2	PSD	prevention of significant deterioration
3	REA	Risk and Exposure Assessment
4	REMAP	Regional Environmental Monitoring and Assessment Program
5	S	sulfur
6	S ₂ O ₃	thiosulfate
7	S ₂ O ₇	heptoxide
8	SAV	submerged aquatic vegetation
9	SF ₆	sulfur hexafluoride
10	SMP	Simple Mass Balance
11	SO	sulfur monoxide
12	SO ₂	sulfur dioxide
13	SO ₃	sulfur trioxide
14	SO ₃ ²⁻	sulfite
15	SO ₄	wet sulfate
16	SO ₄ ²⁻	sulfate ion
17	SOM	soil organic matter
18	SO _x	sulfur oxides
19	SPARROW	SPATIally Referenced Regressions on Watershed Attributes
20	SRB	sulfate-reducing bacteria
21	STORET	STORage and RETrieval
22	TIME	Temporally Integrated Monitoring of Ecosystems
23	TMDL	total maximum daily load
24	TP	total phosphorus
25	USFS	U.S. Forest Service
26	USGS	U.S. Geological Survey
27	µeq/L	microequivalents per liter
28	µg/m ³	micrograms per cubic meter
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LIST OF KEY TERMS

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Acidification: The process of increasing the acidity of a system (e.g., lake, stream, forest soil). Atmospheric deposition of acidic or acidifying compounds can acidify lakes, streams, and forest soils.

Air Quality Indicator: The substance or set of substances (e.g., PM_{2.5}, NO₂, SO₂) occurring in the ambient air for which the National Ambient Air Quality Standards set a standard level and monitoring occurs.

Alpine: The biogeographic zone made up of slopes above the tree line, characterized by the presence of rosette-forming herbaceous plants and low, shrubby, slow-growing woody plants.

Acid Neutralizing Capacity: A key indicator of the ability of water to neutralize the acid or acidifying inputs it receives. This ability depends largely on associated biogeophysical characteristics, such as underlying geology, base cation concentrations, and weathering rates.

Arid Region: A land region of low rainfall, where “low” is widely accepted to be less than 250 mm precipitation per year.

Base Cation Saturation: The degree to which soil cation exchange sites are occupied with base cations (e.g., Ca²⁺, Mg²⁺, K⁺) as opposed to Al³⁺ and H⁺. Base cation saturation is a measure of soil acidification, with lower values being more acidic. There is a threshold whereby soils with base saturations less than 20% (especially between 10%–20%) are extremely sensitive to change.

Ecologically Relevant Indicator: A physical, chemical, or biological entity/feature that demonstrates a consistent degree of response to a given level of stressor exposure and that is easily measured/quantified to make it a useful predictor of ecological risk.

Critical Load: A quantitative estimate of an exposure to one or more pollutants, below which significant (as defined by the analyst or decision maker) harmful effects on specified sensitive elements of the environment do not occur, according to present knowledge.

Denitrification: The anaerobic reduction of oxidized nitrogen (e.g., nitrate or nitrite) to gaseous nitrogen (e.g., N₂O or N₂) by denitrifying bacteria.

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

Ecological Risk: The likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors (U.S. EPA, 1992).

Ecological Risk Assessment: A process that evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors (U.S. EPA, 1992).

Ecosystem: The interactive system formed from all living organisms and their abiotic (i.e., physical and chemical) environment within a given area. Ecosystems cover a hierarchy of spatial scales and can comprise the entire globe, biomes at the continental scale, or small, well-circumscribed systems such as a small pond.

Ecosystem Benefit: The value, expressed qualitatively, quantitatively, and/or in economic terms, where possible, associated with changes in ecosystem services that result either directly or indirectly in improved human health and/or welfare. Examples of ecosystem benefits that derive from improved air quality include improvements in habitats for sport fish species, the quality of drinking water and recreational areas, and visibility.

- 1 **Ecosystem Function:** The processes and interactions that operate within an ecosystem.
- 2 **Ecosystem Services:** The ecological processes or functions having monetary or non-monetary
3 value to individuals or society at large. These are (1) supporting services, such as
4 productivity or biodiversity maintenance; (2) provisioning services, such as food, fiber, or
5 fish; (3) regulating services, such as climate regulation or carbon sequestration; and (4)
6 cultural services, such as tourism or spiritual and aesthetic appreciation.
- 7 **Eutrophication:** The process by which nitrogen additions stimulate the growth of autotrophic
8 biota, usually resulting in the depletion of dissolved oxygen.
- 9 **Nitrogen Enrichment:** The process by which a terrestrial system becomes enhanced by nutrient
10 additions to a degree that stimulates the growth of plant or other terrestrial biota, usually
11 resulting in an increase in productivity.
- 12 **Nitrogen Saturation:** The point at which nitrogen inputs from atmospheric deposition and other
13 sources exceed the biological requirements of the ecosystem; a level beyond nitrogen
14 enrichment.
- 15 **Occult Deposition:** The removal of gases and particles from the atmosphere to surfaces by fog
16 or mist.
- 17 **Semi-arid Regions:** Regions of moderately low rainfall, which are not highly productive and are
18 usually classified as rangelands. “Moderately low” is widely accepted as between 100-
19 and 250-mm precipitation per year.
- 20 **Sensitivity:** The degree to which a system is affected, either adversely or beneficially, by NO_x
21 and/or SO_x pollution (e.g., acidification, nutrient enrichment). The effect may be direct
22 (e.g., a change in growth in response to a change in the mean, range, or variability of
23 nitrogen deposition) or indirect (e.g., changes in growth due to the direct effect of
24 nitrogen consequently altering competitive dynamics between species and decreased
25 biodiversity).
- 26 **Total Reactive Nitrogen:** This includes all biologically, chemically, and radiatively active
27 nitrogen compounds in the atmosphere and biosphere, such as NH₃, NH₄⁺, NO, NO₂,
28 HNO₃, N₂O, NO₃⁻, and organic compounds (e.g., urea, amines, nucleic acids).
- 29 **Valuation:** The economic or non-economic process of determining either the value of
30 maintaining a given ecosystem type, state, or condition, or the value of a change in an
31 ecosystem, its components, or the services it provides.
- 32 **Variable Factors:** Influences which by themselves or in combination with other factors may
33 alter the effects on public welfare of an air pollutant (section 108 (a)(2))
34 (a) Atmospheric Factors: Atmospheric conditions that may influence transformation,
35 conversion, transport, and deposition, and thereby, the effects of an air pollutant on
36 public welfare, such as precipitation, relative humidity, oxidation state, and co-pollutants
37 present in the atmosphere.
38 (b) Ecological Factors: Ecological conditions that may influence the effects of an air
39 pollutant on public welfare once it is introduced into an ecosystem, such as soil base
40 saturation, soil thickness, runoff rate, land use conditions, bedrock geology, and
41 weathering rates.
- 42 **Vulnerability:** The degree to which a system is susceptible to, and unable to cope with, the
43 adverse effects of NO_x and/or SO_x air pollution.
- 44 **Welfare Effects:** The effects on soils, water, crops, vegetation, man-made materials, animals,
45 wildlife, weather, visibility, and climate; as well as damage to and deterioration of
46 property, hazards to transportation, and the effects on economic values and on personal

1 comfort and well-being, whether caused by transformation, conversion, or combination
2 with other air pollutants (Clean Air Act Section 302[h]).
3 **Wet Deposition:** The removal of gases and particles from the atmosphere to surfaces by rain or
4 other precipitation.
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1 This policy assessment is intended to help “bridge the gap” between the scientific
2 assessment contained in the ISA and the judgments required of the EPA Administrator in
3 determining whether it is appropriate to retain or revise the secondary NAAQS for NO_x and SO_x.
4 This policy assessment considers the available scientific evidence and quantitative risk-based
5 analyses, together with related limitations and uncertainties, and focuses on the basic elements of
6 air quality standards: indicators², averaging times, forms³, and levels. These elements, which
7 serve to define each standard, must be considered collectively in evaluating the welfare
8 protection afforded by the secondary NO_x and SO_x NAAQS. Our development of this policy
9 assessment is based on the assessment and integrative synthesis of information presented in the
10 ISA and on staff analyses and evaluations presented in this document, and is further informed by
11 comments and advice received from an independent scientific review committee, the Clean Air
12 Scientific Advisory Committee (CASAC), in their review of the previous integrated science and
13 risk and exposure assessments. The Policy Assessment is further informed by comments
14 submitted by the public⁴. To view related documents developed as part of the planning, science,
15 and risk assessment phases of this review see
16 <http://www.epa.gov/ttn/naaqs/standards/no2so2sec/index.html>.

17 This document is organized around a conceptual framework for a combined NO_x and SO_x
18 secondary NAAQS and is focused on answering key policy questions related to the
19 implementation of that conceptual framework. Chapter 2 provides a summary of ecological
20 effects from the deposition of ambient NO_x and SO_x to sensitive ecosystems, drawing from the
21 ISA and REA. Chapter 3 places those ecological effects within the context of “public welfare”
22 by linking effects to ecosystem services or other benchmarks of public welfare. Chapter 4
23 addresses the adequacy of the current NO_x and SO_x secondary NAAQS in addressing the impacts
24 on public welfare from ecological effects. Chapter 5 develops the conceptual design for
25 ecologically relevant multi-pollutant standards. Chapter 6 presents options for developing critical
26 elements of a secondary NAAQS necessary to implement the conceptual design. Chapter 7
27 describes how secondary NAAQS designed to protect a specific ecological endpoint may also
28 provide protection for other ecological endpoints. Chapter 8 provides a consideration of issues

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

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

⁴ Summary information on public comments will be provided in a later draft of the policy assessment

1 regarding reduced and oxidized forms of nitrogen. Chapter 9 concludes with preliminary staff
2 conclusions regarding ranges of options for pollutant indicators, averaging times, forms, and
3 levels for the secondary NO_x and SO_x NAAQS, including a discussion of staff initial conclusions
4 on what levels of the secondary NAAQS might be requisite to protect public welfare.

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

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

17 EPA will be preparing a second draft Policy Assessment subsequent to receiving advice
18 from the CASAC. The second draft will incorporate responses to comments received from
19 CASAC, as well as comments submitted by the public. The second draft will also provide a more
20 complete development of the conceptual model, and will provide a more complete set of staff
21 conclusions on critical elements of the standards. EPA's final Policy Assessment will address
22 additional CASAC comments on the second draft, and will include sufficient information to
23 inform the Administrator on critical elements of the standards, and staff conclusions regarding
24 alternative levels of the standards.

25 **1.1 DEFINITIONS OF NO_x AND SO_x FOR THIS ASSESSMENT**

26 As discussed in detail in the REA (**REA 1.3.1**), in the atmospheric science community
27 NO_x is typically referred to as the sum of nitrogen dioxide (NO₂), and nitric oxide (NO). From a
28 Clean Air Act perspective, the family of NO_x includes any gaseous combination of nitrogen and
29 oxygen (e.g., NO₂, NO, nitrous oxide [N₂O], nitrogen trioxide [N₂O₃], nitrogen tetroxide [N₂O₄],
30 and dinitrogen pentoxide [N₂O₅]). The term used by the scientific community to represent the

1 complete set of oxidized nitrogen compounds, including those listed in CAA Section 108(c), is
2 total oxidized nitrogen (NO_y). NO_y includes all nitrogen oxides, including e.g. total reactive
3 oxidized atmospheric nitrogen, defined as NO_x (NO and NO₂) and all oxidized NO_x products:
4 NO_y = NO₂ + NO + HNO₃ + PAN + 2N₂O₅ + HONO + NO₃ + organic nitrates + particulate NO₃
5 (Finlayson-Pitts and Pitts, 2000). In this document, unless otherwise indicated, we use the term
6 NO_x interchangeably with NO_y to refer to the complete set of oxidized nitrogen compounds.

7 For this assessment, SO_x is defined to include all oxides of sulfur, including multiple
8 gaseous substances (e.g., SO₂, sulfur monoxide [SO], sulfur trioxide [SO₃], thiosulfate [S₂O₃],
9 and heptoxide [S₂O₇], as well as particulate species, such as ammonium sulfate [(NH₄)₂SO₄]).
10 Throughout this text we refer to sulfate as SO₄ and nitrate as NO₃, recognizing that they have
11 charges of -2 for sulfate and -1 for nitrate.

12 **1.2 POLICY OBJECTIVES**

13 In conducting this periodic review of the NO_x and SO_x secondary NAAQS, EPA has
14 decided to jointly assess the scientific information, associated risks, and standards relevant to
15 protecting the public welfare from adverse effects associated with oxides of nitrogen and sulfur.
16 Although EPA has historically adopted separate secondary standards for oxides of nitrogen
17 (NO_x) and oxides of sulfur (SO_x), EPA is conducting a joint secondary review of these standards
18 because NO_x, SO_x, and their associated transformation products are linked from an atmospheric
19 chemistry perspective, as well as from an environmental effects perspective. The National
20 Research Council (NRC) has recommended that EPA consider multiple pollutants, as
21 appropriate, in forming the scientific basis for the NAAQS (NRC, 2004). There is a strong basis
22 for considering these pollutants together, building upon EPA's and CASAC's past recognition of
23 the interactions of these pollutants and on the growing body of scientific information that is now
24 available related to these interactions and associated ecological effects.

25 EPA sets secondary standards for two criteria pollutants related to NO_x and SO_x: ozone
26 and particulate matter (PM). NO_x is a precursor to the formation of ozone in the atmosphere, and
27 under certain conditions, can combine with atmospheric ammonia to form ammonium nitrate, a
28 component of fine PM. SO_x is a precursor to the formation of particulate sulfate, which is a
29 significant component of fine PM in many parts of the U.S. While there are a number of welfare
30 effects associated with ozone and fine PM, including ozone damage to vegetation, and visibility

1 degradation related to PM, protection against those effects is provided by the ozone and fine PM
2 standards. This review focuses on evaluation of the protection provided by NO_x and SO_x
3 secondary standards for effects associated with direct atmospheric concentrations of NO_x and
4 SO_x, and effects associated with deposition of NO_x and SO_x to ecosystems, including deposition
5 in the form of particulate nitrate and sulfate in their component forms.

6 The ISA highlights the ecological effects associated with deposition of ambient NO_x and
7 SO_x to ecosystems other than commercially managed forests and agricultural lands. This
8 assessment evaluates information on gas-phase effects of NO_x and SO_x via stomatal exposure on
9 vegetation, but primarily focuses on the effects of gas-phase NO_x and SO_x exposure via
10 deposition on multiple ecological receptors. Highlighted effects include those associated with
11 acidification and nitrogen nutrient enrichment. Based on these highlighted effects, EPA's policy
12 objective is to develop a framework for NO_x and SO_x standards that incorporate factors that will
13 lead to standards that are ecologically relevant, and that recognizes the interactions between the
14 two pollutants as they deposit to sensitive ecosystems, with an ultimate goal of setting standards
15 that, based on the ecological criteria described in the ISA, and consistent with the requirements
16 of the Clean Air Act, "are requisite to protect the public welfare from any known or anticipated
17 adverse effects associated with the presence of such air pollutant in the ambient air."

18 In presenting policy options for the Administrator's consideration, we note that the final
19 decision on retaining or revising the current secondary standards for NO_x and SO_x is largely a
20 public welfare policy judgment based on the Administrator's informed assessment of what
21 constitutes requisite protection against adverse effects to public welfare. A final decision should
22 draw upon scientific information and analyses about welfare effects, exposure and risks, as well
23 as judgments about the appropriate response to the range of uncertainties that are inherent in the
24 scientific evidence and analyses. The ultimate determination as to what level of damage to
25 ecosystems and the services provided by those ecosystems is adverse to public welfare is not
26 wholly a scientific question, although it is informed by scientific studies linking ecosystem
27 damage to losses in ecosystem services, and economic information on the value of those losses in
28 ecosystem services. Our approach to informing these judgments, as discussed below, is
29 consistent with the requirements of the NAAQS provisions of the Clean Air Act and with how
30 EPA and the courts have historically interpreted the Act. These provisions require the
31 Administrator to establish secondary NAAQS that, in the Administrator's judgment, are requisite

1 to protect public welfare from any known or anticipated adverse effects associated with the
2 presence of NO_x and SO_x in the ambient air. In so doing, the Administrator seeks to establish
3 standards that are neither more nor less stringent than necessary for this purpose.

4 For this first draft policy assessment, we have chosen to focus much of our discussion on
5 the effects of ambient NO_x and SO_x on ecological impacts associated with acidifying deposition
6 of nitrogen and sulfur, which is a transformation product of ambient NO_x and SO_x. We have the
7 greatest confidence in the causal linkages between NO_x and SO_x and aquatic acidification effects,
8 and we have the most complete information available with which to develop an ecologically
9 meaningful structure for the standards. In future drafts, we expect to be able to explore whether
10 and how the standards can be expanded to directly address effects of acidification on terrestrial
11 ecosystems, and to address the effects of nutrient enrichment in terrestrial and aquatic
12 ecosystems.

13 **1.3 CRITICAL POLICY ELEMENTS**

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

17 Sections 108 and 109 of the CAA govern the establishment and periodic review of the
18 NAAQS and of the air quality criteria upon which the standards are based. The NAAQS are
19 established for pollutants that are listed under section 108, based on three criteria, including
20 whether emissions of the air pollutant cause or contribute to air pollution which may reasonably
21 be anticipated to endanger public health or welfare and whose presence in the ambient air results
22 from numerous or diverse mobile or stationary sources. The NAAQS are based on air quality
23 criteria that reflect the latest scientific knowledge, useful in indicating the types and extent of
24 identifiable effects on public health or welfare that may be expected from the presence of the
25 pollutant in ambient air. The criteria refer to criteria issued pursuant to §108 of the Clean Air
26 Act, which include “(A) those variable factors (including atmospheric conditions) which of
27 themselves or in combination with other factors may alter the effects on public health or welfare
28 of such air pollutant; (B) the types of air pollutants which, when present in the atmosphere, may
29 interact with such pollutant to produce an adverse effect on public health or welfare; and (C) any
30 known or anticipated adverse effects on welfare.”

1 The following critical policy elements for the design of ecologically relevant secondary
2 standards for NO_x and SO_x are identified:

3 (CPE 1) An evaluation of the effects of ambient NO_x and SO_x on ecosystems, and the
4 relationship between those effects and the measure of dose in the ecosystem,
5 indicated by the depositional loadings of N and S.

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

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

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

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

17 (CPE 3) Characterization of the complex atmospheric transformations between
18 ambient concentrations of NO_x and SO_x and deposition of N and S in the
19 specification of a standard.

20 (CPE 4) Specification of those factors, such as precipitation, which interact with
21 ambient NO_x and SO_x to produce adverse effects on welfare, by affecting
22 deposition of N and S.

23 (CPE 5) Specification of the form for the standard(s), including ambient atmospheric
24 indicators for NO_x and SO_x, with consideration of averaging times, and
25 options for levels of the standard(s).

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

1 **1.4 HISTORICAL CONTEXT**

2 **1.4.1 History of NO_x and SO_x NAAQS Review**

3 **1.4.1.1 NO_x NAAQS**

4 EPA began the most recent previous review of the NO_x secondary standards in 1987 and
5 in November 1991, EPA released an updated draft AQCD for CASAC and public review and
6 comment (56 FR 59285). This draft document provided a comprehensive assessment of the
7 available scientific and technical information on health and welfare effects associated with NO₂
8 and other NO_x. CASAC reviewed the draft document at a meeting held on July 1, 1993, and
9 concluded in a closure letter to the Administrator that the document “provides a scientifically
10 balanced and defensible summary of current knowledge of the effects of this pollutant and
11 provides an adequate basis for EPA to make a decision as to the appropriate NAAQS for NO₂”
12 (Wolff, 1993). The AQCD *Air Quality Criteria for Oxides of Nitrogen* was then finalized (U.S.
13 EPA, 1993). EPA also prepared a Staff Paper that summarized and integrated the key studies and
14 scientific evidence contained in the revised NO_x AQCD and identified the critical elements to be
15 considered in the review of the NO₂ NAAQS. CASAC reviewed two drafts of the Staff Paper and
16 concluded in a closure letter to the Administrator that the document provided a “scientifically
17 adequate basis for regulatory decisions on nitrogen dioxide” (Wolff, 1995). In October 1995, the
18 Administrator announced her proposed decision not to revise either the primary or secondary
19 NAAQS for NO₂ (60 FR 52874; October 11, 1995). A year later, the Administrator made a final
20 determination not to revise the NAAQS for NO₂ after careful evaluation of the comments
21 received on the proposal (61 FR 52852; October 8, 1996). The level for both the existing primary
22 and secondary NAAQS for NO₂ is 0.053 ppm (100 micrograms per cubic meter [µg/m³] of air),
23 annual arithmetic average, calculated as the arithmetic mean of the 1-hour NO₂ concentrations.

24 **1.4.1.2 SO_x NAAQS**

25 Based on the 1970 SO_x criteria document (DHEW, 1970), EPA promulgated primary and
26 secondary NAAQS for SO₂ on April 30, 1971 (36 FR 8186). The secondary standards included a
27 standard at 0.02 ppm in an annual arithmetic mean and a 3-hour average of 0.5 ppm, not to be
28 exceeded more than once per year. These secondary standards were established solely on the
29 basis of evidence of adverse effects on vegetation. In 1973, revisions made to Chapter 5

1 (“Effects of Sulfur Oxide in the Atmosphere on Vegetation”) of *Air Quality Criteria for Sulfur*
2 *Oxides* (U.S. EPA, 1973) indicated that it could not properly be concluded that the vegetation
3 injury reported resulted from the average SO₂ exposure over the growing season, rather than
4 from short-term peak concentrations. Therefore, EPA proposed (38 FR 11355) and then finalized
5 (38 FR 25678) a revocation of the annual mean secondary standard. At that time, EPA was aware
6 that SO_x have other public welfare effects, including effects on materials, visibility, soils, and
7 water. However, the available data were considered insufficient to establish a quantitative
8 relationship between specific ambient SO_x concentrations and effects (38 FR 25679).

9 In 1979, EPA announced that it was revising the Air Quality Criteria Document (AQCD)
10 for sulfur oxides concurrently with that for particulate matter and would produce a combined
11 particulate matter and sulfur oxides criteria document. Following its review of a draft revised
12 criteria document in August 1980, CASAC concluded that acid deposition was a topic of
13 extreme scientific complexity because of the difficulty in establishing firm quantitative
14 relationships among (1) emissions of relevant pollutants (e.g., SO₂ and oxides of nitrogen), (2)
15 formation of acidic wet and dry deposition products, and (3) effects on terrestrial and aquatic
16 ecosystems. CASAC also noted that acid deposition involves, at a minimum, several different
17 criteria pollutants: oxides of sulfur, oxides of nitrogen, and the fine particulate fraction of
18 suspended particles. CASAC felt that any document on this subject should address both wet and
19 dry deposition, since dry deposition was believed to account for at least one half of the total acid
20 deposition problem.

21 For these reasons, CASAC recommended that a separate, comprehensive document on
22 acid deposition be prepared prior to any consideration of using the NAAQS as a regulatory
23 mechanism for the control of acid deposition. CASAC also suggested that a discussion of acid
24 deposition be included in the AQCDs for nitrogen oxides and PM and SO_x. Following CASAC
25 closure on the AQCD for SO₂ in December 1981, EPA’s Office of Air Quality Planning and
26 Standards published a Staff Paper in November 1982, but the paper did not directly assess the
27 issue of acid deposition. Instead, EPA subsequently prepared the following documents: *The*
28 *Acidic Deposition Phenomenon and Its Effects: Critical Assessment Review Papers, Volumes I*
29 *and II* (U.S. EPA, 1984a, b), and *The Acidic Deposition Phenomenon and Its Effects: Critical*
30 *Assessment Document* (U.S. EPA, 1985) (53 FR 14935 -14936). These documents, though they

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

3 On April 26, 1988 (53 FR 14926), EPA proposed not to revise the existing primary and
4 secondary standards for SO₂. This proposal regarding the secondary SO₂ NAAQS was due to the
5 Administrator's conclusions that (1) based upon the then-current scientific understanding of the
6 acid deposition problem, it would be premature and unwise to prescribe any regulatory control
7 program at that time, and (2) when the fundamental scientific uncertainties had been reduced
8 through ongoing research efforts, EPA would draft and support an appropriate set of control
9 measures.

10 **1.4.2 History of Related Assessments and Agency Actions**

11 In 1980, the Congress created the National Acid Precipitation Assessment Program
12 (NAPAP) in response to growing concern about acidic deposition. The NAPAP was given a
13 broad 10-year mandate to examine the causes and effects of acidic deposition and to explore
14 alternative control options to alleviate acidic deposition and its effects. During the course of the
15 program, the NAPAP issued a series of publicly available interim reports prior to the completion
16 of a final report in 1990 (NAPAP, 1990).

17 In spite of the complexities and significant remaining uncertainties associated with the
18 acid deposition problem, it soon became clear that a program to address acid deposition was
19 needed. The Clean Air Act Amendments of 1990 included numerous separate provisions related
20 to the acid deposition problem. The primary and most important of the provisions, the
21 amendments to Title IV of the Act, established the Acid Rain Program to reduce emissions of
22 SO₂ by 10 million tons and NO_x emissions by 2 million tons from 1980 emission levels in order
23 to achieve reductions over broad geographic regions. In this provision, Congress included a
24 statement of findings that led them to take action, concluding that (1) the presence of acid
25 compounds and their precursors in the atmosphere and in deposition from the atmosphere
26 represents a threat to natural resources, ecosystems, materials, visibility, and public health; (2)
27 the problem of acid deposition is of national and international significance; and (3) current and
28 future generations of Americans will be adversely affected by delaying measures to remedy the
29 problem.

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

4 Third, Congress considered that further action might be necessary in the long term to
5 address any problems remaining after implementation of the Title IV program and, reserving
6 judgment on the form that action could take, included Section 404 of the 1990 Amendments
7 (Clean Air Act Amendments of 1990, Pub. L. 101-549, § 404) requiring EPA to conduct a study
8 on the feasibility and effectiveness of an acid deposition standard or standards to protect
9 “sensitive and critically sensitive aquatic and terrestrial resources.” At the conclusion of the
10 study, EPA was to submit a report to Congress. Five years later, EPA submitted its report,
11 entitled *Acid Deposition Standard Feasibility Study: Report to Congress* (U.S. EPA, 1995) in
12 fulfillment of this requirement. The Report concluded that establishing acid deposition standards
13 for sulfur and nitrogen deposition may at some point in the future be technically feasible,
14 although appropriate deposition loads for these acidifying chemicals could not be defined with
15 reasonable certainty at that time.

16 Fourth, the 1990 Amendments also added new language to sections of the CAA
17 pertaining to the scope and application of the secondary NAAQS designed to protect the public
18 welfare. Specifically, the definition of “effects on welfare” in Section 302(h) was expanded to
19 state that the welfare effects include effects “...whether caused by transformation, conversion, or
20 combination with other air pollutants.”

21 In 1999, seven Northeastern states cited this amended language in Section 302(h) in a
22 petition asking EPA to use its authority under the NAAQS program to promulgate secondary
23 NAAQS for the criteria pollutants associated with the formation of acid rain. The petition stated
24 that this language “clearly references the transformation of pollutants resulting in the inevitable
25 formation of sulfate and nitrate aerosols and/or their ultimate environmental impacts as wet and
26 dry deposition, clearly signaling Congressional intent that the welfare damage occasioned by
27 sulfur and nitrogen oxides be addressed through the secondary standard provisions of Section
28 109 of the Act.” The petition further stated that “recent federal studies, including the NAPAP
29 Biennial Report to Congress: An Integrated Assessment, document the continued-and increasing-
30 damage being inflicted by acid deposition to the lakes and forests of New York, New England
31 and other parts of our nation, demonstrating that the Title IV program had proven insufficient.”

1 The petition also listed other adverse welfare effects associated with the transformation of these
2 criteria pollutants, including impaired visibility, eutrophication of coastal estuaries, global
3 warming, and tropospheric ozone and stratospheric ozone depletion.

4 In a related matter, the Office of the Secretary of the U.S. Department of Interior
5 requested in 2000 that EPA initiate a rulemaking proceeding to enhance the air quality in
6 national parks and wilderness areas in order to protect resources and values that are being
7 adversely affected by air pollution. Included among the effects of concern identified in the
8 request were the acidification of streams, surface waters, and/or soils; eutrophication of coastal
9 waters; visibility impairment; and foliar injury from ozone.

10 In a Federal Register notice in 2001, EPA announced receipt of these requests and asked
11 for comment on the issues raised in them. EPA stated that it would consider any relevant
12 comments and information submitted, along with the information provided by the petitioners and
13 DOI, before making any decision concerning a response to these requests for rulemaking (65 FR
14 48699).

15 The most recent 2005 NAPAP report states that "... scientific studies indicate that the
16 emission reductions achieved by Title IV are not sufficient to allow recovery of acid-sensitive
17 ecosystems. Estimates from the literature of the scope of additional emission reductions that are
18 necessary in order to protect acid-sensitive ecosystems range from approximately 40-80%
19 beyond full implementation of Title IV.... The results of the modeling presented in this Report to
20 Congress indicate that broader recovery is not predicted without additional emission reductions"
21 (NAPAP, 2005).⁵

22 Given the state of the science as described in the ISA and in other recent reports, such as
23 the NAPAP's above, EPA believes it is appropriate, in the context of evaluating the adequacy of
24 the current NO₂ and SO₂ secondary standards in this review, to revisit the question of the
25 appropriateness and the feasibility of setting a secondary NAAQS to address remaining known
26 or anticipated adverse public welfare effects resulting from the acidic and nutrient deposition of
27 these criteria pollutants

⁵ Note that a new NAPAP report is expected to be released later in 2010. The findings of that report will be considered in the final policy assessment.

1 **1.5 PROPOSED CONCEPTUAL FRAMEWORK FOR COMBINED NO_x**
2 **SO_x STANDARDS**

3 There is a strong basis for considering NO_x and SO_x together at this time, building upon
4 EPA's and CASAC's past recognition of the interactions of these pollutants and on the growing
5 body of scientific information that is now available related to these interactions and associated
6 ecological effects. The REA introduced a conceptual framework for ecologically meaningful
7 secondary standards that recognized the complex processes by which ecosystems are exposed to
8 ambient NO_x and SO_x. That framework provided a flow from ambient concentrations exposures
9 via deposition to ecological indicators and effects (see Figure ES-2 in the REA Executive
10 Summary). This sequence represents the process by which we can determine the risks associated
11 with ambient concentrations of NO_x and SO_x. However, for the purposes of discussing a
12 conceptual framework for design of standards to protect against those risks, a modified version
13 of the risk framework is needed.

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

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

28 The details of this conceptual framework are discussed in Chapter 5, including
29 discussions of modifying factors that alter the relationship between ambient atmospheric
30 concentrations of NO_x and SO_x and depositional loads of nitrogen and sulfur, and those that
31 modify the relationship between deposition loads and the ecological indicator.

1 In setting NAAQS to protect public health and welfare, EPA has historically established
2 standards which require the comparison of monitored concentrations of an air pollutant against a
3 numerical metric of atmospheric concentration that does not vary geographically. This approach
4 has appropriately protected public health as at-risk populations are widely distributed throughout
5 the nation. As more is learned about the effects of pollutants such as NO_x and SO_x and the
6 environment, however, such an approach may not be appropriate to provide the requisite level of
7 protection to public welfare from effects on sensitive ecosystems. EPA is considering in this
8 review of the secondary standard for NO_x and SO_x whether a standard that takes into account
9 variable factors, such as atmospheric variables and ecosystem sensitivities, is the appropriate
10 approach to protect the public welfare from the effects associated with the presence of these
11 pollutants in the ambient air.

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

23 Air quality criteria for an air pollutant shall accurately reflect the latest scientific
24 knowledge useful in indicating the kind and extent of all identifiable effects on public health or
25 welfare which may be expected from the presence of such pollutant in the ambient air, in varying
26 quantities. The criteria for an air pollutant to the extent practicable, shall include information on:

- 27 ▪ (A) those variable factors (including atmospheric conditions) which of themselves or
28 in combination with other factors may alter the effects on public health or welfare of such
29 air pollutants;
- 30 ▪ (B) the types of air pollutants which, when present in the atmosphere, may interact
31 with such pollutants to produce an adverse effect on public health or welfare; and

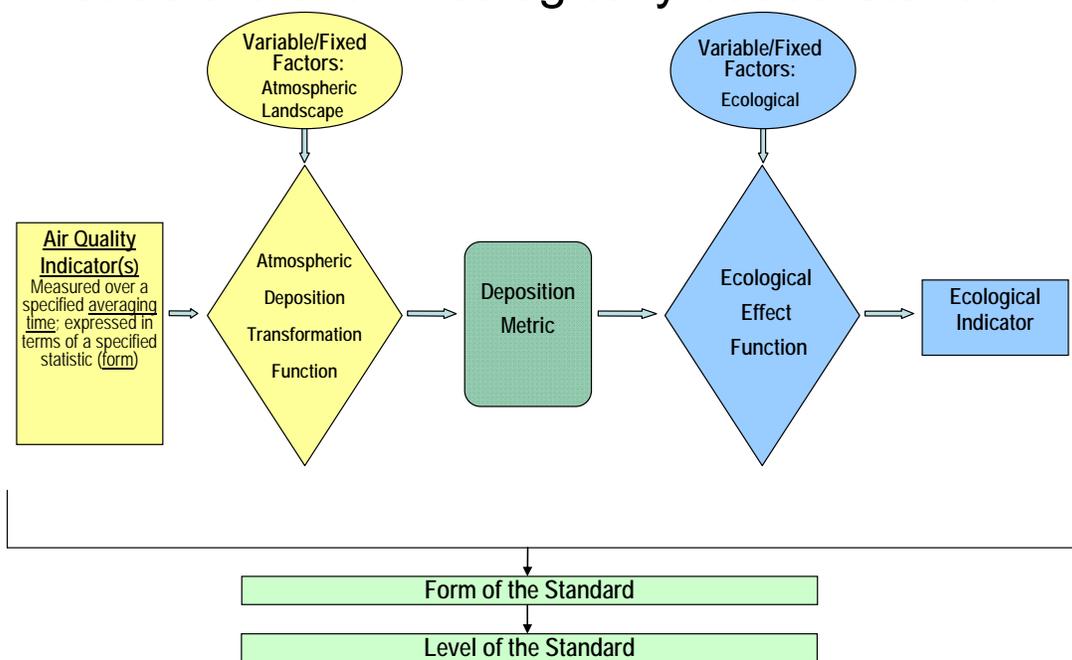
- 1 ▪ (C) any known or anticipated adverse effects on welfare.

2 Based on this extensive review of the air quality criteria for an air pollutant, the
3 Administrator is required to review and to revise, as appropriate, the secondary standard to
4 ensure that the standard “is requisite to protect public welfare from any known or anticipated
5 adverse effects associated with the presence of such air pollutant in the ambient air.” CAA §
6 109(b) & (d). “Effects on welfare,” in turn, is defined to include a broad array of effects,
7 including effects on soil, water, crops, vegetation, and manmade materials, “whether caused by
8 transformation, conversion, or combination with other air pollutants.” CAA § 302(h). Thus, as
9 with the sections of the CAA describing the issuance of air quality criteria, the CAA uses
10 expansive language in describing the scope of EPA’s responsibility and the range of effects that
11 EPA should take into account in setting a standard that is requisite to protect public welfare. The
12 term “requisite,” however, indicates that section 109 is not open-ended. In considering the
13 meaning of the term “requisite” in the context of the primary standards, the Supreme Court has
14 agreed with EPA that such a standard is one that is “sufficient, but not more than necessary” to
15 protect public health. *Whitman v. American Trucking*, 531 U.S. 457, 473 (2001).

16 While EPA has most often considered the results of direct exposure to an air pollutant in
17 the ambient air in assessing effects on public health and welfare, such as the health effects on
18 humans when breathing in an air pollutant or the effects on vegetation through the uptake of air
19 pollutants from the ambient air through leaves, EPA has also considered, where appropriate, the
20 effects of exposure to air pollutants through more indirect mechanisms. For example, both in
21 1978 and in 2008, EPA established a NAAQS for lead that addressed the health effects of
22 ambient lead whether the lead particles were inhaled or were ingested after deposition on the
23 ground or other surfaces. 73 FR 66964 (November 12, 2008), *Lead Industries v. EPA*, 647 F.2d
24 1130 (DC Cir. 1980) (1978 NAAQS). The deposition of ambient NO_x and SO_x to terrestrial and
25 aquatic environments can impact ecosystems through both direct and indirect mechanisms, as
26 discussed in the REA and this document. Given Congress’ instruction to set a standard that “is
27 requisite to protect the public welfare from “any known or anticipated adverse effects associated
28 with the presence of such air pollutant in the ambient air,” 42 U.S.C. § 109 (b)(2) (emphasis
29 added), this review appropriately attempts to take into consideration widely acknowledged
30 effects, such as acidification and nutrient enrichment, which are associated with the presence of
31 ambient SO_x and NO_x.

1 In this review, EPA is also attempting to develop a standard that takes into account the
 2 variability in effects from ambient levels of SO_x and NO_x. The CAA requires EPA to establish
 3 “national” standards, based on the air quality criteria, that provide the requisite degree of
 4 protection, but does not clearly address how to do so under the circumstances present here. One
 5 approach is to develop a secondary standard such as the one discussed in this Policy Assessment
 6 Document. Such a standard is designed to provide a generally uniform degree of protection
 7 throughout the country by allowing for varying concentrations of allowable ambient NO_x and
 8 SO_x, depending on atmospheric conditions and other variabilities, to achieve that degree of
 9 protection. Such a standard protects sensitive ecosystems wherever such ecosystems are found.
 10 This approach recognizes that setting a standard that is sufficient to protect the public welfare but
 11 not more than is necessary calls for consideration of a standard such as the one discussed in this
 12 document.

Structure of an Ecologically-based Standard



13
 14 **Figure 1-1.** Framework of an alternative secondary standard.

15 1.6 POLICY RELEVANT QUESTIONS

16 In this policy assessment, a series of general questions frames our approach to identifying
 17 a range of policy options for consideration by the Administrator regarding secondary NAAQS
 18 for NO_x and SO_x. These questions are drawn from our Integrated Review Plan with

1 modifications based on further consideration by staff and comments from CASAC and the
2 public. Our policy assessment begins by characterizing “known or anticipated adverse effects”
3 on public welfare within our conceptual model (CPE 1). As noted earlier, this review is focusing
4 on effects in unmanaged ecosystems (not commercial forests or agricultural lands⁶) resulting
5 from ambient concentrations of NO_x and SO_x through deposition of N and S. In Chapter 2, we
6 draw from the information and conclusions presented in the ISA and REA to address the
7 following questions:

- 8 1. What are the nature and magnitude of ecosystem responses to reactive nitrogen and
9 sulfur deposition?
 - 10 a. How are these responses affected by landscape factors?
 - 11 b. What types of ecosystems are sensitive to such responses?
- 12 2. To what extent can ecosystem responses to nitrogen deposition be separated into
13 responses related to oxidized and reduced forms of reactive nitrogen compounds?

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

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

23 Once we have described ecological effects, we then provide an assessment of the
24 adequacy of the existing NO_x and SO_x standards (CPE 1.2). We begin this assessment by
25 drawing from the information and conclusions presented in the ISA and REA to address in
26 Chapter 4 the following questions, which allow us to identify whether the structure of the current
27 standards is appropriate relative to the key ecological effects assessed in the ISA and REA,

⁶ The decision to focus on unmanaged ecosystems is based on the weight of evidence of effects in those ecosystems. The majority of the scientific evidence regarding acidification and nutrient enrichment is based on studies in unmanaged ecosystems. Non-managed terrestrial ecosystems tend to have a higher fraction of N deposition resulting from atmospheric N (ISA 3.3.2.5). In addition, the ISA notes that agricultural and commercial forest lands are routinely fertilized with amounts of N (100 to 300 kg N/ha) that exceed air pollutant inputs even in the most polluted areas (ISA 3.3.9)

1 including acidification and excess nutrient enrichment and whether there is adequate information
2 and analyses available at this time to assess the extent to which potentially adverse effects on
3 aquatic and terrestrial ecosystems can be associated with current levels of atmospheric reactive
4 nitrogen, accounting for the contributions of oxidized and reduced forms, and SO_x and with
5 levels that are at or below the current secondary standards:

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

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

- 26 1. (CPE 2.1) Does the available information provide support for the use of ecological
27 indicators to characterize the responses of aquatic and terrestrial ecosystems to
28 oxidized nitrogen and sulfur deposition?
- 29 2. (CPE 1) Does the available information provide support for the development of
30 appropriate ecological response to deposition relationship(s) that meaningfully relates
31 oxidized nitrogen and sulfur deposition to relevant ecological indicators? Does a

- 1 quantified relationship exist between the level of a relevant ecological indicator and
2 an amount of nitrogen and sulfur deposition?
- 3 3. (CPE 2) What are the important variables in the ecological response to deposition
4 relationship(s)? Are these relationships applicable nationally? What are the
5 appropriate temporal scales for these relationships?
- 6 a. How does ecological response to deposition relationship(s) depend upon spatially
7 heterogeneous geologic factors (e.g. bedrock type, weathering rates) that govern
8 sensitivity?
- 9 b. How do we consider areas with high natural background acidification or nutrient
10 loadings?
- 11 4. (CPE 3) Does the available information provide support for the development of
12 appropriate functions that characterize the relationships between atmospheric NO_x
13 and SO_x and the wet and dry deposition of total reactive nitrogen and sulfur? (CPE 4)
14 How do these relationships depend upon relevant atmospheric factors (e.g., reduced
15 forms of nitrogen, meteorological factors) and landscape factors?
- 16 a. What deposition function is appropriate to use for the purpose of relating an
17 amount of nitrogen and/or sulfur deposition in sensitive ecosystems to ambient
18 concentrations of atmospheric reactive nitrogen, including oxides and reduced
19 forms, and/or sulfur? What are the important variables in such a function? What
20 are appropriate spatial and temporal scales to use in specifying such variables?
- 21 Based on the conceptual framework for the structure of the ecologically relevant multi-
22 pollutant standards, we then address in Chapter 6 the elements of the standard needed to develop
23 options for consideration by the Administrator. Development of these options will focus on
24 addressing the following questions:
- 25 1. (CPE 2.1) What ecological indicators are appropriate to use for the purpose of
26 developing an alternative standard for the various ecological effects assessed in this
27 review?
- 28 2. (CPE 5) What indicators of oxides of nitrogen and sulfur are appropriate to use for
29 the purpose of determining whether the resultant deposition is within the target values
30 needed to achieve the desired degree of protection? What averaging times and forms
31 are appropriate to consider?

- 1 3. (CPE 4) What approaches are available to specify non-atmospheric elements of the
2 standard, e.g. weathering rates? Are there approaches that can simplify the structure
3 of the standard by using discrete representations (bins) of continuous variables?
- 4 4. What are the available approaches for accounting for reduced N in the structure of the
5 standard?
- 6 5. What is the most appropriate form for the standards to reflect the relationships
7 between ambient NO_x and SO_x, acidifying deposition, and the ecological indicator for
8 acidification?

9 Several follow-up questions derive from our assessment of options for specifying the
10 elements of a multipollutant standard. In Chapter 7, we address the questions:

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

19 In Chapter 8, we plan to address in the second draft policy assessment issues regarding
20 the adequacy of the current definitions of oxides of nitrogen and sulfur in specifying standards
21 for protection against effects associated with deposition of nitrogen and sulfur. This discussion
22 will be focused on the following questions:

- 23 1. To what extent are effects associated with atmospheric nitrogen deposition reduced
24 when NO_x related deposition is reduced?
- 25 2. To what extent can appropriate protection from relevant ecological effects be
26 achieved by specifying indicators of atmospheric reactive nitrogen and sulfur
27 compounds in terms of gas- and particle-phase nitrogen oxides and/or sulfur oxides?
- 28 3. To what extent does the available information on welfare effects provide a basis for
29 considering expanding the list of criteria pollutants to include all reactive nitrogen or
30 gas-phase ammonia? What are the relative merits of listing total reactive nitrogen
31 versus gas phase ammonia for protection of public welfare effects?

1 We conclude with a discussion of a range of options to consider in selecting pollutant
2 indicators, averaging times, forms, and levels for the secondary NO_x and SO_x standards,
3 including a discussion of staff initial conclusions on what levels of the standard for NO_x and SO_x
4 would be requisite to protect public welfare against adverse ecological effects. This discussion is
5 informed by a consideration of the role of ecosystem services in helping to characterize what
6 adversity to public welfare, focused on the following questions:

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

19

1 **2. KNOWN OR ANTICIPATED ECOLOGICAL EFFECTS**

2 This chapter addresses Critical Policy Element 1, evaluation of the effects of ambient
3 NO_x and SO_x on ecosystems, and the relationship between those effects and the measure of dose
4 in the ecosystem, indicated by the depositional loadings of N and S. In section 302(h) of the
5 Clean Air Act, welfare effects addressed by a secondary NAAQS include, but are not limited to,
6 “effects on soils, water, crops, vegetation, man-made materials, animals, wildlife, weather,
7 visibility and climate, damage to and deterioration of property, and hazards to transportation, as
8 well as effects on economic values and on personal comfort and well-being”. Of these welfare
9 effects categories, the effects of NO_x and SO_x on aquatic and terrestrial ecosystems, which
10 encompass soils, water, vegetation, wildlife, and contribute to economic value and well-being,
11 are of most concern at concentrations typically occurring in the U.S. Direct effects of NO_x and
12 SO_x on vegetation are also discussed in this chapter, and have been the focus of previous
13 reviews. However, for this review, the focus of this chapter is on the known and anticipated
14 effects to ecosystems caused by exposure to NO_x and SO_x through deposition.

15 The information presented here is a concise summary of conclusions from the ISA and
16 the REA. This chapter focuses on effects on specific ecosystems with a brief discussion on
17 critical uncertainties associated with acidification and nutrient enrichment; Chapter 3 evaluates
18 those effects within the context of alternative definitions of, including assessments of potential
19 impacts on ecosystem services. Effects are broadly categorized into acidification and nutrient-
20 enrichment in the proceeding sections. This is background information intended to support new
21 approaches for the design of ecologically relevant secondary NO_x and SO_x standards which are
22 protective of U.S. ecosystems. More detailed information on the conceptual design and specific
23 options for the proposed standards are presented in Chapters 5 and 6 of this policy assessment
24 document. While we provide a summary of effects for all four of the primary effects categories,
25 we reiterate that the focus of this first draft policy assessment is on effects related to aquatic
26 acidification, without downplaying the potential significance of effects in other categories.

1 **2.1 ACIDIFICATION: EVIDENCE OF EFFECTS ON STRUCTURE AND**
2 **FUNCTION OF TERRESTRIAL AND FRESHWATER**
3 **ECOSYSTEMS**

4 Sulfur oxides (SO_x) and nitrogen oxides (NO_x) compounds in the atmosphere undergo a
5 complex mix of reactions and thermodynamic processes in gaseous, liquid, and solid phases to
6 form various acidic compounds. These acidic compounds are removed from the atmosphere
7 through deposition: either wet (e.g., rain, snow), fog or cloud, or dry (e.g., gases, particles).
8 Deposition of these acidic compounds leads to ecosystem exposure and effects on ecosystem
9 structure and function. Following deposition, these compounds can, in some instances, leach out
10 of the soils in the form of sulfate (SO₄²⁻) and nitrate (NO₃⁻), leading to the acidification of surface
11 waters. The effects on ecosystems depend on the magnitude of deposition, as well as a host of
12 biogeochemical processes occurring in the soils and waterbodies (**REA 2.1**). The chemical forms
13 of nitrogen that may contribute to acidifying deposition include both oxidized and reduced
14 species.

15 When sulfur or nitrogen leaches from soils to surface waters in the form of SO₄²⁻ or NO₃⁻,
16 an equivalent amount of positive cations, or countercharge, is also transported. This maintains
17 electroneutrality. If the countercharge is provided by base cations, such as calcium (Ca²⁺),
18 magnesium (Mg²⁺), sodium (Na⁺), or potassium (K⁺), rather than hydrogen (H⁺) and dissolved
19 inorganic aluminum, the acidity of the soil water is neutralized, but the base saturation of the soil
20 is reduced. Continued SO₄²⁻ or NO₃⁻ leaching can deplete the base cation supply of the soil. As
21 the base cations are removed, continued deposition and leaching of SO₄²⁻ and/or NO₃⁻ (with
22 H⁺ and Al³⁺) leads to acidification of soil water, and by connection, surface water. A watershed's
23 ability to neutralize acidic deposition is determined by a host of biogeophysical factors, including
24 base cation concentrations, weathering rates, uptake by vegetation, rate of surface water flow,
25 soil depth, and bedrock. (**REA 2.1**) Some of these factors such as vegetation and soil depth are
26 highly variable over small spatial scales, but others vary over larger spatial scales like geology.
27 For the purpose of a national secondary standard, the most relevant characteristics are those that
28 are less variable over small scales.

29 Acidifying deposition of NO_x and SO_x and the chemical and biological responses
30 associated with these inputs vary temporally. Chronic or long-term deposition processes result in

1 increases of N and S and the associated effects of acidifying deposition in the time scale of years
2 to decades. Episodic or short term (i.e., hours or days) deposition refers to events in which the
3 level of the acid neutralizing capacity (ANC) of a lake or stream is temporarily lowered. In
4 aquatic ecosystems, short-term (i.e., hours or days) episodic changes in water chemistry can have
5 significant biological effects. Episodic chemistry refers to conditions during precipitation or
6 snowmelt events when proportionately more drainage water is routed through upper soil horizons
7 that tend to provide less acid neutralizing than was passing through deeper soil horizons (**REA**
8 **4.2**). Some streams and lakes may have chronic or base flow chemistry that is suitable for aquatic
9 biota, but may be subject to occasional acidic episodes with lethal consequences.

10 The following summary is a concise overview of the known or anticipated effects caused
11 by acidification to ecosystems within the United States. Acidification affects both terrestrial and
12 freshwater aquatic ecosystems. Terrestrial and aquatic processes are often linked; therefore
13 responses to the following questions address both types of ecosystems unless otherwise noted.

14 **2.1.1 What is the nature of acidification related ecosystem responses to reactive** 15 **nitrogen and/ sulfur deposition?**

16 The ISA concluded that deposition of SO_x, NO_x, and NH_x leads to the acidification of
17 ecosystems (EPA 2008). In the process of acidification, geochemical components of terrestrial
18 and freshwater aquatic ecosystems are altered in a way that leads to effects on biological
19 organisms. Deposition to terrestrial ecosystems often moves through the soil and eventually
20 leaches into adjacent water bodies, moreover deposition to the land effects the water as well.

21 The scientific evidence is sufficient to infer a **causal** relationship between acidifying
22 deposition and effects on biogeochemistry and biota in aquatic ecosystems (**ISA 4.2.2**). The
23 strongest evidence comes from studies of surface water chemistry in which acidic deposition is
24 observed to alter sulfate and nitrate concentrations in surface waters, sum and surplus of base
25 cations, acid, ANC, inorganic aluminum, calcium, and surface water pH (**ISA 3.2.3.2**).

26 Consistent and coherent documentation from multiple studies on various species from all major
27 trophic levels of aquatic systems shows that geochemical alteration caused by acidification can
28 result in the loss of acid-sensitive biological species (**ISA 3.2.3.3**). For example, in the
29 Adirondacks, of the 53 fish species recorded in Adirondack lakes about half (26 species) were
30 absent from lakes with pH below 6.0 (Baker et al., 1990b). Biological effects are linked to

1 changes in water chemistry including ANC, inorganic Al, and pH. Decreases in ANC and pH
2 and increases in inorganic Al concentration contribute to declines in taxonomic richness of
3 zooplankton, macroinvertebrates, and fish, which often are sources of food for birds and other
4 animal species in the ecosystem, as well as serving as a source of food and recreation for
5 humans. Acidification of ecosystems has been shown to disrupt food web dynamics causing
6 alteration to the diet, breeding distribution and reproduction of certain species of birds (**ISA**
7 **4.2.2.2. and Table 3-9**). For example, breeding distribution of the common goldeneye
8 (*Bucephala clangula*) an insectivorous duck, may be affected by changes in acidifying deposition
9 (Longcore and Gill, 1993). Similarly, reduced prey diversity and quantity have been observed to
10 create feeding problems for nesting pairs of loons on low-pH lakes in the Adirondacks (Parker
11 1988).

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

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

28 Acidification has been shown to cause decreased growth and increased susceptibility to
29 disease and injury in sensitive tree species. Red spruce (*Picea rubens*) dieback or decline has
30 been observed across high elevation areas in the Adirondack, Green and White mountains
31 (DeHayes et al., 1999). The frequency of freezing injury to red spruce needles has increased over

1 the past 40 years, a period that coincided with increased emissions of S and N oxides and
2 increased acidifying deposition (DeHayes et al., 1999). Acidifying deposition may be
3 contributing to episodic dieback in Sugar maple (*Acer saccharum*) through depletion of nutrient
4 cations from marginal soils (Horsley et al., 2000; Bailey et al., 2004). Grasslands are likely less
5 sensitive to acidification than forests (Blake et al., 1999; Kocky and Wilson 2001).

6 **2.1.2 What types of ecosystems are sensitive to such effects? In which ways are**
7 **these responses affected by atmospheric, ecological, and landscape factors?**

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

18 **2.1.3 What is the magnitude of ecosystem responses to acidifying deposition?**

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

23 **2.1.3.1 Aquatic**

24 Freshwater ecosystem surveys and monitoring in the eastern United States have been
25 conducted by many programs since the mid-1980s, including EPA's Environmental Monitoring
26 and Assessment Program (EMAP), National Surface Water Survey (NSWS), Temporally
27 Integrated Monitoring of Ecosystems (TIME) (Stoddard, 1990), and Long-term Monitoring
28 (LTM) (Ford et al., 1993; Stoddard et al., 1996) programs. Based on analyses of surface water
29 data from these programs, New England, the Adirondack Mountains, the Appalachian Mountains

1 (northern Appalachian Plateau and Ridge/Blue Ridge region), and the Upper Midwest contain
2 the most sensitive lakes and streams (i.e., ANC less than about 50 µeq/L) since the 1980s.
3 Portions of northern Florida also contain many acidic and low-ANC lakes and streams, although
4 the role of acidifying deposition in these areas is less clear. The western U.S. contains many of
5 the surface waters most sensitive to potential acidification effects, but with the exception of the
6 Los Angeles Basin and surrounding areas, the levels of acidifying deposition are low in most
7 areas. Therefore acidic surface waters are uncommon in the western U.S., and the extent of
8 chronic surface water acidification that has occurred in that region to date has likely been very
9 limited (**ISA 3.2.4.2 and REA 4.2.2**).

10 There are a number of species including fish, aquatic insects, other invertebrates and
11 algae that are sensitive to acidification and cannot survive, compete, or reproduce in acidic
12 waters (**ISA 3.2.3.3**). Decreases in ANC and pH have been shown to contribute to declines in
13 species richness and abundance of zooplankton, macroinvertebrates, and fish (Keller and Gunn
14 1995; Schindler et al., 1985). Reduced growth rates have been attributed to acid stress in a
15 number of fish species including Atlantic salmon (*Salmo salar*), Chinook salmon (*Oncorhynchus*
16 *tshawytscha*), lake trout (*Salvelinus namaycush*), rainbow trout (*Oncorhynchus mykiss*), brook
17 trout (*Salvelinus Fontinalis*), and brown trout (*Salmo trutta*) (Baker et al., 1990). In response to
18 small to moderate changes in acidity, acid-sensitive species are often replaced by other more
19 acid-tolerant species, resulting in changes in community composition and richness. The effects of
20 acidification are continuous, with more species being affected at higher degrees of acidification.
21 At a point, typically a pH <4.5 and an ANC <0 µeq/L, complete to near-complete loss of many
22 classes of organisms occur, including fish and aquatic insect populations, whereas others are
23 reduced to only a few acidophilic forms. These changes in species integrity are because energy
24 cost in maintaining physiological homeostasis, growth, and reproduction is high at low ANC
25 levels (Schreck, 1981, 1982; Wedemeyer et al., 1990; **REA appendix 2.3**). Decreases in species
26 richness related to acidification have been observed in the Adirondack Mountains and Catskill
27 Mountains of New York (Baker et al., 1996), New England and Pennsylvania (Haines and Baker,
28 1986), and Virginia (Bulger et al., 2000).

29 From the sensitive areas identified by the ISA, further “case study” analyses on aquatic
30 ecosystems in the Adirondack Mountains and Shenandoah National Park were conducted to
31 better characterize ecological risk associated with acidification (**REA Chapter 4**).

1 In the literature, ANC is the most widely used indicator of acid sensitivity and has been
 2 found in various studies to be the best single indicator of the biological response and health of
 3 aquatic communities in acid-sensitive systems (Lien et al., 1992; Sullivan et al., 2006; ISA). In
 4 the REA, surface water trends in SO₄²⁻ and NO₃⁻ concentrations and ANC levels were analyzed
 5 to affirm the understanding that reductions in deposition could influence the risk of acidification.
 6 ANC values were categorized according to their effects on biota, as shown in Figure 2-1.
 7 Monitoring data from the EPA-administered TIME/LTM and EMAP programs were assessed for
 8 the years 1990 to 2006, and past, present, and future water quality levels were estimated by both
 9 steady-state and dynamic biogeochemical models.
 10

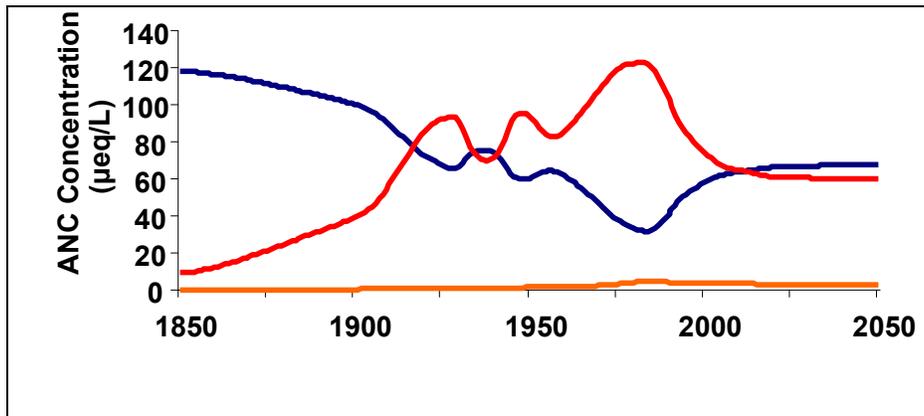
Category Label ANC Levels* Expected Ecological Effects		
Acute Concern	<0 µeq/L (Acidic)	Near complete loss of fish populations is expected. Planktonic communities have extremely low diversity and are dominated by acidophilic forms. The number of individuals in plankton species that are present is greatly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

11
 12 **Figure 2-1.** Ecological Effects Associated with Alternative Levels of Acid
 13 Neutralizing Capacity (ANC)

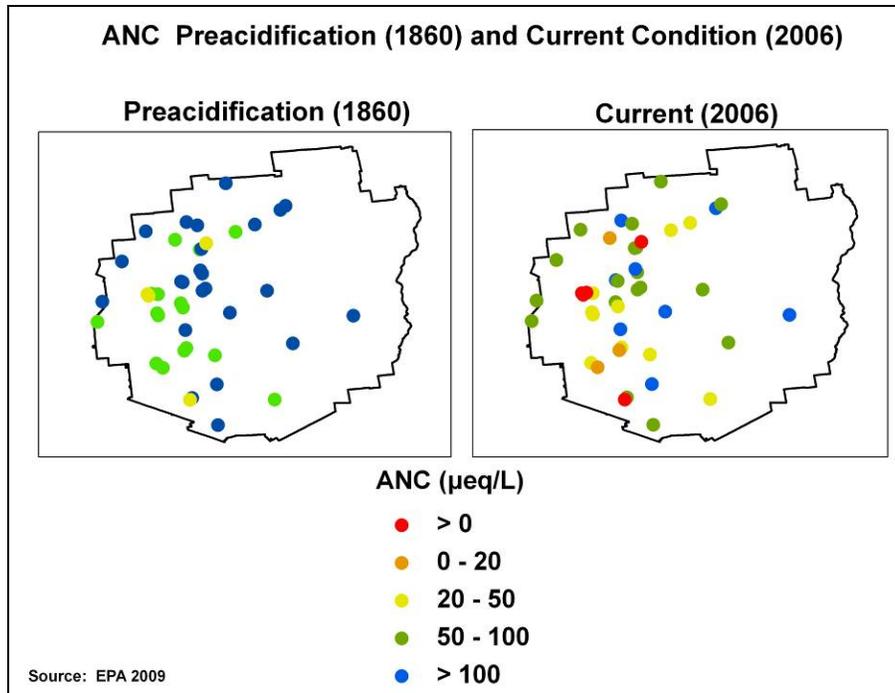
14 The analyses of the Adirondack Case Study Area indicated that although wet deposition
 15 rates for SO₂ and NO_x have been reduced since the mid-1990s, current concentrations are still
 16 well above pre-acidification (1860) conditions. Modeling predicts NO₃⁻ and SO₄²⁻ are 17- and 5-

1 fold higher today, respectively. The estimated average ANC across the 44 lakes in the
2 Adirondack Case Study Area is $62.1 \mu\text{eq/L}$ ($\pm 15.7 \mu\text{eq/L}$); 78 % of all monitored lakes in the
3 Adirondack Case Study Area have a current risk of *Elevated*, *Severe*, or *Acute*. Of the 78%, 31%
4 experience episodic acidification, and 18% are chronically acidic today (**REA 4.2.4.2**).

5 Based on a deposition scenario that maintains current emission levels to 2020 and 2050,
6 the simulation forecast indicates no improvement in water quality in the Adirondack Case Study
7 Area. The percentage of lakes within the *Elevated* to *Acute Concern* classes remains the same in
8 2020 and 2050.

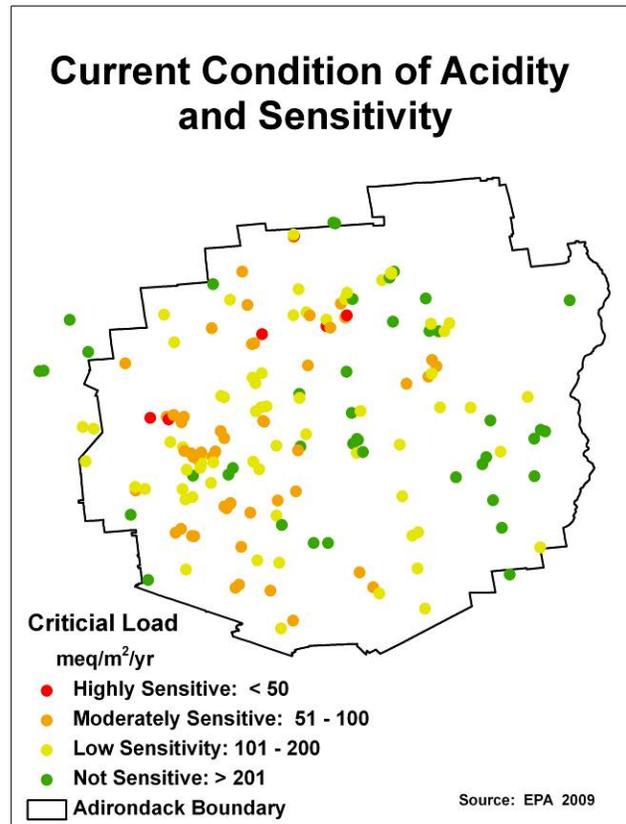


9
10 **Figure 2-2.** Average NO_3^- concentrations (orange), SO_4^{2-} concentrations (red),
11 and ANC (blue) across the 44 lakes in the Adirondack Case Study Area modeled
12 using MAGIC for the period 1850 to 2050.



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Figure 2-3. ANC concentrations of preacidification (1860) and current (2006) conditions based on hindcasts of 44 lakes in the Adirondack Case Study Area modeled using MAGIC. [Note: in this map, the symbol for red is reversed and should be < 0 . The figure will be revised in the next draft.]



1
2 **Figure 2-4.** Critical loads of acidifying deposition that each surface water location
3 can receive in the Adirondack Case Study Area while maintaining or exceeding
4 an ANC concentration of $50 \mu\text{eq/L}$ based on 2002 data. Watersheds with critical
5 load values $<100 \text{ meq/m}^2/\text{yr}$ (red and orange circles) are most sensitive to surface
6 water acidification, whereas watersheds with values $>100 \text{ meq/m}^2/\text{yr}$ (yellow and
7 green circles) are the least sensitive sites.

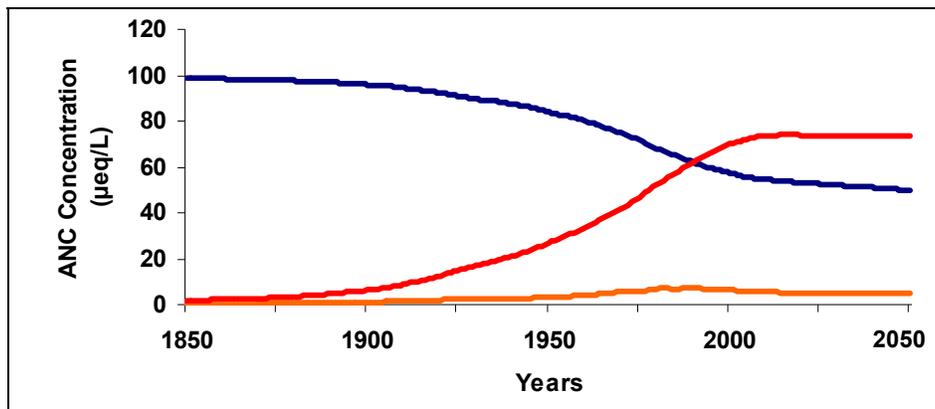
8 It is important to note that studies on fish species richness in the Adirondacks Case Study
9 Area demonstrated the effect of acidification; of the 53 fish species recorded in Adirondack Case
10 Study Area lakes, only 27 species were found in lakes with a $\text{pH} < 6.0$. The 26 species missing
11 from lakes with a $\text{pH} < 6.0$ include important recreational species, such as Atlantic salmon, tiger
12 trout (*Salmo trutta* X *Salvelinus fontinalis*), redbreast sunfish (*Lepomis auritus*), bluegill
13 (*Lepomis macrochirus*), tiger musky (*Esox masquinongy* X *lucius*), walleye (*Sander vitreus*),
14 alewife (*Alosa pseudoharengus*), and kokanee (*Oncorhynchus nerka*) (Kretser et al., 1989), as
15 well as ecologically important minnows that are commonly eaten by sport fish. A survey of
16 1,469 lakes in the late 1980s found 346 lakes to be devoid of fish. Among lakes with fish, there
17 was a relationship between the number of fish species and lake pH , ranging from about one
18 species per lake for lakes having a $\text{pH} < 4.5$ to about six species per lake for lakes having a pH

1 >6.5 (Driscoll et al., 2001; Kretser et al., 1989). In the Adirondacks, a positive relationship exists
 2 between the pH and ANC in lakes and the number of fish species present in those lakes (ISA
 3 **3.2.3.4**).

4 Since the mid-1990s, streams in the Shenandoah Case Study Area have shown slight
 5 declines in NO_3^- and SO_4^{2-} concentrations in surface waters. Current concentrations are still
 6 above pre-acidification (1860) conditions. MAGIC modeling predicts surface water
 7 concentrations of NO_3^- and SO_4^{2-} are 10- and 32-fold higher today, respectively. The estimated
 8 average ANC across 60 streams in the Shenandoah Case Study Area is 57.9 $\mu\text{eq/L}$ ($\pm 4.5 \mu\text{eq/L}$).
 9 55% of all monitored streams in the Shenandoah Case Study Area have a current risk of
 10 *Elevated, Severe, or Acute*. Of the 55%, 18% experience episodic acidification, and 18% are
 11 chronically acidic today (**REA 4.2.4.3**)

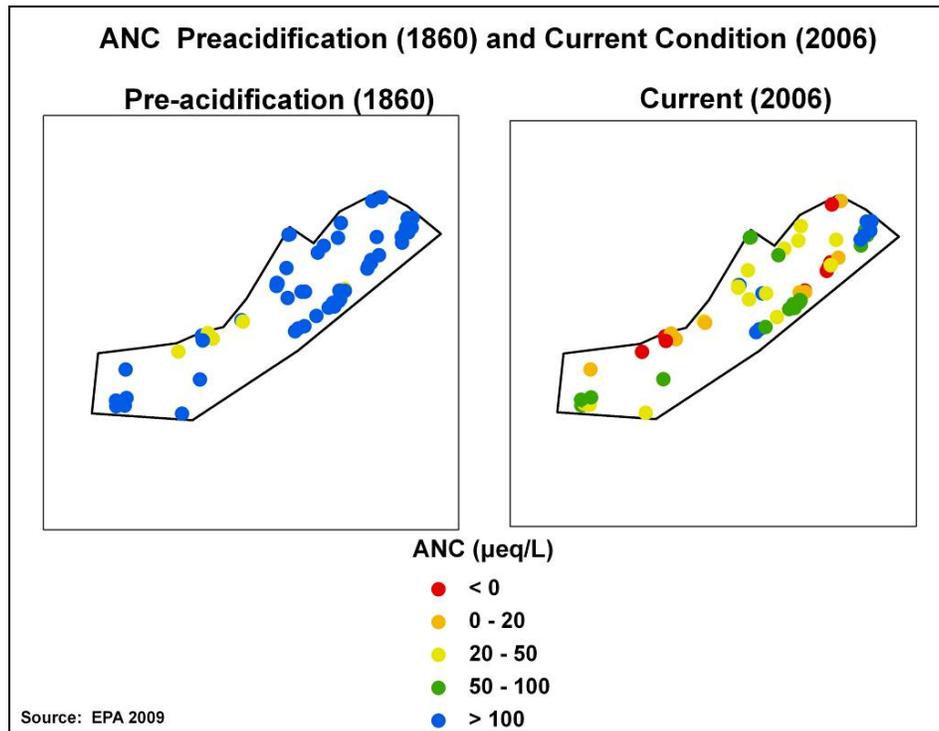
12 Based on a deposition scenario that maintains current emission levels to 2020 and 2050,
 13 the simulation forecast indicates that a large number of streams still have *Elevated to Acute*
 14 problems with acidity. In fact, from 2006 to 2050, the percentage of streams with *Acute Concern*
 15 increases by 5%, while the percentage of streams in Moderate Concern decreases by 5%.

16 Biological effects of increased acidification documented in the Shenandoah Case Study
 17 Area include a reduction in the condition factor in Blacknose Dace (Dennis and Bulgar 1995,
 18 Bulgar et al., 1999) and a decrease in fish biodiversity associated with decreasing stream ANC
 19 (Bulger et al., 1995; Dennis and Bulger, 1995; Dennis et al., 1995; MacAvoy and Bulger, 1995,
 20 Bulgar et al., 1999). On average, the fish species richness is lower by one fish species for every
 21 21 $\mu\text{eq/L}$ decrease in ANC in Shenandoah National Park streams (**ISA 3.2.3.4**).



22
 23 **Figure 2-5.** Average NO_3^- concentrations orange), SO_4^{2-} concentrations (red), and
 24 ANC (blue) levels for the 60 streams in the Shenandoah Case Study Area
 25 modeled using MAGIC for the period 1850 to 2050.

1



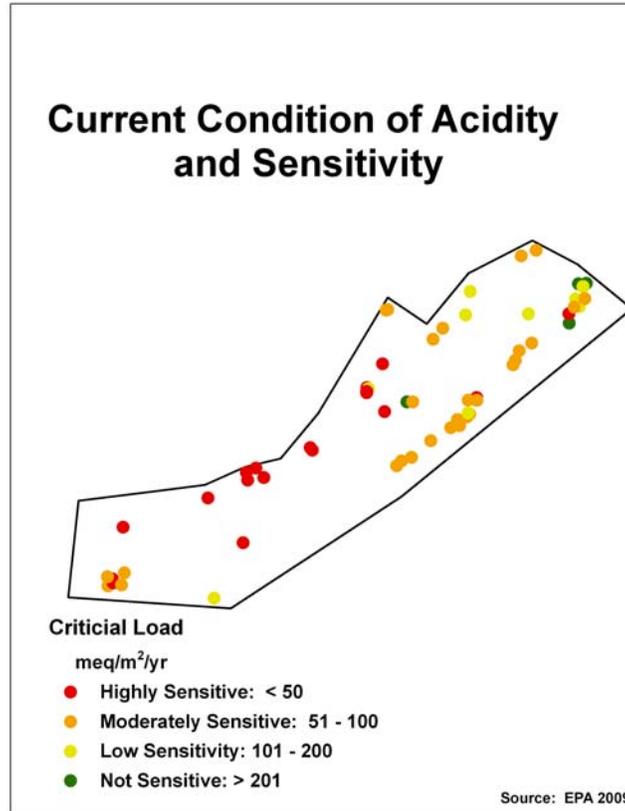
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Figure 2-6. ANC levels of 1860 (preacidification) and 2006 (current) conditions based on hindcasts of 60 streams in the Shenandoah Case Study Area modeled using MAGIC.



1
2 **Figure 2-7.** Critical loads of surface water acidity for an ANC of 50 µeq/L for
3 Shenandoah Case Study Area streams. Each dot represents an estimated amount
4 of acidifying deposition (i.e., critical load) that each stream’s watershed can
5 receive and still maintain a surface water ANC >50 µeq/L. Watersheds with
6 critical load values <100 meq/m²/yr (red and orange circles) are most sensitive to
7 surface water acidification, whereas watersheds with values >100 meq/m²/yr
8 (yellow and green circles) are the least sensitive sites.

9 **2.1.3.2 Terrestrial Acidification**

10 The ISA identified a variety of indicators that can be used to measure the effects of
11 acidification in soils. Tree health has been linked to base cations (Bc) in soil (such as Ca^{2+} , Mg^{2+}
12 and potassium), as well as soil Al content. Tree species show similar sensitivities to Ca/Al and
13 Bc/Al soil solution ratios, therefore these are good chemical indicators because they directly
14 relate to the biological effects. Critical Bc/Al ratios for a large variety of tree species ranged
15 from 0.2 to 0.8 (Sverdrup and Warfvinge, 1993, a meta-data analysis of laboratory and field
16 studies). This range is similar to critical ratios of Ca/Al. Plant toxicity or nutrient antagonism
17 was reported to occur at Ca/Al ratios ranging from 0.2 to 2.5 (Cronan and Grigal, 1995; meta-
18 data assessment) (**REA pg 4-54, REA Appendix 5**).

1 There has been no systematic national survey of terrestrial ecosystems to determine the
2 extent and distribution of terrestrial ecosystem sensitivity to the effects of acidifying deposition.
3 However, one preliminary national evaluation estimated that ~15% of forest ecosystems in the
4 U.S. exceeds the estimated critical load based on soil chemistry for S and N deposition by >250
5 eq ha⁻¹ yr⁻¹ (McNulty et al., 2007). Forests of the Adirondack Mountains of New York, Green
6 Mountains of Vermont, White Mountains of New Hampshire, the Allegheny Plateau of
7 Pennsylvania, and high-elevation forest ecosystems in the southern Appalachians are the regions
8 most sensitive to terrestrial acidification effects from acidifying deposition (**ISA 3.2.4.2**). While
9 studies show some recovery of surface waters, there are widespread measurements of ongoing
10 depletion of exchangeable base cations in forest soils in the northeastern U.S. despite recent
11 decreases in acidifying deposition, indicating a slow recovery time.

12 In the REA, a critical load analysis was performed for sugar maple and red spruce forests
13 in the eastern United States by using Bc/Al ratio in acidified forest soils as an indicator to assess
14 the impact of nitrogen and sulfur deposition on tree health. These are the two most commonly
15 studied species in North America for effects of acidification. At a Bc/Al ratio of 1.2, red spruce
16 growth can be reduced by 20%. Sugar maple growth can be reduced by 20% at a Bc/Al ratio of
17 0.6. The REA analysis determined the health of at least a portion of the sugar maple and red
18 spruce growing in the United States may have been compromised with acidifying total nitrogen
19 and sulfur deposition in 2002. Specifically, total nitrogen and sulfur deposition levels exceeded
20 three selected critical loads for tree growth in 3% to 75% of all sugar maple plots across 24
21 states. For Red Spruce, total nitrogen and sulfur deposition levels exceeded three selected critical
22 loads in 3% to 36% of all red spruce plots across eight states.

23 **2.1.4 What are the key uncertainties associated with acidification?**

24 There are different levels of uncertainty associated with relationships between deposition,
25 ecological effects and ecological indicators. In Chapter 7 of the REA, key uncertainties are
26 characterized as follows to evaluate the strength of the scientific basis for setting a national
27 standard to protect against a given effect (**REA 7.0**):

- 28 ▪ **Data Availability: *high, medium or low quality*.** This criterion is based on the availability
29 and robustness of data sets, monitoring networks, availability of data that allows for
30 extrapolation to larger assessment areas, and input parameters for modeling and

1 developing the ecological effect function. The scientific basis for the ecological indicator
2 selected is also incorporated into this criterion.

- 3 ■ **Modeling Approach: *high, fairly high, intermediate, or low confidence*.** This value is
4 based on the strengths and limitations of the models used in the analysis and how accepted
5 they are by the scientific community for their application in this analysis.
- 6 ■ **Ecological Effect Function: *high, fairly high, intermediate, or low confidence*.** This
7 ranking is based on how well the ecological effect function describes the relationship
8 between atmospheric deposition and the ecological indicator of an effect.

9 ***2.1.4.1 Aquatic Acidification***

10 The REA concludes that the available data are robust and considered *high quality*. There
11 is high confidence about the use of these data and their value for extrapolating to a larger
12 regional population of lakes. The EPA TIME/LTM network represents a source of long-term,
13 representative sampling. Data on sulfate concentrations, nitrate concentrations and ANC from
14 1990 to 2006 used for this analysis as well as EPA EMAP and REMAP surveys, provide
15 considerable data on surface water trends.

16 There is *fairly high confidence* associated with modeling and input parameters.
17 Uncertainties in water quality estimates (.i.e. ANC) from MAGIC was derived from multiple site
18 calibrations. The 95% confidence interval for pre-acidification of lakes was an average of 15
19 µeq/L difference in ANC concentrations or 10% and 8 µeq/L or 5% for streams (**REA 7.1.2**) The
20 use of the critical load model used to estimate aquatic critical loads is limited by the uncertainties
21 associated with runoff and surface water measurements and in estimating the catchment supply
22 of base cations from the weathering of bedrock and soils (McNulty et al., 2007). To propagate
23 uncertainty in the model parameters, Monte Carlo methods were employed to develop an inverse
24 function of exceedences. There is *high confidence* associated with the ecological effect function
25 developed for aquatic acidification. In calculating the ANC function, the depositional load for N
26 or S is fixed by the deposition of the other, so deposition for either will never be zero (**Figure**
27 **7.1-6 REA**).

28 **Terrestrial Acidification**

29 The available data used to quantify the targeted effect of terrestrial acidification are
30 robust and considered *high quality*. The USFS-Kane experimental forest and significant amounts

1 of research work in the Allegheny Plateau have produced extensive, peer-reviewed datasets. A
2 meta-analysis of laboratory studies showed that tree growth was reduced by 20% relative to
3 controls for BC/Al ratios (**ISA 7.2.1 and Figure 7.2-1**). Sugar maple and red spruce were the
4 focus of the REA since they are demonstrated to be negatively affected by Ca²⁺ depletion and
5 high concentrations of available Al, and occur in areas that receive high acidifying deposition,
6 There is high confidence about the use of the REA terrestrial acidification data and their value
7 for extrapolating to a larger regional population of forests.

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

13 **2.2 NITROGEN ENRICHMENT: EVIDENCE OF EFFECTS ON** 14 **STRUCTURE AND FUNCTION OF TERRESTRIAL AND** 15 **FRESHWATER ECOSYSTEMS**

16 The following summary is a concise overview of the known or anticipated effects caused
17 by nitrogen nutrient enrichment to ecosystems within the United States. Nutrient-enrichment
18 affects terrestrial, freshwater and estuarine ecosystems. Nitrogen deposition is often the main
19 source of anthropogenic nitrogen in terrestrial and freshwater ecosystems. In contrast, nitrogen
20 deposition often contributes to nitrogen-enrichment effects in estuaries, but does not drive the
21 effects. Both oxides of nitrogen and reduced forms of nitrogen, e.g. NH_x, contribute to nitrogen
22 deposition. For the most part, nitrogen effects on ecosystems do not depend on whether the
23 nitrogen is in oxidized or reduced form. Thus, this summary focuses on the effects of nitrogen
24 deposition in total. We address the issue of incorporating the relative contributions of oxidized
25 and reduced nitrogen into the standards in Chapters 5, 6, and 8.

26 **2.2.1 What is the nature of terrestrial and freshwater ecosystem responses to** 27 **reactive nitrogen and/ sulfur deposition?**

28 The ISA found that deposition of nitrogen, including NO_x and NH_x leads to the nitrogen
29 enrichment of ecosystems (EPA 2008). In the process of nitrogen enrichment, geochemical

1 components of terrestrial and freshwater aquatic ecosystems are altered in a way that leads to
2 effects on biological organisms.

3 The evidence is sufficient to infer a **causal** relationship between N deposition and the
4 alteration of biogeochemical cycling in terrestrial ecosystems (**ISA 4.3.1.1 and 3.3.2.1**). This is
5 supported by numerous observational, deposition gradient and field addition experiments.
6 Stoddard (1994) identified the leaching of NO₃⁻ in soil drainage waters and the export of NO₃⁻ in
7 stream water as two of the primary indicators of N enrichment. Several N-addition studies indicate
8 that NO₃⁻ leaching is induced by chronic additional of N (Edwards et al., 2002b; Kahl et al.,
9 1999; Peterjohn et al., 1996; Norton et al., 1999). Aber et al. (2003) found that surface water
10 NO₃⁻ concentrations exceeded 1 µeq/L in watersheds receiving about 9 to 13 kg N/ha/yr of
11 atmospheric N deposition. N deposition disrupts the nutrient balance of ecosystems with
12 numerous biogeochemical effects. The chemical indicators that are typically measured include
13 NO₃⁻ leaching, C:N ratio, N mineralization, nitrification, denitrification, foliar N concentration,
14 and soil water NO₃⁻ and NH₄⁺ concentrations. Note that N saturation (N leaching from
15 ecosystems) does not need to occur to cause effects. Substantial leaching of NO₃⁻ from forest
16 soils to stream water can acidify downstream waters, leading to effects described in the previous
17 section on aquatic acidification. Due to the complexity of interactions between the N and C
18 cycling, the effects of N on C budgets (quantified input and output of C to the ecosystem) are
19 variable. Regional trends in net ecosystem productivity (NEP) of forests (not managed for
20 silviculture) have been estimated through models based on gradient studies and meta-analysis.
21 Atmospheric N deposition has been shown to cause increased litter accumulation and carbon
22 storage in above-ground woody biomass. In the West, this has led to increased susceptibility to
23 more severe fires. Less is known regarding the effects of N deposition on C budgets of non-
24 forest ecosystems.

25 The evidence is sufficient to infer a **causal** relationship between N deposition on the
26 alteration of species richness, species composition and biodiversity in terrestrial ecosystems (**ISA**
27 **4.3.1.2**). The most sensitive terrestrial taxa are lichens. Empirical evidence indicates that lichens
28 in the U.S. are affected by deposition levels as low as 3 kg N/ha/yr. Alpine ecosystems are also
29 sensitive to N deposition, changes in an individual species (*Carex rupestris*) were estimated to
30 occur at deposition levels near 4 kg /ha/yr and modeling indicates that deposition levels near 10
31 kg N/ha/yr alter plant community assemblages. In several grassland ecosystems, reduced species

1 diversity and an increase in non-native, invasive species are associated with N deposition (Clark
2 and Tillman, 2008; Schwinning et al., 2005).

3 In freshwater ecosystems, the evidence is sufficient to infer a **causal** relationship between
4 N deposition and the alteration of biogeochemical cycling in freshwater aquatic ecosystems (**ISA**
5 **3.3.2.3**). N deposition is the main source of N enrichment to headwater streams, lower order
6 streams and high elevation lakes. The most common chemical indicators that were studied
7 included NO₃⁻ and dissolved inorganic nitrogen (DIN) concentration in surface waters as well as
8 Chl *a*:total P ratio. Elevated surface water NO₃⁻ concentrations occur in both the eastern and
9 western U.S. Bergstrom and Jansson (2006) report a significant correlation between N deposition
10 and lake biogeochemistry by identifying a correlation between wet deposition and [DIN] and Chl
11 *a*: Total P. Recent evidence provides examples of lakes and streams that are limited by N and
12 show signs of eutrophication in response to N addition.

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

17 **2.2.2 What types of ecosystems are sensitive to such effects? How are these** 18 **responses affected by atmospheric, ecological, and landscape factors**

19 The numerous ecosystem types that occur across the U.S. have a broad range of
20 sensitivity to N deposition. Organisms in their natural environment are commonly adapted to a
21 specific regime of nutrient availability. Change in the availability of one important nutrient, such
22 as N, may result in imbalance in ecological stoichiometry, with effects on ecosystem processes,
23 structure and function (Sturner and Elser, 2002). In general, N deposition to terrestrial
24 ecosystems causes accelerated growth rates in some species, which may lead to altered
25 competitive interactions among species and nutrient imbalances, ultimately affecting
26 biodiversity. The onset of these effects occurs with N deposition levels as low as 3 kg N/ha/yr in
27 sensitive terrestrial ecosystems. In aquatic ecosystems, N that is both leached from the soil and
28 directly deposited can pollute surface water. This causes alteration of the diatom community at
29 levels as low as 1.5 kg N/ha/yr in sensitive freshwater ecosystems.

1 The degree of ecosystem effects lies at the intersection of N loading and N-sensitivity. N-
2 sensitivity is predominately driven by the degree to which growth is limited by nitrogen
3 availability. Grasslands in the western United States are typically N-limited ecosystems
4 dominated by a diverse mix of perennial forbs and grass species (Clark and Tilman, 2008;
5 Suding et al., 2005). A meta-analysis by Lebauer and Treseder (2008) indicated that N
6 fertilization increased aboveground growth in all non-forest ecosystems except for deserts. In
7 other words, almost all terrestrial ecosystems are N-limited and will be altered by the addition of
8 anthropogenic nitrogen. Likewise, a freshwater lake or stream must be N-limited to be sensitive
9 to N-mediated eutrophication. There are many examples of fresh waters that are N-limited or N
10 and P co-limited (**ISA 3.3.3.2**). In a meta-analysis that included 653 datasets, Elser et al. (2007)
11 found that N-limitation occurred as frequently as P-limitation in freshwater ecosystems.
12 Additional factors that govern the sensitivity of ecosystems to nutrient enrichment from N
13 deposition include rates and form of N deposition, elevation, climate, species composition,
14 length of growing season, and soil N retention capacity. (**ISA 4.3**). Less is known about the
15 extent and distribution of the terrestrial ecosystems in the U.S. that are most sensitive to the
16 effects of nutrient enrichment from atmospheric N deposition compared to acidification.

17 **2.2.3 What is the magnitude of ecosystem responses to nitrogen deposition?**

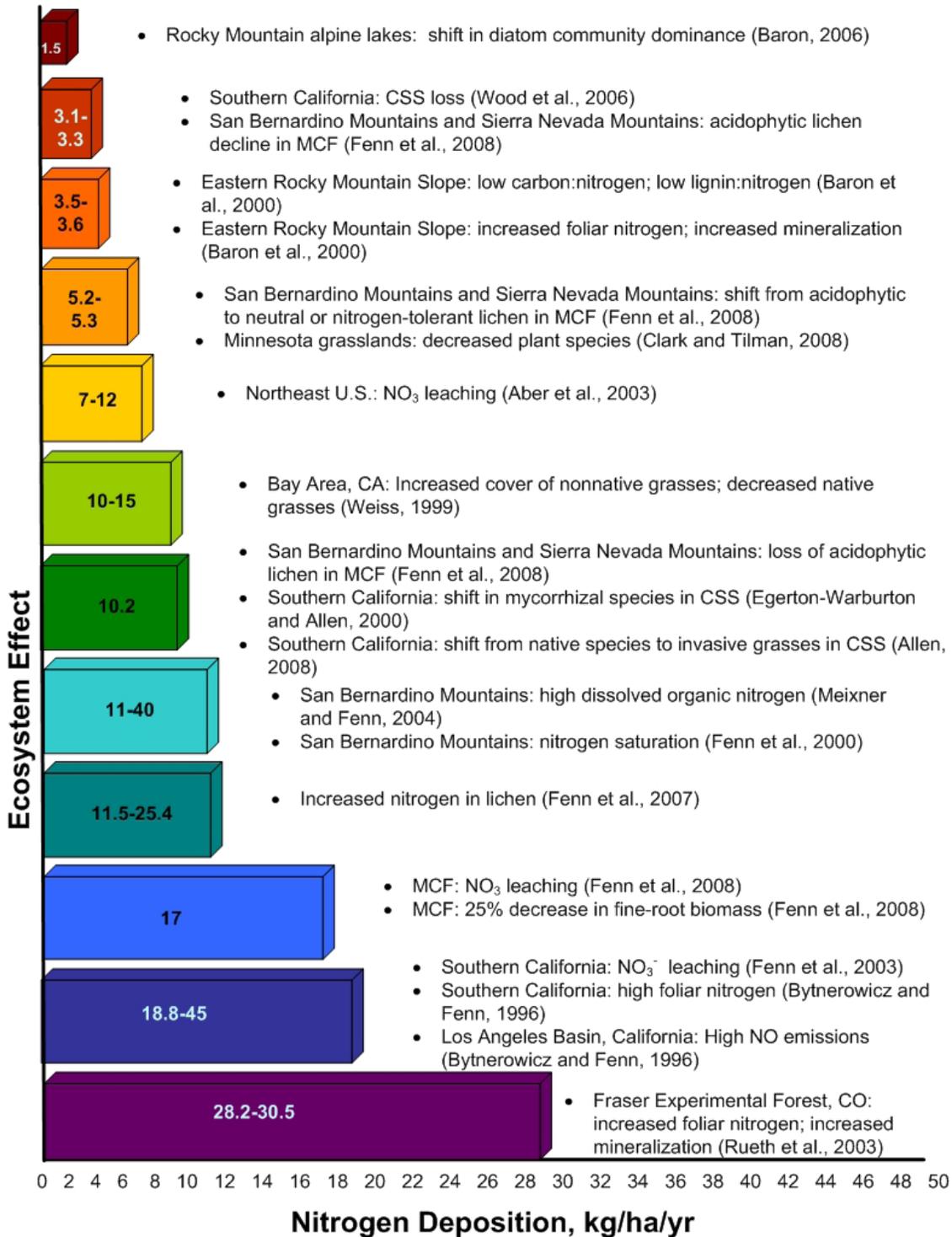
18 **2.2.3.1 Terrestrial**

19 Little is known about the full extent and distribution of the terrestrial ecosystems in the
20 U.S. that are most sensitive to impacts caused by nutrient enrichment from atmospheric N
21 deposition. As previously stated, most terrestrial ecosystems are N-limited, therefore they are
22 sensitive to perturbation caused by N additions (LeBauer and Treseder, 2008). Effects are most
23 likely to occur where areas of relatively high atmospheric N deposition intersect with N-limited
24 plant communities. The alpine ecosystems of the Colorado Front Range, chaparral watersheds of
25 the Sierra Nevada, lichen and vascular plant communities in the San Bernardino Mountains and
26 the Pacific Northwest, and the southern California coastal sage scrub (CSS) community are
27 among the most sensitive terrestrial ecosystems. There is growing evidence that existing
28 grassland ecosystems in the western United States are being altered by elevated levels of N
29 inputs, including inputs from atmospheric deposition (Clark and Tilman, 2008; Suding et al.,
30 2005).

1 In the eastern U.S., the degree of N saturation of the terrestrial ecosystem is often
2 assessed in terms of the degree of NO₃⁻ leaching from watershed soils into ground water or
3 surface water. Stoddard (1994) estimated the number of surface waters at different stages of
4 saturation across several regions in the eastern U.S. Of the 85 northeastern watersheds examined
5 60% were in Stage 1 or Stage 2 of N saturation on a scale of 0 (background or pretreatment) to 3
6 (visible decline). Of the northeastern sites for which adequate data were available for assessment,
7 those in Stage 1 or 2 were most prevalent in the Adirondack and Catskill Mountains. Effects on
8 individual plant species have not been well studied in the U.S. More is known about the
9 sensitivity of particular plant communities. Based largely on results obtained in more extensive
10 studies conducted in Europe, it is expected that the more sensitive terrestrial ecosystems include
11 hardwood forests, alpine meadows, arid and semi-arid lands, and grassland ecosystems (**ISA**
12 **3.8.2**).

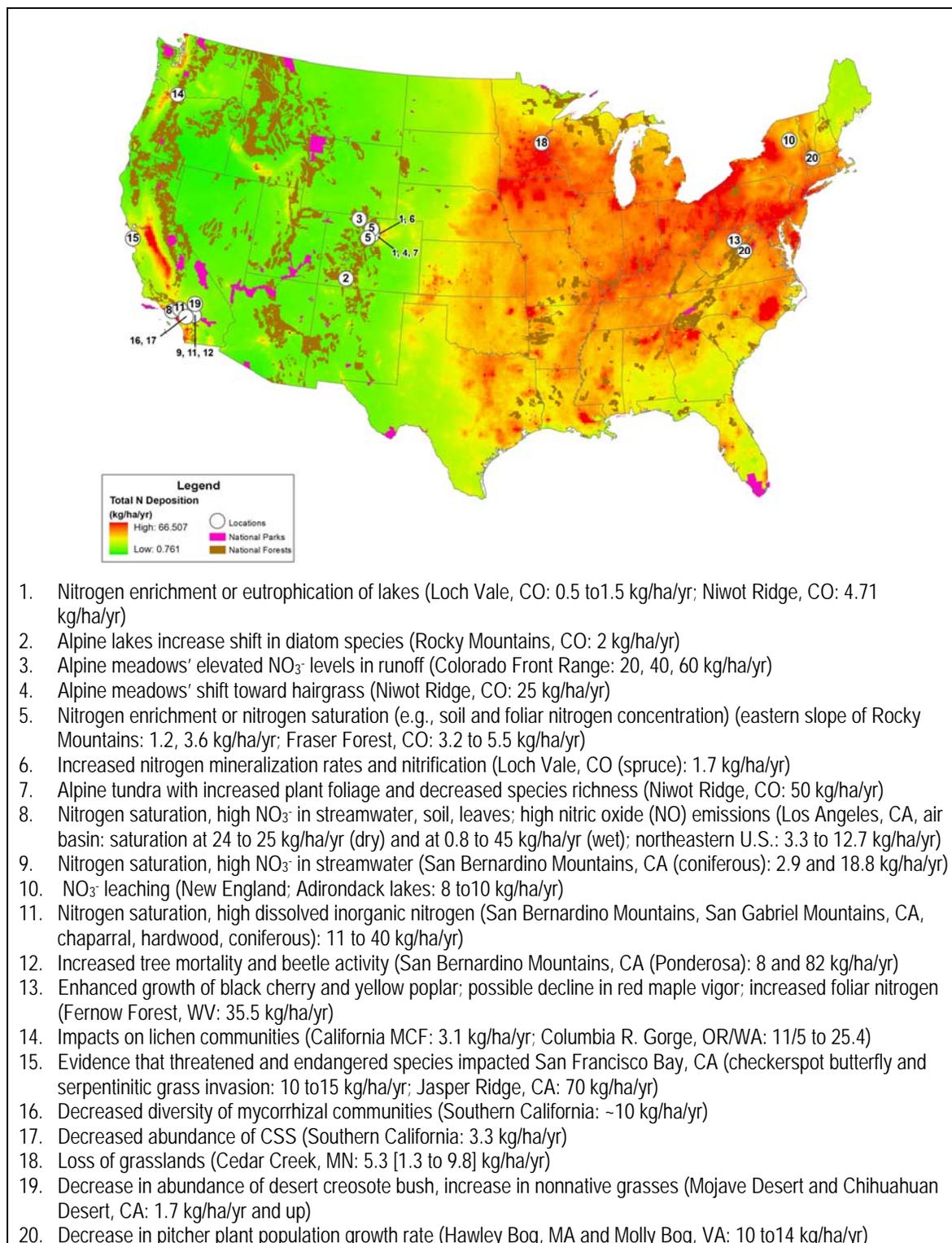
13 The REA used published research results (**REA 5.3.1 and ISA Table 4.4**) to identify
14 meaningful ecological benchmarks associated with different levels of atmospheric nitrogen
15 deposition. These are given by figure 2-8. The sensitive areas and ecological indicators identified
16 by the ISA were analyzed further in the REA to create a national map that illustrates effects
17 observed from ambient and experimental atmospheric nitrogen deposition loads in relation to
18 CMAQ 2002 modeling results and NADP monitoring data. This map, reproduced in Figure 2-9,
19 depicts the sites where empirical effects of terrestrial nutrient enrichment have been observed
20 and site proximity to elevated atmospheric N deposition.

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Figure 2-8. Benchmarks of atmospheric nitrogen deposition for several ecosystem indicators with the inclusion of the diatom changes in the Rocky Mountain lakes (REA 5.3.1.2)



1 **Figure 2-9 (from REA figure 5.3-9).** Observed effects from ambient and
 2 experimental atmospheric nitrogen deposition loads in relation to using CMAQ
 3 2002 modeling results and NADP monitoring data. Citations for effect results are
 4 from the ISA, Table 4.4 (U.S. EPA, 2008).

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

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

- 12 ▪ 3.3 kg N/ha/yr – the amount of nitrogen uptake by a vigorous stand of CSS; above this
13 level, nitrogen may no longer be limiting
- 14 ▪ 10 kg N/ha/yr – mycorrhizal community changes

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

- 16 ▪ 3.1 kg N/ha/yr – shift from sensitive to tolerant lichen species
- 17 ▪ 5.2 kg N/ha/yr – dominance of the tolerant lichen species
- 18 ▪ 10.2 kg N/ha/yr – loss of sensitive lichen species
- 19 ▪ 17 kg N/ha/yr – leaching of nitrate into streams.

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

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

4 **2.2.3.2 Freshwater**

5 The magnitude of ecosystem response may be thought of on two time scales, current
6 conditions and how ecosystems have been altered since the onset of anthropogenic N deposition.
7 As noted previously, Elser et al. (2008) found that N-limitation occurs as frequently as P-
8 limitation in freshwater ecosystems (**ISA 3.3.3.2**). Recently, a comprehensive study of available
9 data from the northern hemisphere surveys of lakes along gradients of N deposition show
10 increased inorganic N concentration and productivity to be correlated with atmospheric N
11 deposition (Bergström and Jansson 2006). The results are unequivocal evidence of N limitation
12 in lakes with low ambient inputs of N, and increased N concentrations in lakes receiving N
13 solely from atmospheric N deposition (Bergström and Jansson, 2006). These authors suggested
14 that most lakes in the northern hemisphere may have originally been N-limited, and that
15 atmospheric N deposition has changed the balance of N and P in lakes.

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

26 Eutrophication effects from N deposition are most likely to be manifested in undisturbed,
27 low nutrient surface waters such as those found in the higher elevation areas of the western U.S.
28 The most severe eutrophication from N deposition effects is expected downwind of major urban
29 and agricultural centers. High concentrations of lake or streamwater NO₃⁻, indicative of
30 ecosystem saturation, have been found at a variety of locations throughout the U.S., including the

1 San Bernardino and San Gabriel Mountains within the Los Angeles Air Basin (Fenn et al., 1996),
2 the Front Range of Colorado (Baron et al., 1994; Williams et al., 1996), the Allegheny mountains
3 of West Virginia (Gilliam et al., 1996), the Catskill Mountains of New York (Murdoch and
4 Stoddard, 1992; Stoddard, 1994), the Adirondack Mountains of New York (Wigington et al.,
5 1996), and the Great Smoky Mountains in Tennessee (Cook et al., 1994) (**ISA 3.3.8**).

6 **2.2.3.3 Nitrogen Enrichment: Evidence of Effects on Estuaries**

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

14 **2.2.3.3.1 What is the nature of estuary responses to reactive nitrogen and sulfur** 15 **deposition?**

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

22 The evidence is sufficient to infer a **causal** relationship between N deposition and the
23 alteration of species richness, species composition and biodiversity in estuarine ecosystems (**ISA**
24 **4.3.4.2 and 3.3.5.4**). Atmospheric and non-atmospheric sources of N contribute to increased
25 phytoplankton and algal productivity, leading to eutrophication. Shifts in community
26 composition, reduced hypolimnetic DO, reduced biodiversity, and mortality of submerged
27 aquatic vegetation are associated with increased N deposition in estuarine systems.

1 **2.2.3.3.2 What types of ecosystems are sensitive to such effects? How are these**
2 **responses affected by atmospheric, ecological, and landscape factors?**

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

15 In the REA, two regions were selected for case study analysis using ASSETS EI, the
16 Chesapeake Bay and Pamlico Sound. Both regions received an ASSETS EI rating of *Bad*
17 indicating that the estuary had moderate to high pressure due to overall human influence and a
18 moderate high to high eutrophic condition (**REA 5.2.4.1 and 5.2.4.2**). These results were then
19 considered with SPATIally Referenced Regression (SPARROW) modeling to develop a response
20 curve to examine the role of atmospheric nitrogen deposition in achieving desired reduction load.
21 To change the Neuse River Estuary’s EI score from *Bad* to *Poor* not only must 100% of the total
22 atmospheric nitrogen deposition be eliminated, but considerably more nitrogen from other
23 sources as well must be reduced (REA section 5.2.7.2). In the Potomac River estuary, a 78%
24 reduction of total nitrogen could move the EI score from *Bad* to *Poor* (**REA 5.2.7.1**). The results
25 of this analysis indicated reductions in atmospheric deposition alone could not solve coastal
26 eutrophication problems due to multiple non-atmospheric nitrogen inputs (**REA 7.3.3**). However,
27 by reducing atmospheric contributions, it may help avoid the need for more costly controls on
28 nitrogen from other sources.

29 In general, estuaries tend to be N-limited (Elser et al., 2008), and many currently receive
30 high levels of N input from human activities to cause eutrophication (Howarth et al., 1996;
31 Vitousek and Howarth, 1991). Atmospheric N loads to estuaries in the U.S. are estimated to

1 range from 2-8% for Guadalupe Bay, TX on the lowest end to as high as 72% for St Catherines-
2 Sapelo estuary, GA (Castro et al., 2003). The Chesapeake Bay is an example of a large, well-
3 studied and severely eutrophic estuary that is calculated to receive as much as 30% of its total N
4 load from the atmosphere.

5 **2.2.3.3.3 What is the magnitude of ecosystem responses to eutrophication?**

6 There is a scientific consensus that nitrogen-driven eutrophication in shallow estuaries
7 has increased over the past several decades and that the environmental degradation of coastal
8 ecosystems due to nitrogen, phosphorus, and other inputs is now a widespread occurrence (Paerl
9 et al., 2001). For example, the frequency of phytoplankton blooms and the extent and severity of
10 hypoxia have increased in the Chesapeake Bay (Officer et al., 1984) and Pamlico estuaries in
11 North Carolina (Paerl et al., 1998) and along the continental shelf adjacent to the Mississippi and
12 Atchafalaya rivers' discharges to the Gulf of Mexico (Eadie et al., 1994).

13 A recent national assessment of eutrophic conditions in estuaries found that 65% of the
14 assessed systems had moderate to high overall eutrophic conditions and generally received the
15 greatest N loads from all sources, including atmospheric and land-based sources (Bricker et al.,
16 2007). Most eutrophic estuaries occurred in the mid-Atlantic region and the estuaries with the
17 lowest degree of eutrophication were in the North Atlantic (Bricker et al., 2007). Other regions
18 had mixtures of low, moderate, and high degree of eutrophication (**ISA 4.3.4.3**).

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

26 **2.2.4 What are the key uncertainties associated with nutrient enrichment?**

27 There are different levels of uncertainty associated with relationships between deposition,
28 ecological effects and ecological indicators. The criteria used in the REA to evaluate the degree
29 of confidence in the data, modeling and ecological effect function are detailed in Chapter 7 of the
30 REA and summarized in section 2.1.4 of this chapter (**REA 7.0**).

1 ***Aquatic***

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

16 ***Terrestrial***

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

22 **2.3 WHAT ECOLOGICAL EFFECTS ARE ASSOCIATED WITH GAS-**
23 **PHASE NO_x AND SO_x?**

24 Acidifying deposition and nitrogen enrichment are the main focus of this policy
25 assessment; however, there are other known ecological effects are attributed to gas-phase NO_x
26 and SO_x. Acute and chronic exposures to gaseous pollutants such as sulfur dioxide (SO₂),
27 nitrogen dioxide (NO₂), nitric oxide (NO), nitric acid (HNO₃) and peroxyacetyl nitrite (PAN) are
28 associated with negative impacts to vegetation. The current secondary NAAQS were set to
29 protect against direct damage to vegetation by exposure to gas-phase NO_x or SO_x, such as foliar

1 injury, decreased photosynthesis, and decreased growth. The following summary is a concise
2 overview of the known or anticipated effects to vegetation caused by gas phase N and S.

3 **2.3.1 What is the nature of ecosystem responses to gas-phase nitrogen and sulfur?**

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

10 *The evidence is sufficient to infer a causal relationship between exposure to NO, NO₂*
11 *and PAN and injury to vegetation (ISA 4.4.2 and 3.4.2.2).* In sufficient concentrations, NO, NO₂
12 and PAN can decrease photosynthesis and induce visible foliar injury to plants. *Evidence is also*
13 *sufficient to infer a causal relationship between exposure to HNO₃ and changes to vegetation*
14 *(ISA 4.4.3 and 3.4.2.3).* Phytotoxic effects of this pollutant include damage to the leaf cuticle in
15 vascular plants and disappearance of some sensitive lichen species.

16 **2.3.2 What types of ecosystems are sensitive to such effects? How are these** 17 **responses affected by atmospheric, ecological, and landscape factors?**

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

26 Entry of gases into a leaf is dependent upon physical and chemical processes of gas phase
27 as well as to stomatal aperture. The aperture of the stomata is controlled largely by the
28 prevailing environmental conditions, such as humidity, temperature, and light intensity. When
29 the stomata are closed, resistance to gas uptake is high and the plant has a very low degree of
30 susceptibility to injury. Mosses and lichens do not have a protective cuticle barrier to gaseous

1 pollutants or stomata and are generally more sensitive to gaseous sulfur and nitrogen than
2 vascular plants (**ISA 3.4.2**).

3 The appearance of foliar injury can vary significantly across species and growth
4 conditions affecting stomatal conductance in vascular plants (**REA 6.4.1**). For example, damage
5 to lichens from SO₂ exposure includes reduced photosynthesis and respiration, damage to the
6 algal component of the lichen, leakage of electrolytes, inhibition of nitrogen fixation, reduced K⁺
7 absorption, and structural changes (Belnap et al., 1993; Farmer et al., 1992, Hutchinson et al.,
8 1996).

9 **2.3.3 What is the magnitude of ecosystem responses to gas phase effects of NO_x** 10 **and SO_x?**

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

17 The ISA states there is very limited new research on phytotoxic effects of NO, NO₂, PAN
18 and HNO₃ at concentrations currently observed in the United States with the exception of some
19 lichen species (**ISA 4.4**). Past and current HNO₃ concentrations may be contributing to the
20 decline in lichen species in the Los Angeles basin (Boonpragob and Nash 1991; Nash and Sigal,
21 1999; Riddell et al., 2008). PAN is a very small component of nitrogen deposition in most areas
22 of the United States (**REA 6.4.2**). Current deposition of HNO₃ is contributing to N saturation of
23 some ecosystems close to sources of photochemical smog (Fenn et al., 1998) such as the MCF's
24 of the Los Angeles basin mountain (Bytnerowicz et al., 1999).

25 **2.4 SUMMARY**

26 In summary, NO_x and SO_x in the atmosphere contribute to effects on individual species
27 and ecosystems through direct contact with vegetation, and more significantly through deposition
28 to sensitive ecosystems. The ISA concludes that the evidence is sufficient to conclude causal
29 relationships between acidifying deposition of N and S and effects on freshwater aquatic
30 ecosystems and terrestrial ecosystems, and between nitrogen nutrient enrichment and effects on

1 sensitive terrestrial and freshwater aquatic ecosystems. The ISA also concludes that a causal
2 relationship is supported between nitrogen nutrient enrichment and effects on estuarine
3 ecosystems; however, the contribution of atmospheric oxidized nitrogen relative to reduced
4 nitrogen and non-atmospheric nitrogen is more difficult to determine.

5 The REA provides additional support that under recent conditions, deposition levels have
6 exceeded benchmarks for ecological indicators of acidification and nutrient enrichment that
7 indicate that effects are likely to be occurring in significant numbers of lakes and streams within
8 sensitive ecosystems.

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3 Fisheries Society.

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1 **3.1.1.1.1 Ozone**

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

15 In the 2008 rulemaking, EPA expanded the characterization of adversity to go beyond the
16 individual plant level and this language is continued in the 2010 ozone reconsideration. The 2008
17 final rule and 2010 proposal conclude that a determination of what constitutes an “adverse”
18 welfare effect in the context of secondary NAAQS review can appropriately occur by
19 considering effects at higher ecological levels (populations, communities, ecosystems) as
20 supported by recent literature. The ozone review uses the example of the construct presented in
21 Hogsett et al. (1997) as a model for assessing risks to forests. This study suggests that adverse
22 effects could be classified into one or more of the following categories: (1) economic production,
23 (2) ecological structure, (3) genetic resources, and (4) cultural values”. Another recent
24 publication, “A Framework for Assessing and Reporting on Ecological Condition: an SAB
25 report” (Young and Sanzone, 2002) provides additional support for expanding the consideration
26 of adversity beyond the species level and at higher levels by making explicit the linkages
27 between stress-related effects at the species level and at higher levels within an ecosystem
28 hierarchy (See Figure 3.1.1).

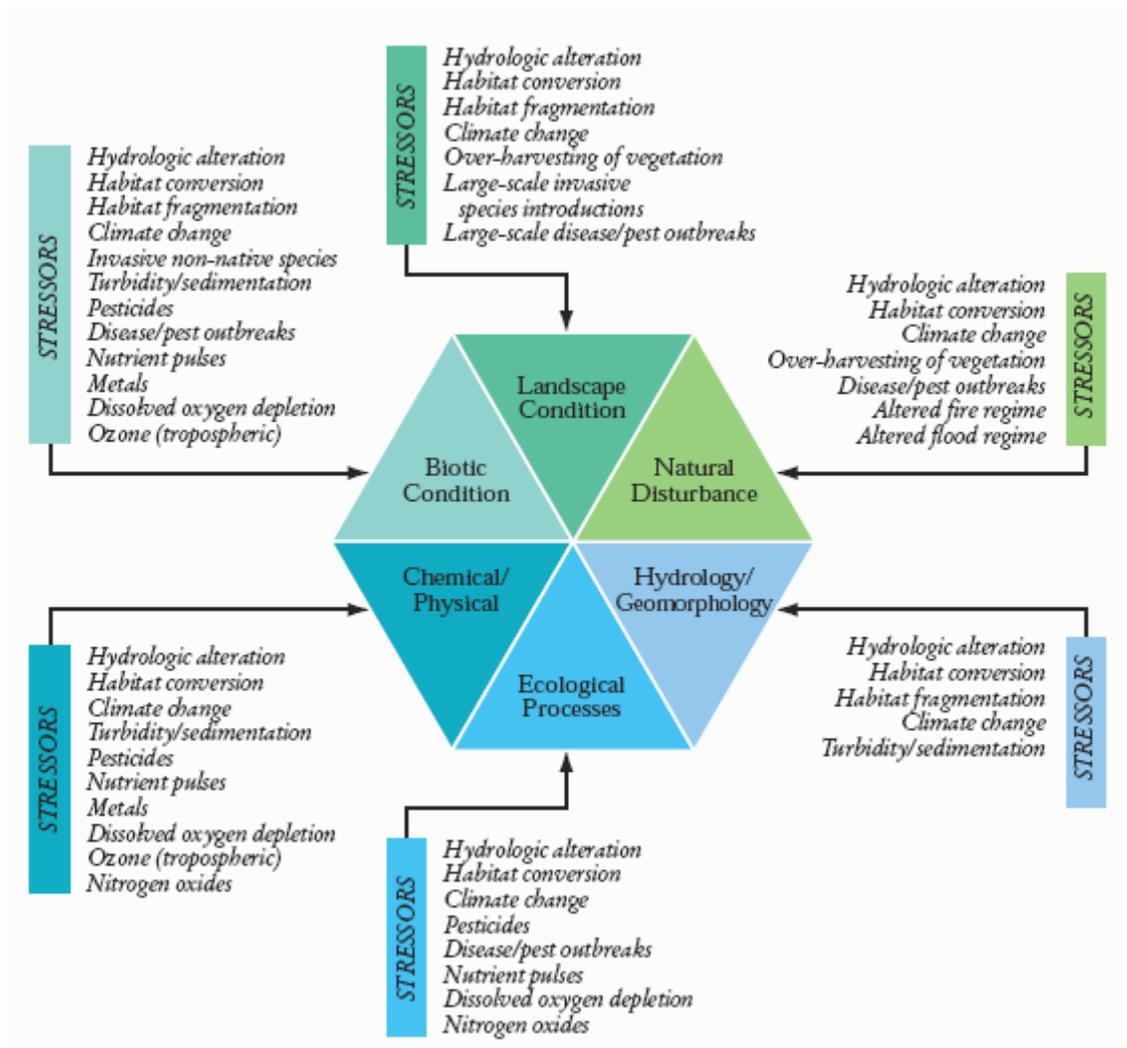


Figure 3-1. Common anthropogenic stressors and the essential ecological attributes they affect. Modified from Young and Sanzone (2002)

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

In the proposed ozone reconsideration in 2010 the Administrator has found that the types of information most useful in informing the selection of an appropriate range of protective levels

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

14 **3.1.1.1.2 PM**

15 [To be added in the second draft policy assessment based on the draft PM policy
16 assessment]

17 **3.1.2 Other EPA Programs and Federal Agencies**

18 Various federal laws and policies exist to protect ecosystem health. How other federal
19 agencies and EPA offices consider ecosystem effects in carrying out their programs can help
20 inform the Administrator when she evaluates the adversity of ecosystem impacts on public
21 welfare. For example, an effect may be considered adverse to public welfare if it contributes to
22 the inability of areas to meet water quality objectives as defined by the Clean Water Act. The
23 following federal statutes and policies may prove helpful to consider.

24 ***EPA Office of Water***

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

1 The CWA also authorizes EPA to develop water quality criteria as a guide for the states
2 to set water quality standards to protect aquatic life. In consideration of acidification effects,
3 EPA’s Redbook, *Quality Criteria for Water*, published originally in 1976, recommends that
4 alkalinity be 20 mg/l or more as CaCO₃ for freshwater aquatic life except where natural
5 concentrations are less. Alkalinity is the sum total of components in the water that tend to elevate
6 the pH of the water above a value of about 4.5.

7 As mentioned in the Redbook, alkalinity is expressed as CaCO₃ in mg/l. Alkalinity
8 differs slightly from ANC in that ANC includes other buffering compounds (Na, Mg, and K) as
9 well and includes buffering capacity of particulates in the water sample. Since alkalinity is
10 expressed as mg/l and ANC is expressed as µeq/l, alkalinity must be multiplied by 20 to be
11 converted to µeq/l. Thus a recommended criterion of 20 mg/l alkalinity is roughly equivalent to
12 an ANC of 400 µeq/l.

13 The **Clean Air Act’s Prevention of Significant Deterioration (PSD)** program (42
14 U.S.C. 7470) purposes include to “preserve, protect and enhance the air quality in national parks,
15 wilderness areas and other areas of natural, recreational, scenic or historic value” Also, the
16 PSD program charges the Federal Land Managers, including the NPS, with “. . . an affirmative
17 responsibility to protect the air quality related values . . . “within federal Class I lands. (42 U.S.C.
18 7475(d)(2)(B)).

19 *National Park Service*

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

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

28 NPS Management Policies (2006) guide all NPS actions including natural resources
29 management. In general, the NPS Management Policies reiterate the NPS Organic Act’s mandate
30 to manage the resources “unimpaired.”

1 ***U.S. Fish and Wildlife Service***

2 On endangered species, Title 16 USC Chapter 35 Section 1531 states “The Congress
3 finds and declares that— these species of fish, wildlife, and plants are of esthetic, ecological,
4 educational, historical, recreational, and scientific value to the Nation and its people and that all
5 Federal departments and agencies will use their authorities to conserve threatened and
6 endangered species.

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

11 ***U.S. Forest Service***

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

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

23 AQRVs in Wilderness areas may receive further protection by the previously mentioned
24 1964 Wilderness Act. For Wilderness Areas in the National Forest System, the Act's
25 implementing regulations are found at 36 C.F.R. §293 requiring these Wilderness Areas be
26 administered to preserve and protect [their] wilderness character.

27 ***Chesapeake Bay Total Maximum Daily Loads***

28 Under section 303(d) of the Clean Water Act, states, territories, and authorized tribes are
29 required to develop lists of impaired waters. These are waters that are too polluted or otherwise
30 degraded to meet the water quality standards set by states, territories, or authorized tribes. The

1 law requires that these jurisdictions establish priority rankings for waters on the lists and develop
2 TMDLs for these waters. A Total Maximum Daily Load, or TMDL, is a calculation of the
3 maximum amount of a pollutant that a waterbody can receive and still safely meet water quality
4 standards. EPA is developing a TMDL for the Chesapeake Bay and its tributaries. The
5 Chesapeake Bay Program has modeled the level of nitrogen that can reach the Bay and still meet
6 the Bay's water quality standards. The TMDL, with full public participation, will set waste load
7 allocations for point source discharges and load allocations for nonpoint sources of nitrogen. Air
8 deposition to the Bay and its watershed, as a source category, will have a specific allocation. The
9 allocation can be used to calculate the level of ambient air concentrations of reactive nitrogen
10 that are likely to meet the deposition allocation. To find the NO_x portion of the allocation one
11 would subtract the reduced forms from the total allocation. If the total load to the Bay of nitrogen
12 from all the allocated source categories remains below the allocations, then the Bay is expected
13 to meet the water quality standards, which are set to protect the designated uses of the Bay. Since
14 the designated uses are set by the states with public input, not meeting the designated uses can be
15 seen as having an adverse effect.

16 ***United Nations Economic Commission for Europe (UNECE)***

17 [This information will be included in the second draft.]

18 ***Critical Loads***

19 The term critical load is used to describe the threshold of air pollution deposition that
20 causes a specified level of harm to sensitive resources in an ecosystem. A critical load is
21 technically defined as “the quantitative estimate of an exposure to one or more pollutants below
22 which significant harmful effects on specified sensitive elements of the environment are not
23 expected to occur according to present knowledge” (Nilsson and Grennfelt, 1988). The
24 determination of when a harmful effect becomes “significant” may be in the view of a researcher
25 or through a policy development process. Researchers often use the term “critical loads” to
26 describe when particular detrimental effects are realized, as is the case in Figure 2-1. In many
27 European countries a critical loads framework is used to determine a level of damages to
28 ecosystem services from pollution that are legally allowed. These critical loads are determined
29 through a policy process.

1 Harmful effects due to acidification have been defined here as those that occur below a
2 given ANC for aquatic systems and below a given Bc:Al ratio for terrestrial systems. However,
3 the level at which an effect becomes harmful in that it causes adverse effects on public welfare is
4 determined by the Administrator.

5 **3.2 WHAT ARE ECOSYSTEM SERVICES AND HOW DOES THIS** 6 **CONCEPT RELATE TO PUBLIC WELFARE?**

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

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

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

18 While the text above lists a number of welfare effects, these effects are not an effect on
19 public welfare in and of themselves.

20 Ecosystem services can be generally defined as the benefits individuals and organizations
21 obtain from ecosystems. Ecosystem services can be classified as provisioning (food and water),
22 regulating (control of climate and disease), cultural (recreational), and supporting (nutrient
23 cycling) (MEA 2005). Conceptually, changes in ecosystem services may be used to aid in
24 characterizing a known or anticipated adverse effect to public welfare. In the context of this
25 review, ecosystem services may also aid in assessing the magnitude and significance to the
26 public of a resource and in assessing how NO_x and SO_x concentrations and deposition may
27 impact that resource. The relationship between ecosystem services and public welfare effects is
28 illustrated in Table 3.2.1.

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

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

1 *All ecosystem services contribute to personal comfort and wellbeing.

2 EPA has defined ecological goods and services for the purposes of a Regulatory Impact
3 Analysis as the “outputs of ecological functions or processes that directly or indirectly contribute
4 to social welfare or have the potential to do so in the future. Some outputs may be bought and
5 sold, but most are not marketed” (US EPA 2006). Though this is not a definition specifically for
6 use in the NAAQS process it may be a useful one in considering the scope of ecosystem services
7 and the effects of air pollutants upon those services. Especially important is the
8 acknowledgement that most of the goods and services supplied by ecosystems cannot be fully
9 measured or monetized. Valuing ecological benefits, or the contributions to social welfare
10 derived from ecosystems, can be challenging as noted in EPA’s Ecological Benefits Assessment
11 Strategic Plan (US EPA 2006) and the Science Advisory Board report “Valuing the Protection of
12 Ecological Systems and Services” (US EPA, 2009). It can be informative in characterizing
13 adversity to public welfare to attempt to place an economic valuation on the set of goods and
14 services that have been identified with respect to a change in policy however it must be noted
15 that this valuation will be incomplete and illustrative only. The stepwise concept leading to the
16 valuation of ecosystem services is graphically depicted in Figure 3-2.

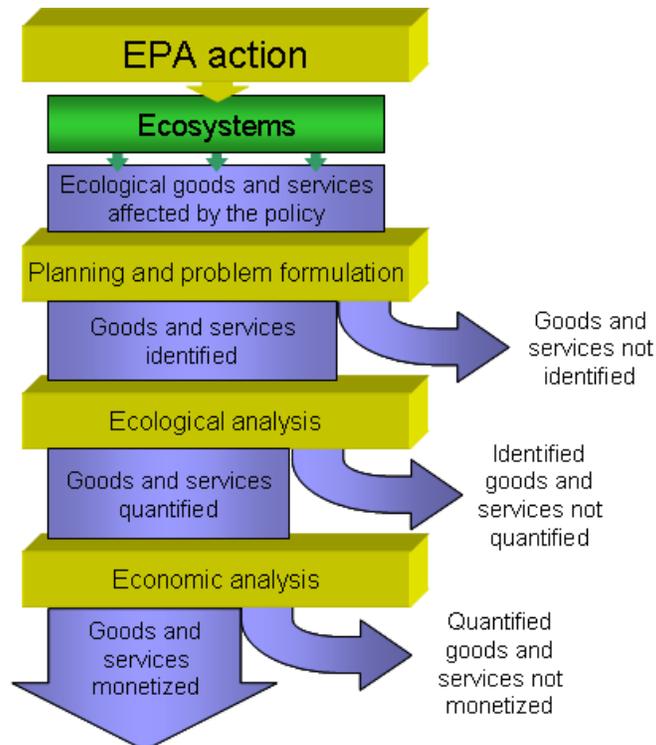


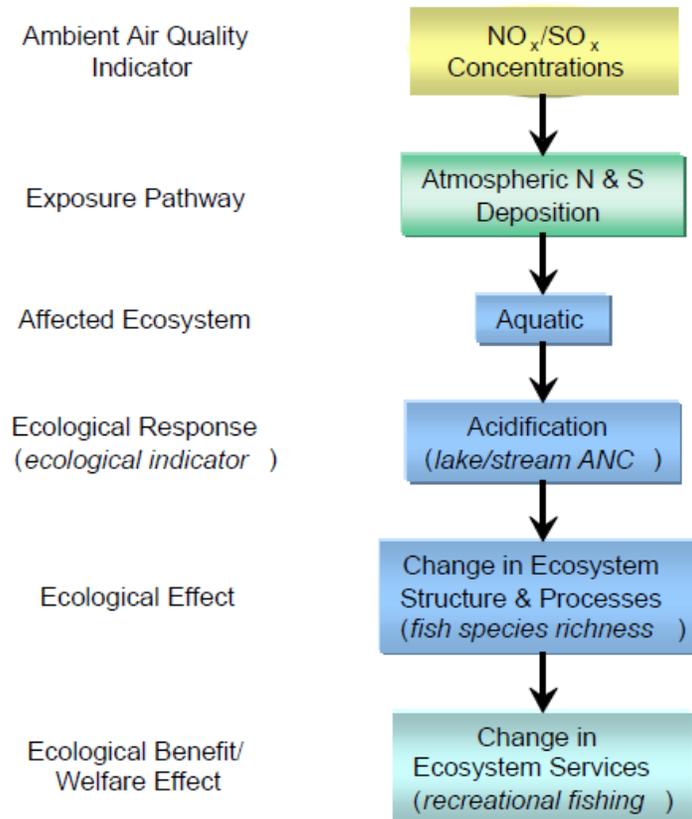
Figure 3-2. Representation of the benefits assessment process indicating where some ecological benefits may remain unrecognized, unquantified, or unmonetized. (Source: EBASP USEPA 2006).

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A conceptual model integrating the role of ecosystem services in characterizing known or anticipated adverse effects to public welfare is shown in Figure 3-3. Under Section 109 of the CAA, the secondary standard is to specify a level of air quality that is requisite to protect public welfare. For this review, the relevant air quality indicator is interpreted as ambient NO_x and SO_x concentrations that can be linked to levels of deposition for which there are ecological effects that are adverse to public welfare. The case study analyses (described in Chapters 4 and 5 of the REA and summarized in Chapter 2 of this document) link deposition in sensitive ecosystems (e.g., the exposure pathway) to changes in a given ecological indicator (e.g., for aquatic acidification, changes in acid neutralizing capacity [ANC]) and then to changes in ecosystems and the services they provide (e.g., fish species richness and its influence on recreational fishing). To the extent possible for each targeted effect area, ambient concentrations of nitrogen and sulfur (i.e., ambient air quality indicators) were linked to deposition in sensitive ecosystems (i.e., exposure pathways), and then deposition was linked to system response as measured by a given ecological indicator (e.g., lake and stream acidification as measured by ANC). The

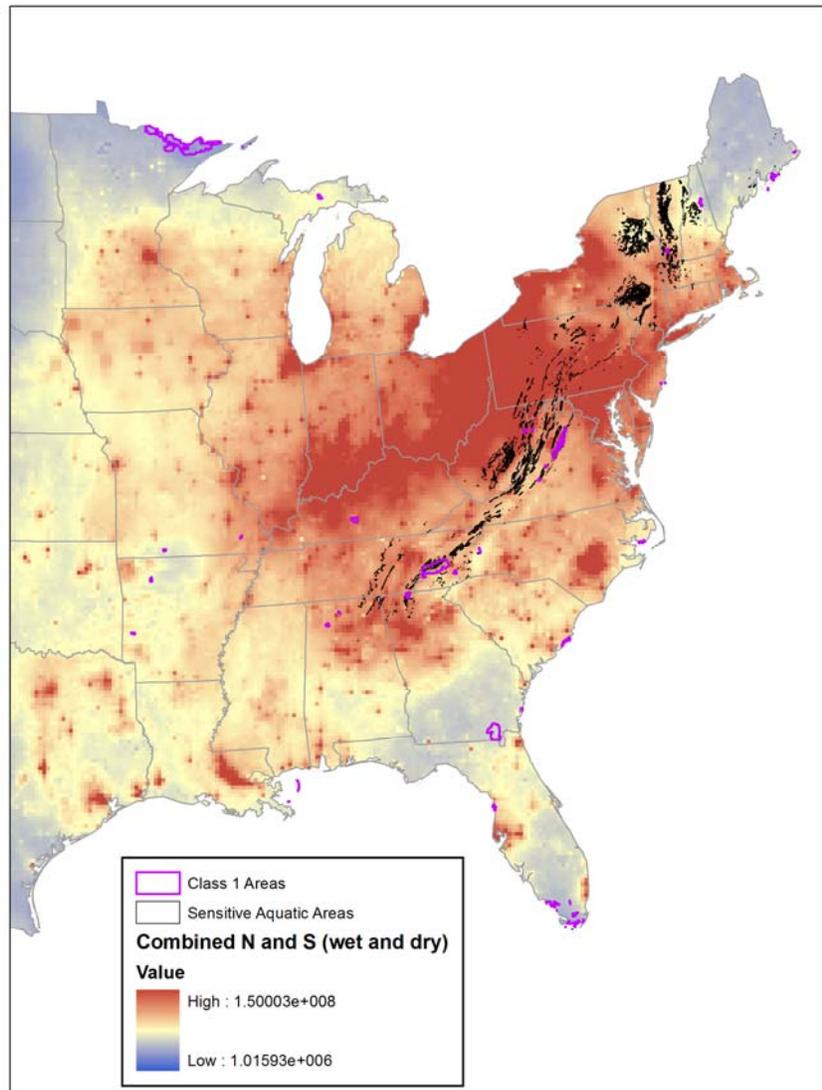
1 ecological effect (e.g., changes in fish species richness, etc.) was then, where possible, associated
2 with changes in ecosystem services and their public welfare effects (e.g., recreational fishing).

3 Knowledge about the relationships linking ambient concentrations and ecosystem
4 services can be used to inform a policy judgment on a known or anticipated adverse public
5 welfare effect. The conceptual model outlined for aquatic acidification in Figure 3-3 can be
6 modified for any targeted effect area where sufficient data and models are available. For
7 example, a change in an ecosystem structure and process, such as foliar injury, would be
8 classified as an ecological effect, with the associated changes in ecosystem services, such as
9 primary productivity, food availability, and aesthetics (e.g., scenic viewing), classified as public
10 welfare effects. Additionally, changes in biodiversity would be classified as an ecological effect,
11 and the associated changes in ecosystem services—productivity, recreational viewing and
12 aesthetics—would be classified as public welfare effects. This information can then be used by
13 the Administrator to determine whether or not the changes described are adverse to public
14 welfare. In subsequent sections these concepts are applied to characterize the ecosystem services
15 potentially affected by nitrogen and/or sulfur for each of the effect areas assessed in the REA.

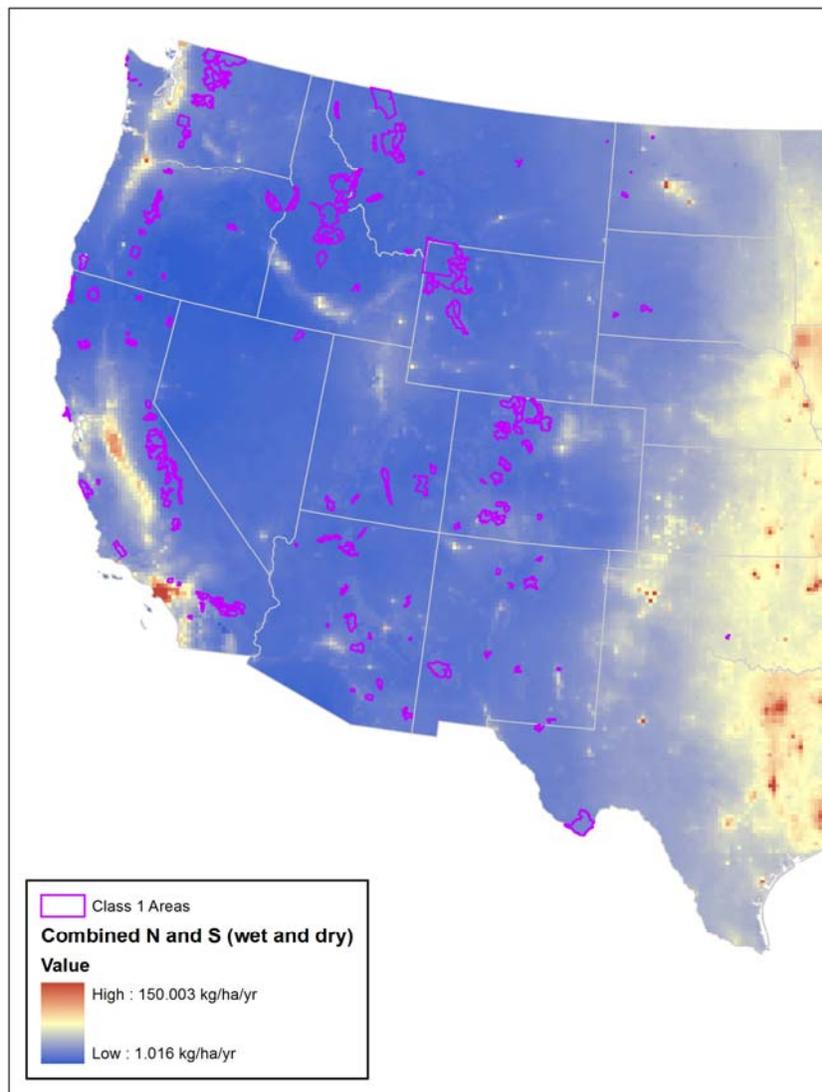


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 2 **Figure 3-3.** Conceptual model showing the relationships among ambient air
 3 quality indicators and exposure pathways and the resulting impacts on
 4 ecosystems, ecological responses, effects and benefits to characterize known or
 5 anticipated adverse effects to public welfare. [This figure to be revised for Second
 6 Draft Policy Assessment Document]

7 These concepts can also be applied to the programs described in section 3.1. National
 8 parks represent areas of nationally recognized ecological and public welfare significance, which
 9 are afforded a higher level of protection. Therefore, staff has also focused on air quality and
 10 deposition in the subset of national park sites and important natural areas. Figures 3-4 and 3-5
 11 illustrate the spatial relationships between sensitive regions, Class 1 areas and nitrogen
 12 deposition levels.



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2 **Figure 3-4.** Locations of Eastern U.S. National Parks (Class I areas) relative to
3 deposition of Nitrogen and Sulfur in sensitive aquatic areas



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Figure 3-5. Location of Western U.S. National Parks (Class I areas) relative to deposition of Nitrogen and Sulfur

[Figures 3-4 and 3-5 will be revised for Second Draft policy Assessment Document]

3.3 WHAT IS THE ROLE OF ECONOMICS?

As discussed earlier in this document, a secondary NAAQS is required to be set at the “level(s) of air quality necessary to protect the public welfare from any known or anticipated adverse effects”. As part of the effort to determine the standard, EPA linked the changes in the ambient air concentrations of NO_x and SO_x to the changes in ecosystem services and ultimately to changes in public welfare (U.S. EPA, 2009). As previously mentioned most ecosystem

1 services are not amenable to monetization a small subset of changes in services can be described
2 by economic valuation methods. And although economics on its own cannot determine which
3 impact on public welfare is “adverse”, economics could be helpful in the context of a secondary
4 NAAQS for determining the degree to which improvements are beneficial to public welfare and
5 illustrating and aggregating those impacts.⁷

6 *The Role of Economics in Defining “Adversity”* There is neither an economic definition
7 of how much loss in public welfare is adverse nor an economic definition of adversity. While an
8 economist might consider a particular scenario adverse because it might imply some harm or
9 potential for improvement, there is no specific threshold level when a loss in welfare (e.g. loss in
10 dollars) becomes adverse. An individual might be willing to give up some of their resources to
11 avoid a threat or negative outcome (i.e., willing to pay to avoid a particular outcome). According
12 to economic theory, if an individual is willing to give up something to avoid the outcome, then
13 imposing the outcome on the individual must make them worse off, at which point an economist
14 might colloquially describe the outcome as adverse. However, the amount they would have been
15 willing to pay to avoid the outcome might be quite small, and might not rise to a level of harm
16 that the Administrator interprets as “adverse” to public welfare. In summary, economics provides
17 little guidance as to how the Administrator should interpret the word “adverse” in the context of
18 public welfare.

19 *Ecosystem Services and Links to Public Welfare* An ecosystem service framework
20 provides a structure to measure changes in public welfare from changes in ecosystem functions
21 affected by air pollution. EPA’s Risk Assessment for this rulemaking defines ecosystem services
22 as “the ecological processes or functions having monetary or nonmonetary value to individuals
23 or society at large” (EPA 2009.) The discipline of economics provides a useful approach for
24 summarizing how the public values changes in the services provided by the environment. An
25 ecosystem services framework (with or without valuation) can provide measures of changes in
26 public welfare.

⁷ Section 109 of the Clean Air Act forbids consideration of the compliance costs of reducing pollution when setting a NAAQS. However, there is no prohibition regarding the consideration of the monetized impacts of welfare effects occurring due to levels of pollution above alternative standards in evaluating the adversity of the impacts to public welfare. Ecosystem services can be characterized as a method of monetizing the impacts of the air pollution. Although a separate regulatory document quantifying the costs and benefits of attaining a NAAQS is prepared simultaneously, this document is not considered when selecting a standard.

1 *Economics as a Framework to Illustrate Changes in Public Welfare* Economics can
2 provide a framework to illustrate how public welfare⁸ changes in response to changes in
3 environmental quality by quantitatively linking changes in ecosystem services to preferences.
4 Economics assumes that the choices that individuals make reflect their preferences over certain
5 outcomes and that, generally speaking, they will make choices that, in expectation, will make
6 them as well off as possible given their resources. In economics revealed and stated preference
7 methods are used to observe the choices individuals make to understand the outcomes
8 individuals prefer. What individuals are willing to give up for an outcome is their willingness-to-
9 pay (WTP) for that outcome. An example of an outcome is an improvement in an ecosystem
10 service. Often, to provide comparability to other goods and services, in economics these
11 tradeoffs are framed relative to dollars for convenience.⁹

12 Economics could inform the Administrator by valuing and characterizing the changes in
13 public welfare from changes in the quantity and quality of ecosystem services. Overall, this
14 assessment intends to characterize changes in ecosystem services from a scientific perspective
15 using effects on ecosystem structures and functions or ecosystem integrity. Economics then
16 estimates the effect on public welfare of these changes in the quantity and quality of ecosystem
17 services. For example, a decrease in a particular bird species can be characterized by its effect on
18 the ecosystem's structure and function, while from an economic perspective, the effects would
19 be based on the impact on public welfare or the value the public places on that species. A simple
20 example is a comparison between a decrease in a bird species that is relatively unknown
21 compared to a decrease in a very prominent species (e.g. Bald Eagle). The public is likely to
22 have a higher WTP to avoid the latter, and thus the decrease would affect the public welfare
23 more.

24 There are important complications with using preferences to understand the effect of
25 pollution on public welfare. For example, while the field of economics generally assumes that
26 public preferences are the paramount consideration; these preferences may change when the
27 public receives new information. Therefore, if individuals do not understand how pollution will

⁸ [A discussion of economic interpretation of "Public Welfare" will be included in the second draft]

⁹ Often groups collectively make choices to engage in activities that improve the collective welfare of the group. For example, a community around an acidified lake might purchase lime and use it to reduce the acidity of the lake. The collective decisions can also be used to understand how people value improvements to ecosystem services.

[Additional discussion will be included in the second draft related to collective actions that reveal preferences for improvements in relevant ecosystem services and how these collective actions, and the absence of these actions, can be interpreted.]

1 affect ecosystem services, or even how those ecosystem services affect their quality of life, then
2 they will have a difficult time valuing changes in those services. Similarly, it may be very costly
3 for individuals to learn and understand how changes in particular ecosystem services may affect
4 them, in part because typically there are significant interdependencies within an ecosystem.
5 Because of this complexity, individuals may implicitly value a species, or habitat, or ecosystem
6 function because it supports an ecosystem service that they do clearly value. Furthermore, the
7 public also has limited understanding regarding irreversibilities, tipping points, and other more
8 complex aspects of ecosystems, which limits the ability to adequately value these ecosystems.¹⁰
9 In addition, where and when a change in an ecosystem takes place is crucial for characterizing
10 the associated change in an ecosystem service, and will also affect the value the public places on
11 that change.

12 **3.4 WHAT IS THE EVIDENCE FOR EFFECTS ON ECOSYSTEM** 13 **SERVICES? HOW DO WE LINK ECOLOGICAL INDICATORS TO** 14 **SERVICES?**

15 The process used to link ecological indicators to ecosystem services is discussed
16 extensively in Appendix 8 of the REA. In brief, for each effect area assessed the ecological
17 indicators were linked to an ecological response that was subsequently linked, to the extent
18 possible, to associated services. For example in the case study for aquatic acidification the
19 chosen ecological indicator is ANC which can be linked to the ecosystem service of recreational
20 fishing as illustrated in the conceptual model shown in Figure 3-6. Although recreational fishing
21 losses are the only service effects that can be quantified or monetized at this time, there are, as
22 can be seen in the Figure, numerous other ecosystem services that may be related to the
23 ecological effects of acidification.

¹⁰ While the public may not fully appreciate the interdependencies within ecosystems, they can learn them, but again it may be costly to do so. It is possible for individuals to value outcomes that are irreversible or result in discrete changes (i.e., tipping points) in the quality and quantity of ecosystem services. Avoiding irreversible outcomes should be and are more valued by individuals than outcomes that are not irreversible (Arrow and Fischer, 1974).

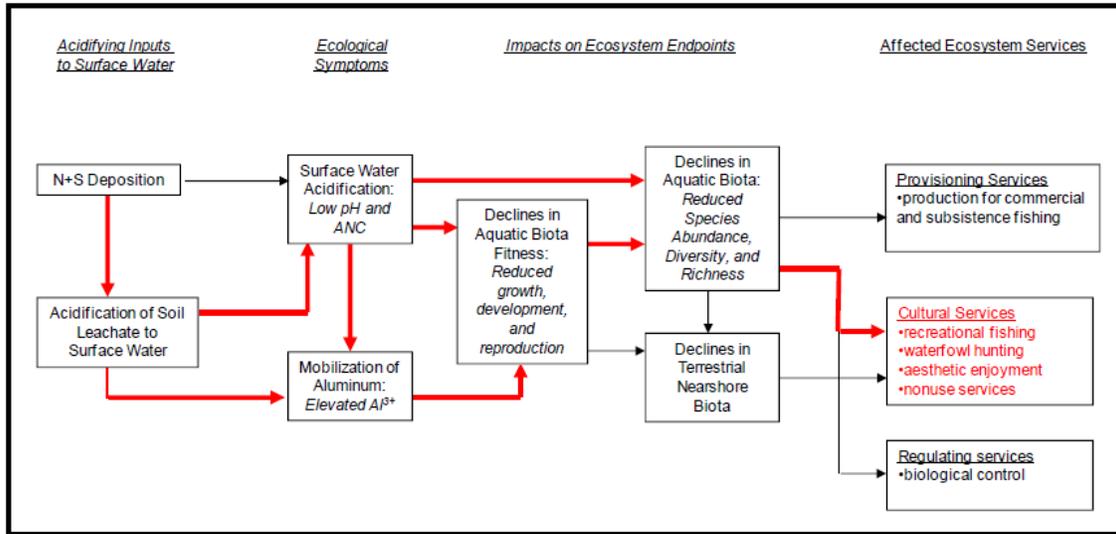


Figure 3-6. Conceptual model linking ecological indicator (ANC) to affected ecosystem services.

The next four sections summarize the current levels of certain ecosystem services for each of the effect areas analyzed in the REA and present results of analyses that have attempted to quantify and monetize the harms to public welfare, as represented by ecosystem services, due to nitrogen and sulfur deposition.

Evidence for Adversity Related to Aquatic Acidification

Acidification primarily affects the ecosystem services that are derived from the fish and other aquatic life found in these surface waters (**REA, Section 5.2.1.3**). Food is generally the most important provisioning services provided by inland surface waters (MEA, 2005). In the northeastern United States, the surface waters affected by acidification are not a major source of commercially raised or caught fish; however, they are a source of food for some recreational and subsistence fishers and for other consumers. Although data and models are available for examining the effects on recreational fishing, relatively little data are available for measuring the effects on subsistence and other consumers. For example, although there is evidence that certain population subgroups in the Northeastern United States, such as the Hmong and Chippewa ethnic groups, have particularly high rates of self-caught fish consumption (Hutchison and Kraft, 1994; Peterson et al., 1994), it is not known if and how their consumption patterns are affected by the reductions in available fish populations caused by surface water acidification.

Inland surface waters support several cultural services, such as aesthetic and educational services; however, the type of service that is likely to be most widely and significantly affected

1 by aquatic acidification is recreational fishing¹¹. Recreational fishing in lakes and streams is
2 among the most popular outdoor recreational activities in the northeastern United States. Data
3 from the 2006 National Survey of Fishing, Hunting, and Wildlife Associated Recreation
4 (FHWAR) indicate that more than 9% of adults in this part of the country participate annually in
5 freshwater fishing with 140 million freshwater fishing days. Based on studies conducted in the
6 northeastern United States, Kaval and Loomis (2003) estimated average consumer surplus values
7 per day of \$35 for recreational fishing (in 2007 dollars). Therefore, the implied total annual value
8 of freshwater fishing in the northeastern United States was \$5 billion in 2006.

9 In general, inland surface waters such as lakes, rivers, and streams provide a number of
10 regulating services, such as hydrological regime regulation and climate regulation. There is little
11 evidence that acidification of freshwaters in the northeastern United States has significantly
12 degraded these specific services; however, freshwater ecosystems also provide biological control
13 services by providing environments that sustain delicate aquatic food chains.

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

20 *What is the value of the impaired recreational fishing services?*

21 The previous section describes the ecosystem services that are most likely to be affected
22 by N and S deposition, and it summarizes evidence regarding the current magnitude and values
23 of recreational fishing services; however, it does not measure the degree to which these services
24 are impaired by existing NO_x/SO_x levels.

25 To address this limitation, the **REA (Appendix 8)** provides insights into the magnitude of
26 ecosystem service impairments.

27 Specifically, the REA focuses on measuring the *benefits* of ecosystem service
28 enhancements resulting from the elimination of anthropogenic sources of NO_x/SO_x. Rather than
29 asking how much public welfare is currently adversely affected relative to a scenario without

¹¹ Banzhaf et al (2006) has shown that non-use services are arguably a more significant source of benefits from reduced acidification than recreational fishing.

1 anthropogenic NO_x/SO_x, it asks a similar question of how much public welfare would improve if
2 the emissions were eliminated. The REA provides quantitative estimates of selected ecosystem
3 services impairments or enhancements for three main categories of ecosystem effects – aquatic
4 acidification, terrestrial acidification, and aquatic nutrient enrichment¹². Within these three
5 categories, the selection of specific ecosystem services for more in-depth analysis depended
6 primarily on the expected magnitude of impairments and on the availability of appropriate data
7 and modeling tools.

8 The analysis of ecosystem service impairments due to aquatic acidification builds on the
9 case study analysis of lakes in the New York Adirondacks. It estimates changes in recreational
10 fishing services, as well as changes more broadly in “cultural” ecosystem services (including
11 recreational, aesthetic, and nonuse services). First, the MAGIC model was applied to 44 lakes to
12 predict what ANC levels would be under both “business as usual” conditions (i.e., allowing for
13 some decline in deposition due to existing regulations) and pre-emission (i.e., background)
14 conditions. When these model runs were initiated staff were interested in a prospective analysis
15 of conditions assuming a 2010 implementation of “zero-out” emissions with a projected lag time
16 to improvement of 10 years thus results were calculated for the year 2020. These predictions
17 were then extrapolated to the full universe of Adirondack lakes. Second, to estimate the
18 recreational fishing impacts of aquatic acidification in these lakes, an existing model of
19 recreational fishing demand and site choice was applied. This model predicts how recreational
20 fishing patterns in the Adirondacks would differ and how much higher the average annual value
21 of recreational fishing services would be for New York residents if lake ANC levels
22 corresponded to background (rather than business as usual) conditions. Aggregating these values
23 across all NY residents implies that acidification of Adirondack lakes due to anthropogenic
24 sources of NO_x/SO_x would impair annual recreational fishing services of NY residents by \$6
25 million to \$11 million in 2020. Current annual impairments are most likely of a similar
26 magnitude because, although current NO_x/SO_x levels are somewhat higher than those expected in
27 2020 (under business as usual – given expected emissions controls associated with Title IV
28 regulations but no additional nitrogen or sulfur controls), the affected NY population is also
29 somewhat smaller (based on U.S. Census Bureau projections).

¹² Estimates for terrestrial nutrient enrichments were not generated due to the limited availability of necessary data and models for this effect category.

1 Third, to estimate impacts on a broader category of cultural ecosystem services, results
2 from an existing valuation survey of NY residents were adapted and applied to this context. The
3 survey used a contingent valuation approach to estimate the average annual household WTP for
4 future reductions (20% and 45%) in the percent of Adirondack lakes impaired by acidification.
5 These WTP estimates were then (1) rescaled to reflect predicted changes between business-as-
6 usual and background conditions in 2020 (MAGIC lake modeling results indicate that the
7 percentage of impaired lakes would be 22 to 31 points lower under background conditions), and
8 (2) aggregated across NY households. The aggregate annual value to NY residents in 2010 for a
9 reduction in lake acidification to background levels by 2020 was estimated to range \$4 million to
10 \$300 million in 2007 dollars. For comparison the previous section estimated the value of
11 recreational fishing in the Northeastern states at approximately \$5 billion in 2006. These results
12 suggest that the value of avoiding current impairments to ecosystem services from Adirondack
13 lakes are even higher than the estimate, because they occur today rather than in 2020 (i.e., no
14 delayed effect) and because the percent of impaired lakes is slightly higher today than expected
15 in 2020 under business-as-usual. These results imply significant value to the public derived from
16 recreational fishing services. The analysis especially illustrates what may be the scale of all
17 impacts to public welfare when viewed as a subset of all services impacted by acidification.

Evidence for Terrestrial Acidification

18
19 A similar model to Figure 3-6 can be drawn for terrestrial acidification that links Bc:Al
20 ratio to reduced tree growth to decreases in timber harvest although we have less confidence in
21 the significance of this linkage than we do for aquatic acidification. There are numerous services
22 expected to be affected, but the means to adequately describe those losses does not as yet exist.
23 These services include effects to forest health, water quality, and habitat, including decline in
24 habitat for threatened and endangered species, decline in forest aesthetics, decline in forest
25 productivity, increases in forest soil erosion and decreases in water retention (ISA, 2009; REA,
26 2009; Krieger, 2001).

27 Forests in the Northeastern United States provide several important and valuable
28 provisioning services, which are reflected in the production and sales of tree products.

29 Sugar maples are a particularly important commercial hardwood tree species in the
30 United States, producing wood products like timber and maple syrup that provide hundreds of

1 millions of dollars in economic value annually (NASS, 2008). Red spruce is also used in a
2 variety of wood products and provides up to \$100 million in economic value annually.

3 Forests in the Northeastern United States are also an important source of cultural
4 ecosystem services, including nonuse (existence value for threatened and endangered species),
5 recreational, and aesthetic services (ISA, 2009; REA, 2009). Red spruce forests are home to two
6 federally listed species.

7 Although we do not have the data to link acidification damages directly to economic
8 values of lost recreational services in forests, these resources are valuable to the public. A recent
9 study suggests that the total annual value of off-road driving recreation was more than \$9 billion,
10 total and value of hunting and wildlife viewing was more than \$4 billion each in the Northeastern
11 United States in 2006(Kaval and Loomis, 2003). In addition, fall color viewing is a recreational
12 activity that is directly dependent on forest conditions. Sugar maple trees, in particular, are
13 known for their bright colors and are, therefore, an essential aesthetic component of most fall
14 color landscapes. Statistics on fall color viewing are much less available than for the other
15 recreational and tourism activities; however, a few studies have documented the extent and
16 significance of this activity. For example, Spencer and Holecek (2007) found that roughly 30%
17 of residents reported at least one trip in the previous year involving fall color viewing. In a
18 separate study conducted in Vermont, Brown (2002) reported that more than 22% of households
19 visiting Vermont in 2001 made the trip primarily for the purpose of viewing fall colors.

20 Two studies that have estimated values for protecting high-elevation spruce forests in the
21 Southern Appalachians. Kramer et al. (2003) conducted a contingent valuation study estimating
22 households' WTP for programs to protect remaining high-elevation spruce forests from damages
23 associated with air pollution and insect infestation (Haefele et al., 1991; Holmes and Kramer,
24 1995). Median household WTP was estimated to be roughly \$29 (in 2007 dollars) for the
25 minimal program and \$44 for the more extensive program. Another study by Jenkins, Sullivan,
26 and Amacher (2002) estimated an aggregate annual value of \$3.4 billion for avoiding a
27 significant decline in the health of high-elevation spruce forests in the Southern Appalachian
28 region.

29 Forests in the Northeastern United States also support and provide a wide variety of
30 valuable regulating services, including soil stabilization and erosion control, water regulation,
31 and climate regulation (Krieger, 2001). Forest vegetation plays an important role in maintaining

1 soils in order to reduce erosion, runoff, and sedimentation that can adversely impact surface
2 waters. In addition to protecting the quality of water in this way, forests also help store and
3 regulate the quantity and flows of water in watersheds. Finally, forests help regulate climate
4 locally by trapping moisture and globally by sequestering carbon. The total value of these
5 ecosystem services is very difficult to quantify and the magnitude of these impacts is currently
6 very uncertain.

7 *What is the value of current ecosystem service impairments?*

8 The analysis of ecosystem service impairments associated with terrestrial acidification
9 specifically addresses impacts on the forest product provisioning services from two
10 commercially important tree species – sugar maple and red spruce--that are particularly sensitive
11 to the effects of acidification. Using data from the USFS Forest Inventory and Analysis (FIA)
12 database, an exposure-response relationship was estimated for each species to measure the
13 average negative effect of critical load exceedances (CLEs) of nitrogen and sulfur deposition on
14 annual tree growth. These estimated relationships were then applied to sugar maple and red
15 spruce stocks in the Northeast and North central regions to estimate the average percent increase
16 in annual tree growth that would occur if all CLEs were eliminated. To estimate the aggregate-
17 level forest market impacts of eliminating CLEs starting in the year 2000, the tree-level growth
18 adjustments were applied using the Forest and Agricultural Sector Optimization Model
19 (FASOM), which is a dynamic optimization model of the U.S. forest and agricultural sectors.
20 The public welfare gains linked to these markets from eliminating CLEs was estimated to be
21 \$0.69 million per year. These estimates can also be interpreted as the current value of
22 impairments to forest provisioning services due to forest acidification effects from nitrogen and
23 sulfur deposition.

24 *Nutrient Enrichment*

25 For the purposes of the following sections nutrient enrichment refers only to that due to
26 NO_y deposition. Additionally these sections focus on the detrimental effects of that deposition.
27 Staff acknowledges that a certain amount of NO_x deposition in managed terrestrial ecosystems
28 may have a beneficial effect. However no attempt has been made to quantify those beneficial
29 effects.

1 *Evidence for Aquatic Nutrient Enrichment*

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

12 Assessing how eutrophication in estuaries affects fishery resources requires bioeconomic
13 models (i.e., models that combine biological models of fish population dynamics with economic
14 models describing fish harvesting and consumption decisions), but relatively few exist (Knowler,
15 2002). Kahn and Kemp (1985) estimated that a 50% reduction in SAV from levels would
16 decrease the net social benefits from striped bass by \$16 million (in 2007 dollars). In a separate
17 analysis, Anderson (1989) modeled blue crab harvests under baseline conditions and under
18 conditions with “full restoration” of SAV. In equilibrium, the increase in annual producer surplus
19 and consumer surplus with full restoration of SAV was estimated to be \$7.9 million (in 2007
20 dollars). Mistiaen, Strand, and Lipton (2003) found that reductions in DO cause a statistically
21 significant reduction in commercial harvest and revenues crab harvests. For the Patuxent River
22 alone, a simulated reduction of DO from 5.6 to 4.0 mg/L was estimated to reduce crab harvests
23 by 49% and reduce total annual earnings in the fishery by \$275,000 (in 2007 dollars).

24 In addition, eutrophication in estuaries may also affect the demand for seafood. For
25 example, a well-publicized toxic pfiesteria bloom in the Maryland Eastern Shore in 1997 led to
26 an estimated \$56 million (in 2007 dollars) in lost seafood sales for 360 seafood firms in
27 Maryland in the months following the outbreak (Lipton, 1999). Surveys by Whitehead, Haab,
28 and Parsons (2003) and Parsons et al. (2006) indicated a reduction in consumer surplus due to
29 eutrophication-related fish kills ranging from \$2 to \$5 per seafood meal.¹³ As a result, they

¹³ Surprisingly, these estimates were not sensitive to whether the fish kill was described as major or minor or to the different types of information included in the survey.

1 estimated aggregate consumer surplus losses of \$43 million to \$84 million (in 2007 dollars) in
2 the month after a fish kill.

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

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

24 *What is the value of current ecosystem service impairments?*

25 The aquatic nutrient enrichment case study relied on the NOAA Eutrophication Index as
26 the indicator, which includes dissolved oxygen, HABs, loss of SAV and loss of water clarity.
27 There are methods available to link some of the components to ecosystem services, most notably
28 loss of SAV and reductions in DO. The REA analysis estimates the change in several ecosystem
29 services including recreational fishing, boating, beach use, aesthetic services and nonuse
30 services. The REA focuses on two major East Coast estuaries – the Chesapeake Bay and the
31 Neuse River. Both estuaries receive between 20%-30% percent of their annual nitrogen loadings

1 through air deposition and both are showing symptoms of eutrophication. The analysis uses and
2 adapts results from several existing studies to approximate effects on several ecosystem services,
3 including commercial fishing, recreation, aesthetic enjoyment, and nonuse values. For example,
4 it is estimated that atmospheric nitrogen reduces the annual benefits of recreational fishing,
5 boating, and beach use in the Chesapeake Bay by \$43-\$217 million, \$3-8 million, and \$124
6 million respectively, and reduces annual aesthetic benefits to nearshore residents by \$39-102
7 million. In the Neuse River, the value of annual commercial crab fishing services would be
8 between \$0.1-1 million higher without the contribution of atmospheric nitrogen, and recreation
9 fishing services in the larger Albermarle Pamlico Sound estuary system (which includes the
10 Neuse) would be \$1-8 million greater per year.

11 *Evidence for Terrestrial Nutrient Enrichment*

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

19 The value that California residents and the U.S. population as a whole place on CSS and
20 MCF habitats is reflected in the various federal, state, and local government measures that have
21 been put in place to protect these habitats. Threatened and endangered species are protected by
22 the Endangered Species Act. The State of California passed the Natural Communities
23 Conservation Planning Program (NCCP) in 1991, and CSS was the first habitat identified for
24 protection under the program (see www.dfg.ca.gov/habcon/nccp). Private organizations such as
25 The Nature Conservancy, the Audubon Society, and local land trusts also protect and restore
26 CSS and MCF habitat.

27 CSS and MCF are found in numerous recreation areas in California. Three national parks
28 and monuments in California contain CSS, including Cabrillo National Monument, Channel
29 Islands National Park, and Santa Monica National Recreation Area. All three parks showcase
30 CSS habitat with educational programs and information provided to visitors, guided hikes, and
31 research projects focused on understanding and preserving CSS. Over a million visitors traveled

1 through these three parks in 2008. MCF is highlighted in Sequoia and Kings Canyon National
2 Park, Yosemite National Park, and Lassen Volcanic National Park, where more than 5 million
3 people visited in 2008.

4 The 2006 FHWAR for California (DOI, 2007) reports on the number of individuals
5 involved in fishing, hunting, and wildlife viewing in California. Millions of people are involved
6 in just these three activities each year. The quality of these trips depends in part on the health of
7 the ecosystems and their ability to support the diversity of plants and animals found in important
8 habitats found in CSS or MCF ecosystems and the parks associated with those ecosystems.
9 Based on analyses in **Section 5.3.1.3 of the REA** (U.S.EPA, 2009), average values of the total
10 benefits in 2006 from fishing, hunting, and wildlife viewing away from home in California were
11 approximately \$947 million, \$169 million, and \$3.59 billion, respectively. In addition, data from
12 California State Parks (2003) indicate that in 2002, 68.7% of adult residents participated in trail
13 hiking for an average of 24.1 days per year. The analyses in the REA (U.S.EPA, 2009) indicate
14 that the aggregate annual benefit for California residents from trail hiking in 2007 was \$11.59
15 billion.

16 CSS and MCF are home to a number of important and rare species and habitat types. CSS
17 displays richness in biodiversity with more than 550 herbaceous annual and perennial species. Of
18 these herbs, nearly half are endangered, sensitive, or of special status (Burger et al., 2003).
19 Additionally, avian, arthropod, herpetofauna, and mammalian species live in CSS habitat or use
20 the habitat for breeding or foraging. Communities of CSS are home to three important federally
21 endangered species. MCF is home to one federally endangered species and a number of state-
22 level sensitive species. The Audubon Society lists 28 important bird areas in CSS habitat and at
23 least 5 in MCF in California (<http://ca.audubon.org/iba/index.shtml>).¹⁴

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

¹⁴ Important Bird Areas are sites that provide essential habitat for one or more species of bird.

1 The CSS and MCF were selected as case studies for terrestrial enrichment because of the
2 potential that these areas could be adversely affected by excessive N deposition. To date, the
3 detailed studies needed to identify the magnitude of the adverse impacts due to N deposition
4 have not been completed. Based on available data, this report provides a qualitative discussion of
5 the services offered by CSS and MCF and a sense of the scale of benefits associated with these
6 services. California is famous for its recreational opportunities and beautiful landscapes. CSS
7 and MCF are an integral part of the California landscape, and together the ranges of these
8 habitats include the densely populated and valuable coastline and the mountain areas. Through
9 recreation and scenic value, these habitats affect the lives of millions of California residents and
10 tourists. Numerous threatened and endangered species at both the state and federal levels reside
11 in CSS and MCF. Both habitats may play an important role in wildfire frequency and intensity,
12 an extremely important problem for California. The potentially high value of the ecosystem
13 services provided by CSS and MCF justify careful attention to the long-term viability of these
14 habitats.

15 The terrestrial nutrient enrichment case study relies on benchmark deposition levels for
16 various species and ecosystems as indicators of ecosystem response. While it would be expected
17 that deposition above those levels would have deleterious effects on the provision of ecosystem
18 services in those areas, at this time it is possible only to describe the magnitude of the some of
19 the services currently being provided. Methods are not yet available to allow estimation of
20 changes in services due to nitrogen deposition.

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1 **4 ADDRESSING THE ADEQUACY OF THE CURRENT STANDARDS**

2 Based on the information in Chapters 2 and 3, we conclude that there is support in the
3 available effects-based evidence for consideration of secondary standards for NO_x and SO_x that
4 are protective against adverse ecological effects associated with deposition of NO_x and SO_x to
5 sensitive ecosystems. Having reached this general conclusion, we then to the extent possible
6 evaluate the adequacy of the current NO_x and SO_x secondary standards by considering to what
7 degree risks to sensitivity ecosystems would be expected to occur in areas that meet the current
8 standards. Staff conclusions regarding the adequacy of the current standards are based on the
9 available ecological effects, exposure and risk-based evidence. In evaluating the strength of this
10 information, staff have taken into account the uncertainties and limitations in the scientific
11 evidence. This chapter addresses key policy relevant questions that inform our determination
12 regarding the adequacy of the structure and levels of the current secondary standards. The
13 chapter begins with a discussion of the structure of the current standards, followed by a
14 presentation of information on recent air quality relative to the existing standards, recent NO_x
15 and SO_x deposition levels, evaluation of recent deposition levels relative to levels where adverse
16 ecological effects have been observed, and a set of conclusions regarding the adequacy of the
17 current structure and levels of the standards.

18 It is also appropriate in this review to consider whether the current standards are adequate
19 to protect against the direct effects on vegetation resulting from ambient NO₂ and SO₂ which
20 were the basis for the current secondary standards. We will include a discussion of this issue in
21 the second draft policy assessment.

22 **4.1 ARE THE STRUCTURES OF THE CURRENT NO_x AND SO_x**
23 **SECONDARY STANDARDS BASED ON RELEVANT**
24 **ECOLOGICAL INDICATORS SUCH THAT THEY ARE**
25 **ADEQUATE TO DETERMINE AND PROTECT PUBLIC WELFARE**
26 **AGAINST ADVERSE EFFECTS ON ECOSYSTEMS?**

27 The current secondary NO_x and SO_x standards are intended to protect against adverse
28 effects to public welfare. For NO_x, the current secondary standard was set identical to the

1 primary standard¹⁵, e.g. an annual standard set for NO₂ to protect against adverse effects on
2 vegetation from direct exposure to ambient NO_x. For SO_x, the current secondary standard is a 3-
3 hour standard intended to provide protection for plants from the direct foliar damage associated
4 with atmospheric concentrations of SO₂.

5 The ISA has established that the major effects of concern for this review of the NO_x and
6 SO_x standards are associated with deposition of N and S associated with atmospheric
7 concentrations of NO_x and SO_x (see Chapter 2). As such, the current secondary standards do not
8 reflect the conclusions of the ISA in the major areas of indicator, form, or averaging times. By
9 using atmospheric NO₂ and SO₂, concentrations as indicators the current standards address only
10 a fraction of total atmospheric NO_x and SO_x, and do not take into account the effects from
11 deposition of total atmospheric NO_x and SO_x. By addressing short-term concentrations of SO₂,
12 the current SO₂ standard, while protective against direct foliar effects from gaseous SO_x, does
13 not take into account the findings of effects in the ISA, which notes the relationship between
14 annual deposition of S and acidification effects which are likely to be more severe and
15 widespread than phytotoxic effects under current ambient conditions. Acidification is a process
16 which occurs over time, as the ability of an aquatic system to counteract acidic inputs is reduced
17 as natural buffers are used more rapidly than they can be replaced through geologic weathering.
18 The relevant period of exposure for ecosystems is therefore not the exposures captured in the
19 short averaging time of the current SO₂ standard. In addition, the ISA has concluded that NO_x
20 and SO_x and their deposition products jointly affect ecosystems, and as such the current separate
21 structure of the NO_x and SO_x secondary standards does not take into account the joint ecological
22 effects of the two pollutants.

23 Current standards are specified as allowable single atmospheric concentration levels for
24 NO₂ or SO₂. This type of structure does not take into account variability in the atmospheric and
25 ecological factors that may alter the effects of NO_x and SO_x on public welfare. Consistent with
26 section 108, the ISA includes in the air quality criteria consideration of how these variable
27 factors impact the effects of ambient NO_x and SO_x on public welfare. Secondary standards are
28 intended to address a wide variety of effects occurring in different types of environments and
29 ecosystems. Ecosystems are not uniformly distributed either spatially or temporally in their

¹⁵ The current primary NO₂ standard has recently been changed to the 3 year average of the 98th percentile of the annual distribution of the 1 hour daily maximum of the concentration of NO₂. The current secondary standard remains as it was set in 1971.

1 sensitivity to air pollution. Therefore, failure to account for the major determinants of variability,
2 especially geologic conditions related to sensitivity to acidification and atmospheric conditions
3 which govern rates of deposition, may lead to standards that do not provide appropriate levels of
4 protection across ecosystems. We can state with confidence the current standards were not
5 designed to be protective against those welfare effects tied to deposition of ambient NO_x and SO_x
6 and thus are not likely to be adequate to protect public welfare against known or anticipated
7 adverse effects from deposition.

8 Because most areas of the U.S. are in attainment with the current NO₂ and SO_x standards,
9 it is possible to evaluate current conditions, and evaluate the impact on public welfare from the
10 current effects on ecosystems from NO_x and SO_x deposition in areas that attain the current
11 standards that use NO₂ and SO₂ as indicators. In addition, this chapter qualitatively addresses the
12 adequacy of the structures of the existing standards relative to ecologically relevant standards for
13 NO_x and SO_x, and sets up arguments for developing an ecologically relevant structure for the
14 standards as described in Chapter 5.

15 **4.2 TO WHAT EXTENT ARE THE STRUCTURES OF THE CURRENT** 16 **NO_x AND SO_x SECONDARY STANDARDS MEANINGFULLY** 17 **RELATED TO RELEVANT ECOLOGICAL INDICATORS OF** 18 **PUBLIC WELFARE EFFECTS?**

19 The current secondary standard for NO_x, set in 1971, using NO₂ as the atmospheric
20 indicator, is 0.053 parts per million (ppm) (100 micrograms per cubic meter of air [$\mu\text{g}/\text{m}^3$]),
21 annual arithmetic average, calculated as the arithmetic mean of the 1-hour NO₂ concentrations.
22 This standard was selected to provide protection to the public welfare against acute injury to
23 vegetation from direct exposure and resulting phytotoxicity. During the last review of the NO_x
24 standards, impacts associated with chronic acidification and eutrophication from NO_x deposition
25 were acknowledged, but the relationships between atmospheric concentrations of NO_x and levels
26 of acidification and eutrophication and associated welfare impacts were determined to be too
27 uncertain to be useful as a basis for setting a national secondary standard (USEPA 1995).

28 The current secondary standard for SO_x, set in 1971, uses SO₂ as the atmospheric
29 indicator, is a 3-hour average of 0.5 ppm, not to be exceeded more than once per year. This
30 standard was selected to provide protection to the public welfare against acute injury to

1 vegetation. In the last review of the SO_x secondary standard, impacts associated with chronic
2 acidification were acknowledged, but the relationships between atmospheric concentrations of
3 SO_x and levels of acidification, along with the complex interactions between SO_x and NO_x in
4 acidification processes, were cited as critical uncertainties which made the setting of secondary
5 NAAQS to protect against acidification inappropriate at that time (USEPA 1982).

6 In the previous independent reviews of the NO_x and SO_x secondary standards, each
7 review acknowledged the additional impacts of NO_x and SO_x on public welfare through the
8 longer term impact of the pollutants once deposited to ecosystems. However, the previous
9 reviews cited numerous uncertainties as the basis for not addressing those impacts in the setting
10 of the standards. In addition, these previous reviews did not consider the common pathways of
11 impact for the two pollutants acting on the same ecosystem endpoints.

12 Three issues arise that call into question the ecological relevance of the current structure
13 of the secondary standards for NO_x and SO_x. One issue is the exposure period that is relevant for
14 ecosystem impacts. The majority of deposition related impacts are associated with depositional
15 loads that occur over periods of months to years. This differs significantly from exposures
16 associated with hourly concentrations of NO₂ and SO₂ as measured by the current standards.
17 Even though the NO₂ standard uses an annual average of NO₂, it is focused on the annual
18 average of 1-hour NO₂ concentrations, rather than a cumulative metric or an averaging metric
19 based on daily or monthly averages. A second issue is the choice of atmospheric indicators. NO₂
20 and SO₂ are used as the component of oxides of nitrogen and sulfur that are measured, but they
21 do not provide a complete link to the direct effects on ecosystems from deposition of NO_x and
22 SO_x as they do not capture all relevant species of oxidized nitrogen and oxidized sulfur that
23 contribute to deposition. The ISA provides evidence that deposition related effects are linked
24 with total nitrogen and total sulfur, and thus all forms of oxidized nitrogen and oxidized sulfur
25 that are deposited will contribute to effects on ecosystems. This suggests that more
26 comprehensive atmospheric indicators should be considered in designing ecologically relevant
27 standards. Further discussions of the need for more ecologically relevant atmospheric indicators
28 as well as the relative contributions to deposition from various species of NO_x and SO_x can be in
29 found in Chapters 5 and 6. The third issue is that the current standards reflect separate
30 assessments of the two individual pollutants, NO₂ and SO₂, rather than assessing the joint
31 impacts of deposition of NO_x and SO_x to ecosystems, recognizing the role that each pollutant

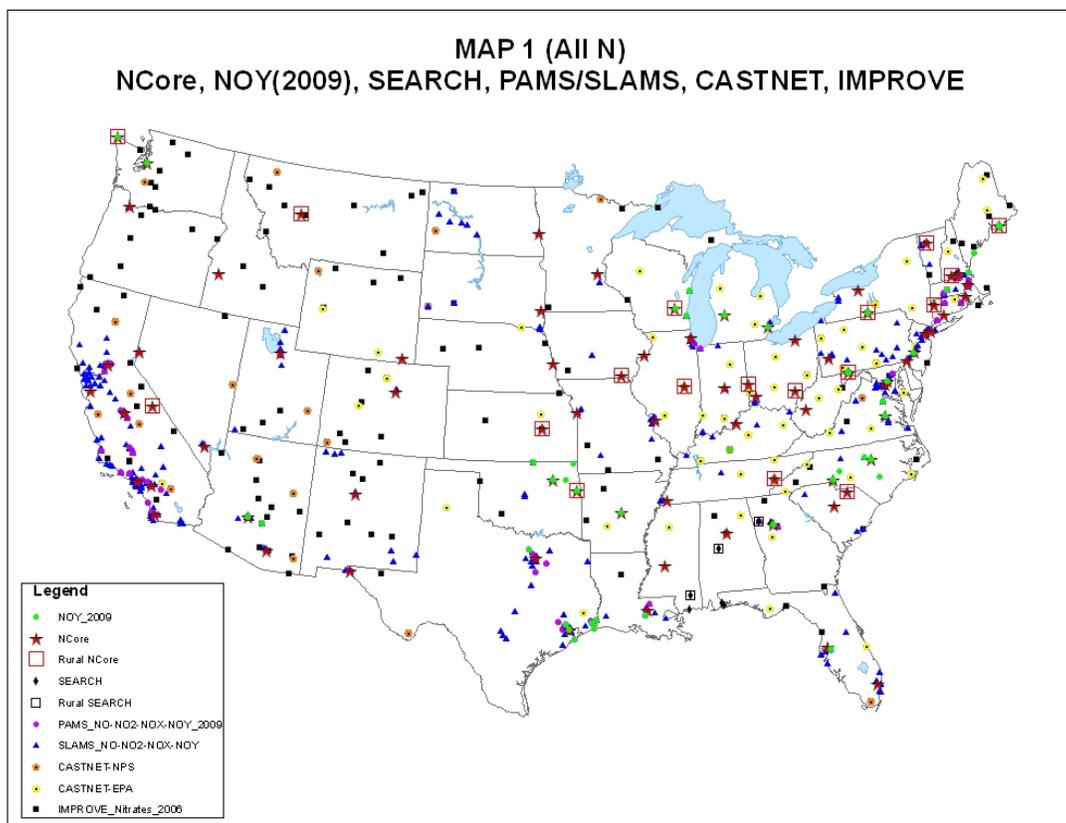
1 plays in jointly affecting ecosystem indicators, functions, and services. The clearest example of
2 this interaction is in assessment of the impacts of acidifying deposition on aquatic ecosystems.

3 Acidification in an aquatic ecosystem depends on the total acidifying potential of the
4 deposition of both N and S from both atmospheric deposition of NO_x and SO_x as well as the
5 inputs from other sources of N and S such as reduced nitrogen and non-atmospheric sources. It is
6 the joint impact of the two pollutants that determines the ultimate effect on organisms within the
7 ecosystem, and critical ecosystem functions such as habitat provision and biodiversity. Standards
8 that are set independently are less able to account for the contribution of the other pollutant. This
9 suggests that interactions between NO_x and SO_x should be a critical element of the conceptual
10 framework for ecologically relevant standards. There are also important interactions between
11 NO_x and SO_x and reduced forms of nitrogen, which also contributes to acidification and nutrient
12 enrichment. While the standards do not address reduced forms of nitrogen in the atmosphere, it is
13 important that the structure of the standards address the role of reduced nitrogen in determining
14 the ecological effects resulting from deposition of atmospheric NO_x and SO_x. Consideration will
15 also have to be given to account for loadings coming from non-atmospheric sources as
16 ecosystems will respond to these sources as well.

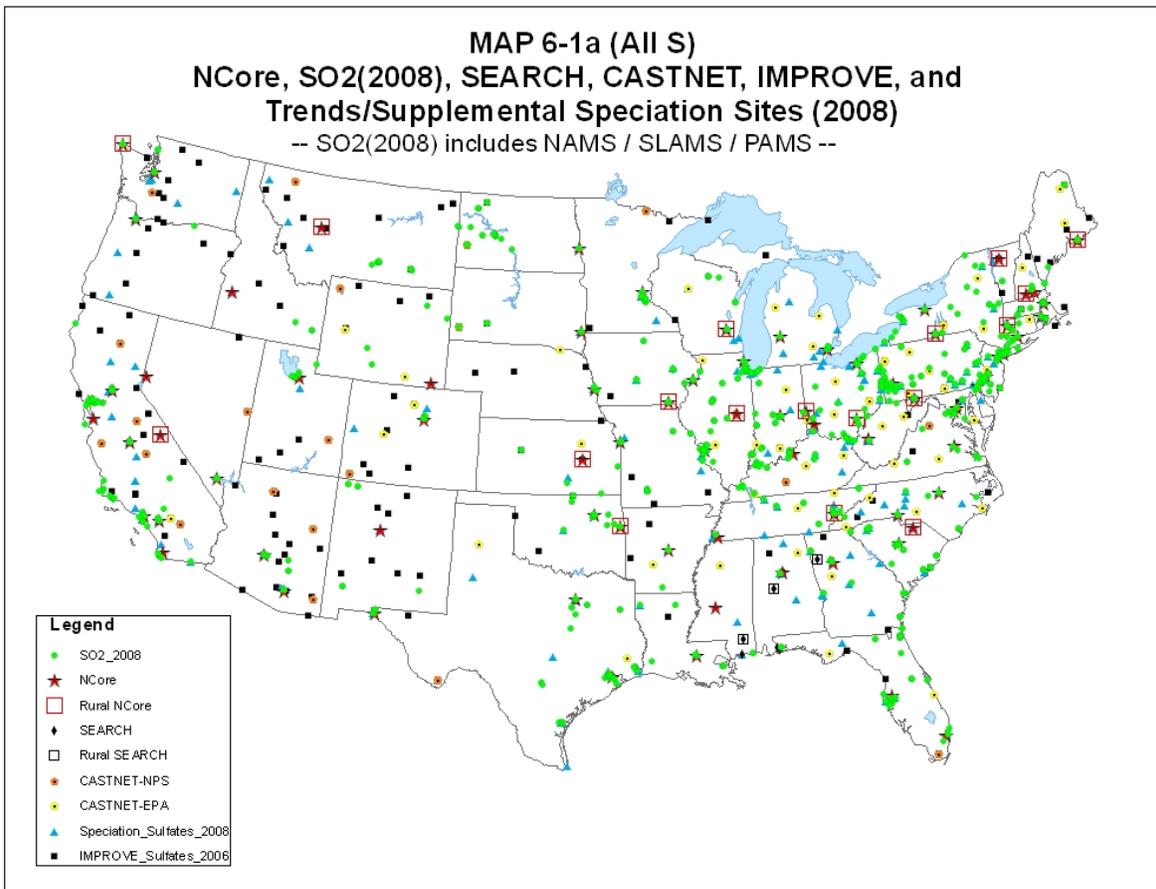
17 In addition to the fundamental issues discussed above, the current structures of the
18 standards do not address the complexities in the responses of ecosystems to deposition of NO_x
19 and SO_x. Ecosystems contain complex grouping of organisms that respond in various ways to the
20 alterations of soil and water that result from deposition of nitrogen and sulfur compounds.
21 Different ecosystems therefore respond in different ways depending on a multitude of factors
22 that control how deposition is integrated into the system. For example, the same levels of
23 deposition falling on limestone dominated soils have a very different effect than those falling on
24 shallow glaciated soils underlain with granite. One system may over time display no obvious
25 detriment while the other may experience a catastrophic loss in fish communities. This degree of
26 sensitivity is a function of many atmospheric factors which control rates of deposition as well as
27 ecological factors which control how an ecosystem responds to that deposition. The current
28 standards do not take into account spatial and seasonal variations not only in depositional
29 loadings but also in sensitivity of ecosystems exposed to those loadings.

1 **4.3 TO WHAT EXTENT DO CURRENT MONITORING NETWORKS**
2 **PROVIDE A SUFFICIENT BASIS FOR DETERMINING THE**
3 **ADEQUACY OF CURRENT SECONDARY NO_x AND SO_x**
4 **STANDARDS?**

5 There are over 1000 ground level monitoring platforms (Figures 4-1 and 4-2) that provide
6 measurements of some form of atmospheric nitrogen or sulfur. The key pollutants for this
7 assessment are total oxidized nitrogen (NO_y), total reduced nitrogen (NH_x), and total sulfur (ST).
8 Total reactive oxidized atmospheric nitrogen, NO_y, is defined as NO_x (NO and NO₂) and all
9 oxidized NO_x products: NO_y = NO₂ + NO + HNO₃ + PAN + 2N₂O₅ + HONO + NO₃ + organic
10 nitrates + particulate NO₃ (Finlayson-Pitts and Pitts, 2000). This definition of NO_y reflects the
11 operational principles of standard measurement techniques in which all oxidized nitrogen species
12 are converted to nitrogen oxide (NO) through catalytic reduction and the resulting NO is detected
13 through luminescence. Thus, NO_y is truly defined as total oxidized nitrogen as converted to NO.
14 NO_y is not a strict representation of the all moles of oxidized nitrogen as the diatomic nitrogen
15 species such as N₂O₅ yield 2 moles of NO. This definition is consistent with the relationship
16 between atmospheric nitrogen and acidification processes as the reported NO_y provides a direct
17 estimate of the potential equivalents available for acidification. Total reduced nitrogen (NH_x)
18 includes ammonia, NH₃, plus ammonium, NH₄ (EPA, 2008). Reduced nitrogen plus oxidized
19 nitrogen is referred to as total reactive nitrogen. Total sulfur (ST) includes SO₂ gas and
20 particulate sulfate, SO₄. Ammonium and sulfate are components of atmospheric particulate
21 matter as well as directly measured and modeled in precipitation as direct deposition
22 components. As discussed in this section, there are only very limited routine measurements of
23 total oxidized and reduced nitrogen. In addition, existing monitoring networks do not provide
24 adequate geographic coverage to fully assess concentrations and deposition of reactive nitrogen
25 and sulfur in and near sensitive ecosystems.



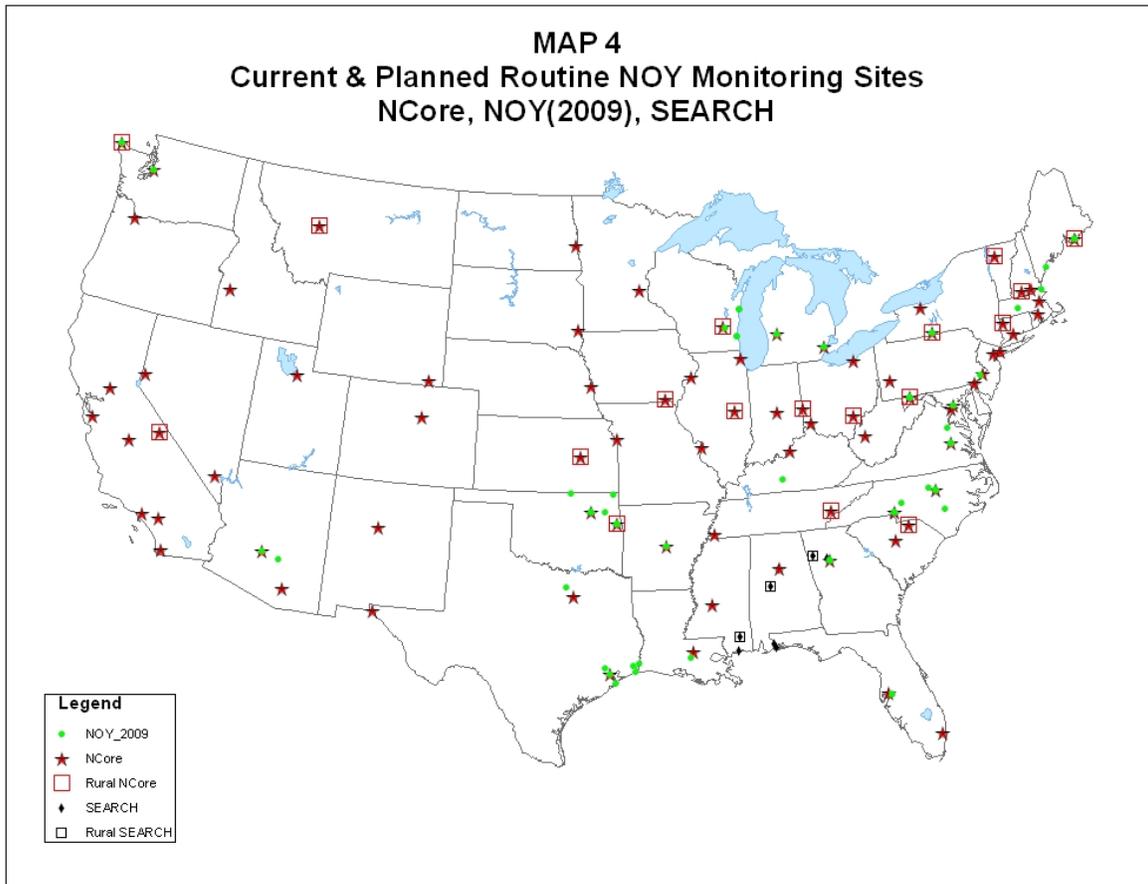
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2 **Figure 4-1.** Routinely operating surface monitoring stations measuring forms of
3 atmospheric nitrogen.



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2 **Figure 4-2.** Routinely operating surface monitoring stations measuring forms of
3 atmospheric sulfur.

4 The principal monitoring networks include the regulatory based State and Local Air
5 Monitoring Stations (SLAMS) providing mostly urban-based SO_2 , NO and NO_x , the $PM_{2.5}$
6 chemical speciation networks Interagency Monitoring of Protected visual Environments
7 (IMPROVE) and EPA's Chemical Speciation Network (CSN) providing particle bound sulfate
8 and nitrate, and the Clean Air Status and Trends Network (CASTNET) providing weekly
9 averaged values of SO_2 , nitric acid, and particle bound sulfate, nitrate and ammonium. The
10 private sector supported SouthEastern Aerosol Research and Characterization (SEARCH) Study
11 network of 4-8 sites in the southeast provides the only routinely operating source of true
12 continuous NO_2 , ammonia, and nitric acid measurements. SEARCH also provides $PM_{2.5}$ size
13 fractions of nitrate and sulfate. Collectively, the SLAMS, Photochemical Assessment
14 Measurement Stations (PAMS), SEARCH and NCore networks will provide over 100 sites
15 measuring NO_y (Figure 4-3). The NCore network (Scheffe et al., 2009) is a multiple pollutant

1 network with co-located measurements of key trace gases (CO, SO₂, O₃, NO and NO_y), PM_{2.5}
2 and PM(10-2.5) mass and PM_{2.5} chemical speciation. Additional air pollutants, particularly
3 volatile organic compounds (VOCs), will be measured at those sites that are part of the existing
4 PAMS and National Air Toxics Trends (NATTS) platforms. The NATTS (EPA, 2008) include
5 27 stations across the U.S. that monitor for a variety of hazardous air pollutants and are intended
6 to remain in place to provide a long term record. Additional measurements of ammonia and
7 possibly true NO₂ are under consideration. True NO₂ is noted to differentiate from the NO₂
8 determined through routine regulatory networks that have known variable positive bias for NO₂.
9 The network currently is being deployed and expected to be operational with nearly 75 sites by
10 January, 2011. The sites are intended to serve as central site monitors capturing broadly
11 representative (e.g., not strongly influenced by nearby sources) air quality in a suite of major and
12 mid size cities, and approximately 20 sites are located in rural locations.



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

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There are significant measurement gaps for characterizing NO_y , NH_x and SO_2 in the nations ambient air observation networks (EPA, 2008) that lead to greater reliance on air quality modeling simulations to describe current conditions. National design of routinely operating ambient air monitoring networks is driven mostly by data uses associated with implementing primary NAAQS, with noted exceptions of the CASTNET and IMPROVE networks. In addition to significant spatial gaps in sensitive ecosystem areas that arise from a population oriented network design, the current measurements for primary and secondary nitrogen are markedly different and in some instances of negligible value for secondary NO_x and SO_x standards. For example, a true NO_x (NO plus NO_2) measurement typically would capture less than 50% (see discussion below) of the total regional NO_y mass in rural locations as the more aged air masses contain significant oxidized nitrogen products in addition to NO_x . Note that the NO_x monitors

1 used for NAAQS primary compliance purposes do capture varying amounts of transformed
2 nitrogen species; however, the method provides biased low estimates with significant airshed
3 induced variability relative to true NO_y. With the exception of the SEARCH network in the
4 southeast, there are virtually no routine networks that measure ammonia, although EPA is
5 considering options for ammonia sampling in CASTNET and NCORE networks. Ammonium is
6 reported in EPA chemical speciation networks, although the values are believed to be biased low
7 due to ammonia volatilization.

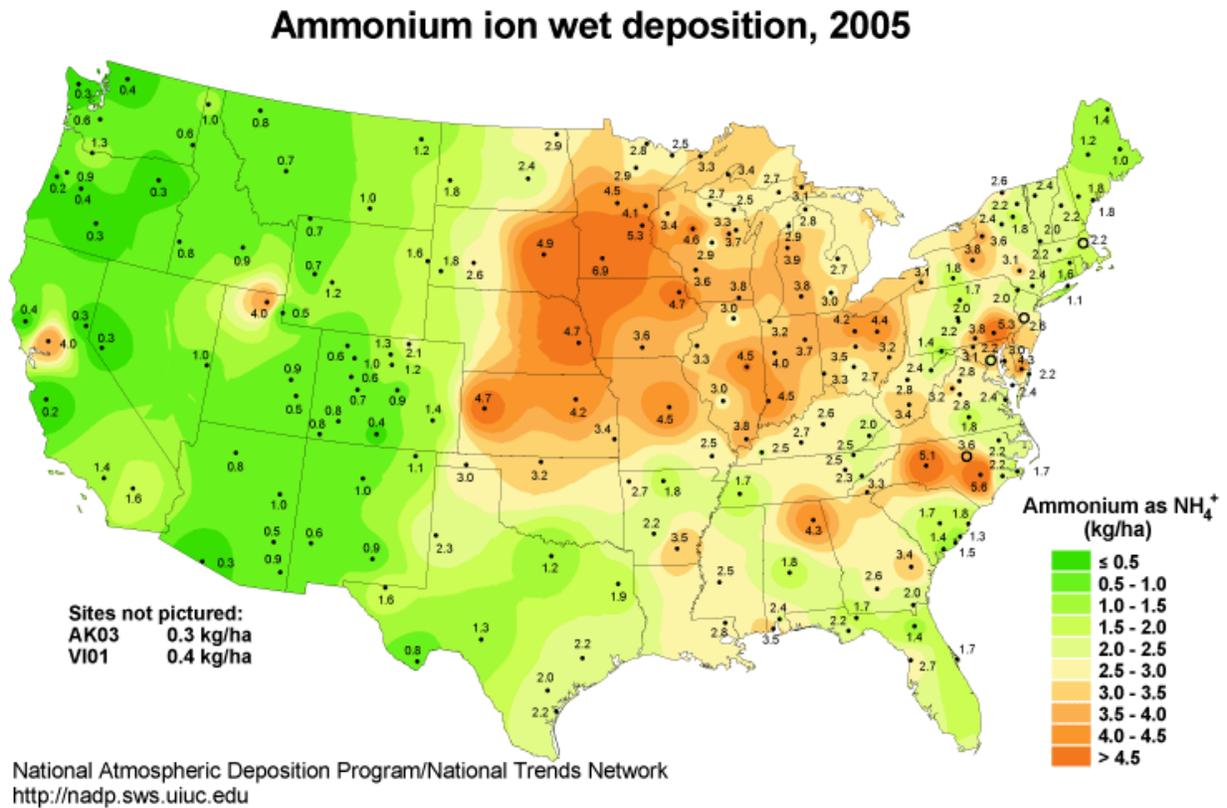
8 CASTNET provides mostly rural measurements of SO₂, total nitrate, and ammonium, and
9 affords an existing infrastructure useful for future monitoring in support of a NO_x and SO_x
10 secondary standard. However, the lack of NO_y, SO_x and NH_x measurements in sensitive
11 ecosystems will require attention in the N/S secondary standard proposal.

12 As a result of the limited monitoring networks for NO_y and SO_x in sensitive ecosystems,
13 we are unable to use current monitoring data to fully assess whether the current standards have
14 resulted in levels of NO_y and SO_x in sensitive ecosystems that would result in deposition levels
15 that are or are not causing ecological effects adverse to public welfare. We supplement the
16 available monitoring data with the use of sophisticated atmospheric modeling conducted using
17 EPA's CMAQ model.

18 **4.3.1 What does the NADP monitoring network provide and what are the major** 19 **limitations?**

20 The National Atmospheric Deposition Program (NADP) includes approximately 250
21 sites (Figure 4-4) across the U.S. providing annual total wet deposition based on weekly
22 averaged measures of wet deposition of nitrate, ammonium and sulfate ions based on the
23 concentrations of these ions in precipitation samples. Meteorological models have difficulty in
24 capturing the correct spatial and temporal features of precipitation events, raising the importance
25 of the NADP as a principal source of precipitation chemistry. The NADP has enabled several
26 organizations to participate in a measurement program with a centralized laboratory affording
27 measurement and analysis protocol consistency nationwide. Virtually every CASTNET site is
28 located at an NADP site and the combined NADP/CASTNET infrastructure is a starting point for
29 discussions addressing future N/S monitoring needs. The Organic bound nitrogen is not analyzed
30 routinely in NADP samples. Consideration might be given to adding NADP sites in locations

1 where ambient air monitoring is conducted to assess compliance with a secondary NO_x/SO_x
 2 standard.



3
 4 **Figure 4-4.** Location of approximately 250 National Atmospheric Deposition
 5 Monitoring (NADP) National Trends Network (NTN) sites illustrating annual
 6 ammonium deposition for 2005. Weekly values of precipitation based nitrate,
 7 sulfate and ammonium are provided by NADP.

8 **4.3.2 How do we characterize deposition through Monitoring and Models?**

9 Routinely available directly measured precipitation to quantify wet deposition of sulfur
 10 and nitrogen species are provided through the NADP. Dry deposition is not a directly measured
 11 variable in routine monitoring efforts and, for all practical purposes, largely will remain a
 12 research endeavor that supports the parameterizations used for estimating dry deposition, as
 13 opposed to striving to develop operational methods. Estimates of dry deposition based on
 14 observations are provided through the CASTNET program. However, dry deposition is a
 15 calculated value represented as the product of ambient concentration (either observed or
 16 estimated through air quality modeling) and deposition velocity, $Dep_i^{Dry} = v_i^{Dry} \cdot C_i^{Amb}$.

1 Deposition velocity is modeled as a mass transfer process through resistance layers
2 associated with the canopy, uptake by vegetation, water and soil which collectively are
3 influenced by micrometeorology, land surface and vegetation types and species specific
4 solubility and reactivity. Dry deposition is calculated through deposition velocity models
5 capturing these features and using species specific ambient air concentrations. This approach
6 conceptually is similar using either observed or modeled air concentrations. Dry deposition
7 estimates from the Community Multi-scale Air Quality (CMAQ) model (EPA, 1999) have been
8 used in this assessment to provide spatially more resolved and extensive estimates of dry
9 deposition for sulfur and all reactive nitrogen (oxidized and reduced) species (CASTNET does
10 not capture important gases such as nitrogen dioxide and peroxyacetyl nitrate). All of the
11 relevant meteorological, land use, vegetation and elevation data required to estimate deposition
12 velocities are generated or accessible in the CMAQ and/or meteorological pre-processors.

13 ***4.3.2.1 Why are we using CMAQ to model deposition? How are we using it? Why is***
14 ***CMAQ the right model to use? What is the spatial and temporal resolution of***
15 ***CMAQ? What are the model years? What are the limitations to CMAQ?***

16 CMAQ provides a platform that allows for a consistent mass accounting approach across
17 ambient concentrations and dry and wet deposition values. Recognizing the limitations of
18 ambient air networks, CMAQ was used to estimate dry deposition to complement NADP wet
19 deposition for MAGIC modeling and for the FAB critical load modeling. CMAQ promotes
20 analytical consistency and efficiency across analyses of multiple pollutants. EPA's Office of
21 Research and Development continues to enhance the underlying deposition science in CMAQ.
22 For the purposes of this policy assessment, CMAQ provides a consistent platform incorporating
23 the atmospheric and deposition species of interest over the entire United States. The caveats and
24 limitations of the use of model predictions are largely associated with the general reliance on
25 calculated values, rather than measurements. Model evaluation addressing the comparison of
26 predictions with observed values is addressed in the REA. Currently, there are efforts to improve
27 a number of nitrogen related processes in CMAQ, recognizing comparatively less uncertainty
28 with the treatment of sulfur. Active areas of model process improvement are in the treatment of
29 lightning generated NO_x and the transference of nitrogen between atmospheric and terrestrial and
30 aquatic media, often referred to as bi-directional flux. Lightning NO_x potentially provides a

1 significant contribution to wet deposition as the resulting NO_x is rapidly entrained into aqueous
2 cloud processes. Both the thermodynamics of soil processes and mass transfer of nitrogen
3 species across the surface-atmosphere interface is governed by an assortment of temperature,
4 moisture, advection and concentration patterns. These processes and mass transfer relationships
5 are coupled within the emissions, meteorological, and chemical simulation processes and
6 associated surface/vegetation and terrain information incorporated in or accessed by the CMAQ.
7 In addition to research activities to improve the characterization of nitrogen-related processes in
8 CMAQ, efforts are also underway to improve the general characterization of ammonia emissions
9 which remains as an area of large uncertainty due to limited source data and the ubiquitous
10 nature of these emissions. Another challenge for regional/national air quality modeling is
11 properly representing the effects on pollutant concentrations, precipitation and therefore
12 deposition of variable terrain features, particularly steep mountain-valley gradients and the
13 interfaces to wide open basins encountered in the Western United States.

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

23 **4.4 WHAT IS OUR BEST CHARACTERIZATION OF ATMOSPHERIC** 24 **CONCENTRATIONS OF NO_y AND SO_x, AND DEPOSITION OF N** 25 **AND S?**

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

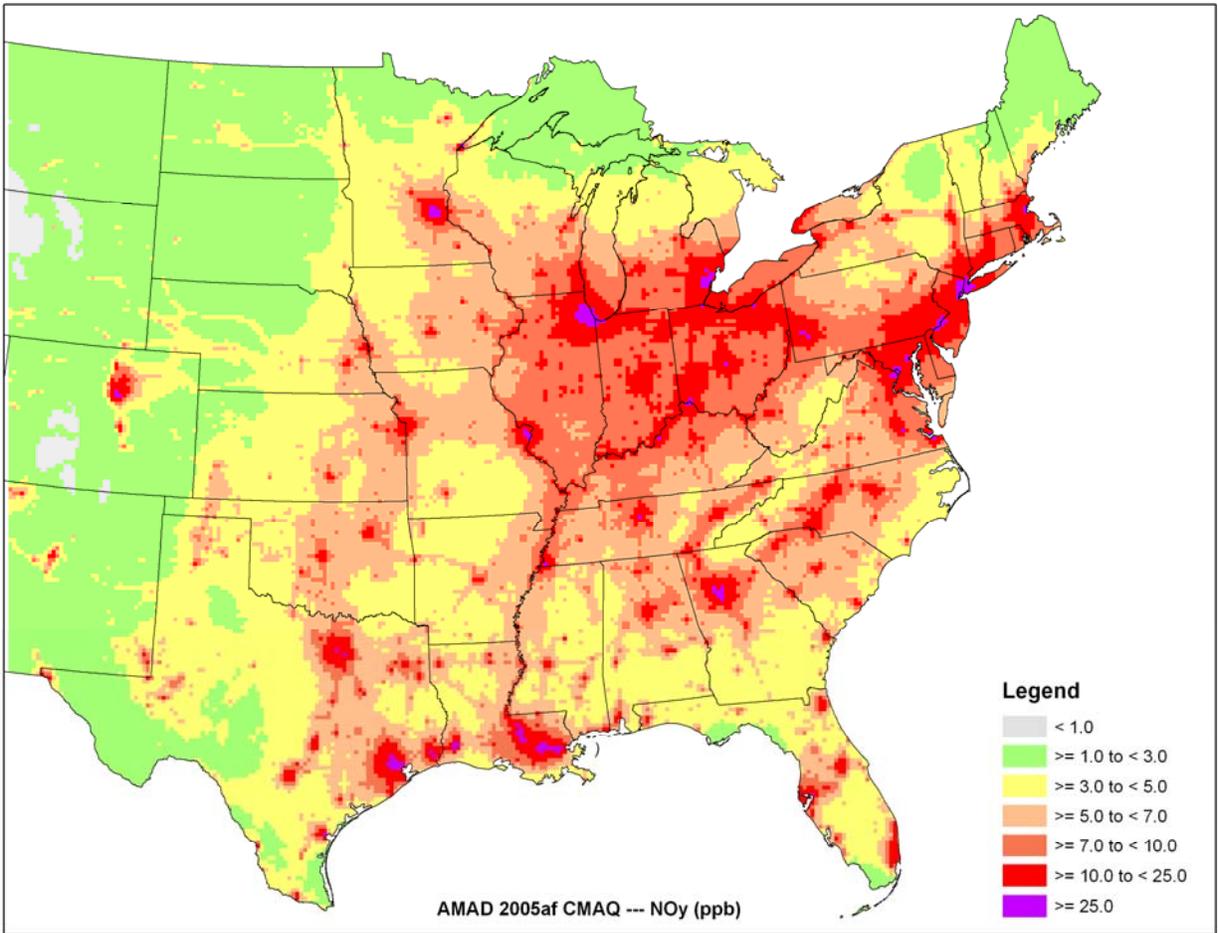
1 **4.4.1 What are the current atmospheric concentrations of reactive nitrogen, NO_y,**
2 **reduced nitrogen, NH_x, sulfur dioxide, SO₂, and sulfate, SO₄?**

3 To provide information for use in characterizing the adequacy of the current standards,
4 we assess the best available data for estimating the ambient concentrations of the major sources
5 of atmospheric nitrogen and sulfur across the U.S. Acidification and nutrient enrichment
6 processes are largely dependent on the cycling of total nitrogen and sulfur species. From an
7 atmospheric perspective, it is convenient and consistent with current measurement and modeling
8 frameworks to consider the reduced and oxidized forms of atmospheric nitrogen. Virtually all
9 atmospheric sulfur is considered oxidized sulfur in the forms of particulate bound sulfate and
10 gaseous sulfur dioxide. In order to assess current concentrations of reactive nitrogen and sulfur
11 we evaluated data available from monitoring the existing networks as well as from the CMAQ
12 model. Regarding the monitoring data, there are a number of important issues in understanding
13 the measurements of NO_y provided by different monitoring networks. In principle, measured
14 NO_y is based on catalytic conversion of all oxidized species to NO followed by
15 chemiluminescence NO detection. We recognize the caveats associated with instrument
16 conversion efficiency and possible inlet losses. The CMAQ treats the dominant NO_y species as
17 explicit species while the minor contributing non-PAN organic nitrogen compounds are
18 aggregated. Atmospheric nitrogen and sulfur are largely viewed as regional air quality issues due
19 to the importance of chemical conversion of primary emissions into secondarily formed species;
20 a combination of ubiquitous sources, particularly mobile source emissions of NO_x, and elevated
21 emissions of NO_x and SO₂ that aid pollutant mass dispersal and broader physical transport over
22 large distances. In effect, the regional nature is due to both transport processes as well as the
23 relatively ubiquitous nature of sources combined with chemical processes that tend to form more
24 stable species with extended atmospheric lifetimes. This regionalized effect, particularly
25 throughout the Eastern United States, dominates the overall patterns discussed below of
26 secondarily formed species such as sulfate or NO_y, which is an aggregate of species where the
27 more aged air masses consisting largely of chemically processed air is dominated by secondarily
28 formed peroxyacetyl nitrate (PAN), particulate nitrate and nitric acid.

29 Nationwide maps of CMAQ-predicted 2005 annual average NO_y, NH_x (NH₃ and NH₄),
30 NH₃, NH₄, S_T, SO₄, and SO₂ are provided in figures 4-5 through 4-11 respectively. Given the
31 considerable gaps in air quality observation networks as discussed in the REA and ISA (2008),

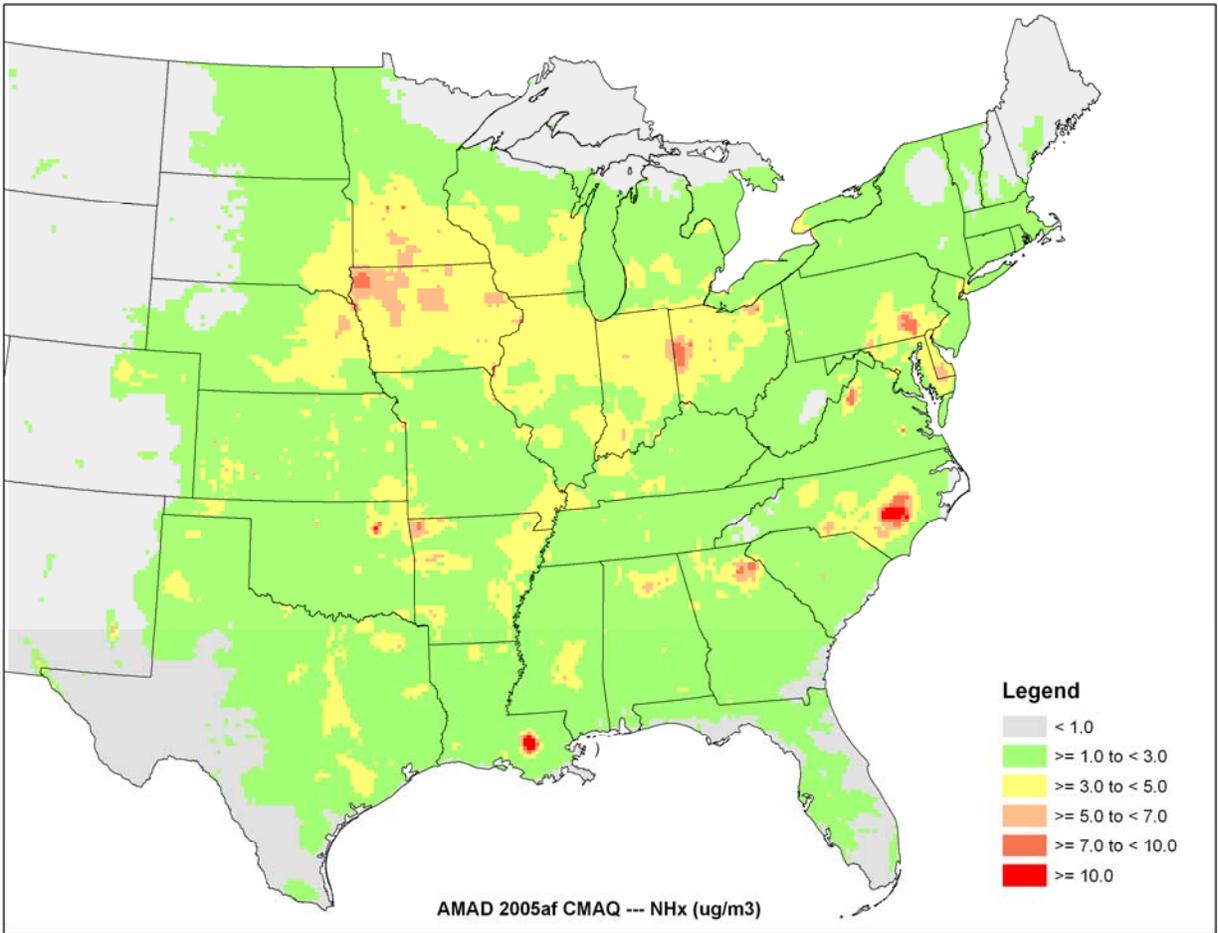
1 modeled concentration patterns are used here to illustrate national representations of current air
2 quality conditions for nitrogen and sulfur. The 2005 model year reflects the most recent available
3 simulation for inclusion in this policy assessment. In addition, figures 4-12 and 4-13 provide
4 maps of 2005 annual average SO₂ and SO₄, respectively based on CASTNET observations. Site
5 specific annual average 2005 NO_y measured concentrations at SLAMS (Figure 4-14) are
6 typically are less than 40 ppb., The spatial patterns for the 2005 modeled and observed NO_y and
7 SO₂ concentrations are similar to the 2002 CMAQ-based maps provided in the REA., largely
8 capturing the influence of major source regions throughout the nation. A spreading of the
9 oxidized sulfur fields (Figures 4-5 and 4-6), relative to SO₂, is consistent with sulfate
10 transformation and associated air mass aging and transport. Ammonia and ammonium
11 concentration patterns (Figure 4-4) are influenced strongly by the ammonia emissions
12 distribution, with marginal spreading associated with the addition of NH₄. The NH_x fields are
13 more strongly influenced by source location, relative to sulfur, based on the fast removal of
14 atmospheric ammonia through deposition. Total deposition for nitrogen and sulfur (Figures 4-15
15 and 4-16) basically follow the patterns of ambient air concentrations.

16 Current conditions indicate that the current SO₂ and NO₂ secondary standards are not
17 exceeded (Figures 4-17 and 4-18) in locations where ecological effects have been observed, and
18 where critical loads of nitrogen and sulfur are exceeded. This is consistent with the fact that NO₂
19 accounts for only a fraction of NO_y, and thus reductions in NO₂ emissions would not be expected
20 to fully address concentrations of NO_y. The map in Figure 4-19 further illustrates this point by
21 showing that the contribution of NO₂ to NO_y is often less than 50% in rural areas.



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Figure 4-5. 2005 CMAQ modeled annual average NO_y (ppb). These maps will be replaced with full CONUS maps in the next draft.



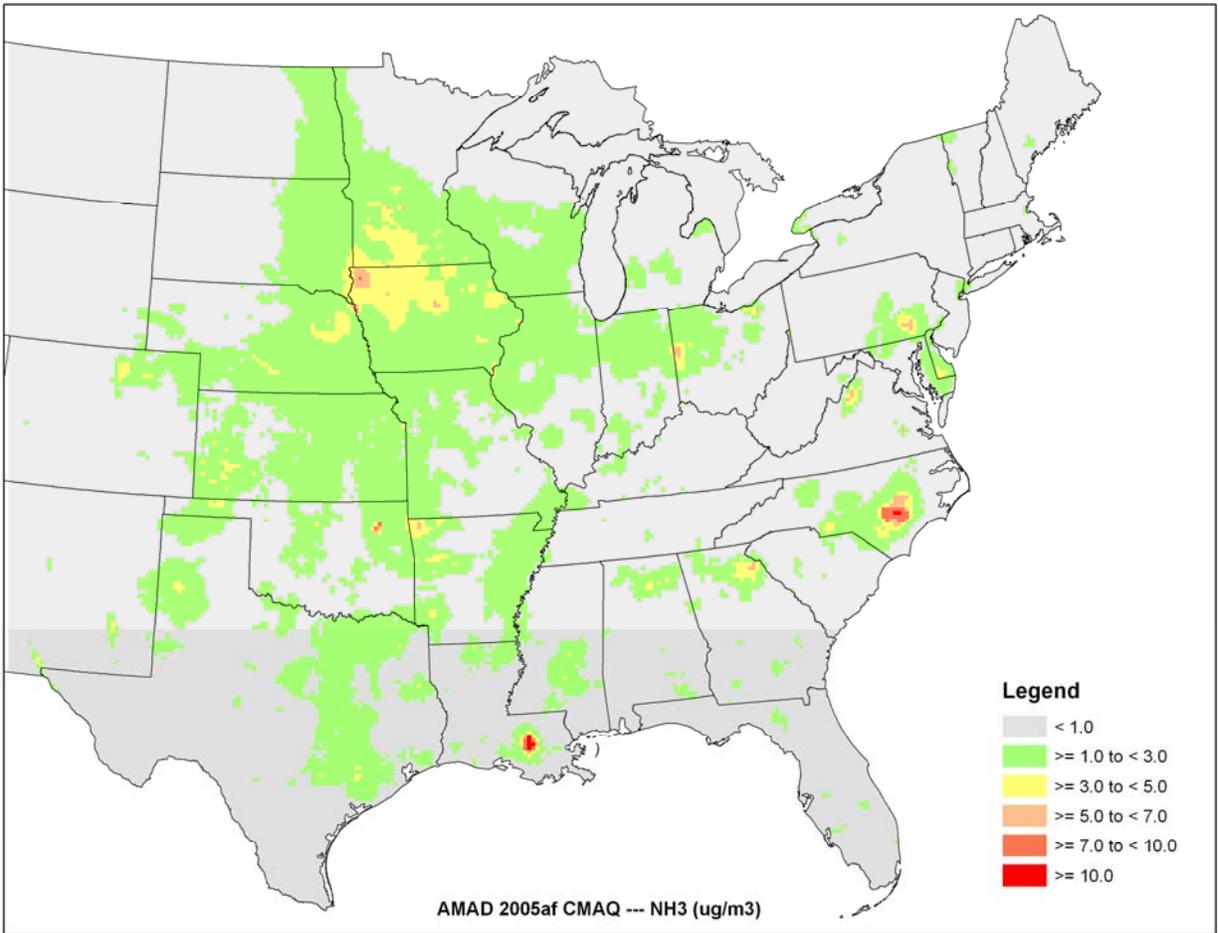
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Figure 4-6. 2005 CMAQ modeled annual average total reduced nitrogen (NH_x) (as $\mu g/m^3$ nitrogen)

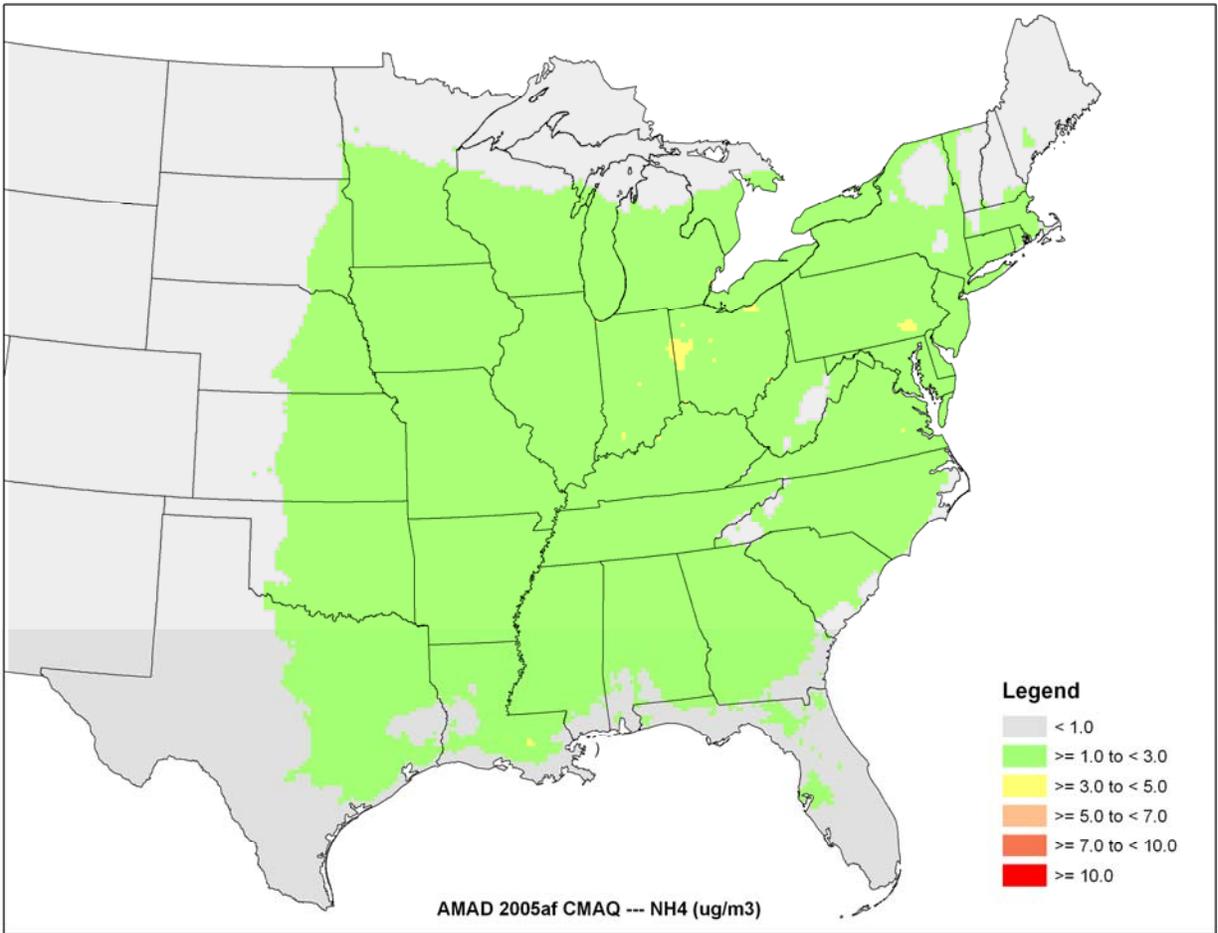


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Figure 4-7. 2005 CMAQ modeled annual average ammonia, NH_3 , (as $\mu g/m^3$ N)

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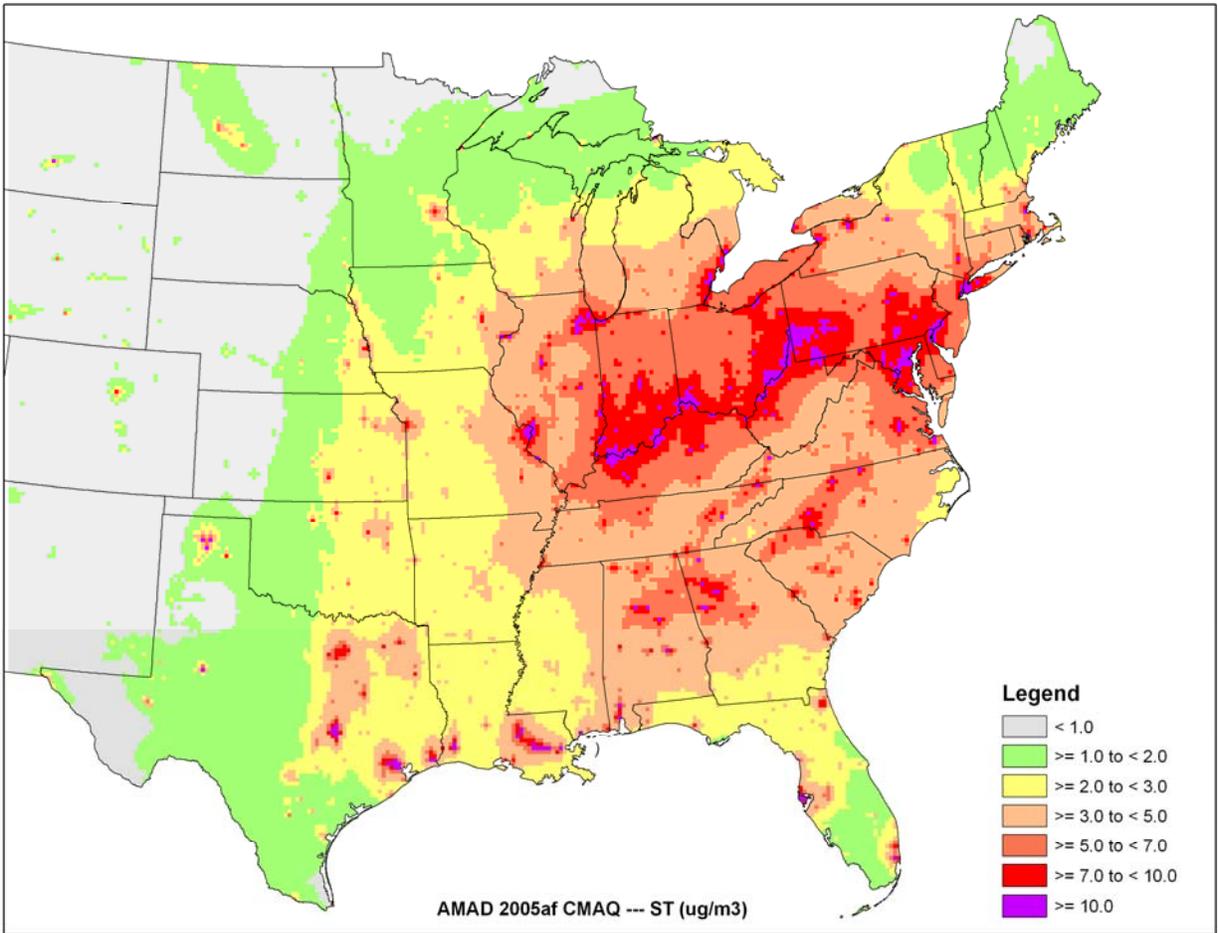


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Figure 4-8. 2005 CMAQ modeled annual average ammonia, NH_4 , (as $\mu g/m^3 N$)

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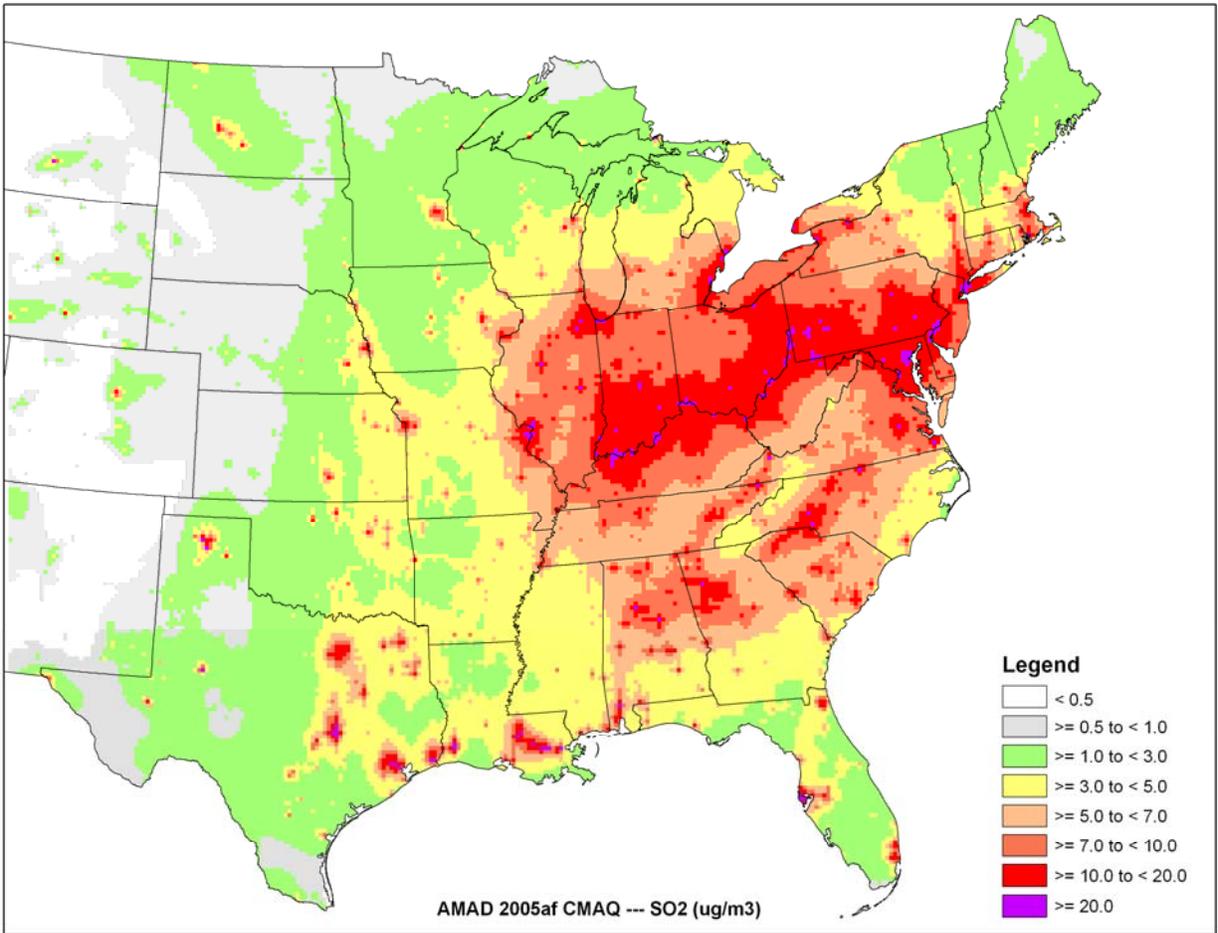
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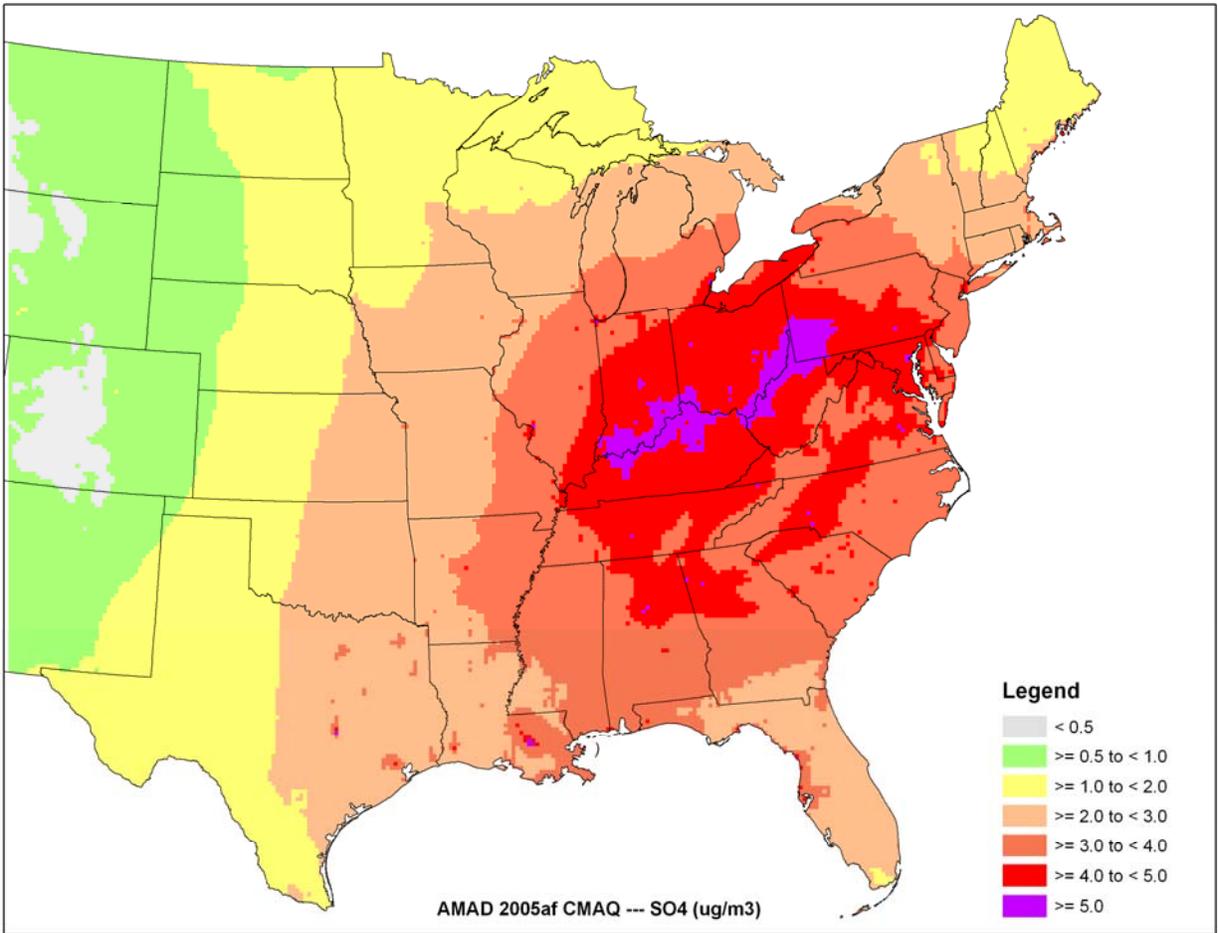
Figure 4-9. 2005 CMAQ modeled annual average SO_x , (as $\mu\text{g}/\text{m}^3$ S from SO_2 and SO_4).



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2 **Figure 4-10.** 2005 CMAQ modeled annual average SO_2 (as $\mu g/m^3$ S)

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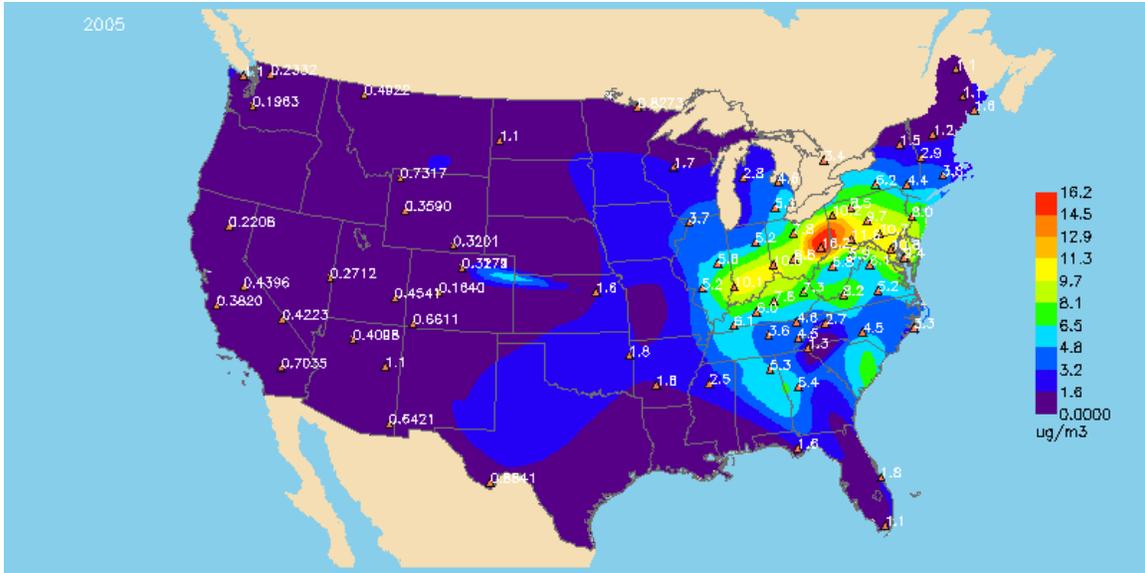


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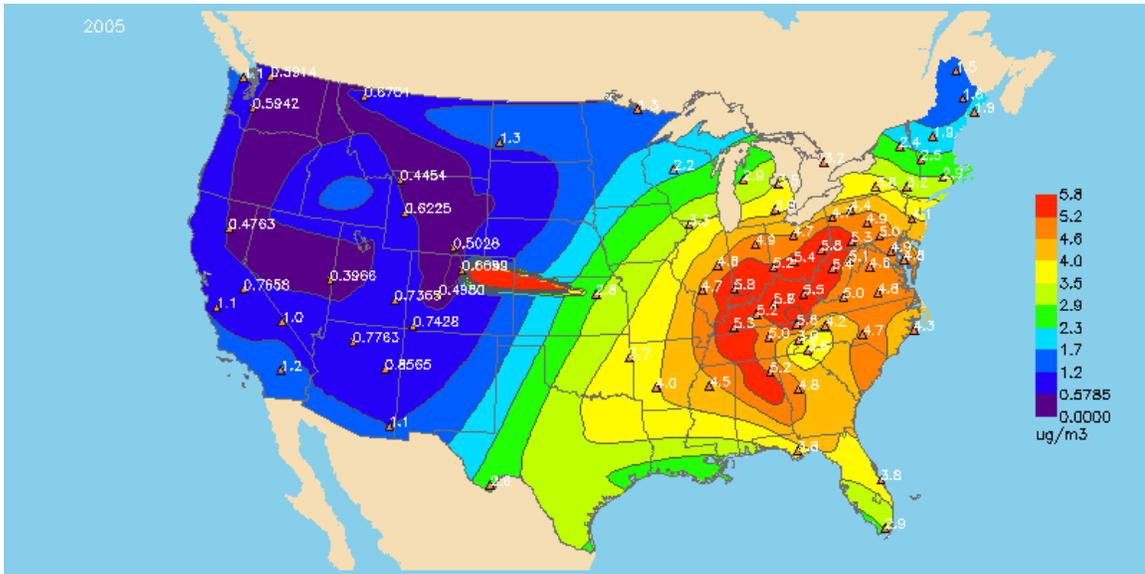
Figure 4-11. 2005 CMAQ modeled annual average SO_4 (as $\mu\text{g}/\text{m}^3$ S).

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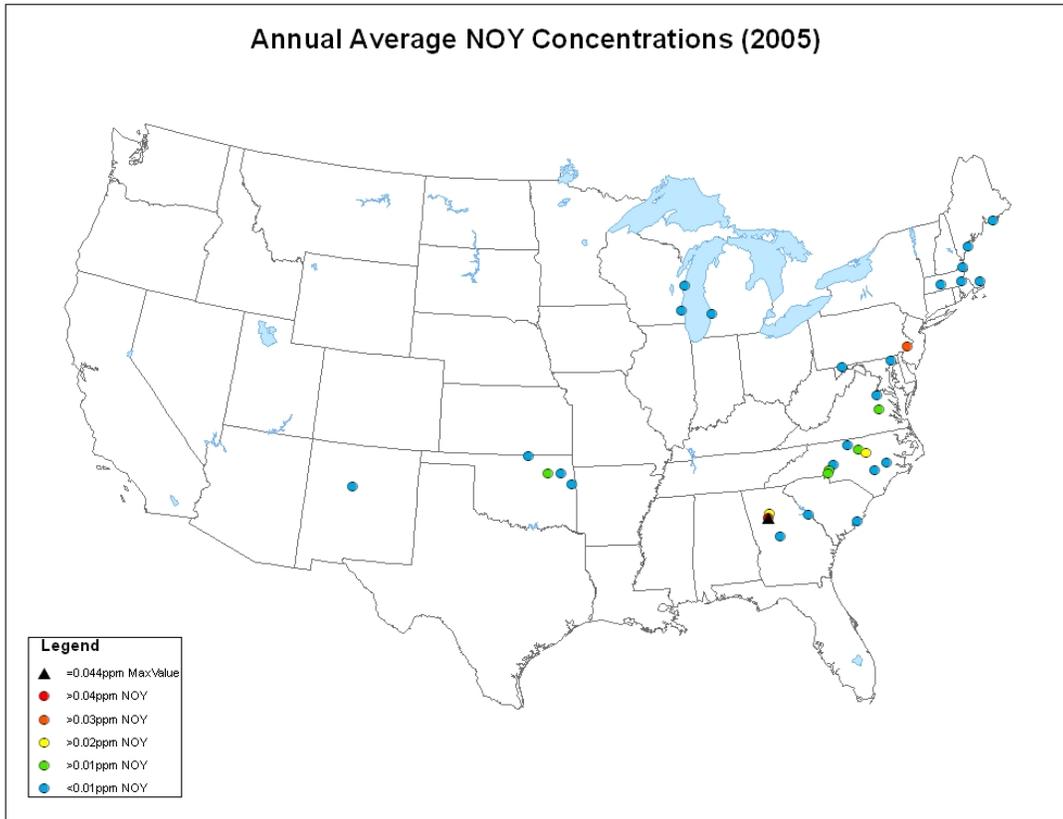
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Figure 4-12. 2005 annual average sulfur dioxide concentrations based on CASTNET generated by the Visibility Information Exchange Web Sysytem (VIEWS).



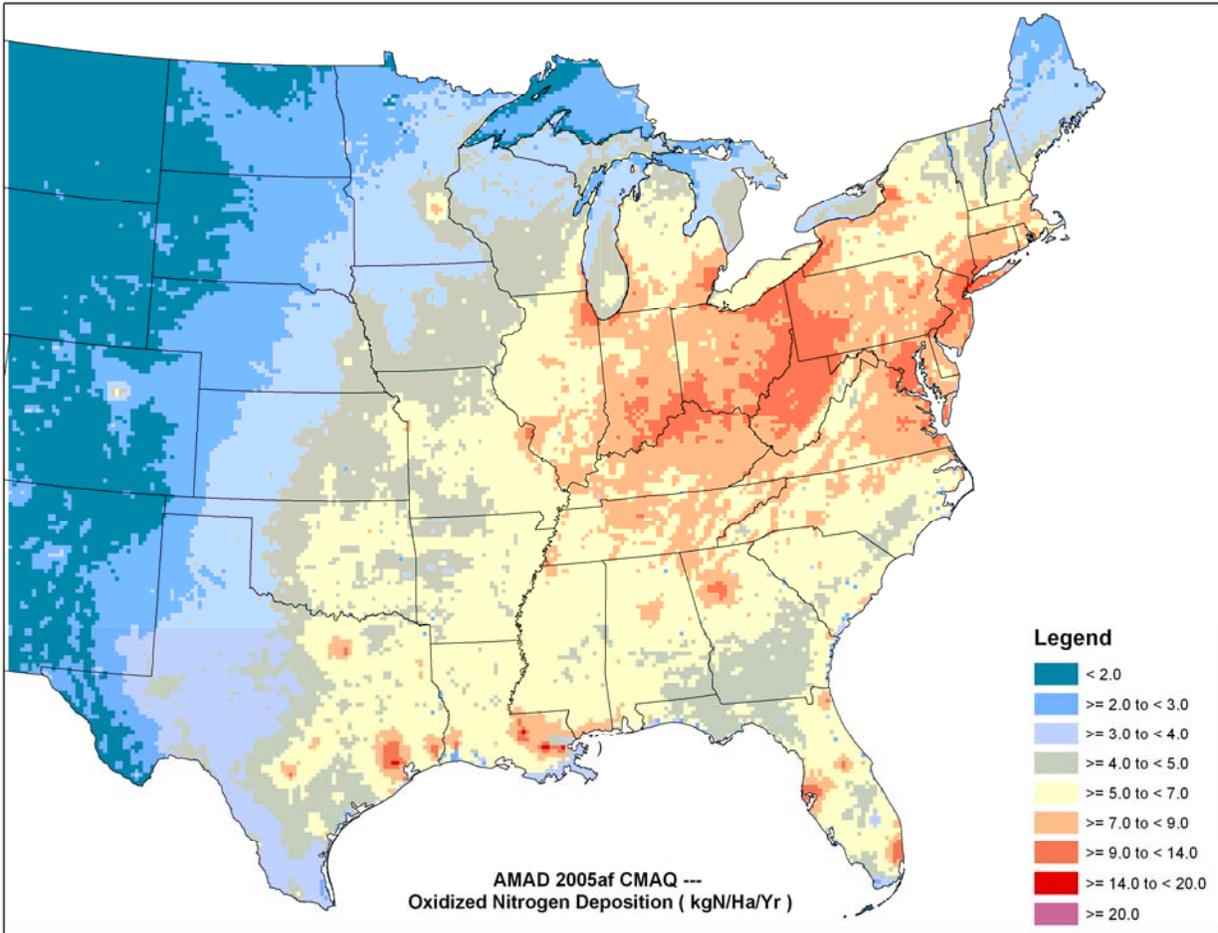
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Figure 4-13. 2005 annual average sulfate concentrations based on CASTNET generated by the Visibility Information Exchange Web Sysytem (VIEWS).



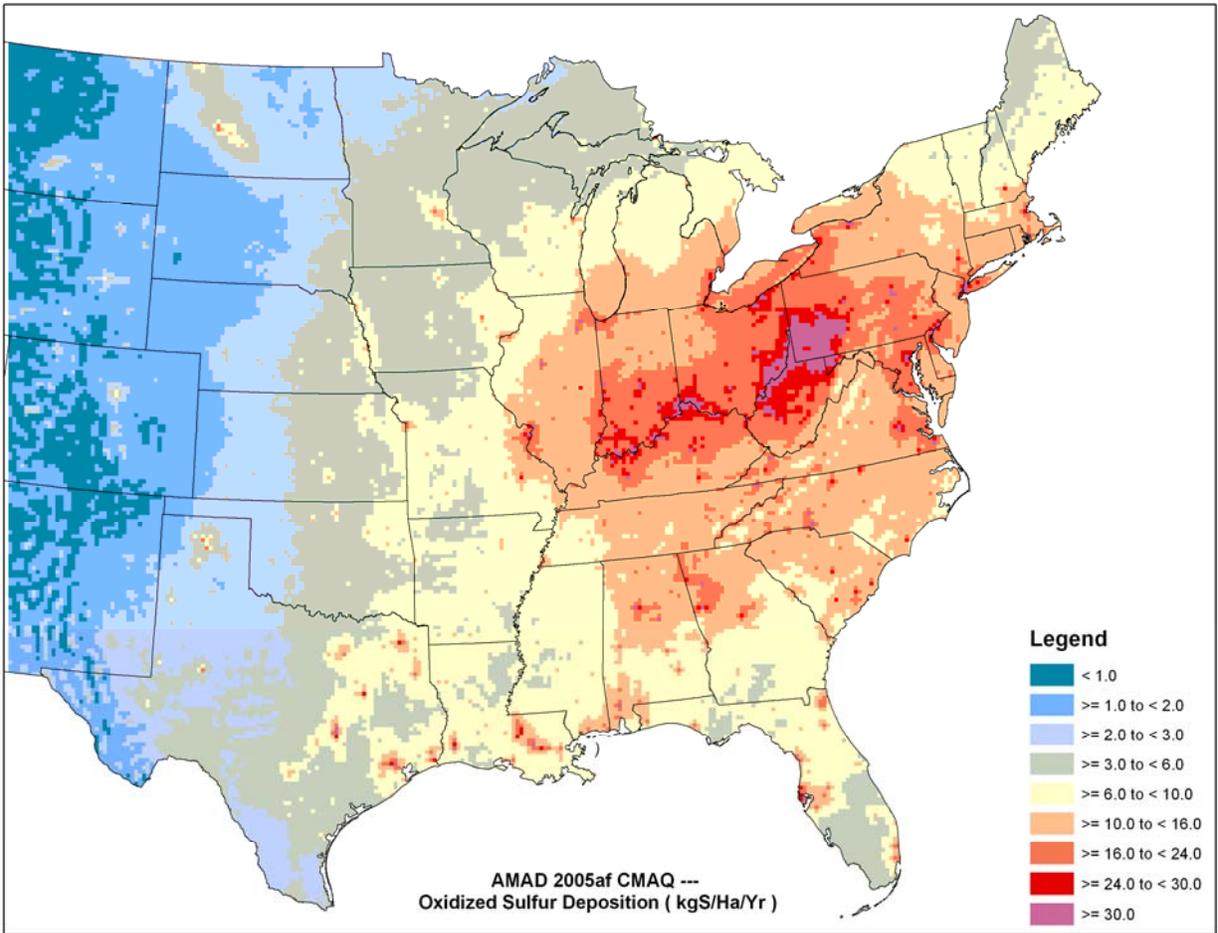
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Figure 4-14. Annual average 2005 NO_y concentrations from reporting stations in AQS.



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Figure 4-15. 2005 CMAQ modeled Oxidized Nitrogen Deposition (kgN/Ha/Yr).

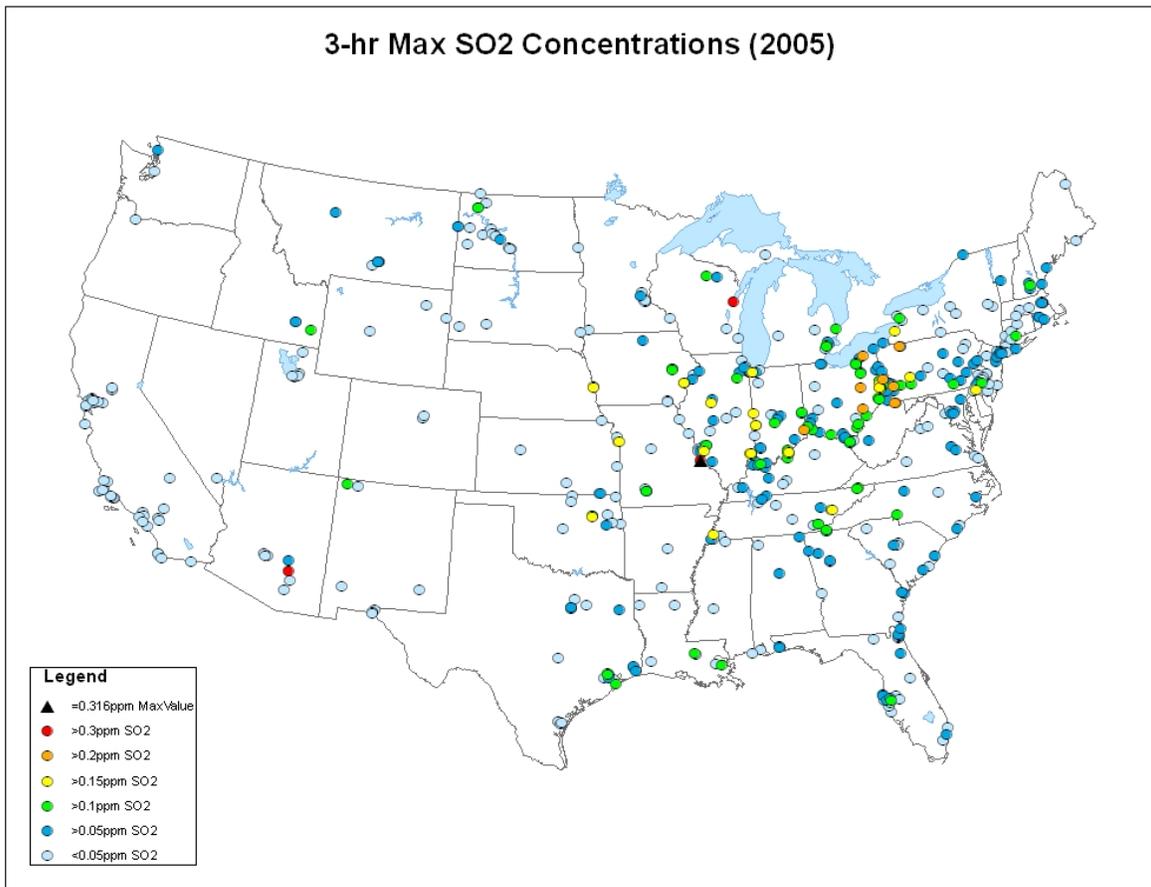


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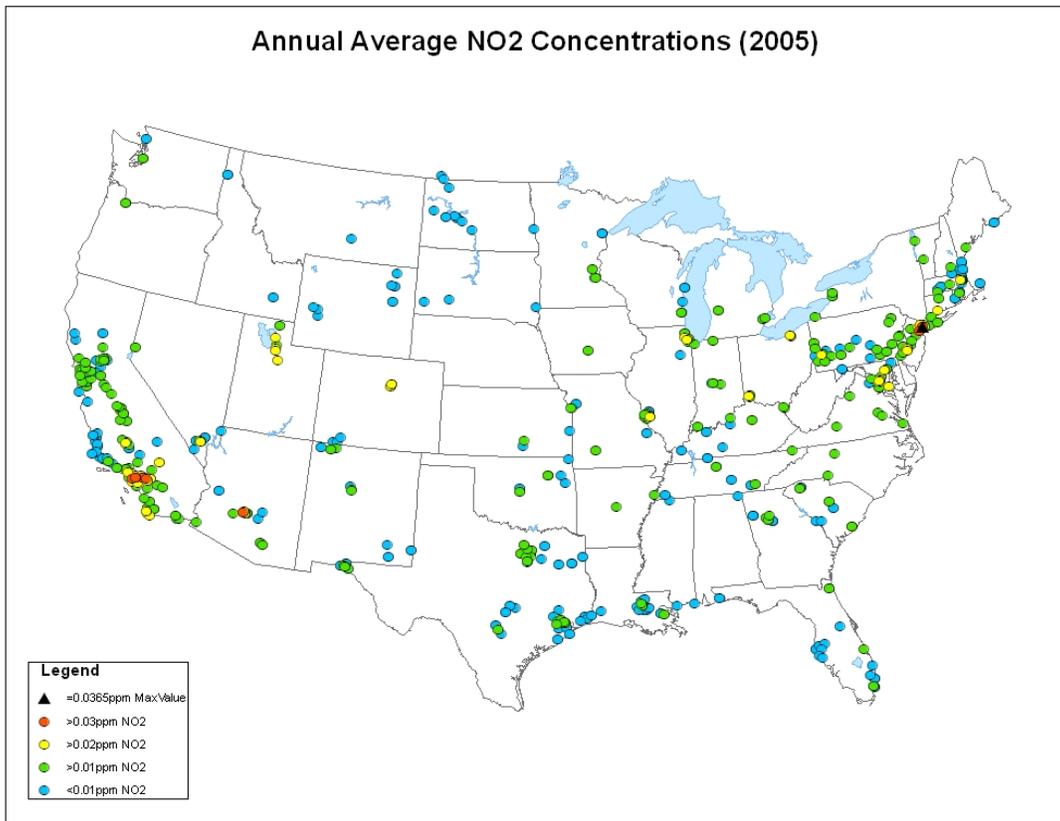
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Figure 4-16. 2005 CMAQ modeled Oxidized Sulfur Deposition (kgS/Ha/Yr).



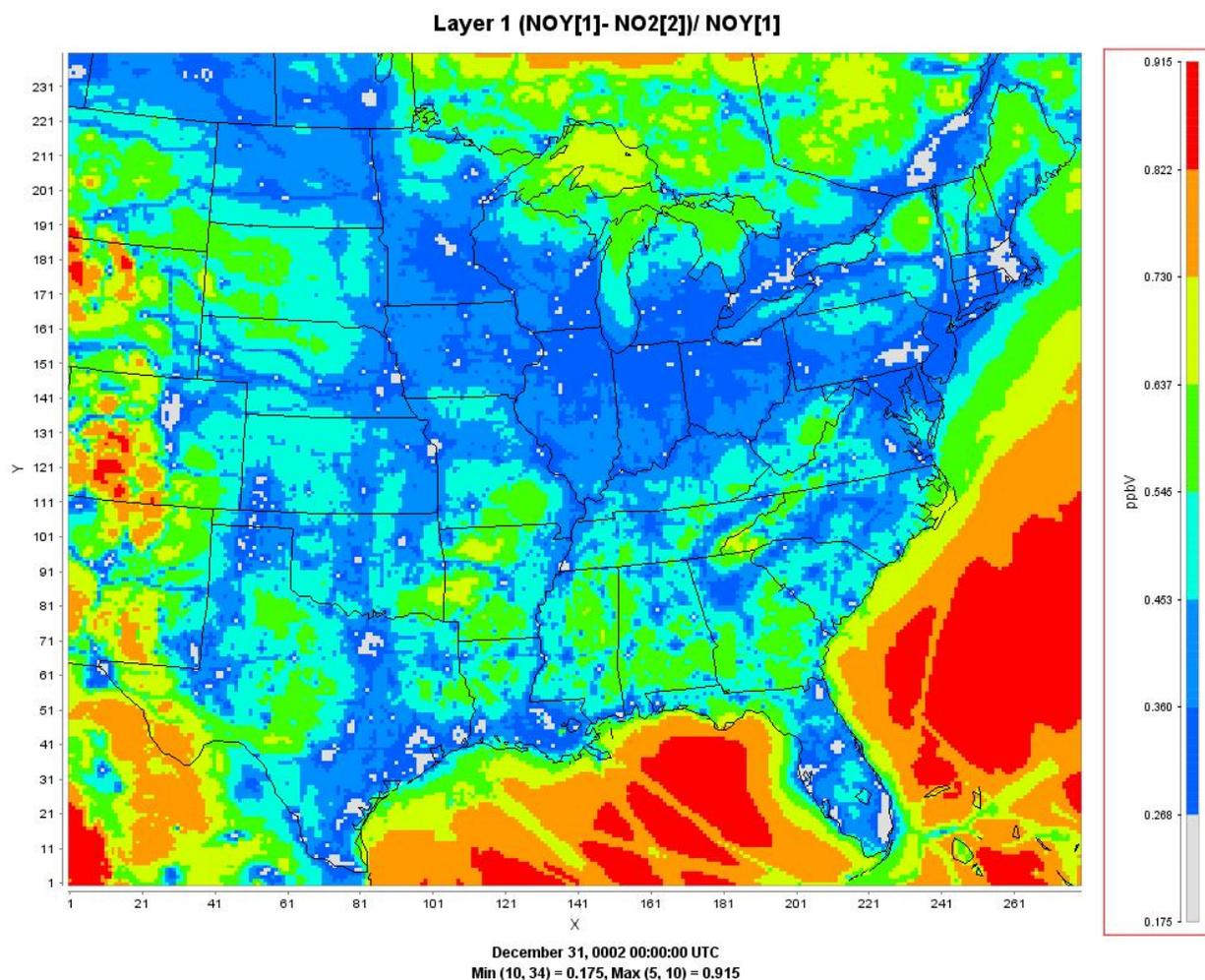
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Figure 4-17. Three hour average maximum 2005 SO₂ concentrations based on the SLAMS reporting to EPA’s Air Quality System (AQS) data base. The current SO₂ secondary standard based on the maximum 3 hour average value is 500 ppb, a value not exceeded. While there are obvious spatial gaps, the majority of these stations are located to capture maximum values generally in proximity to major sources and high populations. Lower relative values are expected in more remote acid sensitive areas.



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Figure 4-18. Annual average 2005 NO_2 concentrations based on the SLAMS reporting to EPA's Air Quality System (AQS) data base. The current NO_2 secondary standard is 53 ppb, a value well above those observed. While there are obvious spatial gaps, the stations are located in areas of relatively high concentrations in highly populated areas. Lower relative values are expected in more remote acid sensitive areas.



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2 **Figure 4-19.** 2005 CMAQ derived annual average ratio of $(\text{NO}_y - \text{NO}_2)/\text{NO}_y$. The
3 fraction of NO_2 contributing to total NO_y generally is less than 50% in the
4 Adirondack and Shenandoah case study areas. The ratio reflects the relative air
5 mass aging associated with transformation of oxidized nitrogen beyond NO and
6 NO_2 as one moves from urban to rural locations.

7 **4.5 ARE ADVERSE EFFECTS ON THE PUBLIC WELFARE**
8 **OCCURRING UNDER CURRENT AIR QUALITY CONDITIONS**
9 **FOR NO_2 AND SO_2 AND WOULD THEY OCCUR IF THE NATION**
10 **MET THE CURRENT SECONDARY STANDARDS?**

11 The previous sections have established that almost all areas of the U.S. were at
12 concentrations of SO_2 and NO_2 below the levels of the current standards. In many locations, SO_2
13 and NO_2 concentrations are substantially below the levels of the standards. This suggests that
14 levels of deposition and any effects on ecosystems due to deposition of NO_x and SO_x under

1 recent conditions are occurring even though areas meet or are below current standards. This
2 section focuses on summarizing the evidence of effects occurring at deposition levels consistent
3 with recent conditions.

4 The ISA summarizes the available studies of relative nitrogen contribution and finds that
5 in much of the U.S., NO_x contributes from 50 to 75 percent of total atmospheric deposition [**ISA**
6 **Section 2.8.4**]. While the proportion of total nitrogen loadings associated with atmospheric
7 deposition of nitrogen varies across locations (N deposition in the Eastern U.S. includes
8 locations with greater than 9 kg N/ha/year, and in the central U.S. high deposition locations with
9 values on the order of 6 to 7 kg N/ha/year), the ISA indicates that atmospheric N deposition is
10 the main source of new anthropogenic N to most headwater streams, high elevation lakes, and
11 low-order streams. Atmospheric N deposition contributes to the total N load in terrestrial,
12 wetland, freshwater, and estuarine ecosystems that receive N through multiple pathways. In
13 several large estuarine systems, including the Chesapeake Bay, atmospheric deposition accounts
14 for between 10 and 40 percent of total nitrogen loadings.

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

23 New scientific evidence exists to address each of the areas of uncertainty raised in the
24 previous reviews (summarized above). Based on the new evidence, the current ISA concludes
25 that:

- 26 (1) The evidence is sufficient to infer a causal relationship between acidifying deposition
27 (to which both NO_x and SO_x contribute) and effects on biogeochemistry related to
28 terrestrial and aquatic ecosystems; and biota in terrestrial and aquatic ecosystems.
- 29 (2) The evidence is sufficient to infer a causal relationship between N deposition, to
30 which NO_x and NH_x contribute, and the alteration of A) biogeochemical cycling of N
31 and carbon in terrestrial, wetland, freshwater aquatic, and coastal marine ecosystems;

1 B) biogenic flux of methane (CH₄), and N₂O in terrestrial and wetland ecosystems;
2 and C) species richness, species composition, and biodiversity in terrestrial, wetland,
3 freshwater aquatic and coastal marine ecosystems.

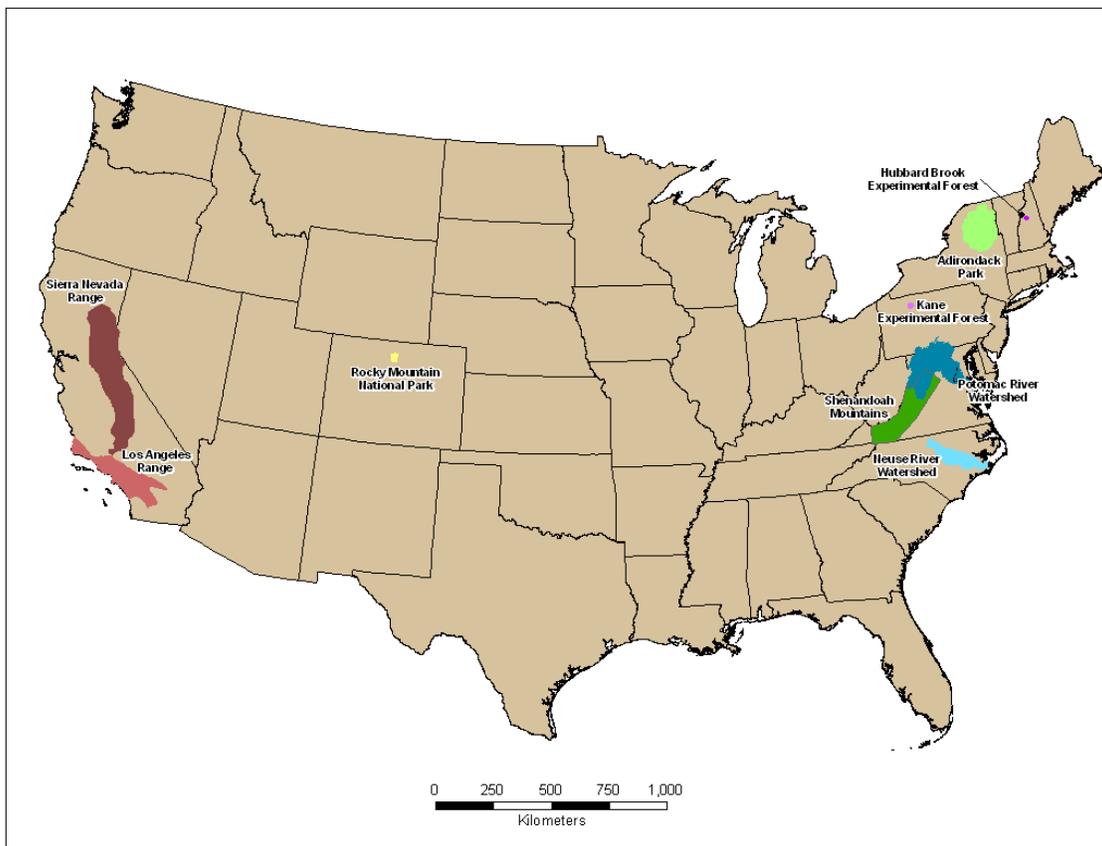
4 (3) The evidence is sufficient to infer a causal relationship between S deposition and
5 increased Hg methylation in wetlands and aquatic environments.

6 Subsequent to the previous review of the NO_x secondary standard, a great deal of
7 information on the contribution of atmospheric deposition associated with ambient NO_x has
8 become available. Chapter 3 of the REA provides a thorough assessment of the contribution of
9 NO_x to nitrogen deposition throughout the U.S., and the relative contributions of ambient NO_x
10 and reduced forms of nitrogen. Staff concludes that based on that analysis, ambient NO_x is a
11 significant component of atmospheric nitrogen deposition, even in areas with relatively high
12 rates of deposition of reduced nitrogen. In addition, staff initially concludes that atmospheric
13 deposition of oxidized nitrogen contributes significantly to total nitrogen loadings in nitrogen
14 sensitive ecosystems.

15 As discussed throughout the risk and exposure assessment document, there are several
16 key areas of risk that are associated with ambient concentrations of NO_x and SO_x. In previous
17 reviews of the NO_x and SO_x secondary standards, the standards were designed to protect against
18 direct exposure of plants to ambient concentrations of the pollutants. A significant shift in
19 understanding of the effects of NO_x and SO_x has occurred since the last reviews, reflecting the
20 large amount of research that has been conducted on the effects of deposition of nitrogen and
21 sulfur to ecosystems. The most significant risks of adverse effects to public welfare are those
22 related to deposition of NO_x and SO_x to both terrestrial and aquatic ecosystems. These risks fall
23 into two categories: acidification and nutrient enrichment. These made up the emphasis of the
24 REA, and are most relevant to evaluating the adequacy of the existing standards in protecting
25 public welfare from adverse ecological effects.

1 **4.5.1 To what extent do the current NO_x and SO_x secondary standards provide**
2 **protection from adverse effects associated with deposition of atmospheric**
3 **NO_x, and SO_x which results in acidification in sensitive aquatic and**
4 **terrestrial ecosystems?**

5 The focus of the REA case studies was on determining whether deposition of sulfur and
6 oxidized nitrogen in locations where ambient NO_x and SO_x was at or below the current standards
7 was resulting in acidification and related effects. This review has focused on identifying
8 ecological indicators that can link atmospheric deposition to ecological effects associated with
9 acidification. NO_x and SO_x contribute to acidification in both aquatic and terrestrial ecosystems,
10 although the indicators of effects differ. While there are some geographic areas with both
11 terrestrial and aquatic ecosystems that are vulnerable to acidification, the case study areas do not
12 fully overlap. Figure 4-20 shows the locations of the case studies evaluated in the REA.



13
14 **Figure 4-20.** National map highlighting the 9 case study areas evaluated in the
15 **REA.**

1 **4.5.1.1 Aquatic Acidification**

2 Based on the case studies conducted for lakes in the Adirondacks and streams in
3 Shenandoah National Park, staff concludes that there is significant risk to acid sensitive aquatic
4 ecosystems at atmospheric concentrations of NO_x and SO_x at or below the current standards.
5 This conclusion is based on application of the MAGIC model to estimate the effects of
6 deposition at levels consistent with atmospheric NO_x and SO_x concentrations that are at or below
7 the current standards. An important ecological indicator for aquatic acidification effects is ANC,
8 measuring the acid buffering capacity of a waterbody, and the case study focused on evaluating
9 whether locations were likely to be below critical values of ANC given deposition levels
10 associated with NO_x and SO_x concentrations that meet the current standards. In addition, the case
11 studies assessed the ecological effects and some of the known ecosystem services that are
12 associated with different levels of ANC in order to associate the ecological indicator with
13 measures of public welfare that may be adversely affected by deposition levels consistent with
14 concentrations of NO_x and SO_x that meet the current standards.

15 Staff concludes that the evidence and risk assessment support strongly a relationship
16 between atmospheric deposition of NO_x and SO_x and ANC, and that ANC is an excellent
17 indicator of aquatic acidification. Staff also concludes that at levels of deposition associated with
18 NO_x and SO_x concentrations at or below the current standards, ANC levels are expected to be
19 below benchmark values that are associated with significant losses in fish species richness (**REA**
20 **Section 4**).

21 Many locations in sensitive areas of the U.S. have ANC levels below benchmark levels
22 for ANC classified as severe, elevated, or moderate concern (see Figure 2-1). The average
23 current ANC levels across 44 lakes in the Adirondack case study area is 62.1 (moderate
24 concern), however, 44 percent of lakes had deposition levels exceeding the critical load for an
25 ANC of 50, and 28 percent of lakes had deposition levels exceeding the critical load for an ANC
26 of 20 µeq/L (**REA Section 4.2.4.2**). This indicates that almost half of the 44 lakes in the
27 Adirondacks case study area are at an elevated concern levels, and almost a third are at a severe
28 concern level. These levels are associated with greatly reduced fish species diversity, and losses
29 in the health and reproductive capacity of remaining populations. Based on assessments of the
30 relationship between number of fish species and ANC level in both the Adirondacks and
31 Shenandoah areas, the number of fish species is decreased by over half at an ANC level of 20

1 μeq/L relative to an ANC level at 100 μeq/L (**REA Figure 4.2-1**). At levels below 20 μeq/L,
2 populations of sensitive species, such as brook trout, may decline significantly during episodic
3 acidification events. When extrapolated to the full population of lakes in the Adirondacks area
4 using weights based on the EMAP probability survey (**REA 4.2.6.1**), 36 percent of lakes
5 exceeded the critical load for an ANC of 50 μeq/L and 13 percent of lakes exceeded the critical
6 load for an ANC of 20 μeq/L.

7 Many streams in the Shenandoah case study area also have levels of deposition that are
8 associated with ANC levels classified as severe, elevated, or moderate concern. The average
9 ANC under recent conditions for the 60 streams evaluated in the Shenandoah case study area is
10 57.9, indicating moderate concern. However, 85 percent of streams had recent deposition
11 exceeding the critical load for an ANC of 50 μeq/L, and 72 percent exceeded the critical load for
12 an ANC of 20 μeq/L. As with the Adirondacks area, this suggests that significant numbers of
13 sensitive streams in the Shenandoah area are at risk of adverse impacts on fish populations under
14 recent conditions. Many other streams in the Shenandoah area are likely to experience conditions
15 of elevated to severe concern based on the prevalence in the area of bedrock geology associated
16 with increased sensitivity to acidification suggesting that effects due to stream acidification could
17 be widespread in the Shenandoah area (**REA 4.2.6.2**).

18 The ISA notes that large portions of the Eastern U.S. are acid sensitive, and that current
19 deposition levels exceed those that would allow recovery of the most acid sensitive lakes in the
20 Adirondacks (**ISA ES**). In addition, because of past loadings, areas of the Shenandoah are
21 sensitive to current deposition levels (**ISA ES**). Much of the West is naturally less sensitive to
22 acidification, and as such, less focus is placed on the adequacy of the existing standards in these
23 areas, with the exception of the mountainous areas of the West, which experience episodic
24 acidification due to deposition.

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

30 The ISA notes that “consideration of episodic acidification greatly increases the extent
31 and degree of estimated effects for acidifying deposition on surface waters.” (**ISA Section**

1 **3.2.1.6)** Some studies show that the number of lakes that could be classified as acidified based on
2 episodic acidification is 2 to 3 times the number of lakes classified as acidified based on chronic
3 ANC. These episodic acidification events can have long term effects on fish populations (**ISA**
4 **Section 3.2.1.6)**. Under recent conditions, episodic acidification has been observed in locations
5 in the Eastern U.S. and in the Mountainous Western U.S. (**ISA Section 3.2.1.6)**.

6 It can therefore be concluded that recent levels of NO_x and SO_x are associated with
7 deposition that leads to ANC values below benchmark values known to cause ecological harm in
8 sensitive aquatic systems, including lakes and streams in multiple areas of the U.S. These
9 changes are known to have impacts on ecosystem services such as reductions in recreational
10 fishing. While other ecosystem services (e.g. habitat provisioning, subsistence fishing, and
11 biological control as well as many others) are potentially affected by reductions in ANC,
12 confidence in the specific translation of ANC values to these additional ecosystem services is
13 much lower.

14 **4.5.1.2 Terrestrial Acidification**

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

28 Many locations in sensitive areas of the U.S. have Bc/Al levels below benchmark levels
29 classified as providing low to intermediate levels of protection to tree health. At a Bc/Al ratio of
30 1.2 (intermediate level of protection), red spruce growth can be reduced by 20 percent. At a

1 Bc/Al ratio of 0.6 (low level of protection), sugar maple growth can be reduced by 20 percent.
2 The REA did not evaluate broad sensitive regions. However, in the sugar maple case study area
3 (Kane Experimental Forest), recent deposition levels are associated with a Bc/Al ratio below 1.2,
4 indicating between intermediate and low level of protection, which would indicate the potential
5 for a greater than 20 percent reduction in growth. In the red spruce case study area (Hubbard
6 Brook Experimental Forest), recent deposition levels are associated with a Bc/Al ratio slightly
7 above 1.2, indicating slightly better than an intermediate level of protection (**REA Section**
8 **4.3.5.1**).

9 Over the full range of sugar maple, 12 percent of evaluated forest plots exceeded the
10 critical load for a Bc/AL ratio of 1.2, and 3 percent exceeded the critical load for a Bc/Al ratio of
11 0.6. However, there was large variability across states. In New Jersey, 67 percent of plots
12 exceeded the critical load for a Bc/Al ratio of 1.2, while in several states on the outskirts of the
13 range for sugar maple, e.g. Arkansas, Illinois, no plots exceeded the critical load for a Bc/Al ratio
14 of 1.2. For red spruce, overall 5 percent of plots exceeded the critical load for a Bc/Al ratio of
15 1.2, and 3 percent exceeded the critical load for a Bc/Al ratio of 0.6. In the major red spruce
16 producing states (Maine, New Hampshire, and Vermont), critical loads for a Bc/AL ratio of 1.2
17 were exceeded in 0.5, 38, and 6 percent of plots.

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

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

1 **4.5.2 To what extent does the current NO_x secondary standard provide protection**
2 **from adverse effects associated with deposition of atmospheric NO_x, which**
3 **results in nutrient enrichment effects in sensitive aquatic and terrestrial**
4 **ecosystems?**

5 Nutrient enrichment effects are due to nitrogen loadings from both atmospheric and non-
6 atmospheric sources. Evaluation of nutrient enrichment effects requires an understanding that
7 nutrient inputs are essential to ecosystem health. The specific long term levels of nutrients in a
8 system affect the types of species that occur over long periods of time. Short term additions of
9 nutrients can affect species competition, and even small additions of nitrogen in areas that are
10 traditionally nutrient poor can have significant impacts. In certain limited situations, additions of
11 nitrogen can increase rates of growth, and these increases can have short term benefits in certain
12 managed ecosystems. As noted earlier, this review of the standards is focused on unmanaged
13 ecosystems. As a result, in assessing adequacy of the current standards, we are focusing on the
14 adverse effects of nutrient enrichment in unmanaged ecosystems. However, the following
15 discussion provides a brief assessment of effects in managed ecosystems.

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

26 Information on the effects of changes in passive nitrogen deposition on forestlands and
27 other terrestrial ecosystems is very limited. The multiplicity of factors affecting forests, including
28 other potential stressors such as ozone, and limiting factors such as moisture and other nutrients,
29 confound assessments of marginal changes in any one stressor or nutrient in forest ecosystems.
30 The ISA notes that only a fraction of the deposited nitrogen is taken up by the forests, most of
31 the nitrogen is retained in the soils (**ISA 3.3.2.1**). In addition, the ISA indicates that forest

1 management practices can significantly affect the nitrogen cycling within a forest ecosystem, and
2 as such, the response of managed forests to NO_x deposition will be variable depending on the
3 forest management practices employed in a given forest ecosystem (**ISA Annex C C.6.3**)
4 Increases in the availability of nitrogen in N-limited forests via atmospheric deposition could
5 increase forest production over large non-managed areas, but the evidence is mixed, with some
6 studies showing increased production and other showing little effect on wood production (**ISA**
7 **3.3.9**). Because leaching of nitrate can promote cation losses, which in some cases create nutrient
8 imbalances, slower growth and lessened disease and freezing tolerances for forest trees, the net
9 effect of increased N on forests in the U.S. is uncertain (**ISA 3.3.9**).

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

24 **4.5.3 Aquatic Nutrient Enrichment**

25 The REA case studies focused on coastal estuaries and revealed that while current
26 ambient loadings of atmospheric NO_x are contributing to the overall depositional loading of
27 coastal estuaries, other non-atmospheric sources are contributing in far greater amounts in total,
28 although atmospheric contributions are as large as some other individual source types. The
29 ability of current data and models to characterize the incremental adverse impacts of nitrogen
30 deposition is limited, both by the available ecological indicators, and by the inability to attribute

1 specific effects to atmospheric sources of nitrogen. The REA case studies used as the ecological
2 indicator for aquatic nutrient enrichment, an index of eutrophication known as the Assessment of
3 Estuarine Trophic Status Eutrophication Index (ASSETS EI). This index is a six level index
4 characterizing overall eutrophication risk in a waterbody. This indicator is not sensitive to
5 relatively large changes in nitrogen deposition. In addition, this type of indicator does not reflect
6 the impact of nitrogen deposition in conjunction with other sources of nitrogen.

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

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

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

1 **4.5.4 Terrestrial Nutrient Enrichment**

2 The scientific literature has many examples of the deleterious effects caused by excessive
3 nitrogen loadings to terrestrial systems. Several studies have set benchmark values for levels of
4 N deposition at which scientifically adverse effects are known to occur. These benchmarks are
5 discussed more thoroughly in Chapter 5 of the REA. Large areas of the country appear to be
6 experiencing deposition above these benchmarks for example, Fenn et al. (2008) found that at
7 3.1 kg N/ha/yr, the community of lichens begins to change from acidophytic to tolerant species;
8 at 5.2 kg N/ha/yr, the typical dominance by acidophytic species no longer occurs; and at 10.2 kg
9 N/ha/yr, acidophytic lichens are totally lost from the community. Additional studies in the
10 Colorado Front Range of the Rocky Mountain National Park support these findings and are
11 summarized in Chapter 6.0 of the *Risk and Exposure Assessment*. These three values (3.1, 5.2,
12 and 10.2 kg/ha/yr) are one set of ecologically meaningful benchmarks for the mixed conifer
13 forest (MCF) of the pacific coast regions. Nearly all of the known sensitive communities receive
14 total nitrogen deposition levels above the 3.1 N kg/ha/yr ecological benchmark according to
15 the 12 km, 2002 CMAQ/NADP data, with the exception of the easternmost Sierra Nevadas.
16 MCFs in the southern portion of the Sierra Nevada forests and nearly all MCF communities in
17 the San Bernardino forests receive total nitrogen deposition levels above the 5.2 N kg/ha/yr
18 ecological benchmark.

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

1 **4.6 TO WHAT EXTENT DO THE CURRENT NO_x AND/OR SO_x**
2 **SECONDARY STANDARDS PROVIDE PROTECTION FROM**
3 **OTHER ECOLOGICAL EFFECTS (E.G., MERCURY**
4 **METHYLATION) ASSOCIATED WITH THE DEPOSITION OF**
5 **ATMOSPHERIC NO_x, AND/OR SO_x?**

6 It is stated in the ISA (**ISA Sections 3.4.1 and 4.5**) that mercury is a highly neurotoxic
7 contaminant that enters the food web as a methylated compound, methylmercury. Mercury is
8 principally methylated by sulfur-reducing bacteria and can be taken up by microorganisms,
9 zooplankton and macroinvertebrates. The contaminant is concentrated in higher trophic levels,
10 including fish eaten by humans. Experimental evidence has established that only inconsequential
11 amounts of methylmercury can be produced in the absence of sulfate. Once methylmercury is
12 present, other variables influence how much accumulates in fish, but elevated mercury levels in
13 fish can only occur where substantial amounts of methylmercury are present. Current evidence
14 indicates that in watersheds where mercury is present, increased SO_x deposition very likely
15 results in additional production of methylmercury which leads to greater accumulation of MeHg
16 concentrations in fish (Munthe et al, 2007; Drevnick et al., 2007).

17 The production of meaningful amounts of methylmercury (MeHg) requires the presence
18 of SO₄²⁻ and mercury, and where mercury is present, increased availability of SO₄²⁻ results in
19 increased production of MeHg. There is increasing evidence on the relationship between sulfur
20 deposition and increased methylation of mercury in aquatic environments; this effect occurs only
21 where other factors are present at levels within a range to allow methylation. The production of
22 methylmercury requires the presence of sulfate and mercury, but the amount of methylmercury
23 produced varies with oxygen content, temperature, pH, and supply of labile organic carbon (**ISA**
24 **Section 3.4**). In watersheds where changes in sulfate deposition did not produce an effect, one or
25 several of those interacting factors were not in the range required for meaningful methylation to
26 occur (**ISA Section 3.4**). Watersheds with conditions known to be conducive to mercury
27 methylation can be found in the northeastern United States and southeastern Canada. The
28 relationship between sulfur and methylmercury production is addressed qualitatively in Chapter
29 6 of the Risk and Exposure Assessment.

1 With respect to sulfur deposition and mercury methylation, the final ISA determined: *The*
2 *evidence is sufficient to infer a causal relationship between sulfur deposition and increased*
3 *mercury methylation in wetlands and aquatic environments.* However, staff did not conduct a
4 quantitative assessment of the risks associated with increased mercury methylation under current
5 conditions. As such, staff are unable to make a determination as to the adequacy of the existing
6 SO₂ standards in protecting against welfare effects associated with increased mercury
7 methylation.

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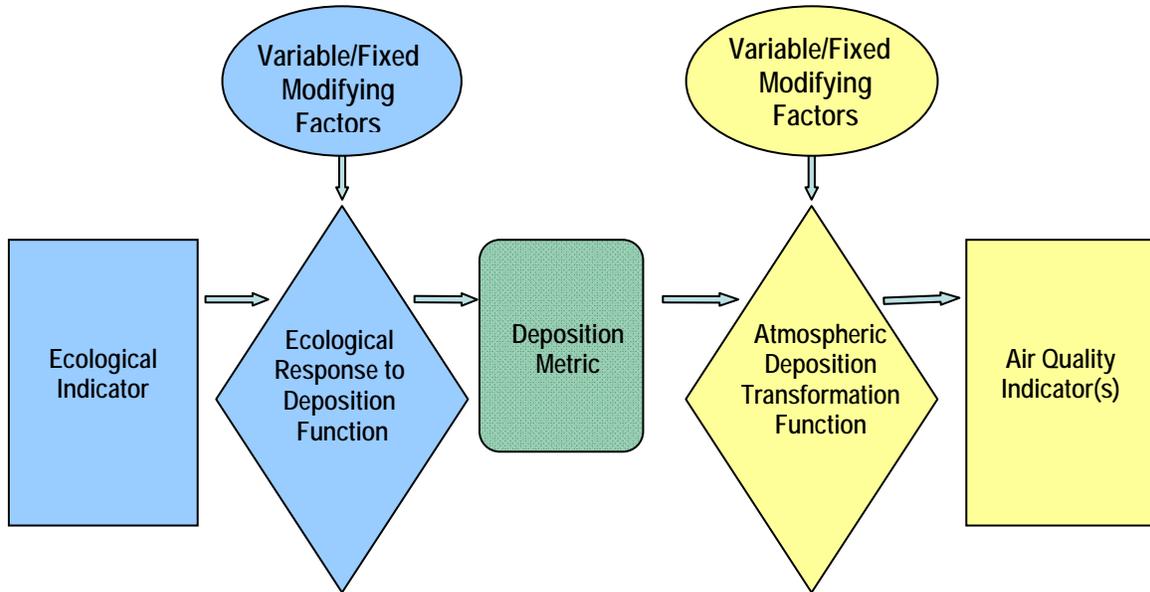
5. CONCEPTUAL DESIGN OF AN ECOLOGICALLY RELEVANT MULTI-POLLUTANT STANDARD

The objective of this chapter is to describe the conceptual design for a national ambient air quality standard that links ecological indicators of concern to ambient air indicators of NO_x and SO_x. In Chapter 4 of this policy assessment, the limitations of the design of the current secondary standards are described as they apply to protection of sensitive ecosystems. The conceptual design described in this chapter addresses those limitations. The overall concept for the standards starts by recognizing that the fundamental welfare effects associated with ambient NO_x and SO_x occur through the process of deposition to sensitive ecosystems. As detailed in Chapter 4, previous NO_x and SO_x NAAQS reviews only considered effects to vegetation via stomatal exposure. There is now sufficient data to link atmospheric concentrations to adverse effects in ecosystems that are caused by exposure via deposition to soils and surface waters. Deposition is a direct consequence of atmospheric concentration; however it is also modified by factors that vary across the landscape (e.g. elevation and groundcover). Likewise, ecological response to deposition can vary according to ecosystem sensitivity and the ecological indicator of concern. This is the first time a secondary standard for deposition effects related to NO_x and SO_x has been developed; therefore the conceptual design of a potential standard is described here prior to the specific details on the indicator, level, form and averaging time for such a potential standard that are presented in chapter 6.

5.1 COMPONENTS OF THE DESIGN

There are four main components to the conceptual design of the standard: atmospheric and ecological indicators, deposition metrics, functions that relate indicators to deposition metrics and factors that modify the functions. These components of the design are illustrated in Figure 5-1. The squares represent indicators. Ecological indicators are chemical or biological components of the ecosystem that can be linked to N and S deposition based on scientific evidence. Air quality indicators are the chemical species of the criteria air pollutants that best represent the atmospheric pollutants that cause ecological harm in the criteria pollutant categories of oxides of nitrogen and oxides of sulfur. Triangles indicate functions in which two variables are related. The ecological effect function is the relationship between the ecological

1 indicator and deposition over a range of values. The atmospheric deposition transformation
2 function is the relationship between deposition and the atmospheric concentration of an air
3 quality indicator. The circles represent factors which will modify the functions. Modifying
4 factors can vary across the landscape. The spatial heterogeneity of modifying factors can be
5 challenging to characterize, and therefore in some cases we present multiple options for how to
6 incorporate them into the design.



7
8 **Fig 5-1.** Schematic diagram of the conceptual design of the standard.

9 **5.1.1 For which effects is there sufficient information to support setting standards?**

10 After review of the ISA and REA, CASAC concluded that aquatic acidification should be
11 the focus for developing a multi-pollutant standard, based on the quantity and quality of data.
12 CASAC also recommended that, in addition to aquatic acidification, the EPA should consider
13 multiple ecological indicators and made the following statement in their letter to the EPA on
14 August 28, 2009:

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

20 The following sections describe the conceptual design for standards based on aquatic
21 acidification, terrestrial acidification, eutrophication of high elevation western lakes and

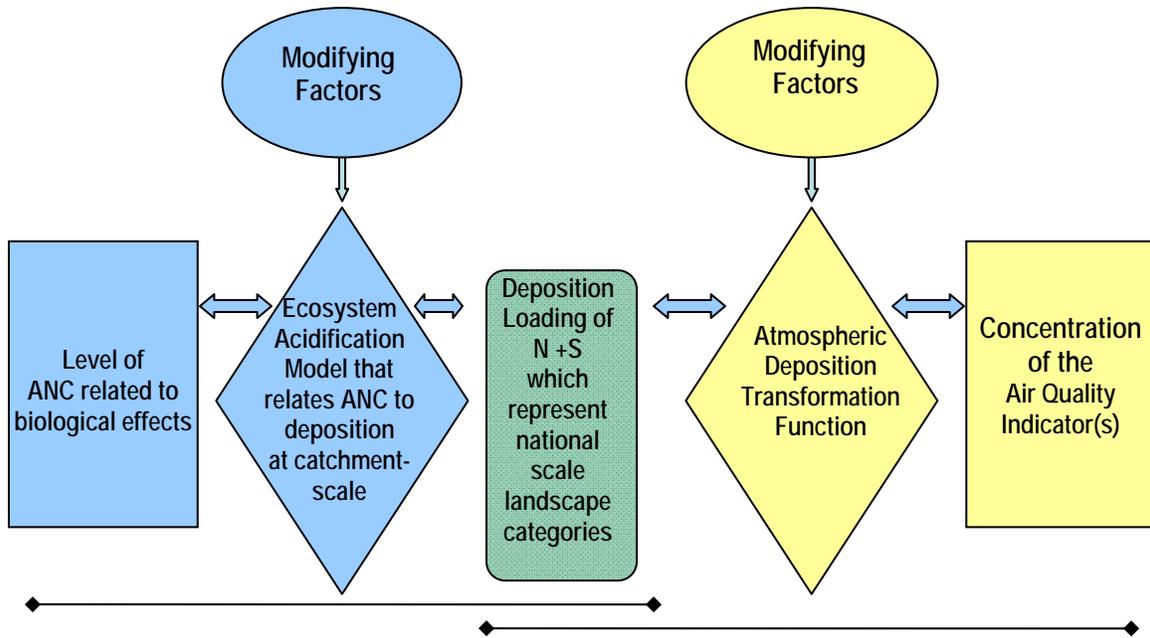
1 terrestrial nutrient enrichment. The focus of the first draft will be on aquatic acidification, but
2 this general conceptual framework will apply to a broader set of potential endpoints.

3 **5.2 ECOLOGICAL COMPONENTS OF THE STANDARD: AQUATIC** 4 **ACIDIFICATION**

5 Details of the conceptual design of the NO_x and SO_x NAAQS based on aquatic
6 acidification effects are presented in this section. A summary of our over all approach is given
7 here to help provide context and support for the more detailed discussions that follow.

8 At the catchment scale, ambient NO_y and SO_x add to the total deposition of N and S that
9 lead to aquatic acidification. NH_x is often another big component of the total N deposition. The
10 load of deposition that causes a desired level of ANC will vary depending on the characteristics
11 of the ecosystem. The level of ANC is tied to the degree of biological harm to the system from
12 aquatic acidification.

13 The components of the standard are modified for application to aquatic acidification and
14 presented in Fig 5-2. The bidirectional arrows emphasize that the order in which one considers
15 the links between ANC and atmospheric concentrations of NO_x and SO_x is conceptually
16 important to the standard design. Moreover, different questions may be answered by working
17 through Fig 5-2 from the left to the right versus the right to the left. For example, working from
18 left to right, when a level of ANC is specified the deposition loadings of N and S that would
19 cause the specified level of ANC can be calculated; in essence this would be a critical load for a
20 specified ANC limit. A comparison between the total amount of deposited N and S to the critical
21 load would determine whether the specified level of ANC is achieved for a catchment. Let's now
22 work through the equation from right to left. If the amount of N and S deposited to a given
23 catchment is known, you could calculate the level of ANC that would result. The calculated
24 ANC could then be compared to a benchmark value of ANC. In both of these approaches the
25 amount of reduced N would be subtracted from the total N deposition to calculate deposition
26 from NO_y. The atmospheric concentrations of NO_y and SO_x would be calculated from the
27 deposition of NO_y and S according to the methods presented in section 5.4. To determine the
28 appropriate conceptual design from the ecological components of the standard, the analysis from
29 the REA is evaluated in which critical loads were calculated for a target value of ANC, thereby
30 working from left to right on Fig 5-2.



Relationship between the amount of deposition and the effect on the selected ecological indicator, ANC (described in 5.2)

Relationship between the amount of deposition and the concentration of NO_x and SO_x (described in 5.4)

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Fig 5-2. Schematic diagram of the conceptual design of the standard based on aquatic acidification. From left to right, if a desired level of ANC is known, then the concentration of the atmospheric indicators that will cause that level may be calculated. From right to left, if the concentration of the air quality indicators are known then the ANC that will be caused may be calculated.

The secondary NAAQS would apply to all areas of the country. It is not practical to evaluate each catchment individually, and that is not the appropriate approach for a national standard. Here, EPA staff proposes to categorize landscape features nationally, such that within a category there are generally similar characteristics as far as the relationship of total deposited N and S to the ANC. Every part of the country would be assigned into one of these bins/ landscape categories.

The secondary NAAQS would be based on a judgment as to a specified level of ANC. For each national acid-sensitivity bin/ landscape category there would be a range of critical loads for a specified ANC limit from the individual catchments within the total population aggregated to an acid-sensitivity category. Given that, the EPA would develop a deposition metric and associated tradeoff curve that represented the percentage of the catchments that would achieve the ANC (DL_{%ECO}). Therefore a judgment would also need to be made to determine the

1 percentage of ecosystems that would be targeted to achieve a specified ANC level that applies to
2 a bin/category.

3 The following discussions in this section focus on the ecological components of the
4 standard (ecological indicator, the deposition metric, the ecological response function and its
5 modifiers). Questions that are relevant to the design of the standard are used to organize these
6 discussions. The first series of questions (section 5.2.1) considers information presented in the
7 ISA and REA relevant to the conceptual design, while the second series of questions (section
8 5.2.2) presents the proposed conceptual design in more detail with an example calculation based
9 on the Adirondacks case study presented in section 5.5.

10 **5.2.1 Conceptual design considerations from the ISA and REA**

11 This section presents discussion of the ecological components of the design based on
12 information in the ISA and REA. The information presented here is considered in the
13 development of the design options that are proposed (section 5.2.2).

14 ***5.2.1.1 Does the available information provide support for the use of ecological*** 15 ***indicators to characterize the responses of aquatic ecosystems to nitrogen and*** 16 ***sulfur deposition?***

17 Ecological indicators of acidification in aquatic ecosystems can be chemical or
18 biological components of the ecosystem that are demonstrated to be altered by the acidifying
19 effects of N and S deposition based on scientific evidence. A desirable ecological indicator for
20 aquatic acidification will be one that is measurable or estimable, linked causally to deposition of
21 N and S, and linked causally to ecological effects known or anticipated to adversely affect public
22 welfare.

23 As summarized in Chapter 2, aquatic acidification is indicated by changes in the surface
24 water chemistry of ecosystems. In turn, the alteration of surface water chemistry has been linked
25 to negative effects on the biotic integrity of freshwater ecosystems. There are a suite of chemical
26 indicators that can be used to assess the effects of acidifying deposition on lake or stream acid-
27 base chemistry. These indicators include acid neutralizing capacity (ANC), surface water pH and
28 concentrations of SO_4^{2-} , NO_3^- , Al, and Ca^{2+} ; the sum of base cations; and the recently developed
29 base cation surplus. ANC is the most widely used chemical indicator of acid sensitivity and has
30 been found in various studies to be the best single indicator of the biological response and health

1 of aquatic communities in acid-sensitive systems (Lien et al., 1992; Sullivan et al., 2006). The
2 utility of the ANC criterion lies in the association between ANC and the surface water
3 constituents that directly contribute to or ameliorate acidity-related stress, in particular pH, Ca²⁺,
4 and Al. ANC is also used because it integrates overall acid status (**ISA 3.2.3 and REA 5.2.1**) and
5 the acid-related stress for biota that occupies the water that can be directly related to biological
6 impairment, specifically the number of fish species (**ISA 3.2.3**).

7 EPA staff thus concludes that the available information provides support for the use of
8 ecological indicators to characterize the responses of aquatic ecosystems to nitrogen and sulfur
9 deposition, and that ANC is the most supportable indicator.

10 ***5.2.1.2 Does the available information provide support for the development of a***
11 ***function that relates total nitrogen and sulfur deposition to ecological***
12 ***indicators?***

13 There is evidence to support the link between deposition of N and S, water chemistry and
14 biota. Atmospheric deposition of NO_x and SO_x causes aquatic acidification through the input of
15 acid anions (e.g. NO₃⁻ and SO₄²⁻). The anions are deposited either directly to the aquatic
16 ecosystem, or indirectly via terrestrial ecosystems. In other words, when the anions are mobile in
17 the terrestrial soil, they can leach into adjacent waterbodies. Acidification of ecosystems is
18 reflected in a robust relationship between ANC of water and the deposition of NO_x and SO_x.

19 In the REA, the relationship between deposition and ANC was investigated using models
20 of ecosystem acidification (**REA Chapter 4 and REA Appendix 4**). These models characterize
21 the relationship between deposition N and S and the ability of an ecosystem to counterbalance or
22 buffer the deposition. The utility of the ecosystem acidification models is for simulating a variety
23 of water and soil acidification responses at the laboratory, plot, hillslope, and catchment scales.
24 For example, the ANC value caused by the current amount of deposition could be calculated, or,
25 the level of deposition that causes a specified level of an ecosystem endpoint could be calculated
26 (i.e. a critical load for ANC=50) (**ISA appendix A**).

27 The models used in the REA were the Steady State Water Chemistry model (SSWC), the
28 First-order Acid Balance model (FAB) and the Model of Acidification of Groundwater in
29 Catchment (MAGIC). The SSWC and FAB models were used to calculate critical loads for
30 specified ANC levels in the case study areas. MAGIC was used to develop weathering rates that

1 were needed for the Shenandoah critical loads calculation and the F-factor was used for
 2 weathering rates in the in the Adirondacks. MAGIC was also used to show long-term trends
 3 between anthropogenic N and S deposition on ANC dating back to pre-industrial times. It is
 4 important to note that acidification models are data intensive. Water chemistry data from the
 5 TIME and LTM programs, which are part of the Environmental Monitoring and Assessment
 6 Program (EMAP), were input to the acidification models. An abbreviated summary of
 7 acidification models and data inputs is given in Table 5.2-1, a complete list is in Appendix A.

Table 5-1. Illustration of how selected models and water chemistry data were used to calculate critical loads in the REA.

	Weathering rate as input to CL model	Water chemistry data input to CL model	CL calculation: single value	CL calculation: critical load function
Adirondack	F-factor	EMAP	SSWC	FAB
Shenandoah	MAGIC	EMAP	SSWC	FAB

8
 9 In summary, the EPA staff concludes that the available information supports using the
 10 acidification models to characterize the relationship between total nitrogen and sulfur deposition
 11 and the ANC ecological indicator.

12 ***5.2.1.3 Does a quantified relationship exist between the level of a relevant ecological***
 13 ***indicator to an amount of nitrogen and sulfur deposition?***

14 A quantified relationship exists between the level of ANC and nitrogen and sulfur
 15 deposition. This relationship was analyzed to determine current risk for two case study areas, the
 16 Adirondacks and Shenandoahs, in the REA using a time series analysis and a critical load
 17 approach. The time series analysis was conducted using MAGIC and recent monitoring data. The
 18 critical loads analysis used water chemistry data from the Temporally Integrated Monitoring of
 19 Ecosystems (TIME) program and Long-term Monitoring (LTM) to calculate critical loads with the
 20 SSWC and FAB models.

21 Long-term trends in surface water nitrate, sulfate and ANC were modeled using MAGIC
 22 for the two case study areas. This data was used to compare current surface water conditions
 23 (2006) with preindustrial conditions (i.e. preacidification or 1860). The results showed a

1 dramatic increase in the number of acidified lakes, characterized as a decrease in ANC levels,
2 since the onset of anthropogenic N and S deposition (**REA Appendix 4 Section 5**)

3 More recent trends in ANC, over the time period from 1990 to 2006, were assessed using
4 monitoring data collected at the two case study areas. In both case study areas, nitrate and sulfate
5 deposition decreased over this time period. In the Adirondacks, this corresponded to a decreased
6 concentration of nitrate and sulfate in the surface waters and an increase in ANC (**REA 4.2.4.2**).
7 In the Shenandoahs, there was a slight decrease in nitrate and sulfate concentration in surface
8 waters corresponding to modest increase in ANC from 50 µeq/L in 1990 to 67 µeq/L in 2006
9 (**REA 4.2.4.3 and REA Appendix 4 Section 3.4**).

10 A critical load for ANC is the amount (or load per year) of N and S deposition above
11 which a selected level of ANC will be exceeded for individual water bodies. In the REA case
12 study analyses, critical loads and their exceedances were calculated for four values of ANC (i.e.,
13 ANC of 0, 20, 50, and 100 µeq/L) for 169 lakes in the Adirondacks and 60 streams in the
14 Shenandoahs. Those four ANC values correspond to important points along the ANC response
15 curve that are associated with levels of ecosystem impairment. The case studies used steady-state
16 critical loads models and focus on the combined load of sulfur and nitrogen deposition, below
17 which the ANC level would still support healthy aquatic ecosystems. For each waterbody, the
18 total deposition in the year 2002 was compared with the estimated critical loads for the four
19 critical limit thresholds to determine which sites exceed their critical limit of deposition and
20 biological protection level. Estimates of deposition were based on the sum of measured wet
21 deposition values from the year 2002 NADP network and modeled dry deposition values based
22 on the year 2002 emissions and meteorology using the Community Multiscale Air Quality
23 (CMAQ) model, respectively (**REA 4.2**). It is important to note that a single level of ANC may
24 be caused by a range of deposition values due to heterogeneous sensitivity among watersheds.

25 In summary, EPA staff concludes that a quantified relationship exists between the level
26 of surface water ANC and an amount of nitrogen and sulfur deposition. This relationship is
27 demonstrated by long-term trends going back to preindustrial conditions in the 1860s, recent
28 trends since the 1990s and critical loads modeling based on 2002 deposition data. Models are the
29 best way to evaluate how multiple environmental factors alter the relationship ANC and
30 deposition.

1 **5.2.1.4 What are the important variables in the ecological response to deposition**
2 **relationship(s)?**

3 There are numerous variables that modify the ANC to deposition relationship. The effects
4 of these modifiers are described by models that parameterize ecosystems to simulate the process
5 of acidification. The steady-state models used for critical loads analysis in the REA required
6 input data for between 17 and 20 environmental parameters.

7 The basic principle of the steady-state approach is to determine the maximum acid input
8 that will balance the system at a biogeochemical safe-limit. Safe-limit is a subjective term that
9 relates to a particular benchmark (e.g. ANC = 20, 50, 100), representing protection against
10 specific types and magnitudes of aquatic ecosystem response. The steady-state models that were
11 used in the REA relate an aquatic ecosystem's critical load to the weathering rate of its drainage
12 basin expressed in terms of the base cation flux. Weathering rate of geologic parent material is
13 the main source of base cations to an ecosystem. It is considered one of the governing factors to
14 ecosystem critical loads, and therefore an important variable in the ecological response to
15 deposition relationship. Landscape features that are correlated to ecosystem acid-sensitivity
16 include lithology, elevation, percent forested watershed, and watershed area (Sullivan et al.
17 2007). A more detailed summary of the models and the environmental variables incorporated
18 into the models that were used in the REA is presented in Appendix A.

19 Numerous environmental variables affect the acidification process. Therefore the input
20 data required to run acidification models is rather extensive. For example, MAGIC, a dynamic
21 process based model of acidification, requires atmospheric deposition fluxes for the base cations
22 and strong acid anions as inputs to the model. The volume discharge for the catchment must also
23 be provided to the model. Values for soil and surface water temperature, partial pressure of
24 carbon dioxide and organic acid concentrations must also be provided at the appropriate
25 temporal resolution. The aggregated nature of the model requires that it be calibrated to
26 observational data from a system before it can be used to examine potential system response. The
27 calibration procedure requires that stream water quality, soil chemical and physical
28 characteristics, and atmospheric deposition data be available for each catchment. The water
29 quality data needed for calibration are the concentrations of the individual base cations (Ca, Mg,
30 Na, and K) and acid anions (Cl, SO₄²⁻, and NO₃⁻) and the pH. The soil data used in the model
31 include soil depth and bulk density, soil pH, soil cation-exchange capacity, and exchangeable

1 bases in the soil (Ca, Mg, Na, and K). The atmospheric deposition inputs to the model must be
2 estimates of total deposition (wet and dry).

3 In summary, the EPA staff concludes there are numerous variables which modify the
4 ANC to deposition relationship. The relationships between environmental factors are described
5 by models that parameterize ecosystems to simulate the process of acidification. Weathering rate
6 of geologic parent material is the main source of base cations to an ecosystem, and it is therefore
7 considered one of the governing factors of ecosystem critical loads. Landscape features that are
8 correlated to ecosystem acid-sensitivity include lithology, elevation, percent forested watershed,
9 and watershed area. Consideration of the effects of environmental variables on the relationship
10 between environmental variables is extensive in ecosystem acidification models. The calibration
11 procedure requires that stream water quality, soil chemical and physical characteristics, and
12 atmospheric deposition data be available for each catchment.

13 ***5.2.1.5 Are these relationships applicable regionally?***

14 The relationship between ANC and N + S deposition based on catchment- scale modeling
15 is applicable regionally. Response to N and S deposition will vary catchment by catchment.
16 However, modeling every catchment in a region (i.e. a spatial area that includes a large
17 population of individual catchments) is implausible due to the extensive data requirements to
18 inform the simulations. A method to extrapolate watershed-scale analysis to a region was
19 developed in the REA. In that method, the critical loads (combined N+S load) developed for the
20 case study sites were applied over a region using water quality data. Critical load exceedance
21 (i.e., the amount of actual deposition above the critical load, if any) was calculated for each
22 waterbody in the region to quantify the number of lakes or streams that receive harmful levels of
23 deposition. Lakes and streams with positive exceedance values, where actual deposition was
24 above its critical load, were not protected at that critical limit (e.g. ANC= 20, 50, 100; REA
25 appendix 4).

26 In the Adirondack case study conducted in the REA, critical load exceedances were
27 extrapolated to lakes defined by the New England EMAP probability survey. The EMAP
28 probability survey was designed to estimate, with known confidence, the status, extent, change,
29 and trends in condition of the nation's ecological resources, such as surface water quality. For
30 the Adirondack Case Study Area, the regional EMAP probability survey of 117 lakes were used

1 to infer the number of lakes and percentage of lakes that receive acidifying deposition above
2 their critical load of a population of 1,842 lakes. ANC limits of 20, 50, and 100 µeq/L were
3 examined.

4 In the Shenandoah case study, critical load exceedances were extrapolated using the
5 SWAS-VTSSS LTM quarterly monitored sites to the population of brook trout streams that do
6 not lie on limestone bedrock and/or are not significantly affected by human activity within the
7 watershed. The total number of brook trout streams represented by the SWAS-VTSSS LTM
8 quarterly monitored sites is approximately 310 streams out of 440 mountain headwater streams
9 known to support reproducing brook trout. ANC limits of 20, 50, and 100 µeq/L were examined.
10 **(REA Appendix 4.3.1).**

11 In summary, approaches were developed in the REA to extrapolate the ANC-deposition
12 relationship across a region. The data requirements for these approaches include (1) calculation
13 of critical loads of ANC using a catchment-scale model (2) stream chemistry data across the
14 region of concern, and (3) deposition loads across the region. With this information the
15 deposition load that would cause the stream to exceed the critical limit of ANC was calculated as
16 the critical load exceedance.

17 ***5.2.1.6 Are these relationships applicable nationally?***

18 The relationship between ANC and N + S deposition is applicable nationally. Areas that
19 have similar geologic underpinnings and weathering rates should show similar sensitivity to NO_x
20 and SO_x deposition. The critical load modeling that was used in the REA case studies requires
21 parameterization to each catchment. The spatial scale is small (e.g. catchment level) and the data
22 requirements are great (17+ environmental variables for each catchment) to use this method to
23 determine critical loads across all sensitive regions of the U.S. at this time. It is important to note
24 that acid-sensitivity often varies from catchment to catchment. Even if we did calculate critical
25 loads data for each catchment, aggregation of the catchment-scale data is appropriate for a
26 national standard.

27 The technique developed in the REA for extrapolating catchment-specific results to a
28 regional area determines the number of streams in a given area that show critical load (CL)
29 exceedances based on a selected value of ANC and deposition values for 2002. The approach
30 developed in the case study for extrapolating catchment-specific results to a regional area is not

1 immediately applicable across the U.S. because data for surface water chemistry and data for
2 other input parameters is not available at a national scale.

3 To summarize, the relationship between ANC and N + S deposition is applicable
4 nationally. However the data required for critical loads analysis and extrapolation that is
5 available on the regional scale is not available at the national scale. Considering this current data
6 limitation the utility of the extrapolation approach developed in the REA to the national-scale is
7 limited. Additional national-scale approaches are discussed in section 5.2.3.

8 **5.2.1.7 Summary**

9 In summary, EPA staff concludes that the available information from the ISA and REA
10 supports the following characterization of aquatic acidification. First, there is sufficient support
11 for the use of ecological indicators to characterize the responses of aquatic ecosystems to
12 nitrogen and sulfur deposition, and that ANC is the most supportable indicator. The available
13 information supports using the acidification models to characterize the ecological response, using
14 ANC as the indicator, to nitrogen and sulfur deposition. Models are the best way to evaluate how
15 multiple environmental factors alter the relationship ANC and deposition.

16 Heterogeneous sensitivity among watersheds is due in part to landscape features.
17 Weathering rate of geologic parent material is the main source of base cations to an ecosystem,
18 and is therefore considered one of the governing factors of ecosystem critical loads. Landscape
19 features that are correlated to ecosystem acid-sensitivity include lithology, elevation, percent
20 forested watershed, and watershed area.

21 Modeling every catchment in a region is implausible due to the extensive data
22 requirements. The relationship between ANC and N + S deposition is applicable regionally. A
23 method to extrapolate watershed-scale analysis to a region was developed in the REA. In that
24 method, the critical loads (combined N+S load) developed for the case study sites were applied
25 over a region using water quality data. The data requirements for the regional extrapolation
26 include (1) calculation of critical loads for ANC using a catchment-scale model (2) stream
27 chemistry data across the region of concern, and (3) deposition loads across the region. The
28 approach developed in the case study areas is not immediately applicable across the U.S. because
29 data for critical loads modeling and surface water chemistry is not available at a national scale.
30 However, it is important to note that the relationship between ANC and N + S deposition is

1 applicable nationally. Areas that have similar geologic underpinnings should show similar
2 sensitivity to NO_x and SO_x deposition.

3 **5.2.2 Design options for aquatic acidification**

4 The following design options describe the conceptual approach to integrating the
5 ecological components of the standard outlined in section 5.1: ecological indicator, modifying
6 factors, ecological response function and deposition metric. The goal is to illustrate how levels of
7 NO_x and SO_x can be set to protect areas of the U.S. from acidic deposition.

8 ***5.2.2.1 Is it appropriate to use ANC as the ecological indicator for the conceptual*** 9 ***design of the NO_x and SO_x standard based on aquatic acidification?***

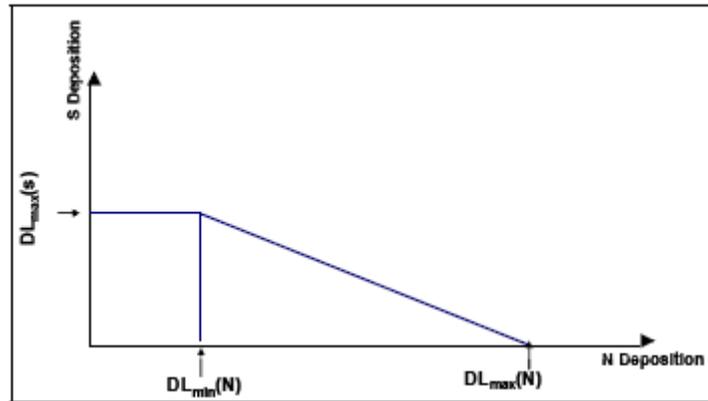
10 There is strong evidence supporting that ANC is an appropriate ecological indicator for
11 aquatic acidification as discussed in Chapter 2 and Section 5.1.1 (as well as **ISA 3.2.3** and **REA**
12 **5.2.1**). Options for the level of the indicator are discussed in Chapter 6. The options for the levels
13 are derived from experimental and observed evidence in the scientific literature showing the
14 biological effects over a range of ANC values.

15 ***5.2.2.2 What is the appropriate ecosystem acidification model(s) to represent the*** 16 ***ecological response function?***

17 In the REA, critical loads were calculated for specified ANC levels using the SSWC and
18 FAB models, these are referred to as acidification models, acid balance models or critical loads
19 models. The different assumptions of each modeling approach have implications that should be
20 considered in the conceptual design of a deposition-based NO_x and SO_x standard. Most notably,
21 biogeochemical pathways of N and S deposition are considered differently in the two models. In the
22 SSWC model, sulfate is assumed to be a mobile anion (i.e. S leaching = S deposition), while nitrogen is
23 retained in the catchment by various processes. This assumption that all N is retained by the ecosystem
24 and does not contribute to acidification is incorrect in many instances because nitrate leaching is
25 observed. If nitrogen is leaching out of an ecosystem, obviously it has not been retained. Nitrate leaching
26 is determined from the sum of the measured concentrations of nitrate and ammonia in the runoff. The
27 critical load for sulfur that is calculated by SSWC can be corrected for the amount of nitrogen that
28 contributes to acidification. When an exceedence value for the critical load is calculated, the critical load
29 is subtracted from S deposition plus the amount of nitrate leaching, as it represents the difference between

1 N deposition and N retention by the ecosystem. N leaching data used in this calculation is considered
 2 robust.

3 In contrast to the SSWC approach, the FAB model includes more explicit modeling of N
 4 processes including soil immobilization, denitrification, and wood removal, in-lake retention of N
 5 and S, as well as lake size. Although N cycling is more detailed in the FAB model, there is
 6 greater uncertainty in the input data needed to characterize the components of the N cycle. The
 7 FAB model yields a deposition load function for a specified level of an endpoint. This function is
 8 characterized by three nodes that are illustrated on Figure 5-3: 1) the maximum of amount of N
 9 deposition when S deposition equals zero ($DL_{max}(N)$), 2) the amount of N deposition that will
 10 be captured by the ecosystem before it leaches ($DL_{min}(N)$) and 3) the maximum amount of S
 11 sulfur deposition considering the N captured by the ecosystem ($DL_{max}(S)$). The function
 12 represents many unique pairs of N and S deposition that will equal the critical load for acidifying
 13 deposition. The slope portion of the function will vary according to attributes of the water body
 14 that is modeled, including lake size and in-lake retention.



15
 16 **Figure 5-3.** The depositional load function.

17 A third modeling approach, which synthesizes components of each model used in the
 18 REA, is suggested by staff for catchment scale modeling in developing the NAAQS. The
 19 foundation of the proposed approach is the SSWC model because there is high confidence in the
 20 input data required. The SSWC model for aquatic acidification is expressed as equation 1.

21
$$DL_{ANC\lim}(N + S) = ([BC]_o^* - [ANC_{\lim}])Q \quad (1)$$

22 where,

1 $DL_{ANClim}(N+S)$ = depositional load of S and N that does not cause the ecosystems to exceed a
 2 given ANC_{lim}
 3 $[BC]_0^*$ = the preindustrial concentration of base cations (equ/L)
 4 ANC_{limit} = a “target” ANC level (equ/L)
 5 Q = surface water runoff (m/yr) (this is typically equal to precipitation –evapotranspiration
 6

7 This model could be further constrained by a quantity of N which would which would be
 8 taken up, immobilized or denitrified by ecosystems and adjust the quantity of deposition required
 9 to meet a specified critical load. This term is represented as $DL_{min}(N)$ in the FAB model and
 10 illustrated in Fig. 5-3. For application in the NAAQS and in the following discussion, the
 11 parameter is designated with the abbreviation N_{ECO} . The acid-base model constrained by N_{ECO} is
 12 expressed by equation 2.

$$13 \quad DL_{ANClim}(N + S) = ([BC]_0^* - [ANC_{lim}])Q + N_{eco} \quad (2)$$

14
 15 where,

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

18
 19 The term N_{eco} could be derived multiple ways, each yielding different ultimate results.
 20 The first is by taking the mean value calculated to represent the long-term amount of N an
 21 ecosystem can immobilize and denitrify before leaching (i.e. N saturation) that is derived from
 22 the FAB model [denoted as $DL_{min}(N)$ in the FAB model]. This approach requires the input of
 23 multiple ecosystem parameters. Its components are expressed by eq 3.

$$24 \quad N_{eco} = fN_{upt} + N_{ret} + (1 - r)(N_{imm} + N_{den}) \quad (3)$$

25 where,

26 N_{upt} = nitrogen uptake by the catchment

27 N_{imm} = nitrogen immobilization by the catchment

28 N_{den} =denitrification of nitrogen in the catchment,

- 1 N_{ret} = in-lake retention of nitrogen
- 2 f = forest cover in the catchment (dimensionless parameter)
- 3 r = fraction lake/catchment ratio (dimensionless parameter)
- 4

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

$$7 \qquad \qquad \qquad N_{eco} = DL(N) - N_{leach} \qquad \qquad \qquad (4)$$

8 It is unclear which approach for calculating N_{ECO} should be used in developing the
9 NAAQS. The two equations can result in quite different values (See section 5.4 for an example
10 calculation).

11 To summarize, the SSWC model assumes N deposited to the ecosystem is retained by the
12 ecosystem, while also assuming that all S deposition is leached and contributes to aquatic
13 acidification. The critical load is calculated for S deposition, and the N that contributes to
14 acidification is incorporated into the exceedance calculation. The FAB model considers a
15 detailed accounting of the N cycle; however confidence in the input data to the model is more
16 uncertain. The FAB approach yields a function which may be solved by many unique pairs of N
17 and S deposition. A minimum amount of N deposition that will be captured by the ecosystem
18 before it leaches is included in the calculation of the maximum amount of S deposition. A third
19 approach is suggested by staff as the most appropriate approach for informing the structure of the
20 NO_x and SO_x secondary standard. This approach constrains the critical load calculated from a
21 SSWC method by a value of N_{ECO} [previously defined as DLmin(N)] which accounts for the
22 amount of N deposition that would be taken up by the ecosystem and, therefore, would not
23 contribute to acidification.

24 **5.2.2.3 How are results of acidification models aggregated to adequately represent a**
25 **larger spatial area and inform a deposition metric?**

26 So far in this section, the ecological indicator would be established as ANC. Acidification
27 models are considered the best way to describe the relationship between ANC and deposition and
28 to describe how this relationship is altered by modifying factors. If deposition is known the
29 model may be run to calculate the resultant ANC. If a target ANC level is desired the model may

1 be run to calculate the corresponding deposition load that should not be exceeded (i.e. the critical
2 load). The following discussion will focus on the critical load application of the acidification
3 model. It is important to emphasize that the acidification models are only applied at the spatial
4 scale of the catchment. Spatial aggregation of critical loads are necessary to inform the
5 discussion of appropriate design and levels of a national standard.

6 Acidification models are parameterized for catchments. The critical loads that they
7 calculate for N and S deposition based on a specified ANC limit vary at the small spatial scale of
8 the catchment to the degree that acid-balancing properties of the catchments vary. Despite this
9 variation, the goal of aggregating critical loads from multiple catchments is to develop an
10 appropriately representative deposition value, which is adequately protective of ecosystems and
11 could be applied over larger spatial areas.

12 Staff proposes evaluating the critical loads for a specified ANC limit of a population of
13 waterbodies to calculate a benchmark depositional load in which a specified percentage of the
14 population does not exceed their critical load. This approach uses the distribution of critical loads
15 from a population to derive a value that is intended to provide protection over a spatial area that
16 is larger than the individual catchment for which a single critical load may be calculated. An
17 example of this technique is calculated in section 5.5. The ecological indicator would be a single
18 value of ANC, and the acidification models would calculate the critical loads for the specified
19 ANC level for individual catchments across a spatial area. The deposition metric would be an
20 amount of deposition such that a specified percentage of a population of water bodies does not
21 exceed a critical load for the specified value of ANC. The deposition metrics could be calculated
22 for populations of catchments that are categorized according to acid-sensitivity, as described in
23 the next section.

24 ***5.2.2.4 How are modifying factors of the ecological response to deposition function*** 25 ***considered at the national-scale?***

26 As previously noted, critical loads for ANC vary at a small spatial scale, catchment by
27 catchment. As it is implausible to model the acidification status of every catchment in the U.S.,
28 an alternative is to develop a deposition metric for a population of catchments, as suggested in the
29 previous section. The following design options focus on relating acid-sensitivity, based on ANC,
30 to a feature(s) of the landscape at a national-scale by creating acid-sensitivity categories. A

1 population of catchments could then be defined to represent these categories and a representative
2 deposition metric chosen.

3 **Acid sensitivity classes based on bed rock geology**

4 Here an approach is presented in which ecosystem sensitivity to acidification is
5 categorized into classes based on bedrock geology/ lithology. The approach is supported by
6 conclusions from the ISA in which geologic bedrock is determined to be the governing factor
7 that drives ecosystem sensitivity to acidification (**ISA 3.2.4.1**). Specifically, geologic bedrock
8 with a low base cation supply leads to ecosystems that are sensitive to acidifying deposition. A
9 method to develop a deposition metric, based on the distribution of critical loads of a
10 representative population, for each category of acid-sensitivity is presented here.

11 A map was developed to capture the heterogeneity of geologic bedrock that occurs across
12 the eastern U.S. and link it to ecosystem acid-sensitivity (Fig5-4). The method is based on
13 Sullivan et al.(2007) in which 70+ primary lithologies are grouped into 5 categories of acid-
14 sensitivity, using ANC as the ecosystem indicator upon which acid-sensitivity is based. Sullivan
15 et al. (2007) evaluated multiple features of the landscape and found that geology is the landscape
16 parameter that governs ecosystem sensitivity to acidic deposition. The analysis in Sullivan et al.
17 2007 was conducted in the Southern Appalachian Mountains region, which included sites from
18 the states of GA, TN, NC, KT, VA and WV. EPA is conducting additional analyses to further
19 test the concept that lithology correlates to acid sensitivity in case study areas and in the western
20 U.S. EPA staff intends that some of these additional analyses will be available at for review in
21 the second draft of the policy assessment.

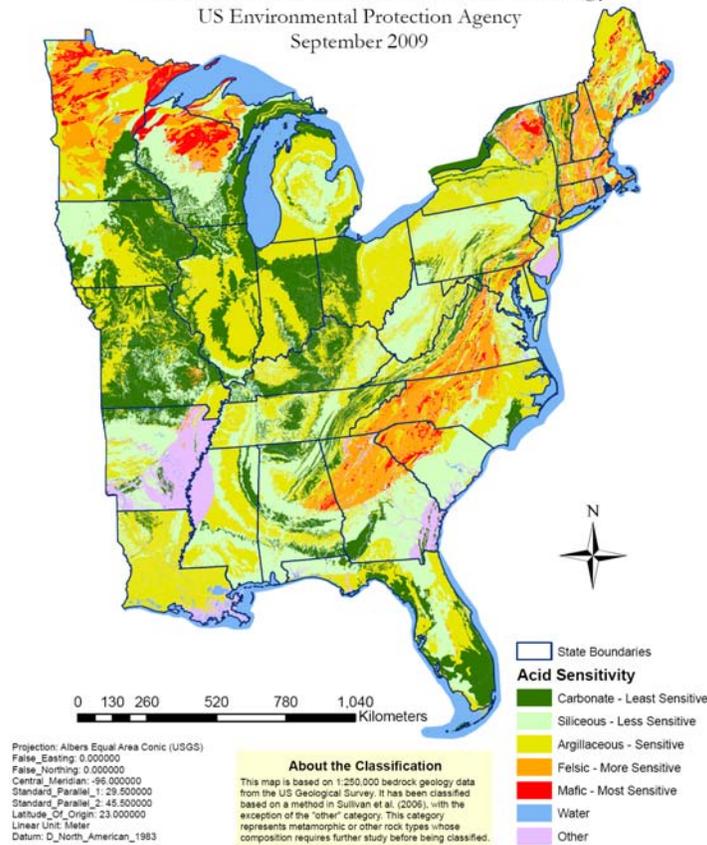
22 As previously stated, acidification often varies catchment by catchment. Therefore there
23 will be variation in terms of acid-sensitivity among catchments within each acid-sensitivity class
24 designated by the map. Despite this variation, lithology is a nationally applicable landscape
25 feature which is known to govern acid-sensitivity. Ultimate detail and rigor would be provided
26 by modeling deposition and consequential acidification of each catchment in the U.S., an
27 approach which would require knowledge of 17+ environmental parameters for each catchment.
28 However classification of the landscape into categories based on geology provides a national-
29 scale landscape feature to extrapolate the results of catchment-scale modeling.

Acid-Sensitive Areas of the Eastern United States

A Classification based on Bedrock Geology

US Environmental Protection Agency

September 2009



1

2

3

4

Fig 5-4. A map of acid sensitive areas of the Eastern U.S. developed from a lithology-based five-unit geologic classification system after methods in Sullivan et al. (2007).

5

Acid sensitivity based on multiple landscape features

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Although bedrock geology is a governing factor of acid sensitivity, multiple factors have been shown to contribute to sensitivity. Topography is a characteristic of the landscape that is often shown to correlate with acid-sensitivity, specifically low elevations, which generally receive some cations from higher elevation sites, are less sensitive than higher elevation sites (ISA 3.2.4.1). Could both topography and bedrock geology be included a national map of acid-sensitivity? A map of high elevation could be layered over the map of bedrock categories. If all high elevation areas were within the sensitive geologic categories, then the additional parameter would further refine the spatial resolution of sensitivity within the bedrock categorization. Moreover, the approach will provide more spatial detail on the sensitivity within areas already considered sensitive based on bedrock geology. It's unclear if elevation alone would help

1 identify new sensitive areas. It's also unclear if greater spatial resolution of sensitivity within
2 areas already identified as sensitive would be helpful in terms of relating the national-scale
3 landscape features to critical loads. Should additional multiple features be considered when
4 categorizing the landscape according to acid-sensitivity? We are providing this design option to
5 elicit comment; it is presented as a conceptual idea.

6 ***5.2.2.5 How is a deposition metric developed so that critical loads for catchments are***
7 ***aggregated to adequately represent classes of acid sensitivity based on***
8 ***geology?***

9 The values that represent a deposition metric for the acid-sensitivity categories could be
10 derived from the critical loads calculated for the case study analysis in the REA. The case study
11 sites (Adirondack and Shenandoah areas) occur in areas that are predominately composed of the
12 two most acid-sensitive types of bedrock geology. Therefore the case study sites would represent
13 those sensitivity categories. The deposition and atmospheric concentration tradeoff curves for a
14 specified level of ANC for each bedrock geology site would be based on a deposition metric
15 derived from the distribution of critical loads within the case study areas. It could be a central
16 value such as the mean or median value or a value representing a percentile of the distribution,
17 such as the 95th percentile. Central estimates, such as the mean, would likely not be projected to
18 achieve the target ANC of the majority of acid-sensitive ecosystems; therefore it may be
19 preferable to calculate the spatially aggregated value for some percentage of catchments to
20 project achieving the ANC for the more sensitive ecosystem types. For example, if projecting
21 85%, 90% or 95% of the aquatic ecosystems achieving the ANC is selected, then the deposition
22 metric that represents the critical load for the 85th, 90th or 95th percentile of the population would
23 be selected. An example calculation for the Adirondacks is presented in section 5.5.

24 ***5.2.2.6 How is reduced nitrogen appropriately considered in the deposition metric?***

25 Reduced forms of nitrogen deposition are quickly converted to nitrate in the environment
26 and use up the assimilative capacity of ANC at the same rate as oxidized forms of nitrogen
27 deposition; therefore, reduced nitrogen deposition must be accounted for in the watershed. There
28 are two basic approaches to accounting for the use of this assimilative capacity.

29 The suggested approach is to subtract the loadings of reduced forms of nitrogen derived
30 for a given spatial area from the deposition metric that represents selected percentage of critical

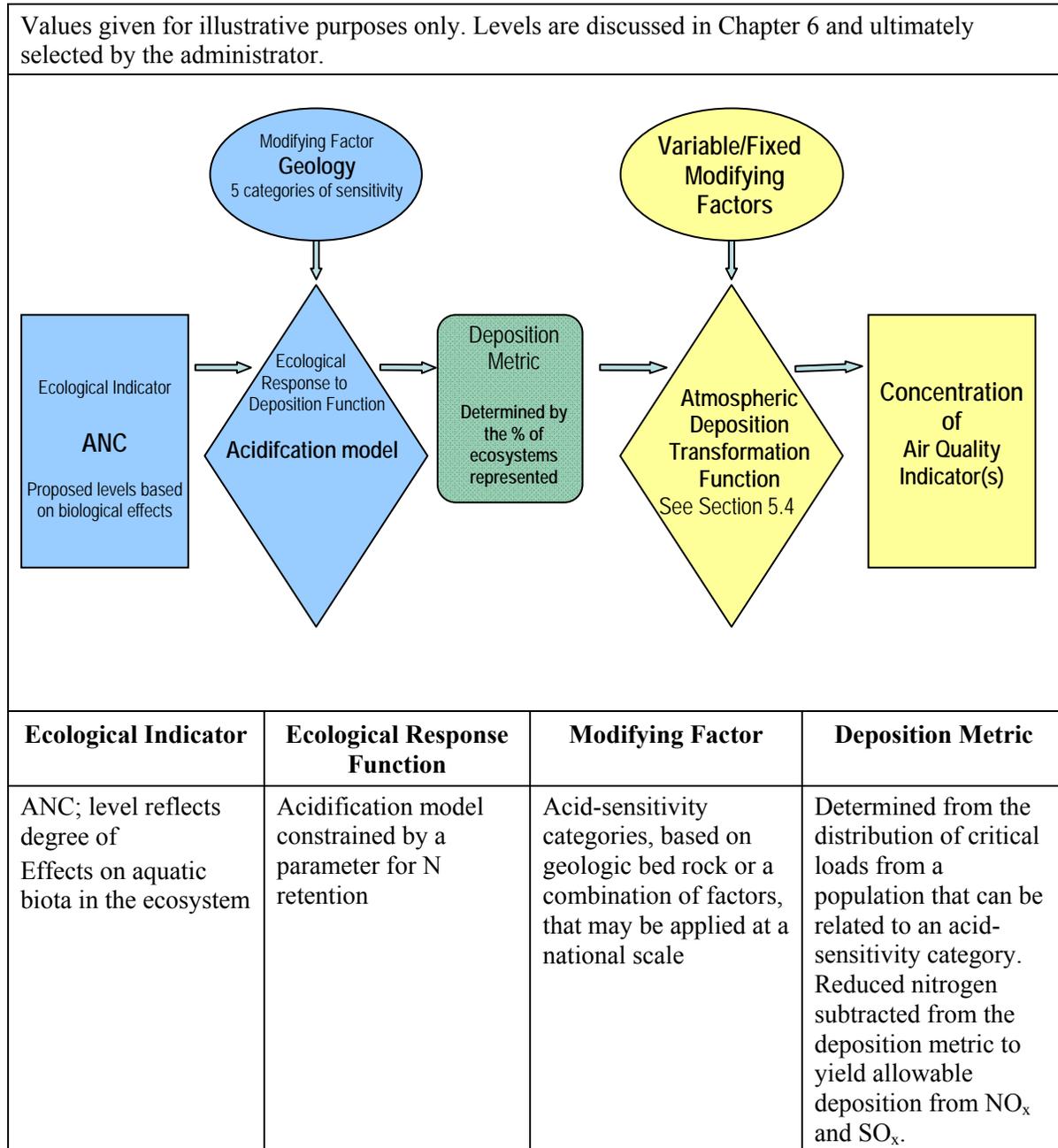
1 loads for a given population, such that the resultant deposition metric is for sulfur and oxidized
2 nitrogen only. This approach assumes that the reduced forms of nitrogen deposition are relatively
3 constant over time. This assumption could lead to over or under protection for an area depending
4 on whether the actual concentrations of reduced forms of nitrogen increase or decrease over
5 time. An example for how to subtract reduced nitrogen from the deposition metric based on
6 nitrogen and sulfur is given in section 5.5.

7 **5.2.2.7 Summary**

8 In summary, the ecological components of the conceptual design for a standard base on
9 aquatic acidification include the ecological indicator, ecological response function and its
10 modifiers and the deposition metric. A summary how each component is considered in the
11 conceptual design is given in Table 5-2. Using ANC as the ecological indicator, an approach is
12 suggested for using an acidification model constrained by a parameter for ecosystem N retention
13 to represent the ecological response function. The best way to calculate ecosystem N retention is
14 as of yet unclear. It is proposed that the national landscape is categorized in terms of criteria that
15 denote acid-sensitivity. It is well known that bedrock geology is a governing factor of acid-
16 sensitivity, in other words ecosystem response is modified across the landscape due in part to
17 bedrock geology. It is unclear if landscape categorization based on geology is the best approach
18 or other criteria/combination of criteria should be used.

19 The distribution of critical loads for a specified target ANC from a population of
20 catchments representing an acid-sensitivity category, based on geology or some combination of
21 factors, can be calculated. From this a deposition metric, an amount of deposition, could be
22 calculated such that a specified target percentage of the population of water bodies in the acid-
23 sensitivity category does not exceed a critical load for the specified value of ANC. Moreover, the
24 deposition metric would reflect both the selected level of ANC and the percentage of catchments
25 in the representative population that do not exceed their critical load. Reduced nitrogen
26 deposition, average over a determined spatial scale, would be subtracted from the deposition
27 metric yielding a value for allowable deposition from NO_y and SO_x. The deposition from NO_y
28 and SO_x would be converted to atmospheric concentrations of NO_y and SO_x by the methods
29 described in section 5.4.

Table 5-2. Summary of the ecological components of design option 1.



1 **5.3 ECOLOGICAL COMPONENTS OF THE STANDARD:**
2 **TERRESTRIAL ACIDIFICATION, TERRESTRIAL NUTRIENT**
3 **ENRICHMENT AND SURFACE WATER NUTRIENT**
4 **ENRICHMENT**

5 These effects were not included in the conceptual design for the first draft of the PA,
6 however a brief summary of our approach for developing standards that are protective of these
7 ecological effects follows.

8 **5.3.1 Terrestrial Acidification**

9 The deleterious effects of terrestrial acidification on tree species is indicated by base
10 cation to aluminum ratio (Bc:Al) of soils. Critical load functions were developed in the REA that
11 relate Bc:Al threshold values (0.6, 1.2 and 10) to values of N+S deposition using the simple mass
12 balance (SMB) model. The exceedance of these critical loads were calculated at the two study
13 sites and then extrapolated over 24 states. Like aquatic acidification, sensitivity of terrestrial
14 ecosystems to acidification is linked to the geologic bedrock. Moreover, areas that are sensitive
15 to aquatic acidification should also be sensitive to terrestrial acidification. Therefore, an
16 approach similar to that described for aquatic acidification could be developed. This would mean
17 that a critical load based on Bc:Al at either 1.2 or 10 would be calculated to protect a percentage
18 of the terrestrial landscape. This value would then be assigned to categories of acid sensitivity
19 based on geology.

20 This could result in two standards, one for aquatic ecosystems and one for terrestrial
21 ecosystems. This leads to the question, are aquatic or terrestrial ecosystem more sensitive? To
22 answer this question, an analysis was conducted in which critical loads for the Adirondacks and
23 Shenandoah case study areas were calculated based on the terrestrial ecosystem indicator, Bc:Al,
24 at the level of 1.2 and 10. The terrestrial critical loads were compared to the critical loads for
25 aquatic ecosystems. A full description of this analysis and results is available in Chapter 7, the
26 results are briefly summarized here. In the Adirondacks case study area, 7 of the 16 watersheds
27 had terrestrial critical acid loads (based on a Bc:Al of 10.0) that were lower and therefore more
28 sensitive to acidification than all the lakes in the watershed. However, when the terrestrial critical
29 loads were calculated with a Bc:Al soil solution ratio of 1.2, only 5 of the 16 watersheds were
30 protected by a terrestrial critical load that was lower than the aquatic critical loads of the lakes. In

1 the Shenandoah case study area terrestrial critical loads offered a higher level of protection than
2 aquatic critical loads in only one watershed. If two standards were proposed, the one that allows
3 lower ambient levels of NO_x and SO_x would be controlling in a given area.

4 **5.3.2 Terrestrial and surface water nutrient enrichment**

5 NO_x and NH_x are the main contributors to nitrogen deposition. The effects of nitrogen
6 deposition on terrestrial ecosystems and surface waters are many. Most notable are the effects on
7 ecosystem biodiversity found across the U.S and affecting multiple taxonomic groups including
8 vascular plants, algae, mycorrhiza and lichens (**ISA 3.3**). Unlike terrestrial and aquatic
9 acidification, there is no one, well-supported chemical or biological indicator of ecosystem
10 effects that occurs across the nation. In order to develop a NAAQS based on nitrogen enrichment
11 effects there needs to be one indicator that can be applied across the nation. It is possible that we
12 could develop an index in which information on different ecological indicators could be input
13 and the output would be an index score that could be consistently applied across the U.S. It is not
14 clear how to develop such an index.

15 Nitrogen critical loads are known for many ecosystem endpoints in the U.S. and are
16 published in the scientific literature. Additionally, critical loads for ecosystems in Europe, many
17 of which are similar to U.S. ecosystems, have been reported for over a decade, they are
18 continually refined through periodic assessments of the scientific literature, and they are
19 currently supported by a strong weight of peer-reviewed scientific information (**ISA 3.3**).
20 Additional critical load modeling was not conducted in the REA because of two factors. There
21 are numerous reports in the peer-reviewed scientific literature and there is no model available to
22 conduct such analysis for multiple endpoints and ecosystems. However, based on nitrogen
23 critical loads published in the literature, the REA evaluated the extent of the landscape
24 represented by those critical loads and their exceedances (**REA 5.0**).

25 A standard that integrates acidification and nutrient effects could conceptually be quite
26 simple. The total nitrogen deposition allowed for a deposition metric based on acidification could
27 be constrained so that it does not exceed a value based on a deposition metric for a nutrient
28 related effect.

5.3.3 Summary

Conceptual design of NO_x and SO_x NAAQS were not developed for terrestrial acidification and terrestrial/surface water nitrogen enrichment in the first draft PA, however a brief summary of a potential structure for these ecological effects is presented. The ecological indicator for terrestrial acidification would be Bc:Al because it relates to both atmospheric deposition of N+S and deleterious effects on tree growth. Critical loads would be related to acid-sensitivity categories and calculated according to similar methods presented for aquatic acidification effects. This could result in two standards, one for aquatic ecosystems and one for terrestrial ecosystems. If two standards were proposed, the one that allows lower ambient levels of NO_x and SO_x would be controlling in a given area. Unlike terrestrial and aquatic acidification, there is no one, well-supported ecological indicator of nitrogen deposition effects that occurs across the nation. In order to develop a NAAQS based on nitrogen enrichment effects there needs to be one indicator that can be applied across the nation. Although, the specifics of an approach are unclear, it may be possible that we could develop an index in which information on different ecological indicators could be input and the output would be an index score that could be consistently applied across the U.S. A standard that integrates acidification and nutrient effects could conceptually be quite simple. The total nitrogen deposition allowed for a deposition metric based on acidification could be constrained so that it does not exceed a value based on a deposition metric for a nutrient related effect.

5.4 LINKING DEPOSITION TO ATMOSPHERIC CONCENTRATION

5.4.1 Background

Atmospheric pollutants deposit onto land and water surfaces through at least two major mechanisms: direct contact with the surface (dry deposition), and transfer into liquid precipitation (wet deposition). The magnitude of each deposition process is related to the ambient concentration through the time-, location-, process- and species-specific *deposition velocity* (Seinfeld and Pandis, 1998) and can be conceptualized as:

$$Dep_i^{Dry} = v_i^{Dry} \cdot C_i^{Amb} \quad (1)$$

$$Dep_i^{Wet} = v_i^{Wet} \cdot C_i^{Amb} \quad (2)$$

1 where v_i^{Dry} and v_i^{Wet} are the dry and wet deposition velocities, Dep_i^{Dry} and Dep_i^{Wet} are the dry and
 2 wet deposition fluxes, C_i^{Amb} is the ambient concentration, and the i subscript indicates the
 3 pollutant species under study. The wet deposition velocity term is a conceptualized term and not
 4 a state variable that allows for the grouping of wet and dry deposition. The total deposition of
 5 each pollutant is

$$6 \quad Dep_i^{Tot} = Dep_i^{Dry} + Dep_i^{Wet} \quad (3)$$

7 Substituting Equations 1 and 2 into Equation 3 yields

$$8 \quad Dep_i^{Tot} = v_i^{Dry} \cdot C_i^{Amb} + v_i^{Wet} \cdot C_i^{Amb} \quad (4)$$

9 The total deposition of sulfur or nitrogen would therefore be:

$$10 \quad Dep_{S/N}^{Tot} = \sum_i (v_i^{Dry} + v_i^{Wet}) \cdot m_i \cdot C_i^{Amb} \quad (5)$$

11 where m_i is the molar ratio of the atom (sulfur or nitrogen) of interest to the i th pollutant.
 12 Ambient sulfur- and nitrogen-containing pollutants include gases such as sulfur dioxide (SO₂),
 13 ammonia (NH₃), various nitrogen oxides (NO, NO₂, HONO, N₂O₅), nitric acid (HNO₃), and
 14 organic nitrates such as peroxyacetyl nitrates (PAN); as well as particulate species such as sulfate
 15 (SO₄²⁻), nitrate (NO₃⁻), and ammonium (NH₄⁺). As discussed in chapter 4, the definitions of NO_y
 16 and SO_x species for the purposes of this review include the sulfur-containing species above and
 17 the above oxidized forms of nitrogen (NO_y); ammonia and ammonium are not currently included
 18 as listed pollutants (see Chapter 8 for an expanded discussion of the role of NH_x).

19 **5.4.2 Aggregation Issues**

20 Equation 5 provides a relationship for converting sulfur or nitrogen deposition to
 21 “equivalent” ambient concentrations. A major issue to consider during such conversion is the
 22 treatment of spatial, temporal and chemical resolutions of the deposition data and the resulting
 23 standards. Since the objective is to set an ambient air quality standard for total oxidized sulfur
 24 and nitrogen, and this is also the chemical resolution provided by the ecosystem models, it is
 25 convenient to use a relationship with the following form:

1
$$Dep_{S/N}^{Tot} = V_{S/N} \cdot C_{S/N}^{Amb} \tag{6}$$

2 where $V_{S/N}$ can be considered an aggregated deposition to ambient air transformation ratio,
3 referred to herein as the deposition transformation ratio, that relates total deposition of sulfur or
4 nitrogen to the total ambient concentration, and represents an average of the species specific v_i^{Tot}
5 ($= v_i^{Dry} + v_i^{Wet}$) values in Equation 5. The sulfur and nitrogen concentrations are the result of
6 applying the m_i values to the C_i^{Amb} values in Equation 5.

7 Since the deposition critical loads are expressed in terms of annual total deposition, the
8 most relevant averaging time for equivalent ambient concentrations is the annual average. Data
9 used to derive annual $V_{S/N}$ values will need to have the same spatial representativeness as the
10 depositional loads. To be clear, the deposition transformation ratio is not a state variable, but
11 simply is a calculated term that facilitates the linkage between deposition and concentrations
12 which is a necessary step in developing ambient air indicators that are used to assess compliance
13 with a NAAQS. There will be a tendency that is not scientifically defensible to compare
14 deposition ratios with deposition velocities that are uniquely determined on a species by species
15 basis influenced by numerous factors as discussed earlier.

16 **5.4.3 Air Quality Simulation Models**

17 Ideally, $V_{S/N}$ values would be derived for each area of interest from concurrently collected
18 sulfur and nitrogen deposition and concentration measurements. However, no monitoring
19 network currently exists that can provide such information. We therefore propose using output of
20 the CMAQ model for initial calculation of $V_{S/N}$ values.

21 CMAQ provides both concentrations and depositions for a large suite of pollutant species
22 on an hourly basis for 12 km grids across the continental U.S. Its comprehensive structure is
23 ideal for providing $V_{S/N}$ values that appropriately address the chemical and temporal aggregation
24 issues discussed above, and weighted spatial averages of the gridded data can be used for areas
25 that span multiple grid cells. Potential concerns with using CMAQ-predicted concentrations and
26 depositions for this purpose stem from the various, but unquantifiable uncertainties in model
27 formation and input data, which will be discussed in the next draft of this PAD.

28 CMAQ does not directly calculate or use $V_{S/N}$ values; instead the following procedures
29 are used in the code to model deposition:

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

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

8 3) v^{wet} values are not explicitly calculated. Wet deposition is derived from the cloud
9 processing module of CMAQ, which performs simulations of mass transfer into cloud droplets
10 and aqueous chemistry to incorporate pollutants into rainwater, all of which is conceptually
11 contained in the v^{wet} parameter in Equation 2.

12 Due to lack of direct measurements, no performance evaluations of CMAQ's dry
13 deposition calculations can be found; however, the current state of MCIP is the product of
14 research that has been based on peer-reviewed literature from the past two decades (EPA, 1999)
15 and is considered to be EPA's best estimate of dry deposition velocities. Some bias has been
16 found between CMAQ's wet deposition predictions and measured values (Morris et al., 2005);
17 recent analyses suggest that poor simulation of precipitation could be responsible for this (Davis
18 and Swall, 2006), which can potentially be dealt with by recalculating wet deposition using
19 precipitation measurements. Although the model is continually undergoing improvement,
20 CMAQ is EPA's state-of-the-science computational framework for calculating deposition
21 velocities, and was therefore the logical first choice as a source for V_{SN} values.

22 **5.4.4 Oxidized Sulfur and Nitrogen Pollutant Species**

23 Ideally, all possible air pollutant species that contribute to ecological adversity would be
24 considered for V_{SN} values. The pollutant list is constrained by the source of V_{SN} values, which is
25 currently CMAQ output. Table 1 lists the oxidized sulfur and nitrogen species currently available
26 in CMAQ whose data will be used for V_{SN} values.

27 One issue that needs explicit consideration is the contributions of particles larger than
28 $PM_{2.5}$ to sulfur and nitrogen deposition. A recent review of particle deposition measurements
29 (Grantz, Garner, and Johnson, 2003) showed that coarse particles generally deposit far more
30 sulfate and nitrate in forest ecosystems than fine particles. However, CMAQ does not currently

1 provide simulationsof coarse particulate sulfate and nitrate. This is an issue that needs to be
2 addressed by developers of either the model or the future SO_x/NO_x measurement network to set
3 scientifically sound standards.

4 **5.4.5 Example Calculations**

5 Figure 5-5 shows annual inverse $V_{S/N}$ values¹⁶ calculated for each 12 km grid in the
6 eastern and western domains for a 2002 CMAQ v4.6 simulation, which is the quantity that would
7 be used for conversion of deposition load tradeoff curves which illustrate (see Section 6) the
8 combinations of NO_y and SO_x concentrations that would correspond to an established critical
9 load. Figure 5-6 shows an example application of these ratios for a lake in the Adirondacks.
10 Deposition load tradeoff curves for this lake (see Section 6for their calculation) are multiplied by
11 the inverse $V_{S/N}$ value from the appropriate grid cell in Figure 1 to convert those depositions to
12 ambient concentrations of sulfur and nitrogen.

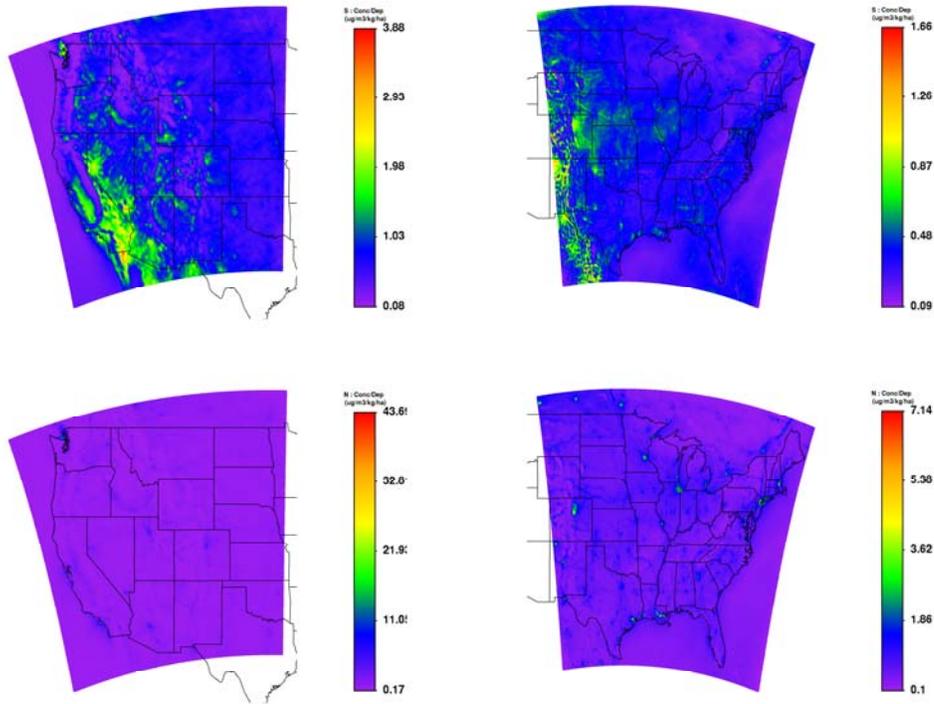
13 A CMAQ v4.7 simulation for multiple years (2002-2005) recently became available,
14 which was used to examine the inter-annual variability of inverse $V_{S/N}$ values. The grid-specific
15 coefficients of variation (CV) are shown in Figure 3. Figure 5-7 shows that CV values are
16 relatively small (< 25%) in the Adirondacks and Shenandoah case study areas. This suggests that
17 a 3-year average of the ratios may be a sufficiently stable representation of deposition velocities
18 for converting the deposition load curves to ambient concentrations in future applications.

¹⁶ Inverse $V_{S/N}$ values represent the multiplier needed to convert deposition levels into atmospheric concentrations of NO_x and SO_x.

Table 5-3. Oxidized sulfur and nitrogen species currently available in CMAQ simulations. Note that PNA concentrations are not available in current CMAQ extractions.

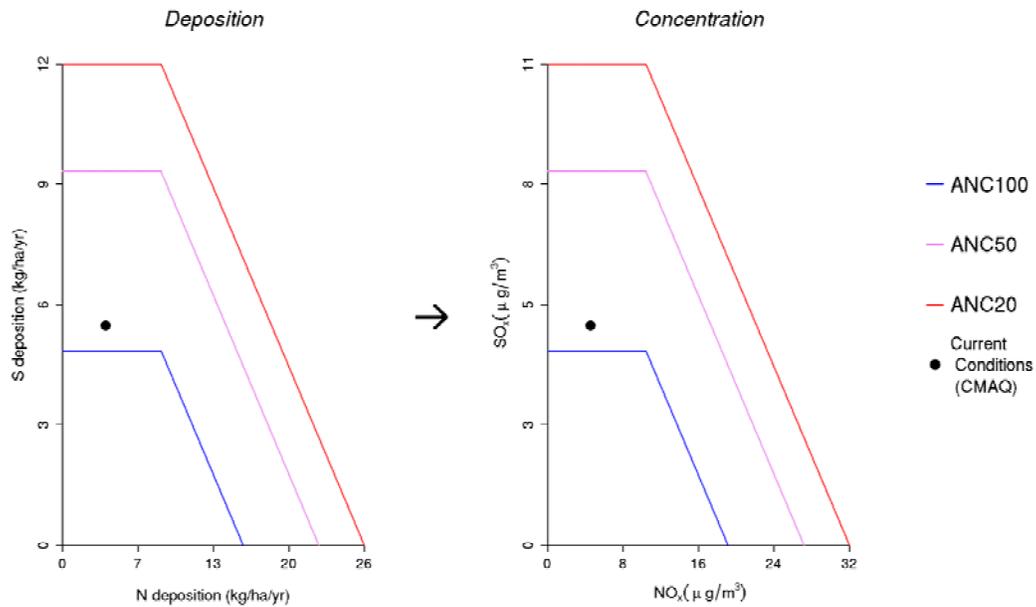
Pollutant Class	Chemical/CMAQ Species Symbol	Species Name	Notes
Sulfur Oxides	SO_2	Sulfur Dioxide	
	SO_4^{2-}	Sulfate	Predominantly particulate
Nitrogen Oxides	NO	Nitrogen Oxide	
	NO_2	Nitrogen Dioxide	
	NO_3^-	Nitrate	Predominantly particulate
	N_2O_5	Dinitrogen pentoxide	
	HONO	Nitric Acid	
	PAN	Peroxyacetyl nitrate	
	PANX	Higher order peroxyacetyl nitrates	
	NTR	Organic Nitrates	
	PNA	HNO_4	

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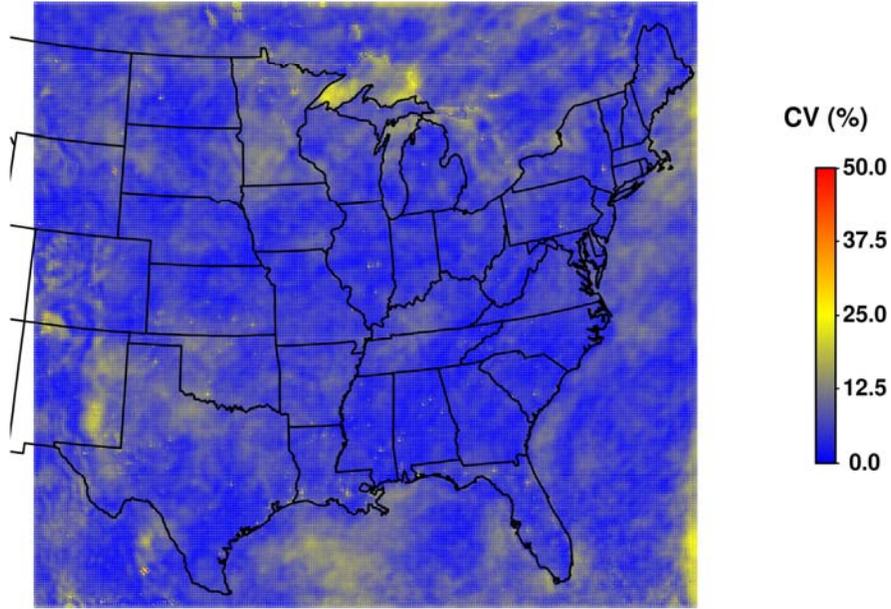
Figure 5-5. $V_{S/N}$ values for each grid cell in the eastern (right) and western (left) U.S. domains. The top maps are for sulfur and the bottom are for nitrogen.



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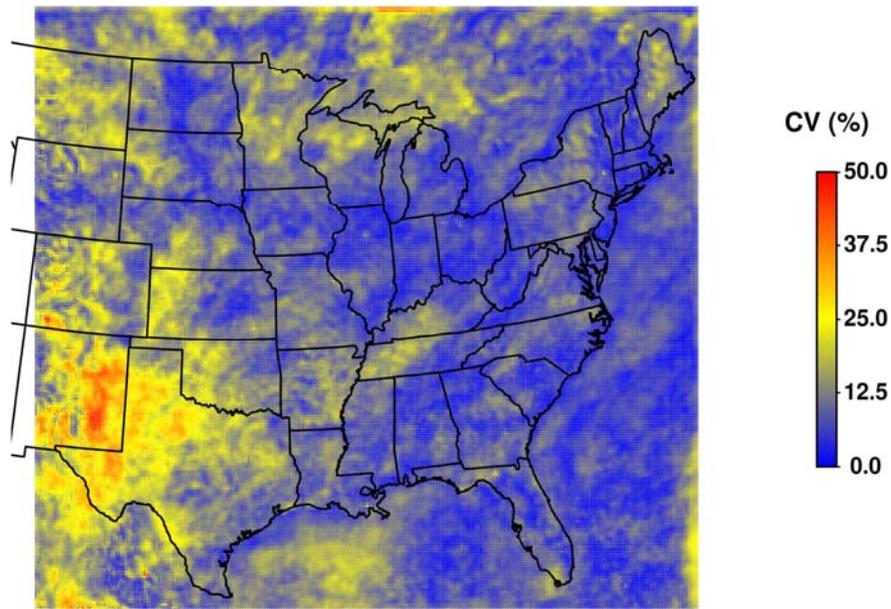
Figure 5-6. Schematic Diagram illustrating the procedure for converting deposition tradeoff curves of sulfur and nitrogen to atmospheric concentrations of SO_x and NO_x .

Coefficient of Variation of N Conc/Dep ratio, 2002-2005



1 a)

Coefficient of Variation of S Conc/Dep ratio, 2002-2005



2 b)

Figure 5-7. Inter-annual coefficients of variation (CV) of a) nitrogen and b) sulfur $V_{S/N}$ values, based on a series of 2002-2005 CMAQ v4.7 simulation.

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1 **5.5 EXAMPLE CALCULATION FOR THE CONCEPTUAL DESIGN**
2 **AND DERIVATION OF AAPI**

3 Section 5.2 describes a proposed conceptual design for a NO_x and SO_x NAAQS based on
4 aquatic acidification. To summarize the process of acidification, atmospheric deposition of NO_x
5 and SO_x contributes to acidification in aquatic ecosystems through the input of acid anions, such
6 as NO₃⁻ and SO₄²⁻. The acid-base balance of headwater lakes and streams is controlled by the
7 level of this acidifying deposition of NO₃⁻ and SO₄²⁻ and a series of biogeochemical processes
8 that produce and consume acidity in the watershed. The biotic integrity of freshwater ecosystems
9 is then a function of the, acid-base balance and the resulting acidity-related stress on the biota
10 that occupy the water. Given some “benchmark level” of ANC [ANClimit]) that appropriately
11 protects biological integrity, the depositional load of acidity DL(N+S) is simply the input flux of
12 acid anions from atmospheric deposition that result in a surface water ANC level equal to the
13 [ANClimit] when balanced by the sustainable flux of base cations input and the sinks of nitrogen
14 and sulfur in the watershed catchment.

15 **5.5.1 Example calculation for the conceptual design**

16 This section summarizes and provides an example calculation of the approach proposed
17 by EPA staff to calculate (1) the acid-base balance of a catchment for a specified ANC level, (2)
18 the N and S deposition tradeoff curves for a deposition metric, which represents a specified
19 percentage of the total population of water bodies that do not exceed their critical load at a
20 specified ANC level and (3) the conversion from tradeoff curves for N and S deposition to those
21 for atmospheric concentrations of NO_y and SO_x. The equations representing deposition loads and
22 associated tradeoff curves for a specified level of ANC are the basis for deriving the form of the
23 standard discussed above in section (5.5.2).

24 Equation (1) expresses the model that we suggest using to determine the amount of N and
25 S that may be deposited onto a catchment to yield a specified level of ANC.

26
$$DL_{ANC\lim}(N + S) = ([BC]_O^* - [ANC_{\lim}])Q + N_{eco} \quad (1)$$

27 where,

1 $DL_{ANClim}(N+S)$ = depositional load of S and N that does not cause the ecosystems to exceed a
 2 given ANC_{lim}
 3 $[BC]_0^*$ = the preindustrial concentration of base cations (equ/L)
 4 ANC_{limit} = a “target” ANC level (equ/L)
 5 Q = surface water runoff (m/yr) (this is typically equal to precipitation – evapotranspiration)
 6 N_{eco} = nitrogen retention and denitrification by terrestrial catchment and nitrogen retention in the
 7 lake

8 The term N_{eco} could be derived multiple ways. The first is by taking the mean value
 9 calculated to represent the long-term amount of N an ecosystem can immobilize and denitrify
 10 before leaching (i.e. N saturation) that is derived from the FAB model. This approach requires
 11 the input of multiple ecosystem parameters. Its components are expressed by eq 2.

$$12 \quad N_{eco} = fN_{upt} + N_{ret} + (1 - r)(N_{imm} + N_{den}) \quad (2)$$

13 where,

14 N_{upt} = nitrogen uptake by the catchment
 15 N_{imm} = nitrogen immobilization by the catchment soil
 16 N_{den} = denitrification of nitrogen in the catchment,
 17 N_{ret} = in-lake retention of nitrogen
 18 f = forest cover in the catchment (dimensionless parameter)
 19 r = fraction lake/catchment ratio (dimensionless parameter)

20
 21 The second approach for estimating N_{eco} is to take the difference between N deposition
 22 and measured N leaching in a catchment as expressed by eq 3.

$$23 \quad N_{eco} = DL(N) - N_{leach} \quad (3)$$

24 N deposition is composed of NH_x deposition (NH_{xdep}) and NO_y deposition. It is known that
 25 NH_{xdep} contributes to acidification, however the definition of NO_x in the CAA does not include
 26 NH_x , and as such is not defined to provide protection from the acidifying effects of NH_x .
 27 Therefore, $DL_{ANClim}(N)$ is separated into NH_x and NO_y .

$$28 \quad DL_{ANClim}(Noy + S) = [DL_{ANClim}(N) - DL_{ANClim}(NHx)] + DL_{ANClim}(SOx) \quad (4)$$

1 Equation 1 and 4 will differ catchment by catchment because the acid-base balance of a
2 catchment is a function of site-specific characteristics. However, for the standard it is desirable to
3 calculate a deposition load for a specified ANC not for an individual catchment, but a larger
4 population of catchments. The site specific values from equation 1 can be used to derive such a
5 deposition loading, here called the deposition metric, which represents a group or percentage of
6 water bodies that reach a specified ANC (or higher). For example, if it is desired that all water
7 bodies reach a specified ANC, the allowable amount of deposition for all water bodies is equal to
8 the lowest value calculated from equation 1 for the population of water bodies. Because the
9 deposition metric represents a percentage of individual catchments from a population of water
10 bodies, and not an individual catchment like $DL_{ANClim}(S+N)$, the deposition metric is noted by
11 the follow abbreviation $DL_{\%ECO}$.

12 As an example of the above approach, we evaluate the population of 169 waterbodies in
13 the Adirondacks used in the REA analysis. For each individual waterbody in the population
14 $DL_{ANClim}(S+N)$ at $ANC_{lim} = 50$ was calculated using the two equations for deriving the Neco
15 term (eq 2 and 3). The distribution of deposition loads for the population was assessed and Table
16 5-5 shows the a few selected values for $DL_{\%ECO}$. The mean value for $DL_{\%ECO}$ for the 169 water
17 bodies is presented, as well as the values for which 50, 75, 85, 95 and 100% of the water bodies
18 in the population will not exceed their critical load at $ANC=50$. Note, only 32% of water bodies
19 would not exceed their critical load at $ANC=50$ for the mean value $DL_{\%ECO}$ because variability is
20 high in the data set. The deposition and atmospheric concentration tradeoff curves for $DL_{\%ECO}$
21 equal to 32% and 50% are plotted in the subsequent figures. The Administrator will choose
22 which % of water bodies are projected to reach a targeted level of ANC as part of the overall
23 decision on the elements of the standard; this selection may be higher or lower than the examples
24 given here.

Table 5-4. Example Calculations for Determining the Percent of Water Bodies Achieving Target ANC Levels

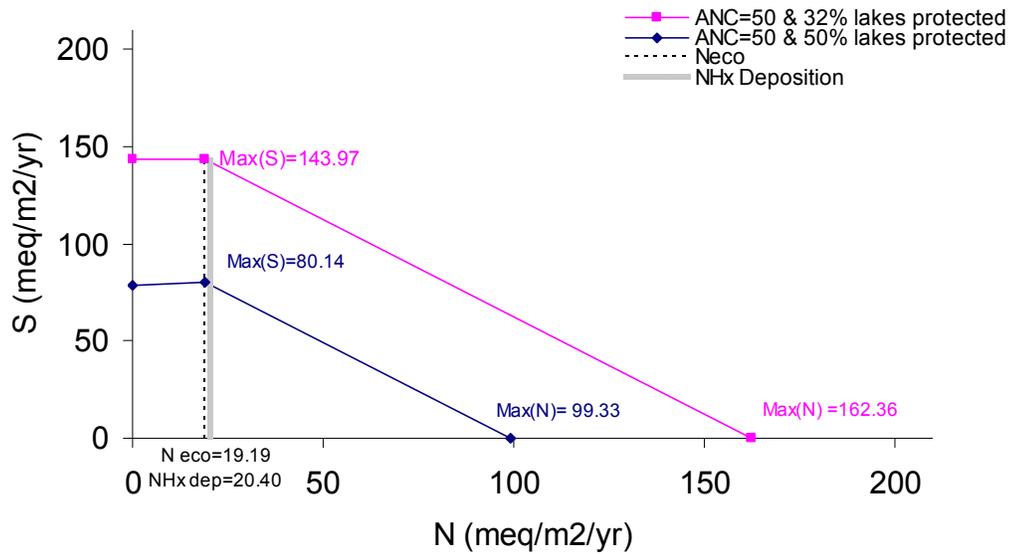
This example is based the population of DL_{ANCLim} for and ANC=50 for 169 catchments in the Adirondacks. These catchments occur across on three categories of geologic sensitivity. We could separate the DL_{ANCLim} values into sensitivity categories (if info is available) and do the analysis for each category or calculate one DL_{ANCLim} for combined geologic categories. Units are in meq/m²/yr.

	NH _x dep	Neco (eq2)	DL _{%ECO} (S+N) using N _{eco} eq 2	Neco (eq3)	DL _{%ECO} (S+N) using N _{eco} eq 3	% of lakes within the population that have ANC ≥ 50
Mean	20.40	19.19	162.36	63.95	207.55	31.7%
St dev	3.22	3.03	162.92	11.15	165.42	
St er	0.25	0.23	13.04	0.86	13.24	
Rank %tile						
50%			99.33		139.22	50%
75%			65.62		110.37	75%
85%			54.89		95.53	85%
95%			45.12		83.99	95%
100%			30.22		59.07	100%

1
2 The deposition tradeoff curves for N and S based on DL_{%ECO} at ANC=50 using the two
3 approaches for Neco and protective of 32 and 50% of the population of water bodies, are plotted
4 on Fig 5-8 and 5-9. The values for the maximum deposition values for N and S are given in
5 Table 5-5.
6

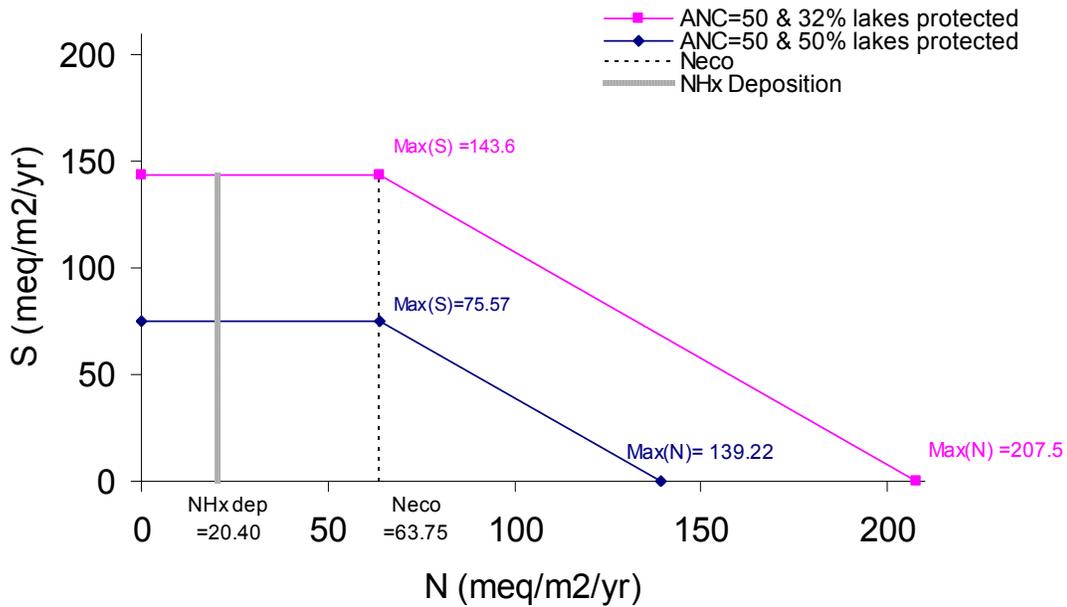
Table 5-5. Values for N and S deposition tradeoff curves for ANC = 50, protecting 32 and 50% of the population, in Adirondacks case study area as illustrated on Fig 5-8 and Fig 5-9. Units are in meq/m²/yr unless noted otherwise.

% protection		NH _x dep	Neco	DL _{%ECO} (max N)	DL _{%ECO} (max S)	DL _{%ECO} (max NOY)
32	Eq 2	20.4	19.19	162.36	143.97	141.96
50	Eq 2	20.4	19.19	99.33	80.14	78.9.3
32	Eq 3	20.4	63.75	207.5	143.6	187.15
50	Eq 3	20.4	63.75	139.22	75.27	118.82



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Figure 5-8. Tradeoff curve for S and N deposition to protect from aquatic acidification in the Adirondacks using N_{eco} equation 2.



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Figure 5-9. Tradeoff curve for S and N deposition to protect from aquatic acidification in the Adirondacks using N_{eco} equation 3.

1 As previously stated, it is known that NH_x deposition (NH_{xdep}) contributes to
 2 acidification. However, the criteria pollutant listed by EPA pursuant to section 108 (a) of the Act
 3 is oxides of nitrogen does not include NH_x, and as such is not defined to provide protection from
 4 the acidifying effects of NH_x. Therefore, in order to represent the role of NH_{xdep} as a component
 5 of acidification it is subtracted from DL_{%ECO}(S+N). The difference is the total allowable
 6 deposition from NO_y and SO_x to protect a selected % of catchments in the population at a
 7 selected level of ANC [DL_{%ECO} (S + NO_y)] as expressed in equation 5.

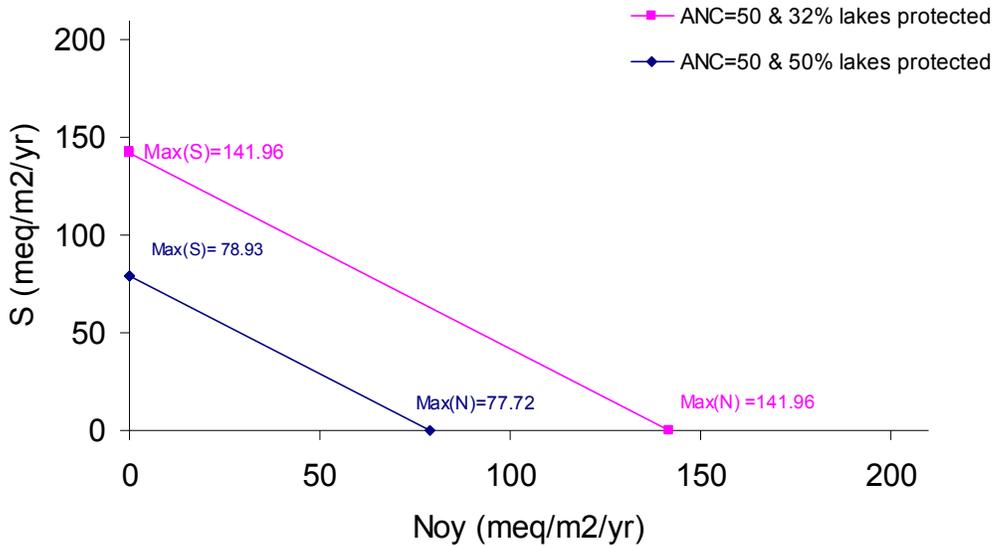
$$8 \quad DL_{\%ECO}(N_{OY} + S) = DL_{\%ECO}(N + S) - NH_{X_{DEP}} \quad (5)$$

9 The NO_y and S deposition tradeoff curves for ANC =50, protecting 32 and 50% of the
 10 water bodies, are presented in Table 5-6 and plotted on Fig 5-10 and 5-11. If NH_x deposition is
 11 greater than Neco, then Neco disappears from the tradeoff curve (i.e. Fig 5-11).

Table 5-6. Values for NO_y and S deposition tradeoff curves for ANC = 50, protecting 32 and 50% of the population in Adirondacks case study area as illustrated on Fig 5.10 and Fig 5.11. Units are in meq/m2/yr unless noted otherwise.

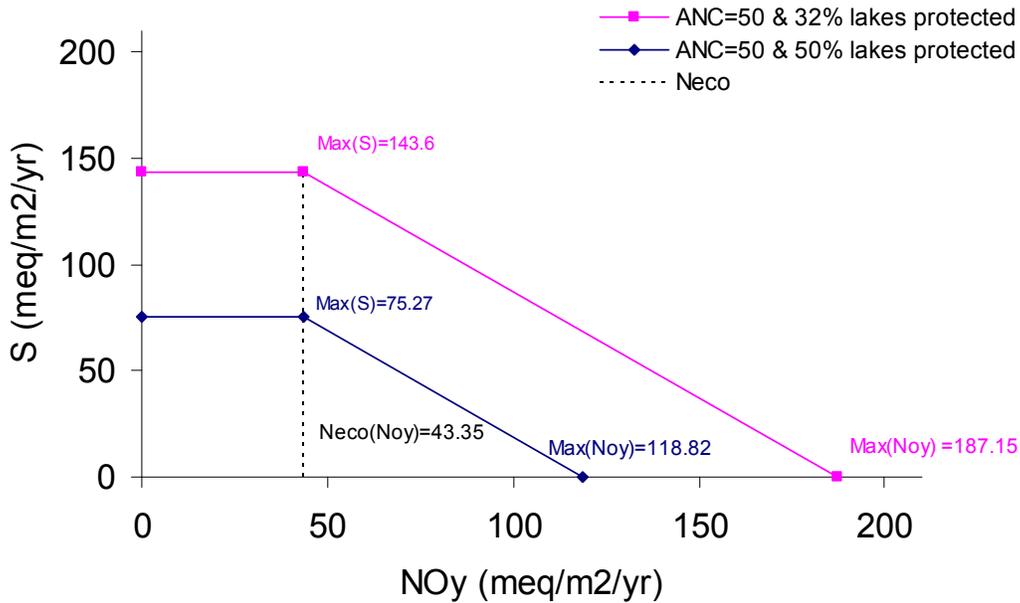
% protection		NH _x dep	Neco (Noy)	DLmax(S)	DLmax(Noy)
32	Eq 2	20.4	Neco < NH _x dep	141.96	141.96
50	Eq 2	20.4	Neco < NH _x dep	78.93	78.93
32	Eq 3	20.4	43.35	143.6	187.15
50	Eq 3	20.4	43.35	75.27	118.82

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Figure 5-10. Tradeoff curve for S and NO_y deposition to protect from aquatic acidification in the Adirondacks using N_{eco} equation 2.



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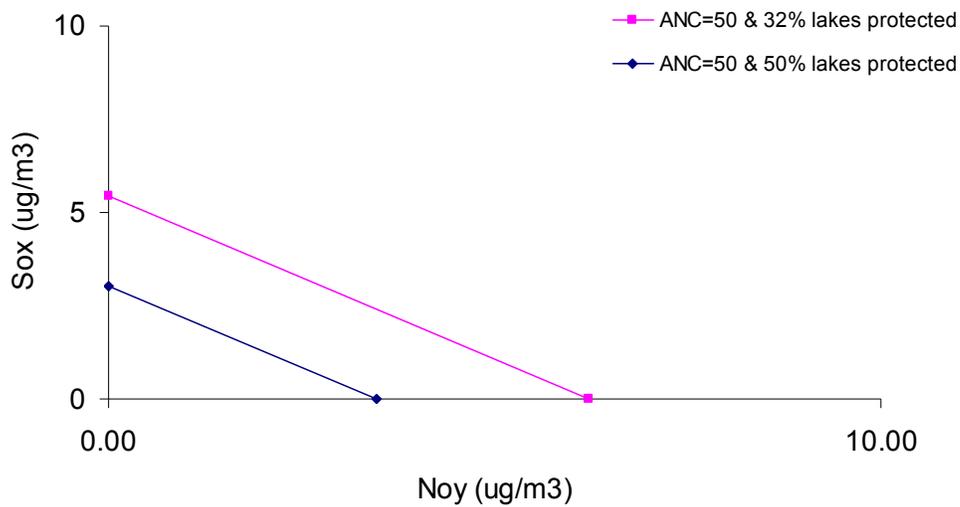
Figure 5-11. Tradeoff curve for S and NO_y deposition to protect from aquatic acidification in the Adirondacks using N_{eco} equation 3.

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The tradeoff curves for the atmospheric concentration of NO_y and SO_x are presented in Fig 5-12 and 5-13. Deposition values for NO_y and S (from Table 5-6, Fig 5-10 and 5-11) were multiplied by the ratio of concentrations to depositions (previously referred to as aggregate

1 effective deposition velocities¹⁷) for NO_x and SO_x ($V_{SO_x} = 0.03824755 \mu\text{g}/\text{m}^3/\text{meq}/\text{m}^2$ and
 2 $V_{NO_x} = 0.04386373 \mu\text{g}/\text{m}^3/\text{meq}/\text{m}^2$). This is expressed in equation 5. These velocities were
 3 calculated by taking the median value of the concentration of oxidized N to deposition of
 4 oxidized N ratio in CMAQ for all grid cells over the Adirondack case study area.

$$5 \quad [DL_{\%ECO}(N_{OY}) \cdot V_{noy}] + [DL_{\%ECO}(S) \cdot V_{sox}] = DL_{\%ECO}(N + S) - NHx_{DEP} \quad (6)$$



6
 7 **Figure 5-12.** Tradeoff curve for atmospheric concentration of SO_x and NO_y to
 8 protect from aquatic acidification in the Adirondacks using N_{cco} equation 2.

¹⁷ Note to reviewers: in previous drafts we have referred to the ratios of deposition to concentration for NO_y and SO_x as “aggregate effective velocities.” We are revisiting this choice of terms, as it is not as accurate a reflection of the parameter as we might prefer. The concern with continuing to use the term “velocity” in this context is that it will be misinterpreted by the scientific community, and in order to avoid confusion, we will likely replace the term with “deposition ratio” or some other term that more accurately describes the parameter.

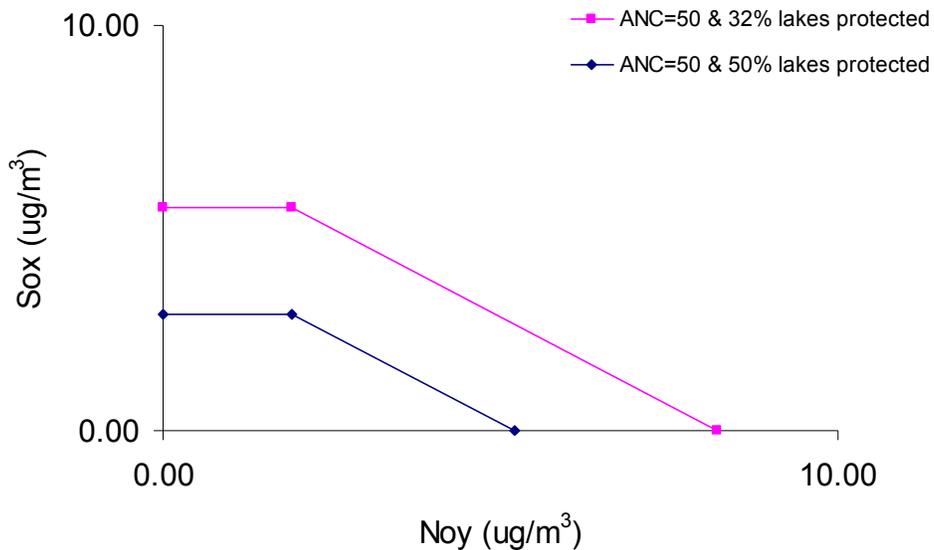


Figure 5-13. Tradeoff curve for atmospheric concentration of SO_x and NO_y to protect from aquatic acidification in the Adirondacks using N_{eco} equation 3.

5.5.2 Derivation of the Atmospheric Acidification Potential Index (AAPI):

While the conceptual framework above provides a means for calculating tradeoff curves associated with a specific level of protection (indicated by a target ANC level) and a specific percentage of ecosystems protected within an overall sensitive area, it does not provide a clearly integrated statement that can be expressed as a level such as would be needed for the secondary standard. The goal of this development of the AAPI is to create an index which can be applied across the nation to convey the potential of an ecosystem to become acidified from atmospheric deposition.

The definition of the AAPI form considered here is:

Annual Average AAPI: Natural background ANC minus the contribution to acidifying deposition from NH_x , minus the acidifying contribution of NO_y and SO_x . This term is essentially a calculated ANC value that represents a percentage of catchments in a population.

In order to derive the AAPI, we start with the basic framework of critical loads discussed in the example above.

The approach used to calculate N and S deposition values for a specified ANC at a catchment-scale is expressed in Equation 1. The deposition value for a specified ANC will vary

1 from catchment to catchment based on how the properties that counterbalance the acidifying
 2 deposition vary among catchments. Equation 5 expresses how to calculate a deposition metric for
 3 a specified ANC for a population of waterbodies that could represent a national acid-sensitivity
 4 category. Moreover, the quantity of deposition equal to a specified ANC limit (i.e. critical load)
 5 will vary in eq 1 and 5 depending on the characteristics of the catchment or population of
 6 catchments, respectively. The goal for a secondary NO_x and SO_x NAAQS is to develop a form
 7 for the standards that allows us to set a single value for the standard across the U.S. To
 8 accomplish this, we rearrange equation (1) to solve for ANC (place ANC on the left hand side of
 9 the equation):

$$10 \quad Q \cdot ANC_{lim} = N_{eco} + [BC]_o^* \cdot Q - [DL(N) + DL(S)] \quad (7)$$

$$11 \quad ANC_{lim} = \frac{1}{Q} N_{eco} + [BC]_o^* - \frac{1}{Q} [DL(N) + DL(S)] \quad (8)$$

12 In order to develop a form for the standard in which the level can be expressed as a single
 13 national value related to protection against effects that occur at specific values of ANC, a
 14 simplified version of equation (8) is:

$$15 \quad ANC_{lim} = g(\cdot) - \frac{1}{Q} DL(N + S) \quad (9)$$

16 where, $g(\cdot)$ = sustainable flux of base cations from the ecosystem + ecological sinks of N. This
 17 term is equivalent to the pre-industrial ANC level, or the natural background ANC, expressed as:

$$18 \quad g(\cdot) = \frac{1}{Q} \cdot N_{eco} + [BC]_o^* \quad (10)$$

19 Building from equation 9, total nitrogen deposition is split into oxidized and reduced
 20 nitrogen because we need to be able to specify the standards in terms of oxides of nitrogen, and
 21 so the contribution of reduced nitrogen has to be separated.

$$22 \quad ANC_{lim} = g(\cdot) - \frac{1}{Q} [DL(N_{ox}) + DL(S)] - \frac{1}{Q} \cdot DL(NHx) \quad (11)$$

1 where,
2 DL(NO_x)= the depositional load of oxidized nitrogen
3 DL(NH_x)= the depositional load of reduced nitrogen, NH_x.

4
5 In order to judge whether an ecosystem or group of ecosystems meets the ANC_{limit} given
6 observed NO_y and SO_x levels, the associated depositional loadings of NO_y and S can be
7 compared directly against calculated deposition tradeoff curves (eq 4), atmospheric
8 concentrations of NO_y and SO_x can be compared against the atmospheric concentration tradeoff
9 curves (eq 5) or, loadings of NO_x and SO_x can be input into the following equations to obtain the
10 calculated value of ANC, equal to ANC*:

$$11 \quad ANC^* = g(\cdot) - [L(NO_y) + L(SO_x)] - L(NH_x) \quad (11)$$

12 where,
13 ANC*= the calculated value of ANC given loadings of N and S for comparison against an
14 ANC_{limit}.
15 L(N_{ox}+S)= the load of N_{ox}+S anions based on observed atmospheric concentrations of NO_y and
16 SO_x
17 L(NH_x) = the load of reduced nitrogen deposition
18 [Note that L(N) = L(N_{ox}+NH_x)]

19
20 In equation 11, the ANC* will vary based on the deposition load inputs of N_{ox}, NH_x and
21 S at the site of interest. The deposition loads caused by NO_y and S and NH_x are inputs, leading to

$$22 \quad ANC^* = g - \frac{1}{Q} [L(N_{ox}) + L(S)] - \frac{1}{Q} \cdot DL(NH_x) \quad (12)$$

23 If ANC* < ANC_{lim}, then the deposition of N and S exceeds the deposition load to maintain
24 ANC_{limit}. ANC* is still representative of the calculated ANC based on specific catchment level
25 estimates of g, Q and NH_x.

26 AAPI is equivalent to the equation for calculating ANC* when the catchment specific
27 values for g in equation (9) in Section 5.5.1. are replaced by representative values for acid
28 sensitive areas (based on a percentile of water bodies targeted for an ANC level selected by the

1 Administrator), Q and NH_x are replaced by average values for aggregate ecosystem areas, and
2 L(NO_x) and L(S) are replaced by terms translating atmospheric NO_y and SO_x into deposition:

3
$$AAPI = g(\cdot) - \frac{1}{Q} L(NHx) - \frac{1}{Q} [V_{NOy} \cdot NOy + V_{SOx} \cdot SOx] \quad (13)$$

4 where NO_y and SO_x are concentrations of NO_y and SO_x, respectively, V_{NO_y} and V_{SO_x} are the
5 ratios of deposition to concentrations (deposition transformation ratios) for NO_y and SO_x,
6 respectively.

7 **5.6 REFERENCES**

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7

6. OPTIONS FOR ELEMENTS OF THE STANDARD

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

EPA has historically established NAAQS so that the locally-monitored ambient concentration of an air pollutant indicator is compared against a specified numerical level of atmospheric concentration, using a specified averaging time and statistical form. For example, the current secondary standard for oxides of nitrogen uses ambient concentrations of NO₂ as the indicator. Attainment is determined by comparing the annual arithmetic mean of the measured maximum daily 1-hour NO₂ concentrations, for a calendar year, against the level of 0.053 ppm. As discussed in Chapters 4 and 5, a standard using this kind of approach for defining indicator, averaging time, form, and level is not the most appropriate way to protect sensitive ecosystems from effects associated with ambient concentrations of NO_x and SO_x. Moreover, the inherently complex and variable linkages between ambient concentrations of NO_x and SO_x, their deposited forms of nitrogen and sulfur, and the ecological responses that are associated with public welfare effects call for consideration of a more complex and ecologically relevant design of the standard that reflects these linkages.

Chapter 5 provided a conceptual framework for a secondary standard that is designed to provide protection of ecosystems against the effects associated with deposition of ambient concentrations of NO_x and SO_x. This conceptual framework takes into account variable factors, such as atmospheric and ecosystem conditions that modify the amounts of deposited NO_x and SO_x, and the associated effects of deposited N and S on ecosystems. Based on the conceptual framework described in Chapter 5, this chapter provides a set of potential options for specifying the elements of the framework to define a secondary standard for NO_x and SO_x. Our development of options for the standards recognizes the need for a nationally applicable standard for protection against adverse effects to public welfare, while recognizing the complex and heterogeneous interactions between atmospheric concentrations of NO_x and SO_x, deposition, and

1 ecological response. These options will include elements of the framework related to the air
2 quality indicator, the averaging time, the form, and the level, which are based on the ecological
3 indicator, the ecological response to deposition function, the deposition metric, and the
4 atmospheric deposition transformation function.

5 To make the transition from the conceptual framework in Chapter 5, which is developed
6 largely around the concept of critical loads, to elements of the standard, we propose to focus on
7 developing a form of the standard that is based on the concepts of critical loads of NO_x and SO_x
8 deposition linked to target ANC values, recognizing the limitations in available data and related
9 uncertainties. Our goal in developing the form of the standard is to create an index, directly
10 expressed in terms of atmospheric concentrations of NO_y and SO_x, that can be applied across the
11 nation to convey the potential of an ecosystem to become acidified from atmospheric deposition.

12 This chapter is structured around questions related to the various elements of a standard.
13 The chapter begins in section 6.1 with a discussion of atmospheric indicators. Section 6.2 then
14 discusses averaging times for the atmospheric indicators. Section 6.3 suggests a possible
15 ecologically relevant form of the standard. Section 6.4 provides a discussion of issues regarding
16 the spatial area over which a standard might be evaluated, and related issues regarding spatial
17 averaging within areas. Section 6.5 discusses options for specifying target levels for the
18 ecological indicator for aquatic acidification. Section 6.6 addresses issues relating to monitoring
19 of the atmospheric indicators. Section 6.7 concludes with a discussion of potential ranges of
20 levels for the standard.

21 **6.1 WHAT ATMOSPHERIC INDICATORS OF OXIDIZED NITROGEN**
22 **AND SULFUR ARE APPROPRIATE FOR USE IN A SECONDARY**
23 **NAAQS THAT PROVIDES PROTECTION FOR PUBLIC WELFARE**
24 **FROM EXPOSURE RELATED TO DEPOSITION OF N AND S?**
25 **WHAT AVERAGING TIMES AND STATISTICS FOR SUCH**
26 **INDICATORS ARE APPROPRIATE TO CONSIDER?**

27 Staff concludes that indicators other than NO₂ and SO₂ should be considered as the
28 appropriate pollutant indicators for protection against the acidification effects associated with
29 deposition of NO_x and SO_x. This conclusion is based on the recognition that all forms of

1 oxidized nitrogen and sulfur in the atmosphere contribute to deposition and resulting
2 acidification, and as such NO₂ and SO₂ are incomplete indicators. Furthermore, staff concludes
3 that NO_y (total oxidized nitrogen) should be considered as an appropriate indicator for oxides of
4 nitrogen. NO_y is defined as NO_x (NO and NO₂) and all oxidized NO_x products: including NO,
5 NO₂, and all other oxidized N-containing compounds transformed from NO and NO₂ (Finlayson-
6 Pitts and Pitts, 2000). As described in Chapter 4, this set of compounds includes NO₂ + NO +
7 HNO₃ + PAN + 2N₂O₅ + HONO + NO₃ + organic nitrates + particulate NO₃. Staff concludes that
8 SO_x should be considered as an appropriate indicator for oxides of sulfur. SO_x includes sulfur
9 monoxide (SO), sulfur dioxide, sulfur trioxide (SO₃), and disulfur monoxide (S₂O), and
10 particulate-phase S compounds that result from gas-phase sulfur oxides interacting with particles.

11 In principle, measured NO_y based on catalytic conversion of all oxidized species to NO
12 followed by chemiluminescence NO detection is consistent with this definition. We recognize
13 the caveats associated with instrument conversion efficiency and possible inlet losses which are
14 discussed in Section 5.6. The development of the function that converts atmospheric
15 concentrations of NO_y and SO_x to N and S deposition which incorporates NO_y estimates is based
16 on the Community Multi-scale Air Quality (CMAQ) model (EPA, 1999). CMAQ treats the
17 dominant NO_y species as explicit species while the minor contributing non-PAN organic
18 nitrogen compounds are aggregated. Total oxidized sulfur, SO_x, requires independent
19 measurements of particle bound sulfate and gaseous sulfur dioxide; methodology and network
20 considerations are discussed in Section 5.6. The CMAQ treatment of SO_x is the simple addition
21 of both species which are treated explicitly in the model formulation. All particle size fractions
22 are included in the CMAQ SO_x estimates. At this time, we consider the contribution of coarse
23 fraction (aerodynamic diameters between 2.5 and 10 microns) particle bound sulfate to be
24 insignificant from a measurement perspective. Consequently, the routinely measured sulfate
25 from IMPROVE and EPA speciation networks, as well as CASTNET, are viable candidates for
26 measurement consideration. Consistent with units and the charge balance relationships applied in
27 ecosystem acidification models, only mass as sulfur or nitrogen is considered requiring
28 conversion of reported particle bound sulfate and nitrate. Precipitation mass is not included
29 explicitly as part of an atmospheric NAAQS indicator.

1 **6.2 WHAT IS THE APPROPRIATE AVERAGING TIME FOR THE AIR**
2 **QUALITY INDICATORS NO_y AND SO_x TO PROVIDE**
3 **PROTECTION OF PUBLIC WELFARE FROM ADVERSE EFFECTS**
4 **FROM ACIDIFICATION?**

5 Based on the review of the scientific evidence, welfare effects associated with
6 acidification result from annual cumulative deposition of nitrogen and sulfur, reflected in effects
7 on the chronic ANC level (measured as annual ANC). It is important to note that chemical
8 changes can occur over both long- and short-term timescales. Short-term (i.e., hours or days)
9 episodic changes in water chemistry can also have significant biological effects. Episodic
10 chemistry refers to conditions during precipitation or snowmelt events when proportionately
11 more drainage water is routed through upper soil horizons that tend to provide less acid
12 neutralizing than was passing through deeper soil horizons. Surface water chemistry has lower
13 pH and acid neutralizing capacity (ANC) during events than during baseflow conditions. One of
14 the most important effects of acidifying deposition on surface water chemistry is the short-term
15 change in chemistry that is termed “episodic acidification.” Some streams may have chronic or
16 base flow chemistry that is suitable for aquatic biota, but may be subject to occasional acidic
17 episodes with lethal consequences. Episodic declines in pH and ANC are nearly ubiquitous in
18 drainage waters throughout the eastern United States and are caused partly by acidifying
19 deposition and partly by natural processes. As noted in Chapter 3 of the ISA, while ecosystems
20 are also affected by episodic increases in acidity due to pulses of acidity during high rainfall
21 periods and snowmelts, protection against these episodic acidity events can be achieved by
22 establishing a higher chronic ANC level. Episodic acidification can result from either shorter
23 term deposition episodes, or from longer term deposition on snowpack. Snowmelt can release
24 stored N deposited throughout the winter, leading to episodic acidification in the absence of
25 increased deposition during the actual episodic acidification event. Protection against a low
26 chronic ANC level is provided by reducing overall annual average deposition levels for nitrogen
27 and sulfur. This supports the conclusion that long term NO_x and SO_x concentrations are
28 appropriate to provide protection against low chronic ANC levels, which protects against both
29 long term acidification and acute acidic episodes.

1 Long term concentrations are often measured using annual averages. However, given the
2 multi-year nature of responses to chronic acidification, multi-year averages of concentrations of
3 NO_y and SO_x may also be appropriate. In the second draft policy assessment, we will provide an
4 expanded discussion of the support for different options for the averaging time to best represent
5 long-term concentrations of NO_y and SO_x related to chronic acidification.

6 **6.3 WHAT FORM(S) OF THE STANDARD ARE MOST APPROPRIATE**
7 **TO PROVIDE PROTECTION OF SENSITIVE ECOSYSTEMS**
8 **FROM THE EFFECTS OF ACIDIFYING DEPOSITION RELATED**
9 **TO AMBIENT NO_x AND SO_x CONCENTRATIONS?**

10 Based on the evidence for joint effects of NO_x and SO_x through acidifying deposition,
11 staff concludes that it is appropriate to consider changes to the form of the existing NO_x and SO_x
12 secondary standards to provide protection to ecosystems. Staff notes that in recent reviews of the
13 secondary ozone standards, EPA has considered use of a form of the standard that reflects
14 ecologically relevant exposures, by using a cumulative index which weights exposures at higher
15 concentrations greater than those at lower concentrations based on scientific literature
16 demonstrating the cumulative nature of O₃-induced plant effects and the need to give greater
17 weight to higher concentrations (EPA, 2007). See 75 FR 2938, 2999 (January 19, 2010) In order
18 to recognize the roles that NO_x and SO_x play in acidification based on their acidifying potentials,
19 and to incorporate the important roles that reduced nitrogen and non-atmospheric variables play
20 in determining the acidifying potentials of NO_x and SO_x, staff suggests using an Atmospheric
21 Acidification Potential Index (AAPI) that is a more ecologically relevant form relative to the
22 current ambient concentration based forms, based on the derivations in Section 5.5.1. The intent
23 of the AAPI is in effect to weight atmospheric concentrations of NO_x and SO_x by their
24 propensity to contribute to acidification through deposition, given the fundamental acidifying
25 potential of each pollutant, and the ecological factors that govern acid sensitivity in different
26 ecosystems. Thus the APPI is more relevant to protecting ecosystems from acidifying deposition
27 compared to simple ambient concentration forms which do not reflect factors that affect
28 acidifying potential.

29 The AAPI is closely tied to the ecological indicator of acidification, ANC, so that the
30 form of AAPI is intended to identify the atmospheric concentrations of NO_x and SO_x that will

1 result in an equivalent level of a target ANC for a percentage of aquatic ecosystems within a
2 particular acid sensitive area. Thus, this form is ecologically relevant as it is tied directly to the
3 ecological indicator that is most directly linked with known ecological effects.

4 The AAPI incorporates the processes which modify both rates of deposition and
5 ecological response to deposition caused by NO_x and SO_x. There is strong evidence in the
6 scientific literature demonstrating that the amount of deposition caused by NO_x and SO_x is
7 modified by atmospheric and landscape factors. Within the ecosystem there are factors, such as
8 bedrock geology and topography, which modify the acidifying potential of the nitrogen and
9 sulfur deposition resulting from ambient NO_x and SO_x concentrations. In addition reduced
10 nitrogen contributes to total nitrogen loading. In this review, reduced nitrogen is treated as an
11 additional modifying factor within the ecosystem, which reduces the buffering capacity of the
12 ecosystem, and therefore it increases the impact or sensitivity to additional loading from oxidized
13 forms of nitrogen. In effect this leaves less allowable deposition loading from NO_x and SO_x
14 before the ecosystem fails to achieve a target ANC level. Based on this evidence staff concludes
15 that the form should include landscape and atmospheric factors, including reduced nitrogen,
16 which modify the acidifying potential of ambient NO_x and SO_x concentrations. This form is
17 consistent with the language of the CAA as discussed in Section 1.5.

18 Selecting a more ecologically-relevant secondary standard form would also be directly
19 responsive to the recommendation of the 2004 National Research Council's report titled Air
20 Quality Management in the United States (NRC, 2004) which encourages the Agency to evaluate
21 its historic practice of setting the secondary NAAQS equal to the primary.

22 In theory, the AAPI could address acidification potential related to both terrestrial
23 acidification and aquatic acidification. For this first draft policy assessment, as discussed in
24 Chapter 5, we define the AAPI for protection against aquatic acidification. In the second draft
25 policy assessment, we will explore the potential to include protection against terrestrial
26 acidification in the AAPI or a related index.

27 The definition of the AAPI form considered here is:

28 Annual Average AAPI: Natural background ANC minus the contribution to
29 acidifying deposition from NH_x, minus the acidifying contribution of deposition
30 from NO_y and SO_x.

31 Building from the derivation of ANC* provided in Section 5.5.2, the AAPI is equivalent
32 to the equation for calculating ANC* when the catchment specific values for g in equation (9) in

1 Section 5.5.2. are replaced by representative values for acid sensitive areas (based on a percentile
2 of water bodies targeted for an ANC level selected by the Administrator), Q and NH_x are
3 replaced by average values for aggregate ecosystem areas, and L(NO_x) and L(S) are replaced by
4 terms translating atmospheric NO_y and SO_x into deposition:

$$5 \quad AAPI = g(\cdot) - \frac{1}{Q} L(NHx) - \frac{1}{Q} [V_{NO_y} \cdot NO_y + V_{SO_x} \cdot SO_x] \quad (1)$$

6 where NO_y and SO_x are concentrations of NO_y and SO_x, respectively, V_{NO_y} and V_{SO_x} are the
7 ratios of deposition to concentrations (deposition transformation ratios) for NO_y and SO_x,
8 respectively. Deposition transformation ratios are the estimated relationships between
9 atmospheric concentrations of NO_y and SO_x and the collocated deposition of NO_x and S. See
10 Chapter 5.4.4 and 5.4.5 for further description of calculation of ratios of deposition to
11 concentrations.

12 Note that while equation (1) is used to calculate the value of AAPI for any observed
13 values of NO_y and SO_x, the level of the standard for AAPI selected by the administrator should
14 reflect a wide number of factors, including desired level of protection indicated by a target
15 ANC_{limit}, the specified percentile of waterbodies projected to achieve the target ANC, and the
16 various factors and uncertainties involved in specifying all of the other aspects of the standard,
17 such as the classification of landscape areas, the specification of reduced nitrogen deposition, the
18 methodology to determine deposition of NO_y and SO_x, and the averaging time. As such the
19 administrator may choose an AAPI level higher or lower than the target ANC_{limit} to reflect the
20 combined effect of the all of the components of the standard and their related uncertainty, such
21 that the chosen AAPI, in the context of the overall standard, reflects her informed judgment as to
22 a standard that is sufficient but not more than necessary to protect against adverse public welfare
23 effects.

24 *How are AAPI parameters determined?*

25 Other than ambient levels of NO_x and SO_x, which would be measured values, EPA would
26 determine and specify all of the values for the AAPI parameters, as discussed below.

27 The natural background ANC, g, is a calculated value and is determined by two
28 components: [BC]_o* which is closely associated with underlying bedrock which strongly
29 influences the contribution of base cations due to weathering, for which a representative value

1 could be determined for a limited set of geologic acid sensitivity classes, and N_{eco} , which
2 represents the amount of deposited nitrogen that is available for acidification due to uptake,
3 denitrification and immobilization. N_{eco} is estimated using two different approaches: (1) the
4 individual terms are estimated through available data and modeling or (2) N_{eco} is calculated as
5 nitrogen deposited minus nitrogen leached, using streamwater measurements of nitrate for
6 leaching and estimates of nitrogen deposition based on model results and measurements. The
7 details of these procedures are addressed in chapter 4 and Appendix 4 of the REA.

8 The runoff parameter Q for each acid sensitive area is determined based on USGS
9 mapping of runoff values (REFERENCE NEEDED).

10 V_{NO_y} , V_{SO_x} are calculated from CMAQ by dividing the annual average NO_y , SO_x
11 concentration by the total NO_y or SO_x deposition, respectively, for each grid cell and then
12 aggregating all grid cells in the acid sensitive area.

13 $L(NH_x)$ is calculated using the same procedures applied to CMAQ results for deposited
14 NH_x .

15 The V_{NO_y} and V_{SO_x} are spatially variable, and for the purposes of setting the standard,
16 are determined based on the ratios of total sulfur and nitrogen depositions to concentrations from
17 CMAQ model outputs (see Chapter 5 for details of calculation of deposition ratios). V_{NO_y} , V_{SO_x}
18 are calculated from CMAQ by dividing the annual average NO_y or SO_x concentration by the total
19 NO_y or SO_x deposition, respectively, for each grid cell and then computing the mean or median
20 of all grid cells in the acid sensitive area (the decision on whether the median or mean value
21 should be used is an option for discussion; the mean will give more weight to outlier values
22 relative to the median).

23 NH_x is spatially variable and determined based on monitored and/or CMAQ modeled
24 outputs. The average NH_x deposition across grid cells within an acid sensitive region will be
25 used to represent the depositional load of NH_x .

26 There will be multiple combinations of concentrations of NO_x and SO_x that result in a
27 specific value of the AAPI. There will be no single combination of NO_x and SO_x that solves for a
28 particular value of AAPI in all locations. Measured concentrations of annual average NO_x and SO_x
29 necessary to meet the standards are thus expressed conditionally by the equality in (1), and not
30 by fixed quantities.

1 In order to provide a set of values for elements of the form, e.g. to develop a specific set
2 of parameter values for g , V_{NO_y} , V_S , and N_x , we propose to classify locations in the U.S. into a
3 set of areas based on sensitivity to acidification. Each area would be assigned a classification for
4 the g parameter; for example, as described in Section 5.2.2.4, a set of classes of acidification
5 sensitivity might be able to be developed based on underlying bedrock geology, or bedrock
6 geology plus other ecosystem variables. The g parameter (natural background, or preindustrial,
7 ANC) would then be estimated for each of those sensitivity classes, based on the critical load
8 modeling available for each class. Each acid sensitive area would then be assigned a value of g
9 based on the geology class in which it falls. In the case of V_{NO_y} , V_S , and NH_x , values for specific
10 areas would be estimated based on the best available monitoring and/or modeling data. Given the
11 limited availability of measured deposition velocities, staff concludes that the calculated
12 deposition ratios based on the CMAQ modeling from 2005 provides the best available source of
13 estimates of V_{NO_y} and V_S . Evaluation of the stability of these estimates of deposition ratios over
14 time (see Chapter 5) suggests that in most acid sensitive areas, deposition ratios are quite stable,
15 with a coefficient of variation less than 25 percent across a four year period. While there are a
16 limited number of sites that directly measure deposition of reduced nitrogen, staff concludes that
17 the most widely available and defensible estimates of reduced nitrogen deposition (NH_x) are the
18 estimates obtained from the CMAQ modeling from 2005.¹⁸

19 It is important to note for this form of the standard that the same AAPI can be obtained
20 with different combinations of ambient NO_x and SO_x concentrations. The implication of the form
21 of the standard expressed in equation (1) is that there will be a tradeoff curve that reflects the
22 combinations of NO_x and SO_x that satisfy equation (1) for any specific value of the standard. The
23 shape of the tradeoff curve will depend on the specific values of G , V_{NO_y} , V_S , and NH_x for a
24 limited number of specific areas classified based on acid-sensitivity. As discussed in Chapter 5,
25 all parts of the U.S. would be classified into areas based on acid-sensitivity. Within each such
26 area, EPA would specify the parameter values of APPI, leading to a specific tradeoff curve for
27 each area. The levels of NO_y and SO_x that meet an AAPI standard expressed for a given
28 $g(\cdot)$ [preindustrial ANC], Q , $L(NH_x)$ and V_{NO_y} and V_{SO_x} :

¹⁸ Note to readers: Maps of CMAQ 2005 estimates of NH_x deposition will be included in the second draft policy assessment, along with an evaluation of the representativeness of the 2005 NH_x deposition for characterizing conditions over a multiyear period.

$$V_{NO_y} \cdot NO_y + V_{ST} \cdot ST = g(\cdot) \cdot Q - L(NHx) - AAPI \cdot Q \quad (2)$$

Note that $[V_{NO_y} \cdot NO_y + V_{ST} \cdot ST]$ is essentially the critical load of NO_y and S, expressed in terms of atmospheric concentrations. As such, equation (2) can also be expressed in a form similar to a typical critical load equation as discussed in Chapter 5, e.g.

$$V_{NO_y} \cdot NO_y + V_{ST} \cdot ST = (BC_0^* - APPI)Q - N_{eco} - L(NHx) \quad (3)$$

This expression is based on

$$g(\cdot) = (BC_0^* +) - L(NHx) - AAPI \cdot Q \quad (4)$$

The pairs of NO_y and SO_x that will meet a given AAPI limit are related through the following equations

$$NO_y^* = C_{\min}(NO_y) \quad (5)$$

$$SO_x^* = C_{\max}(SO_x) \forall NO_y < C_{\min}(NO_y) \quad (6)$$

$$SO_x^* = C_{\max}(SO_x) + \left[\frac{C_{\max}(SO_x)}{(C_{\min}(NO_y) - C_{\max}(NO_y))} \right] \cdot NO_y^* \forall NO_y > C_{\min}(NO_y) \quad (7)$$

where,

NO_y^{*} is the coordinate point for NO_y

SO_x^{*} is the coordinate point for SO_x

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

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

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

$$C_{\max}(SO_x) = \frac{1}{V_S} DL_{\max}(S) \quad (8)$$

$$1 \quad C_{\min}(NO_y) = \frac{1}{V_{NO_y}} DL_{\min}(N - NH_x) \forall NH_x < DL_{\min}(N) \quad (9)$$

$$2 \quad = 0 \forall NH_x > DL_{\min}(N)$$

$$3 \quad C_{\max}(NO_y) = \frac{1}{V_N} DL_{\max}(N) \quad (10)$$

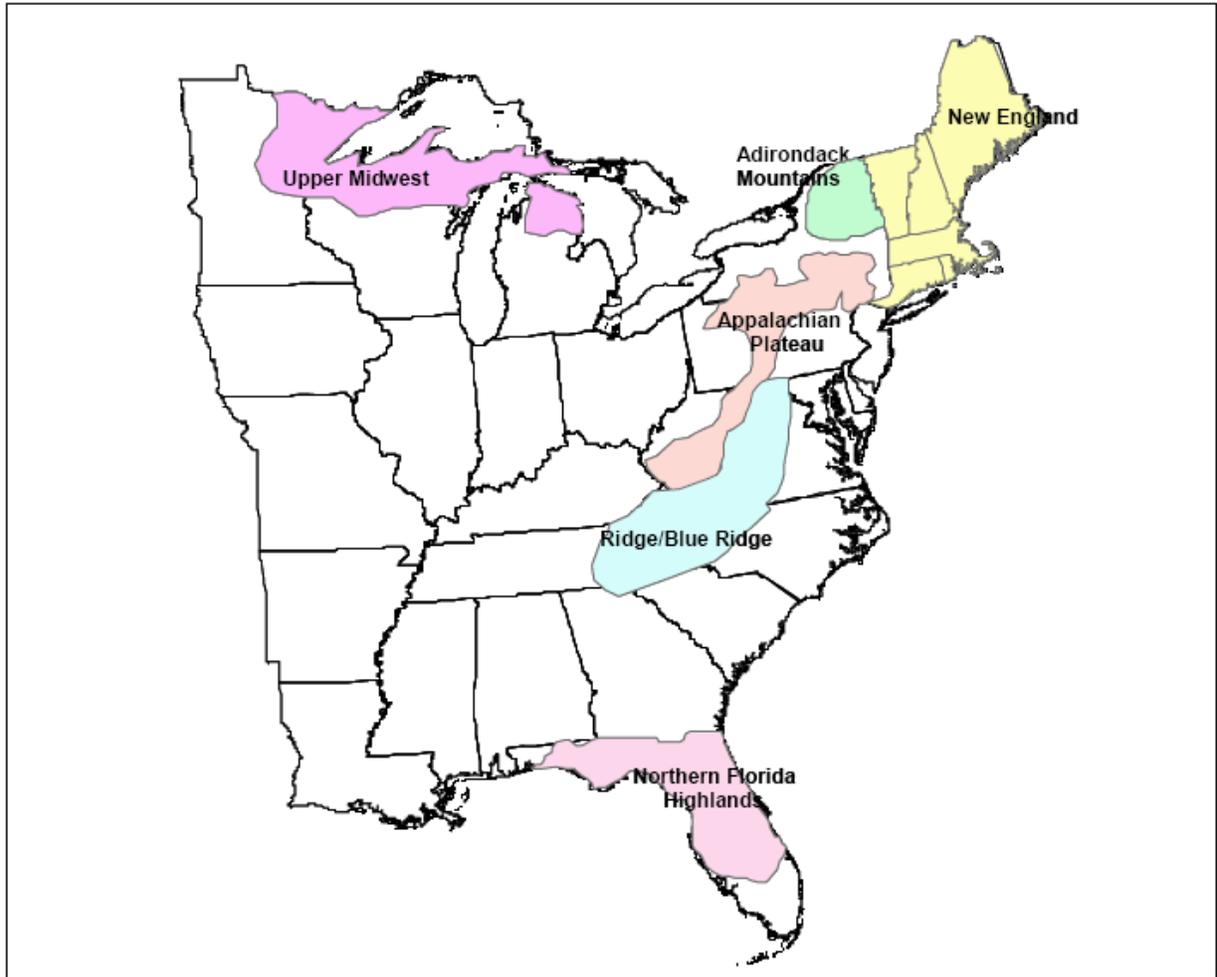
4 where $DL_{\max}(S)$, $DL_{\max}(N)$, and $DL_{\min}(N)$ are based on the critical load within a sensitive
 5 areas that protects a specified percentile (e.g. 95%) of water bodies in the area.

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

14 Recall that these three variables are conditional on the chosen level of APPI, and reflect
 15 the depositional loadings that are associated with an equivalent level of ANC, e.g. for an APPI of
 16 50, the $DL_{\max}(S)$, $DL_{\max}(N)$, and $DL_{\min}(N)$ are associated with an ANC of 50. Also recall that
 17 $DL_{\max}(S)$ for a given ANC is a function of the “natural” flux of base cations to a watershed,
 18 runoff, and the amount of sulfur retention within a waterbody; $DL_{\min}(N)$ is the minimum amount
 19 of deposition of total nitrogen ($NH_x + NO_x$) that catchment processes can effectively remove
 20 without contributing to the acidic balance; and $DL_{\max}(N)$ for a given ANC is a function of
 21 $DL_{\min}(N)$ and the “natural” flux of base cations to a watershed, runoff, and the amount of
 22 nitrogen retention within a waterbody, assuming S is zero. In our framework, $DL_{\min}(N)$ is
 23 calculated from the FAB critical load modeling (equation 5 from Attachment A of the REA) or
 24 estimated through measured or modeled values of total nitrogen deposition and nitrate leaching.

25 As discussed in Chapter 5, the specific estimation of G, V_{NO_y} , V_S , and NH_x in a specific
 26 sensitive area will depend on the spatial scale of the sensitive area. Sensitivity can be assessed at
 27 the level of individual catchments, however, this presents practical limitations for establishing

1 meaningful standards, as there are thousands of catchments within the U.S. Binning classes of
2 sensitivity within larger spatial areas, e.g. the sensitive ecosystem areas displayed in Figure 6-1
3 (reproducing Figure 4.2-2 in the REA), can provide a more manageable set of values of G, V_{NO_y},
4 V_S, and NH_x. These parameters can be estimated in several ways for the larger spatial areas.
5 Mean or median values can be generated across catchments, however, this would lead to
6 parameter estimates that do not reflect conditions in the more sensitive lakes in the region.
7 Alternatively, in order to provide a desired level of protection in these larger defined spatial
8 areas, estimates based on higher percentiles of the distributions of parameters across catchments
9 can be generated, e.g. the 75th or 95th percentile values of G, V_{NO_y}, V_S, and NH_x could be used to
10 provide protection for the more vulnerable aquatic ecosystems, however this would potentially
11 lead to over-protection for less vulnerable ecosystems in the area. The Administrator may
12 consider the balance between protection of particularly sensitive ecosystems and the overall
13 protection for ecosystems in an area as an important element to consider in making decisions
14 about the target level of ANC and the percent of aquatic ecosystems within an area targeted to
15 achieve the specified ANC level. One potentially important modification to this process would
16 be to first remove water bodies that are naturally acidic (e.g. that will not benefit from reductions
17 in atmospheric NO_x and SO_x deposition) from the distribution of water bodies in the area prior to
18 determining the mean or 95th percentile. This will increase the likelihood that the estimated g
19 parameter will be representative of ecosystems within an area that are sensitive to NO_x and SO_x
20 deposition. The second draft policy assessment will explore the implications of alternative
21 combinations of target ANC and percent of aquatic ecosystems protected at the target ANC in
22 areas of different sizes. The second draft policy assessment will also explore methods for
23 determining values of g for areas that are clearly not sensitive to acidification from deposition of
24 NO_x and SO_x. These areas may be areas that have very high levels of natural buffering, or may
25 also be areas that are naturally acidified, such that the value of g is less than the target value of
26 ANC. In these naturally acidified areas, reducing deposition from NO_x and SO_x will not be
27 beneficial, because the areas are adapted to high levels of acidity.



1
2 **Figure 6-1.** Ecosystems sensitive to acidifying deposition in the Eastern U.S.
3 (Note that Florida represents a special case where high levels of natural
4 acidification exist unrelated to deposition) This map does not include all sensitive
5 areas in the U.S. Certain mountainous areas of the Western U.S. are also sensitive
6 to acidifying deposition.

1 **6.4 WHAT ARE THE APPROPRIATE SPATIAL EXTENTS OF THE**
2 **BOUNDARIES FOR EVALUATING AAPI? WITHIN THOSE**
3 **BOUNDARIES, WHAT ARE THE APPROPRIATE STATISTICS TO**
4 **USE IN CALCULATING THE PARAMETERS OF THE AAPI, E.G.**
5 **G, V_{NOY} , V_S , AND NH_x ? WITHIN THOSE BOUNDARIES, WHAT S**
6 **THE APPROPRIATE SPATIAL AVERAGING FOR THE AIR**
7 **QUALITY INDICATORS NO_y AND SO_x TO PROVIDE**
8 **PROTECTION OF PUBLIC WELFARE FROM ADVERSE EFFECTS**
9 **FROM ACIDIFICATION?**

10 *[Note to reviewers: This section will be added in the second draft policy assessment. In*
11 *the second draft we plan to provide initial sets of parameter values for acid sensitive areas of*
12 *the U.S., and include an exploration of how the standard might be specified for areas of the U.S.*
13 *that are not sensitive to deposition of NO_x and SO_x . In addition, we plan to discuss the*
14 *correlation between the extent of a spatial area and the importance of evaluating alternative*
15 *percentiles of critical loads to protect a percentage of water bodies in an area, and to discuss*
16 *how averaging of the $VNOY$, VSO_x , and NH_x should be conducted to best represent the*
17 *parameters for an area.]*

18 **6.5 WHAT ARE THE OPTIONS FOR SPECIFYING THE TARGETS**
19 **FOR THE ECOLOGICAL INDICATOR FOR AQUATIC**
20 **ACIDIFICATION?**

21 Chapter 5 discusses the rationale for use of ANC as the ecological indicator best suited to
22 reflect the sensitivity of aquatic ecosystems to acidification. ANC as an indicator of acidification
23 is causally linked to a number of measures of adversity to ecosystems, including declines in fish
24 populations and diversity of aquatic species. ANC is also causally linked with deposition of
25 nitrogen and sulfur. ANC is thus ideally suited to serve as the bridge between deposition and
26 ecological effects. As such, staff concludes that ANC is the best available choice as the
27 ecological indicator. CASAC has agreed that ANC represents a suitable ecological indicator for
28 aquatic acidification (EPA-CASAC-09-013). Results from the REA confirm that ANC may be

1 used to establish impacts from current depositional loadings (**REA 4.2.6**). As explained above,
2 ANC is an indicator of the effects expected to occur given the natural buffering capacity of an
3 ecosystem and the loadings of nitrogen and sulfur resulting from atmospheric deposition. A
4 target ANC limit based on a desired level of protection is an important input to the decisions of
5 the level of AAPI and the percent of ecosystems to be protected.

6 **6.5.1 What levels of impairment are related to alternative levels of ANC?**

7 As discussed in Chapters 2, 3, and 4, specific levels of ANC are associated with differing
8 levels of ecosystem impairment, with higher levels of ANC resulting in fewer ecosystem
9 impacts, and lower levels resulting in both higher intensity of impacts and a broader set of
10 impacts. Logistic regression of species presence/absence data against ANC provides a
11 quantitative dose-response function, which indicates the probability of occurrence of an
12 organism for a given value of ANC. For example, the number of fish species present in a
13 waterbody has been shown to be positively correlated with the ANC level in the water, with
14 higher values supporting a greater richness and diversity of fish species (Figure 6-2). The
15 diversity and distribution of phyto-zooplankton communities are also positively correlated with
16 ANC.

17 The relationship between ANC and ecosystem impacts is non-linear, with a sigmoidal
18 shape. For freshwater systems, ANC levels can be grouped into five major classes: <0, 0–20, 20–
19 50, 50–100, and >100 microequivalents per liter ($\mu\text{eq/L}$), with each range representing a
20 probability of ecological damage to the community. The five categories of ANC and expected
21 ecological effects are described Table 2-1 in Chapter 2 and are supported by a large body of
22 research completed throughout the eastern United States (Sullivan et al., 2006).

23 Biota are generally not harmed when ANC values are >100 microequivalents per liter
24 ($\mu\text{eq/L}$). The number of fish species also peaks at ANC values >100 $\mu\text{eq/L}$. This suggests that at
25 ANC greater than 100, little risk from acidification exists in most aquatic ecosystems. At ANC
26 levels below 100 $\mu\text{eq/L}$, overall health of an aquatic community can be maintained; however,
27 fish fitness and community diversity begin to decline. At ANC levels between 100 and 50 $\mu\text{eq/L}$,
28 the fitness of sensitive species (e.g., brook trout, zooplankton) also begins to decline. When ANC
29 concentrations are <50 $\mu\text{eq/L}$, negative effects on aquatic biota are observed, including large
30 reductions in diversity of fish species, and changes in health of fish populations, affecting

1 reproductive ability and fitness. ANC levels below 50 are generally associated with death or loss
2 of fitness of biota that are sensitive to acidification. (**ISA 5.2.2.1 and REA 5.2.1.2**).

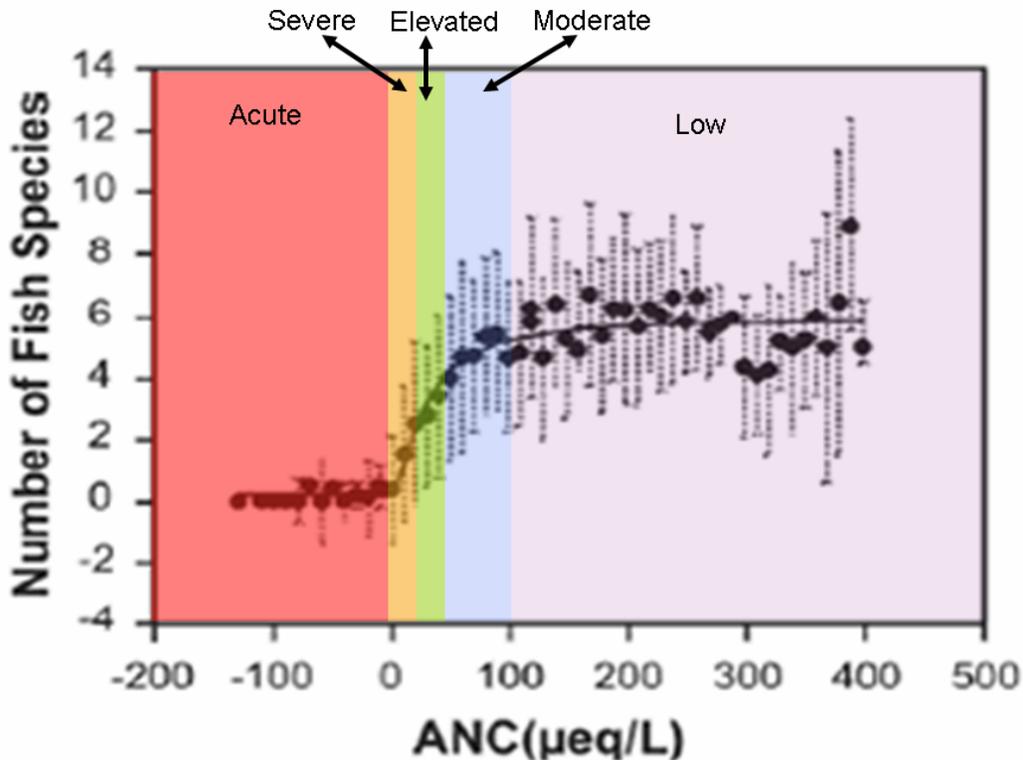
3 Based on the field data from the Adirondacks and Shenendoah case study areas, ANC
4 levels less than 50 are clearly adverse to ecosystem health, and are likely to lead to reductions in
5 ecosystem services related to recreational fishing. ANC levels between 50 and 100 are
6 potentially adverse to ecosystem health, and may result in losses in ecosystem services, but the
7 effects are less severe and greater uncertainty exists as to the magnitude of ecosystem service
8 impacts. A more comprehensive discussion of uncertainties related to ecological effects at
9 different ANC levels and related ecosystem services will be included in the second draft policy
10 assessment.

11 The implications of the data from the Adirondacks and Shenendoah case study areas for
12 relating ANC to adverse ecological impacts is transferable to other acid sensitive areas of the
13 U.S. The relationship between species diversity and ANC is quite similar between the two case
14 study areas (see **REA Figure 4.2-1**), which have different water body types and different
15 geological and topographical features. While the species composition and thereby relative
16 sensitivities of species are likely to vary across the landscape, the rate of impact is likely to be
17 similar. The plot in Figure 6-2 shows a rapid decrease in fish species between an ANC of 100
18 and an ANC of 0. This trend is what would be expected in many systems given similar changes
19 in ANC.

20 Consideration of the appropriate levels of ANC to target in the standard to reduce the
21 likelihood of effects from aquatic acidification can be based upon the above presented categories
22 of aquatic status in Table 2-1. Using this information as well as information provided by both the
23 ISA and REA, the lowest two categories (0 and 0<20) would appear inadequate to protect against
24 catastrophic loss of ecosystem function. While ecological effects occur at ANC levels below 50,
25 the degree and nature of those effects is less significant than at levels below 20. Therefore, three
26 levels of ANC – 20, 50, and 100 - would provide the Administrator with reasonable range of
27 options in designing an AAPI for protecting public welfare.

28 Given the level of ecosystem impairment occurring at ANC levels below 50, staff suggest
29 that the greatest support is for the Administrator to consider a range for the target ANC between
30 50 and 100 as a basis for the design of the standard. Selection of target ANC values closer to 50
31 places less weight on the vulnerability of sensitive aquatic ecosystems, while selection of target

1 ANC values closer to 100 places more weight on sensitive species within acid sensitive
2 ecosystems. Staff conclude that while target ANC values between 20 and 50 will not result in
3 complete impairment of aquatic systems, the level of damages due to ANC as you get lower in
4 this range are highly likely to result in adverse impacts to public welfare in many locations, due
5 to the significant reductions in the number of fish species in affected waterbodies, and the
6 reductions in health and reproductive fitness of fish populations and other aquatic organisms.



7
8 **Figure 6-2.** Number of fish species per lake or stream versus ANC level and
9 aquatic status category¹⁹ (colored regions) for lakes in the Adirondack Case Study
10 Area (Sullivan et al., 2006).

11 The target ANC level specified in designing the standard is only one part in determining
12 the overall protectiveness of the standard. The degree of protectiveness is based on all elements
13 of the standard, including the target ANC, the size of the spatial areas over which the standard is
14 applied, the percent of aquatic ecosystems targeted within a spatial area that is selected by the
15 Administrator to achieve the selected ANC level, the atmospheric indicator, the method for
16 calculating g , the calculated values for the deposition transformation ratios (VNO_x and VSO_x),

¹⁹ The aquatic status categories are based on the literature and are discussed in detail in the REA (REA Appendix 4-20)

1 and the calculated value for reduced nitrogen deposition (NH_x). There are widely varying
2 degrees of uncertainty associated with all of these elements, some being much more certain and
3 others being much less certain. The specified target ANC level is a crucial part of developing a
4 standard that is requisite to protect, but it is the overall design and content of the standard that
5 must be considered in judging the adequacy of protection it provides.

6 Consideration of the target ANC should also reflect that an adequate level of ANC should
7 protect against episodic as well as long term effects. Selecting a higher chronic ANC level can
8 provide greater protection against short term peaks in acidification. In addition, selection of ANC
9 values in the range of 20 to 50 provides less protection against these short term episodic effects.
10 Selection of target ANC values in the range from 50 to 100 provides additional protection
11 against episodic peaks in acidification.

12 When considering the appropriate level of a standard to protect against aquatic
13 acidification, it is necessary to take into account both the time period desired for recovery as well
14 as the potential of recovery. Ecosystems become adversely impacted by acidifying deposition
15 over long periods of time and have variable time frames and abilities to recover from such
16 perturbations. Modeling presented in the REA (**REA Section 4.2.4**) shows the estimated ANC
17 values for Adirondack lakes and Shenandoah streams under pre-acidification conditions and
18 indicates that for a small percentage of lakes and streams, natural ANC levels would have been
19 below 50. Therefore, for these waterbodies, no reduction in input is likely to achieve an ANC of
20 50 or greater. Conversely, for some lakes and streams the level of perturbation from long periods
21 of acidifying deposition has resulted in very low ANC values compared to estimated natural
22 conditions. For such waterbodies, the time to recovery would be largely dependent on future
23 inputs of acidifying deposition. These concepts become important in the consideration of the
24 desired level of protection of a standard and will be discussed further in the next draft of this
25 document.

1 **6.6 WHAT ARE THE APPROPRIATE AMBIENT AIR MONITORING**
2 **METHODS TO CONSIDER IN DEVELOPING THE STANDARDS?**

3 **6.6.1 What measurements would be used to characterize NO_y and SO_x ambient air**
4 **concentrations for the purposes of the AAPI based standard?**

5 Ambient NO_y, gaseous SO₂ and particulate sulfate concentrations would be used in
6 determining compliance with the AAPI. This would require measurements of NO_y, sulfate and
7 sulfur dioxide, all which are conducted as part of current routine monitoring networks (section
8 3.2). There are issues requiring resolution associated with Federal Reference or Equivalency
9 Measurement (FRM/FEM) status of measurement techniques, that to date have served as
10 supplemental information, which will require resolution. A FRM for SO₂ exists, but not for NO_y
11 or sulfate. Only recently have NO_y measurements, which historically were viewed as research
12 venue measurements, been incorporated as “routine” observations, partly as a result of the NCore
13 program. Acquiring FRM status may require better characterization of the conversion
14 efficiencies, mass loss and clear guidance on operating and siting procedures. Particulate sulfate
15 has been measured for several years in the IMPROVE, CASTNET and EPA CSN networks. The
16 nation has over 500 24-hour average, every third day sulfate measurements produced by the
17 PM_{2.5} speciation networks (IMPROVE and EPA CSN) and nearly 80 CASTNET sites that
18 provide continuous weekly average samples of sulfate with an open inlet accommodating all
19 particle sizes. However, with minor exceptions, the PM_{2.5} fraction accounts for nearly all sulfate
20 mass. The sample collection period is not an issue for gaseous measurements of NO_y and SO₂
21 that operate continuously. Some concerns have been raised about the possibility of exclusion of
22 coarse particles from NO_y samplers operating at low flow conditions as well as potential
23 difficulties of reducing organically bound and mineralized nitrate. These conversion efficiency
24 and particle size fraction issues are viewed by EPA as relatively minor mass accounting issues
25 that require more clarification but not necessarily technical resolution.

26 **6.6.2 What sampling frequency would be required?**

27 The averaging time for the standard is likely to be an annual average. Conceptually,
28 extended sampling periods as long as one year would be adequate for the specific purposes of
29 comparing to a standard. However, future assessments that characterize acidification and form

1 the scientific basis for subsequent standards reviews and allow for systematic checking of
2 progress through accountability procedures benefit from more highly resolved data, especially
3 the evaluation of air quality models that are key components of N/S deposition assessments. In
4 addition, many of the monitoring approaches that are used throughout the nation sample (or at
5 least report out) on daily (PM_{2.5} chemical speciation), weekly (CASTNET) and hourly (all
6 inorganic gases) periods. There is a tradeoff to consider in sampling period design. For example,
7 the weekly CASTNET collection scheme covers all time periods throughout a year, but only
8 provides weekly resolution that misses key temporal and episodic features valuable for
9 diagnosing model behavior. The every third day, 24-hour sampling scheme used in IMPROVE
10 and EPA speciation monitoring does provide more information for a specific day of interest yet
11 misses 2/3 of all sampling periods. The missing sampling period generally is not a concern when
12 aggregating upward to a longer term average value as the sample number adequately represents
13 an aggregated mean value. Additionally, there is a benefit to leveraging existing networks which
14 should be considered in sampling frequency recommendations. A possible starting point would
15 be to assume gaseous oxidized species, NO_y and SO₂, are run continually all year reporting
16 values every hour, consistent with current routine network operations. Sulfate sampling periods
17 should coincide with either the chemical speciation network schedules or CASTNET. There are
18 advantages to coordinating with either network. Ammonia gas and ammonium ion present
19 challenges in that they are not routinely sampled and analyzed for, and the combined quantity,
20 NH_x is of interest. Because NH_x is of interest, some of the problems of volatile ammonia loss
21 from filters may be mitigated. However, for model diagnostic purposes, delineation of both
22 species at the highest temporal resolution is preferred. While levels of deposited reduced
23 nitrogen would be specified by EPA for purposes of the APPI, monitoring of reduced nitrogen
24 would be important but would not be used in the APPI itself.

25 **6.6.3 What are the spatial scale issues associated with monitoring for compliance,** 26 **and how should these be addressed?**

27 The observation network for NO_y, NH_x and SO_x is very modest and includes a
28 monitoring network infrastructure that is largely population oriented. While there is platform and
29 access infrastructure support provided by CASTNET, NADP and IMPROVE, those locations by
30 themselves are not likely to provide the needed spatial coverage to address acid sensitive

1 watersheds across the United States. Ambient monitoring at every watershed may not be required
2 due to the nature of the ambient air quality in acid sensitive areas. An understanding of the
3 spatial variability of NO_y, NH_x, sulfate and SO₂ will help inform monitoring. Critical load
4 models are based on annual averages, which effectively serves to dampen much of the spatial
5 variability. Furthermore, the development of an area-wide depositional load tradeoff curve
6 implies focus on region wide characterization. Toward that end, CMAQ concentration fields will
7 provide insight into the likely spatial representativeness of monitors leading to efficient
8 application of monitoring resources. For example, the CMAQ based spatial coefficient of
9 variation (standard deviation/mean) of oxidized nitrogen in the Adirondacks was 1.46%.
10 Improved dry deposition estimates will result from enhancements of ambient monitoring
11 addressing the N/S secondary standards as each additional location could serve a similar role
12 that existing CASTNET sites provide in estimating dry deposition.

13 **6.7 TAKING INTO CONSIDERATION INFORMATION ABOUT**
14 **ECOSYSTEM SERVICES AND OTHER FACTORS RELATED TO**
15 **CHARACTERIZING ADVERSITY FOR THE ECOLOGICAL**
16 **EFFECTS BEING ASSESSED IN THIS REVIEW, WHAT IS AN**
17 **APPROPRIATE RANGE OF ALTERNATIVE STANDARDS FOR**
18 **THE AGENCY TO CONSIDER?**

19 The secondary NAAQS will reflect the public welfare policy judgments of the
20 Administrator, based on the science, as to the level of air quality which is requisite to protect the
21 public welfare from any known or anticipated adverse effects associated with the pollutant in the
22 ambient air. The exposure and risk assessment provide information regarding the effects
23 associated with a number of different welfare endpoints at different levels of air quality,
24 expressed in terms of the joint annual mean concentrations of NO_x and SO_x determined such that
25 specific levels of ecosystem protection (for example, ANC greater than 50) are met. Staff also
26 recognizes that in certain naturally acidic ecosystems, even though the ecological benchmarks
27 are exceeded, e.g. ANC may be quite low; NO_x and SO_x are not contributing to effects because
28 those systems have chronic natural acidity and will not benefit from reductions in atmospheric
29 deposition. The secondary NAAQS are not intended to provide protection in these types of

1 naturally acidic systems. As noted earlier, we will be exploring methods to address the design of
2 the standard relative to these naturally acidic systems in the second draft policy assessment. The
3 secondary NAAQS are focused on providing protection in areas where ambient NO_x and SO_x are
4 resulting in effects in ecosystems with low natural levels of acidification that are highly sensitive
5 to additional inputs of acid deposition.

6 Staff believes that ecosystem effects of NO_x and SO_x deposition in aquatic ecosystems
7 are an important public welfare effect of concern. There are several sources of benchmark values
8 for ANC that can help to inform a determination of adversity. [Additional information on
9 benchmark values will be provided in the second draft policy assessment] Staff concludes that
10 achieving ANC in the range of 50 to 100 would be likely to provide adequate protection against
11 the effects of acidification on ecosystems.

12 Based on our analyses of risks of impacts on aquatic species diversity and fitness and on
13 the basis of the scientific effects literature, we anticipate that achieving the upper end of this
14 ANC range would substantially decrease the effects of acidification due to NO_x and SO_x on
15 aquatic ecosystems. Additionally, it is anticipated that achieving the upper end of this range
16 would provide increased protection from NO_x and SO_x in areas with higher levels of variability
17 in ecosystem sensitivity due to variability in meteorology, bedrock geology, topography, land
18 use characteristics, or reduced nitrogen deposition.

19 These ANC levels are estimated to protect sensitive aquatic ecosystems from significant
20 negative effects of NO_x and SO_x deposition on aquatic biota, including large reductions in
21 diversity of fish species, and changes in health of fish populations, affecting reproductive ability
22 and fitness. It is recognized, however, that a standard set within this range would not protect the
23 most sensitive aquatic ecosystems or species within those ecosystems from the effects of NO_x
24 and SO_x. At ANC levels below 100, while overall health of an aquatic community can be
25 maintained, ANC levels are expected to be such that fish fitness and community diversity begin
26 to decline. At ANC levels between 100 and 50, ANC levels are expected to be such that the
27 fitness of sensitive species (e.g., brook trout, zooplankton) also begins to decline. Staff notes that
28 at levels of ANC above 100, biota are generally not harmed. As such, achieving an ANC of
29 greater than 100 would be expected to result in little damage from NO_x and SO_x deposition to
30 aquatic ecosystems.

1 Specifying an appropriate range of levels for an AAPI standard that is designed and
2 specified as discussed above involves consideration of the degree to which any specific AAPI
3 would lead to achieving the desired ANC level, and a judgment as to the degree of protection of
4 public welfare that is warranted. In general, staff initially conclude that it would be appropriate
5 for the Administrator to consider an AAPI in the range of 50 to 100. Selection of a range of
6 AAPI and selection of a specific level of AAPI within that range should incorporate a wide
7 number of considerations, including the percent of water bodies within acid sensitive areas that
8 the Administrator determines should be protected at the targeted ANC level.

9 The Administrator should consider the uncertainties in the ecological effects observed in
10 the literature and the adversity to public welfare associated with those effects. In determining the
11 requisite level of protection for the public welfare from effects on aquatic ecosystems, the
12 Administrator will need to weigh the importance of the predicted risks of these effects in the
13 overall context of public welfare protection, along with a determination as to the appropriate
14 weight to place on the associated uncertainties and limitations of this information.

15 In addition, selection of a specific level of AAPI should consider uncertainties in the
16 design and calculation of the parameters included in the AAPI, including uncertainties in the
17 characterization of natural background ANC (indicated by g in the AAPI equation), spatial and
18 temporal averaging of aggregate effective deposition velocities (indicated by V_{NOY} and V_{SO_x} in
19 the AAPI equation), and spatial and temporal averaging of NH_x deposition (indicated by NH_x in
20 the AAPI equation).

21

1 **7. CO-PROTECTION FOR OTHER EFFECTS USING**
2 **STANDARDS TO PROTECT AGAINST ACIDIFICATION**

3 To this point, the standard for NO_x and SO_x centers on ecosystem protection against
4 aquatic acidification. This chapter focuses on the level of co-protection that this standard would
5 provide for other ecological effects, including terrestrial acidification, terrestrial nutrient
6 enrichment, and estuarine eutrophication.

7 **7.1 TO WHAT EXTENT WOULD A STANDARD SPECIFICALLY**
8 **DEFINED TO PROTECT AGAINST AQUATIC ACIDIFICATION**
9 **LIKELY PROVIDE PROTECTION FROM TERRESTRIAL**
10 **ACIDIFICATION?**

11 In order to understand the level of protection provided by a NO_x/SO_x standard based on
12 aquatic acidification to protect against terrestrial acidification effects, an analysis was conducted
13 comparing the critical loads for lakes and streams that would be developed to protect for an
14 aquatic ANC of 50 to the critical loads to protect for either a terrestrial Bc:Al ratio of 1.2 or 10
15 averaged across a watershed area. See Appendix B for full analysis results. The analysis selected
16 16 watersheds with 29 lakes in the Adirondacks case study area, 4 watersheds randomly selected
17 from each of 4 categories of sensitivity reported in the REA: highly sensitive, moderately
18 sensitive, low sensitivity, and not sensitive. In the Shenandoah case study area, there were a
19 limited number of watersheds in the low sensitivity and not sensitive range, so 18 of the 20
20 streams in 16 watersheds selected were located in highly and moderately sensitive categories.

21 Results for the Adirondacks showed that critical loads for 29 lakes at an ANC of 50 were
22 lower for 13 lakes than the critical load for the terrestrial watershed areas at a Bc:Al ratio of 10
23 and for 21 lakes at a Bc:Al ratio of 1.2. Perhaps more significant was the result that 13 of the 16
24 lakes in the highly and moderately sensitive areas had a lower critical load than the Bc:Al 10
25 areas and 16 of 16 lakes in the highly and moderately sensitive areas had lower critical loads
26 than the Bc:Al 1.2 areas. The Shenandoah region reflected similar results. See table 7.1 below
27 for tabulated results.
28

Table 7-1. Results of comparing aquatic ANC50 critical loads to average terrestrial watershed area Bc:Al ratios. Left numbers in each column are the number of lakes or streams that had a lower critical load than the terrestrial calculated critical load. Right numbers in each column are the number of lakes that had a higher critical load than the watershed calculated terrestrial critical loads.

	Highly Sensitive	Moderately Sensitive	Low Sensitivity	Not Sensitive
Adirondack Bc:Al 10	7-0	6-3	0-7	0-6
Adirondack Bc:Al 1.2	7-0	9-0	5-2	0-6
Shenandoah Bc:Al 10	13-0	5-0	0-1	0-1
Shenandoah Bc:Al 1.2	13-0	5-0	0-1	0-1

1
 2 In summary, a comparison of the terrestrial and aquatic critical acid loads for watersheds
 3 in the Adirondacks and Shenandoah Case Study Areas indicated that, in general, the aquatic
 4 critical acid loads offered greater protection to the watersheds than did the terrestrial critical
 5 loads. Generally in situations where the terrestrial critical loads were more protective, the lakes
 6 or streams in the watershed were rated as having “Low Sensitivity” or “Not Sensitive” to
 7 acidifying nitrogen and sulfur deposition. Conversely, when the water bodies were more
 8 sensitive to deposition (“Highly Sensitive” or “Moderately Sensitive”), the aquatic critical acid
 9 loads generally provided a greater level of protection against acidifying nitrogen and sulfur
 10 deposition in the watershed. In the next draft of the Policy Assessment Document, we intend to
 11 expand this analysis by comparing more levels of ANC to other Bc:Al ratios.

12 **7.2 TO WHAT EXTENT WOULD A STANDARD SPECIFICALLY**
 13 **DEFINED TO PROTECT AGAINST AQUATIC ACIDIFICATION**
 14 **LIKELY PROVIDE PROTECTION FROM TERRESTRIAL**
 15 **NUTRIENT ENRICHMENT?**

16 This question will be answered in the next draft of the Policy Assessment Document.
 17 Once maximum depositional loads are calculated for broad areas, we can compare the derived
 18 maximum NO_y limits to nutrient enrichment benchmarks found in the REA. Benchmarks for
 19 lichens, grasses, mychorrhizae, and diatoms will be compared to the aquatic acidification limits
 20 for nitrogen.

1 **7.3 TO WHAT EXTENT WOULD A STANDARD SPECIFICALLY**
2 **DEFINED TO PROTECT AGAINST AQUATIC ACIDIFICATION**
3 **LIKELY PROVIDE PROTECTION FROM AQUATIC NUTRIENT**
4 **ENRICHMENT?**

5 The REA found that deposition of reactive nitrogen contributed to eutrophication of
6 estuaries; however, it was also noted that atmospheric deposition of nitrogen is only part of the
7 total nitrogen load to the estuaries. Due to the complications of separating out the effects of
8 atmospheric deposition from the effects of other nitrogen loads, CASAC did not recommend that
9 a secondary NAAQS be set to specifically protect against estuarine eutrophication. In the next
10 draft of the Policy Assessment Document, we will attempt to analyze the benefit to the
11 Chesapeake Bay that attaining an aquatic acidification standard would provide by decreasing
12 nitrogen deposition to the watershed.

13
14

1 **8. CONSIDERATION OF ISSUES REGARDING REDUCED**
2 **AND OXIDIZED FORMS OF NITROGEN**

3 [To be added in the second draft Policy Assessment]
4
5

9. INITIAL CONCLUSIONS

1
2 Staff initial conclusions on the elements of the secondary NO_x and SO_x standards for the
3 Administrator's consideration in making decisions on the secondary NO_x and SO_x standards are
4 summarized below, together with supporting conclusions from previous chapters. We recognize
5 that selecting from among alternative policy options will necessarily reflect consideration of
6 qualitative and quantitative uncertainties inherent in the relevant evidence and in the assumptions
7 of the quantitative exposure and risk assessments. Any such standard should protect public
8 welfare from any known or anticipated adverse effects associated with the presence of the
9 pollutant(s) in the ambient air. In providing these options for consideration, we are mindful that
10 the Act requires standards that, in the judgment of the Administrator, are requisite to protect
11 public welfare. The standards are to be neither more nor less stringent than necessary.

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

20 Staff notes that since the last review, additional policy-relevant developments have
21 occurred that may also warrant consideration by the Administrator when making decisions about
22 what is requisite to protect public welfare. The NRC report (described in Chapter 6) states:
23 "Whatever the reason that led EPA to use identical primary and secondary NAAQS in the past, it
24 is becoming increasingly evident that a new approach will be needed in the future. There is
25 growing evidence that the current forms of the NAAQS are not providing adequate protection to
26 sensitive ecosystems and crops" (NRC, 2004).

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

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

- 1 2) Lack of adequate quantitative evidence on the relationship between deposition rates
2 and environmental impacts
- 3 3) Significant uncertainties with regard to the long-term role of nitrogen deposition in
4 surface water acidity and with regard to the quantification of the magnitude and
5 timing of the relationship between atmospheric deposition and the appearance of
6 nitrogen in surface water.

7 In this current review, staff concludes that important new information has become
8 available since the last review that supports revising the current NO_x and SO_x standards.
9 Specifically, the ISA has concluded that there are causal relationships between NO_x and SO_x
10 acidifying deposition and effects on aquatic and terrestrial ecosystems, and the ISA and REA
11 provide substantial quantitative evidence of effects occurring in locations that meet the current
12 NO₂ and SO₂ standards. In addition, substantial new information, based on observational data
13 and rigorous atmospheric modeling, has become available regarding the role of both nitrogen and
14 sulfur deposition in acidification of sensitive water bodies. This information is sufficient to
15 inform the development of revised secondary standards for NO_x and SO_x to protect against the
16 effects of acidification²⁰. While there is also new information available on the role of nitrogen
17 deposition on nutrient enrichment effects in terrestrial and aquatic ecosystems, and the ISA
18 concludes there is a causal relationship between NO_x and nutrient enrichment effects, for this
19 first draft policy assessment, staff have focused on acidification effects due to the substantially
20 greater amount of information available to inform the development of secondary standards.

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

²⁰ As we have note earlier in the document, in this draft we have focused on aquatic acidification. However, in the second draft policy assessment we plan to more fully explore the possibility of expanding the conceptual model to address terrestrial acidification.

1 **9.1 CONCLUSIONS**

2 As noted throughout this document, because of the complex interactions between NO_x
3 and SO_x in the atmosphere and their impacts once deposited in ecosystems, the consideration of
4 indicators, averaging times, forms, and levels for the two pollutants is being conducted jointly. In
5 addition, as discussed in Chapters 5 and 6, we are considering structures for the standards that
6 reflect a more scientifically derived understanding of the relationships between atmospheric
7 concentrations of NO_x and SO_x and the primary indicators of ecosystem impacts.

8 With respect to soil and water effects information, we have evaluated the conclusions
9 drawn at the end of the last review in light of more recent evidence from studies for a variety of
10 ecological effects endpoints. We place greater weight on U.S. studies due to the species-, site-,
11 and climate-specific nature of ecological responses. With respect to quantitative exposure- and
12 risk-based considerations, we have relied on both monitored and modeled NO_x and SO_x ambient
13 concentrations and related deposition, as described in Chapter 3 of the REA.

14 Uncertainties associated with the exposure and risk assessments are also discussed,
15 including, where possible, some sense of the direction and/or magnitude of the uncertainties that
16 should be taken into account as one considers these estimates. As with any analysis that relies on
17 complex scientific models, there are a number of unknown and unquantifiable sources of
18 uncertainty. However, each model that has been applied in the risk and exposure assessment
19 represents the best available science and the models have all been subject to substantial levels of
20 peer-review.

21 The following secondary NAAQS conclusions encompass the breadth of policy-relevant
22 considerations described in this policy assessment:

- 23 (1) Based on the policy-relevant findings from the ISA described in Chapter 2, and while
24 recognizing that important uncertainties and research questions remain, staff conclude
25 that great progress has been made since the last reviews of the secondary standards
26 for NO_x and SO_x. We generally find support in the available effects-based evidence
27 for consideration of NO_x and SO_x standards that are at least as protective as the
28 current standard and do not find support for consideration of NO_x and SO_x standards
29 that are less protective than the current standard. The staff also concludes that
30 consideration of joint standards for NO_x and SO_x is appropriate given the common
31 atmospheric processes governing the deposition of NO_x and SO_x to sensitive

1 ecosystems, and given the combined effects of N and S deposition on acidification of
2 soil and water.

3 (2) Staff concludes that ambient NO_x is a significant component of atmospheric nitrogen
4 deposition, even in areas with relatively high rates of deposition of reduced nitrogen.
5 Staff make this conclusion based on the analysis in Chapter 3 of the REA, which
6 provides a thorough assessment of the contribution of NO_x to nitrogen deposition
7 throughout the U.S., and the relative contributions of ambient NO_x and reduced forms
8 of nitrogen.

9 (3) Staff concludes based on the case study results provided in the REA, that current
10 levels of NO_x and SO_x are associated with deposition that leads to ANC values below
11 benchmark values that cause ecological harm and losses in ecosystem services. Staff
12 concludes that the evidence and risk assessment support strongly a relationship
13 between atmospheric deposition of NO_x and SO_x and ANC, and that ANC is an
14 excellent indicator of aquatic acidification. Staff also concludes that at levels of
15 deposition associated with NO_x and SO_x concentrations at or below the current
16 standards, ANC levels are expected to be below benchmark values that are associated
17 with significant losses in fish species richness, which is associated with reductions in
18 recreational fishing services. While there are many other ecosystem services
19 potentially affected by reductions in ANC, including subsistence fishing, natural
20 habitat provision, and biological control, confidence in the specific translation of
21 ANC values to these additional ecosystem services is much lower.

22 (4) Losses in aquatic resources associated with ANC levels below 50 are clearly
23 associated with significant losses in economic value. Based on the best available data,
24 just in the northeastern U.S., current acidification levels are resulting in \$4 million to
25 \$300 million in damages annually from lost recreational fishing. This estimate
26 represents only a fraction of the total economic value of ecosystem damages as many
27 impacted resources are not amenable to economic valuation methods. In addition,
28 economic damages are also likely to occur in other areas affected by acidification,
29 including New England, the Appalachian Mountains (northern Appalachian Plateau
30 and Ridge/Blue Ridge region), and the Upper Midwest. Staff concludes that reducing
31 acidifying deposition of NO_x and SO_x will result in improvements in public welfare

- 1 by increasing the quantity and quality of ecosystem services, including recreational
2 fishing and other services associated with improved water quality.
- 3 (5) Staff initially concludes based on the case study results that current levels of ambient
4 NO_x and SO_x are associated with deposition that leads to BC:Al values below
5 benchmark values that cause ecological harm and losses in ecosystem services. Staff
6 concludes that the evidence and risk assessment support strongly a relationship
7 between atmospheric deposition of NO_x and SO_x and BC:Al, and that BC:Al is a
8 good indicator of terrestrial acidification. Staff also concludes that at levels of
9 deposition associated with NO_x and SO_x concentrations at or below the current
10 standards, BC:Al levels are expected to be below benchmark values that are
11 associated with significant losses in tree health and growth, which are associated with
12 reductions in timber production. While there are many other ecosystem services,
13 including maple syrup production, natural habitat provision, and regulation of water,
14 climate, and erosion, potentially affected by reductions in BC:Al, confidence in the
15 specific translation of BC:Al values to these additional ecosystem services is much
16 lower.
- 17 (6) On the basis of the acidification and nutrient enrichment effects that have been
18 observed to still occur under current ambient conditions and those predicted to occur
19 under the scenario of just meeting the current secondary NAAQS, staff concludes that
20 the current secondary NAAQS are inadequate to protect the public welfare from
21 known and anticipated adverse welfare effects from aquatic and terrestrial
22 acidification associated with deposition of NO_x and SO_x. As discussed above, this
23 conclusion derives from several lines of evidence.
- 24 (7) Staff has concluded, based on the completeness of the available evidence and
25 quantitative risk information, that effects due to aquatic and terrestrial acidification
26 are most suitable for defining secondary standards for NO_x and SO_x. Staff notes that
27 in developing a standard designed to protect against the effects of acidification due to
28 deposition of NO_x and SO_x, the resulting standards may not provide protection
29 against known effects associated with nutrient enrichment in aquatic and terrestrial
30 ecosystems.

- 1 (8) It is appropriate to consider using indicators other than NO₂ and SO₂ as the indicators
2 for a standard that is intended to address the ecological effects associated with
3 deposition of NO_x and SO_x to sensitive ecosystems. Given the reasons discussed in
4 Chapters 2, 4, and 5 of this policy assessment, staff concludes that NO_x, as defined in
5 the CAA, is best represented by the atmospheric indicator NO_y, defined as NO₂ + NO
6 + HNO₃ + PAN + 2N₂O₅ + HONO + NO₃ + organic nitrates + particulate NO₃ is the
7 more appropriate indicator of oxides of nitrogen, and that SO_x, defined to include
8 sulfur monoxide (SO), sulfur dioxide, sulfur trioxide (SO₃), and disulfur monoxide
9 (S₂O), and particulate-phase S compounds, is the more appropriate indicator of
10 oxides of sulfur.
- 11 (9) It is appropriate to use the annual average of concentrations of NO_y and SO_x as the
12 averaging time for the secondary standards, based on the chronic nature of
13 acidification, and the protection against episodic acidification provided by a standard
14 based on annual average concentrations.
- 15 (10) It is appropriate to consider changing the form of the secondary standards for NO_x
16 and SO_x as the current form does not take into account the linkages between NO_x and
17 SO_x in the causation of effects associated with acidification of aquatic ecosystems.
18 Based on the causal linkages between NO_x and SO_x, deposition of N and S, and the
19 indicator of acidification, ANC, staff concludes that the current forms should be
20 replaced with an atmospheric acidification potential index (AAPI), which reflects the
21 important roles of underlying ecosystem characteristics, determinants of deposition,
22 and reduced nitrogen deposition in determining the potential effects from deposition
23 of NO_x and SO_x.
- 24 (11) Staff initial conclusions regarding the elements of the standard, e.g. the target ANC,
25 spatial extent of areas in which the standard will be evaluated, percentiles of aquatic
26 ecosystems within sensitivity classes to be protected for alternative target ANC
27 values, calculated values of deposition transformation ratios, natural buffering
28 capacity, and reduced nitrogen deposition will be provided in the second draft of the
29 policy assessment. In addition, staff initial conclusions regarding consideration of
30 uncertainty and variability in elements of the standard will be developed in the second
31 draft.

1 **9.2 SUMMARY OF KEY UNCERTAINTIES AND RESEARCH**
2 **RECOMMENDATIONS RELATED TO SETTING A SECONDARY**
3 **STANDARD FOR NO_x AND SO_x**

4 [This section is still under development. Summary of key uncertainties to be added in
5 second draft policy assessment. Research and data needs are partial lists that will be more
6 completely developed in subsequent versions.]

7 **9.2.1 Research Needs to Reduce Uncertainty in the Next Review (focused on**
8 **aquatic acidification)**

9 Based on the information presented in this policy assessment, several information gaps
10 arise that suggest further research is needed in the following areas:

- 11 ■ Developing relationships between aquatic acidity as measured by ANC, and effects on
12 ecological effects and ecosystem services, especially due to incremental changes
- 13 ■ Developing nationwide weathering rates, or weathering rates for aquatic ecosystems
14 sensitive to acidification
- 15 ■ Developing a better understanding of the uncertainty in critical loads for acidity
- 16 ■ Developing methods for calculating critical loads for surface water acidity when data are
17 absent or of poor quality
- 18 ■ Evaluating ways to combine multiple critical load estimates for surface waters and soils on
19 a national scale
- 20 ■ Estimating ways to determine critical load parameters across different media (e.g., surface
21 waters, soils).

22 **9.2.2 Data Needs to Reduce Uncertainty in the Next Review (focused on aquatic**
23 **acidification)**

24 Improved measurements of reduced nitrogen: Nitrification processes within watershed
25 soil, sediment and vegetation systems effectively convert ammonia gas and ammonium ions to
26 nitrates, which contribute to the overall acidifying loads in ecosystems; consequently, the
27 atmospheric contributions of reduced nitrogen must be accounted for in acidification
28 assessments. We would expect that all or a subset of ambient monitoring platforms supporting

1 the N/S secondary standard will measure both ammonia gas and ammonium ion along with
2 oxidized sulfur and nitrogen species.

3 Extended modeling of air quality and deposition to inform monitoring network design: In
4 addition to providing deposition inputs for watershed models and critical loads analysis, the
5 spatial and temporal flexibility afforded by air quality modeling can support monitoring network
6 design and in inform the averaging time period (one or more years) to more appropriately
7 account for inter-annual variability in NO_x and SO_x concentrations.

8 Development of data fusion approaches to combine model results with observational
9 data: Consideration also will be given to fusing model results with observation fields to improve
10 spatial resolution by taking advantage of the landscape, emissions and meteorological
11 information that affect spatial gradients while relying on observations to reduce the influence of
12 model uncertainties.

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APPENDIX A
CHAPTER 5: CONCEPTUAL DESIGN OF THE
STANDARD

First External Review Draft

Prepared by:

U.S. Environmental Protection Agency
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APPENDIX A

CHAPTER 5: CONCEPTUAL DESIGN OF THE STANDARD

This is supplemental information to support the discussion of the conceptual design of the standard that is presented in Chapter 5 of the Policy Assessment Document. The aquatic acidification analyses developed in the REA used a number of different models and calculation techniques that are important for the development of the standard. The goal of this Appendix is to summarize information from the REA analysis that is most relevant to the Policy Assessment. A brief summary of the REA analyses are presented in section 1. In section 2 there is a general summary and technical discussion of the critical loads modeling approaches that were used in the REA, followed by a brief description of MAGIC model data requirements.

A.1 TECHNICAL SUMMARY OF METHODS USED IN THE REA AQUATIC ACIDIFICATION ANALYSIS

The aquatic acidification analysis is presented in Chapter 4 and Appendix 4 of the REA. The analysis uses multiple techniques to show the relationship between ANC and NO_x and SO_x deposition, as well as determine the current level of risk to water bodies that occur in sensitive areas. A brief summary of the techniques and objectives of the REA analysis is given in Table 1.

Table A.1. Brief summary of objects and methods used in the REA Aquatic Acidification analysis.

Technique	Objectives	
Time-series graphs of current conditions	1	Data from monitoring networks collected from 1990 to 2006 were plotted to show trends in concentrations of pollutants, deposition and acidification for each case study site. The data included surface water concentration of nitrate, sulfate and ANC; deposition of sulfate and nitrate; as well as air concentration of SO_x , NO_x and NH_4
MAGIC	1	Used to estimate the relationship between ANC values and anthropogenic NO_x and SO_x emission from the past (preacidification ~1860), present (2002 and 2006) and projected into the future (2020 and 2050). Analysis included 44 lakes from Adirondacks and 60 streams from Shenandoah.
	2	Used to develop input parameters for critical loads modeling (i.e. weathering rates)
	3	Used for uncertainty analysis

Technique	Objectives	
Critical Loads modeling	1	SSWC and FAB models used to calculate critical loads for critical limits of ANC = 0, 20, 50, 100
	2	Critical loads for ANC critical limits calculated for 169 lakes in the Adirondacks and 60 streams in the Shenandoah using water quality data from monitoring sites collected in 2006
	3	Critical loads exceedences calculated by comparing the critical loads that were calculated by SSWC with deposition data from NADP for wet deposition and CMAQ for dry deposition, both for the year 2002
Regional Extrapolation	1	117 of the critical loads calculated for the Adirondacks were extrapolated to lakes defined by the New England EMAP probability survey, representing 1842 lakes, to infer the # of lakes that exceeded their critical load
	2	69 of the critical loads calculated for the Shenandoah were extrapolated to 330 streams based on bed rock geology classification.

1

2 **A.2 TECHNICAL SUMMARY OF CRITICAL LOADS MODELING IN** 3 **THE REA**

4 The critical load of acidity for lakes or streams was derived from present-day water
5 chemistry using a combination of steady-state models. Both the Steady-State Water Chemistry
6 (SSWC) model and First-order Acidity Balance model (FAB) is based on the principle that
7 excess base-cation production within a catchment area should be equal to or greater than the acid
8 anion input, thereby maintaining the ANC above a preselected level (Reynolds and Norris, 2001;
9 Posch et al. 1997). These models assume steady-state conditions and assume that all SO_4^{2-} in
10 runoff originates from sea salt spray and anthropogenic deposition. Given a critical ANC
11 protection level, the critical load of acidity is simply the input flux of acid anions from
12 atmospheric deposition (i.e., natural and anthropogenic) subtracted from the natural (i.e.,
13 preindustrial) inputs of base cations in the surface water. Final Risk and Exposure Assessment
14 September 2009 Appendix 4, Attachment A – 15 *Aquatic Acidification Case Study* Atmospheric
15 deposition of NO_x and SO_x contributes to acidification in aquatic ecosystems through the input of
16 acid anions, such as NO_3^- and SO_4^{2-} . The acid balance of headwater lakes and streams is
17 controlled by the level of this acidifying deposition of NO_3^- and SO_4^{2-} and a series of
18 biogeochemical processes that produce and consume acidity in watersheds. The biotic integrity
19 of freshwater ecosystems is then a function of the acid-base balance, and the resulting acidity-

1 related stress on the biota that occupy the water. The calculated ANC of the surface waters is a
2 measure of the acid-base balance:

$$3 \quad \text{ANC} = [\text{BC}]^* - [\text{AN}]^* \quad (1)$$

4 where $[\text{BC}]^*$ and $[\text{AN}]^*$ are the sum of base cations and acid anions (NO_3^- and SO_4^{2-}),
5 respectively. Equation (1) forms the basis of the linkage between deposition and surface water
6 acidic condition and the modeling approach used. Given some “target” ANC concentration
7 $[\text{ANClimit}]$) that protects biological integrity, the amount of deposition of acid anions (AN) or
8 depositional load of acidity $\text{CL}(\text{A})$ is simply the input flux of acid anions from atmospheric
9 deposition that result in a surface water ANC concentration equal to the $[\text{ANClimit}]$ when
10 balanced by the sustainable flux of base cations input and the sinks of nitrogen and sulfur in the
11 lake and watershed catchment.

12 Critical loads for nitrogen and sulfur ($\text{CL}(\text{N}) + \text{CL}(\text{S})$) or critical load of acidity $\text{CL}(\text{A})$
13 were calculated for each waterbody from the principle that the acid load should not exceed the
14 nonmarine, nonanthropogenic base cation input and sources and sinks in the catchment minus a
15 neutralizing to protect selected biota from being damaged:

$$16 \quad \text{CL}(\text{N}) + \text{CL}(\text{S}) \text{ or } \text{CL}(\text{A}) = \text{BC}^*\text{dep} + \text{BCw} - \text{Bcu} - \text{AN} - \text{ANClimit} \quad (2)$$

17 Where,

18 $\text{BC}^*\text{dep} = (\text{BC}^* = \text{Ca}^* + \text{Mg}^* + \text{K}^* + \text{Na}^*)$, nonanthropogenic deposition flux of base cations $\text{BCw} =$
19 the average weathering flux, producing base cations

20 Bcu ($\text{Bc} = \text{Ca}^* + \text{Mg}^* + \text{K}^*$) = the net long-term average uptake flux of base cations in the biomass
21 (i.e., the annual average removal of base cations due to harvesting)

22 AN = the net long-term average uptake, denitrification, and immobilization of nitrogen anions
23 (e.g. NO_3^-) and uptake of SO_4^{2-}

24 ANClimit = the lowest ANC-flux that protects the biological communities.

25 Since the average flux of base cations weathered in a catchment and reaching the lake or
26 streams is difficult to measure or compute from available information, the average flux of base
27 cations and the resulting critical load estimation were derived from water quality data (Henriksen
28 and Posch, 2001; Henriksen et al., 1992; Sverdrup et al., 1990). Weighted annual mean water
29 chemistry values were used to estimate average base cation fluxes, which were calculated from
30 water chemistry data collected from the Temporally Integrated Monitoring of Ecosystems

1 (TIME)/Long-Term Monitoring (LTM) monitoring networks, that include Adirondack Longterm
 2 Monitoring (ALTM), Virginia Trout Stream Sensitivity Study (VTSSS), and the Shenandoah
 3 Watershed Study (SWAS), and Environmental Monitoring and Assessment Program (EMAP)
 4 (see Section 4.1.2.1 of Chapter 4).

5 The preacidification nonmarine flux of base cations for each lake or stream, BC^*0 , is

$$6 \quad BC^*0 = BC^*dep + BCw - Bcu \quad (3)$$

7 Thus, critical load for acidity can be rewritten as

$$8 \quad CL(N) + CL(S) = BC^*0 - AN - ANClimit = Q.([BC^*]0 - [AN] - [ANC]limit), \quad (4)$$

9 where the second identity expresses the critical load for acidity in terms of catchment runoff (Q)
 10 m/yr and concentration ($[x] = X/Q$). The sink of nitrogen in the watershed is equal to the uptake
 11 (Nupt), immobilization (Nimm), and denitrification (Nden) of nitrogen in the catchment. Thus,
 12 critical load for acidity can be rewritten as

$$13 \quad CL(N) + CL(S) = \{fNupt + (1 - r)(Nimm + Nden)\} + ([BC^*]0 - [ANC]limit)Q \quad (5)$$

14 where f and r are dimensionless parameters that define the fraction of forest cover in the
 15 catchment and the lake/catchment ratio. The in-lake retention of nitrogen and sulfur was assumed
 16 to be negligible. Equation 5 described the FAB model that was applied when sufficient data was
 17 available to estimate the uptake, immobilization, and denitrification of nitrogen and the
 18 neutralization of acid anions (e.g. NO_3^-) in the catchment. In the case where data was not
 19 available, the contribution of nitrogen anions to acidification was assumed to be equal to the
 20 nitrogen leaching rate (Nleach) into the surface water. The flux of acid anions in the surface
 21 water is assumed to represent the amount of nitrogen that is not retained by the catchment, which
 22 is determined from the sum of measured concentration of NO_3^- and ammonia in the stream
 23 chemistry. This case describes the SSWC model and the critical load for acidity is

$$24 \quad CL(A) = Q.([BC^*]0 - [ANC]limit) \quad (6)$$

25 where the contribution of acid anions is considered as part of the exceedances calculation (see
 26 Section 1.2.5, below). For the assessment of current condition in both case study areas, the
 27 critical load calculation described in Equation 6 was used for most lakes and streams. The lack of
 28 sufficient data for quantifying nitrogen denitrification and immobilization prohibited the wide
 29 use of the FAB model. In addition, given the uncertainty in quantifying nitrogen denitrification

1 and immobilization, the flux of nitrogen anions in the surface water was assumed to more
 2 accurately reflect the contribution of NO_3^- to acidification. Several major assumptions are made:
 3 (1) steady-state conditions exist, (2) the effect of nutrient cycling between plants and soil is
 4 negligible, (3) there are no significant nitrogen inputs from sources other than atmospheric
 5 deposition, (4) ammonium leaching is negligible because any inputs are either taken up by biota
 6 or adsorbed onto soils or nitrate compounds, and (5) longterm sinks of sulfate in the catchment
 7 soils are negligible.

8 **1.2.1 Preindustrial Base Cation Concentration**

9 Present-day surface water concentrations of base cations are elevated above their
 10 steady-state preindustrial concentrations because of base cation leaching through ion exchange in
 11 the soil due to anthropogenic inputs of SO_4^{2-} to the watershed. For this reason, present-day
 12 surface water base cation concentrations are higher than natural or preindustrial levels, which, if
 13 not corrected for, would result in critical load values not in steady-state condition. To estimate
 14 the preacidification flux of base cations, the present flux of base cations was estimated,

$$15 \quad \text{BC}^*_t, \text{ given by } \text{BC}^*_t = \text{BC}^*_{\text{dep}} + \text{BC}_w - \text{BC}_u + \text{BC}_{\text{exc}}, \quad (7)$$

16 Where BC_{exc} = the release of base cations due to ion-exchange processes. Assuming that
 17 deposition, weathering rate, and net uptake have not changed over time, BC_{exc} can be obtained
 18 by subtracting Equation 5 from Equation 7:

$$19 \quad \text{BC}_{\text{exc}} = \text{BC}^*_t - \text{BC}^*_0 \quad (8)$$

20 This present-day excess production of base cations in the catchment was related to the long-term
 21 changes in inputs of nonmarine acid anions ($\Delta\text{SO}^*_2 + \Delta\text{NO}_3$) by the F-factor (see below):

$$22 \quad \text{BC}_{\text{exc}} = F (\Delta\text{SO}^*_2 + \Delta\text{NO}_3) \quad (9)$$

23 For the preacidification base cation flux, solving Equation 5 for BC^*_0 and then substituting
 24 Equation 8 for BC_{exc} and explicitly describing the long-term changes in nonmarine acid ion
 25 inputs:

$$26 \quad \text{BC}^*_0 = \text{BC}^*_t - F (\text{SO}^*_{4,t} - \text{SO}^*_{4,0} + \text{NO}^*_{3,t} - \text{NO}^*_{3,0}) \quad (10)$$

27 The preacidification NO_3^- concentration, $\text{NO}^*_{3,0}$, was assumed to be zero.

1.2.2 F-factor

An F-factor was used to correct the concentrations and estimate preindustrial base concentrations for lakes in the Adirondack Case Study Area. In the case of streams in the Shenandoah Case Study Area, the preindustrial base concentrations were derived from the MAGIC model as the base cation supply in 1860 (hindcast) because the F-factor approach is untested in this region. An F-factor is a ratio of the change in nonmarine base cation concentration due to changes in strong acid anion concentrations (Henriksen, 1984; Brakke et al., 1990):

$$F = ([BC^*]_t - [BC^*]_0) / ([SO_4^*]_t - [SO_4^*]_0 + [NO_3^*]_t - [NO_3^*]_0), \quad (12)$$

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

$$F = \sin(\pi/2 Q[BC^*]_t/[S]) \quad (13)$$

where

Q = the annual runoff (m/yr). $[S]$ = the base cation concentration at which $F=1$; and for $[BC^*]_t > [S]$ F is set to 1. For Norway $[S]$ has been set to 400 milliequivalents per cubic meter (meq/m³) (circa. 8 mg Ca/L) (Brakke et al., 1990). The preacidification SO_4^{2-} concentration in lakes, $[SO_4^*]_0$, is assumed to consist of a constant atmospheric contribution and a geologic contribution proportional to the concentration of base cations (Brakke et al., 1989). The preacidification SO_4^{2-} concentration in lakes, $[SO_4^*]_0$ was estimated from the relationship between $[SO_4^{2-}]_0$ and $[BC]_t$ based on work completed by Henriksen et al., 2002 as described by the following equation:

$$[SO_4^{2-}]_0 = 15 + 0.16 * [BC]_t \quad (14)$$

1 **Table A.2** Illustrates SSWC Approach – Environmental Variables

2
$$CL(A) = BC_{dep}^* + BC_w - Bc_u - ANC_{limit}$$

3
$$CL(A) = Q([BC^*]_0 - [ANC]_{limit})$$

	Variable Code	Description	Source
1	BC_{dep}^*	Sum ($Ca^*+Mg^*+K^*+Na^*$), nonanthropogenic deposition flux of base cations	Wet NADP and Dry CASTNET
2	BC_w	Average weathering flux of base cations	Calculated (5-17)
3	Bc_u	Sum ($Ca+Mg+K$), the net long-term average uptake flux of base cations in the biomass	USFS-FIA data
4	ANC_{limit}	Lowest ANC-flux that protects the biological communities	Set
5	Ca^*	Sea Salt corrected Surface water concentration ($\mu eq/L$) growing season average. ($Ca - (CL \times 0.0213)$)	Water quality data
6	Mg^*	Sea Salt corrected Surface water concentration ($\mu eq/L$) growing season average. ($Mg - (CL \times 0.0669)$)	Water quality data
7	Na^*	Sea Salt corrected Surface water concentration ($\mu eq/L$) growing season average. ($Na - (CL \times 0.557)$)	Water quality data
8	K^*	Sea Salt corrected Surface water concentration ($\mu eq/L$) growing season average. ($K - (CL \times 0.0206)$)	Water quality data
9	SO_4^*	Sea Salt corrected Surface water concentration ($\mu eq/L$) growing season average. ($SO_4 - (CL \times 0.14)$)	Water quality data
10	CL	Surface water concentration ($\mu eq/L$) growing season average.	Water quality data
11	SO_4^*	Surface water concentration ($\mu eq/L$) growing season average.	Water quality data
12	NO_3^*	Surface water concentration ($\mu eq/L$) growing season average.	Water quality data
13	Q	The annual runoff (m/yr)	USGS
14	$[BC^*]_0$	Preindustrial flux of base cations in surface water, corrected for sea salts	Calculated from water quality data
15	$[SO_4^*]_0$	Preindustrial flux of sulfate in surface water, corrected for sea salts	Estimated
16	$[NO_3^*]_0$	Preindustrial flux of nitrate, corrected for sea salts	Equal to 0
17	F	Calculated factor	Fix values

4
5

1 **Table A.3 FAB Approach – Environmental Variables**

2
$$DL(N) + DL(S) = \{fN_{upt} + (1 - r)(N_{imm} + N_{den}) + (N_{ret} + S_{ret})\} + ([BC]_0^* - [ANC_{limit}])Q$$

	Variable Code	Description	Source
1	Ndepo	Total N deposition	NADP/CMAQ
2	ANCLimit	Lowest ANC-flux that protects the biological communities	Set
3	[BC*] ₀	Preindustrial flux of base cations in surface water, corrected for sea salt	Calculated from water quality data
4	Ca*	Sea Salt corrected Surface water concentration (µeq/L) growing season average. (Ca – (CL × 0.0213))	Water quality data
5	Mg*	Sea Salt corrected Surface water concentration (µeq/L) growing season average. (Mg – (CL × 0.0669))	Water quality data
6	Na*	Sea Salt corrected Surface water concentration (µeq/L) growing season average. (Na – (CL × 0.557))	Water quality data
7	K*	Sea Salt corrected Surface water concentration (µeq/L) growing season average. (K – (CL × 0.0206))	Water quality data
8	SO ₄ *	Sea Salt corrected Surface water concentration (µeq/L) growing season average. (SO ₄ – (CL × 0.14))	Water quality data
9	CL	Surface water concentration (µeq/L) growing season average.	Water quality data
10	SO ₄ *	Surface water concentration (µeq/L) growing season average.	Water quality data
11	NO ₃ *	Surface water concentration (µeq/L) growing season average.	Water quality data
12	Q	The annual runoff (m/yr)	USGS
13	f	f is a dimensionless parameter that define the fraction of forest cover in the catchment	
14	r	r is a dimensionless parameter that define the lake/catchment ratio	
14	N _{ret}	The in-lake retention of nitrogen	Estimated
15	S _{ret}	The in-lake retention of sulfur	Estimated
16	N _{upt}	The net long-term average uptake flux of N in the biomass	USFS-FIA data
17	N _{imm}	Immobilization of N in the soils	Estimated fix value
18	N _{den}	Denitrification	Estimated fix value
19	Lake Size	Lake size (ha)	DLMs
20	WSH	Watershed area (ha)	Calculated

3

Data requirements for MAGIC

The MAGIC model (Cosby et al., 1985a; 1985b; 1985c) is a mathematical model (a lumped-parameter model) of soil and surface water acidification in response to atmospheric deposition based on process-level information about acidification. A process model, such as MAGIC, characterizes acidification into (1) a section in which the concentrations of major ions are assumed to be governed by simultaneous reactions involving SO_4^{2-} adsorption, cation exchange, dissolution-precipitation- speciation of aluminum, and dissolution-speciation of inorganic carbon; and (2) a mass balance section in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering, net uptake and loss in biomass and losses to runoff. At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time owing to changes in atmospheric deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. The degree and rate of change of surface water acidity thus depend both on flux factors and the inherent characteristics of the affected soils.

There are numerous input data required to run MAGIC making it rather data intensive. Atmospheric deposition fluxes for the base cations and strong acid anions are required as inputs to the model. These inputs are generally assumed to be uniform over the catchment. The volume discharge for the catchment must also be provided to the model. In general, the model is implemented using average hydrologic conditions and meteorological conditions in annual simulations, i.e., mean annual deposition, precipitation and lake discharge are used to drive the model. Values for soil and surface water temperature, partial pressure of carbon dioxide and organic acid concentrations must also be provided at the appropriate temporal resolution.

The aggregated nature of the model requires that it be calibrated to observed data from a system before it can be used to examine potential system response. Calibrations are based on volume weighted mean annual or seasonal fluxes for a given period of observation. The length of the period of observation used for calibration is not arbitrary. Model output will be more reliable if the annual flux estimates used in calibration are based on a number of years rather than just one year. There is a lot of year-to-year variability in atmospheric deposition and catchment runoff. Averaging over a number of years reduces the likelihood that an “outlier” year (very dry, etc.) is used to specify the primary data on which model forecasts are based. On the other hand,

1 averaging over too long a period may remove important trends in the data that need to be
2 simulated by the model.

3 The calibration procedure requires that stream water quality, soil chemical and physical
4 characteristics, and atmospheric deposition data be available for each catchment. The water
5 quality data needed for calibration are the concentrations of the individual base cations (Ca, Mg,
6 Na, and K) and acid anions (Cl, SO_4^{2-} , and NO_3^-) and the pH. The soil data used in the model
7 include soil depth and bulk density, soil pH, soil cation-exchange capacity, and exchangeable
8 bases in the soil (Ca, Mg, Na, and K). The atmospheric deposition inputs to the model must be
9 estimates of total deposition, not just wet deposition. In some instances, direct measurements of
10 either atmospheric deposition or soil properties may not be available for a given site with stream
11 water data. In these cases, the required data can often be estimated by: (a) assigning soil
12 properties based on some landscape classification of the catchment; and (b) assigning deposition
13 using model extrapolations from some national or regional atmospheric deposition monitoring
14 network. Soil data for model calibration are usually derived as aerially averaged values of soil
15 parameters within a catchment. If soils data for a given location are vertically stratified, the soils
16 data for the individual soil horizons at that sampling site can be aggregated based on horizon,
17 depth, and bulk density to obtain single vertically aggregated values for the site, or the stratified
18 data can be used directly in the model.

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**Methodologies for National Terrestrial and Aquatic
Acidification Maximum Depositional Load
Approaches: Determining Weathering Rates**

First External Review Draft

Prepared for:

**U.S. Environmental Protection Agency
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5	capacity are means based on quarterly measurements from 1987 to 1994. The regression	
6	analysis shows a highly significant relationship ($p < .0001$) between mean stream acid	
7	neutralizing capacity and the number of fish species.	5
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2

1 **1. PURPOSE**

2 The purpose of this Work Assignment Task is to develop methodologies for estimating
3 national terrestrial and aquatic acidification maximum depositional loads. Separate approaches
4 are developed for terrestrial and aquatic acidification because biogeochemical processes in
5 aquatic and terrestrial ecosystems for nitrogen and sulfur are not identical. Information about the
6 key physical, chemical, and biological parameters needed to predict acidification potential in
7 ecosystems is not always available. For example, weathering rates are key to acidification but are
8 not available in all parts of the U.S. Knowledge of an ecosystem's weathering characteristics
9 enables a more accurate assessment of whether acidifying deposition can be neutralized or
10 exceeds an ecosystem's critical load beyond which negative effects in aquatic and terrestrial
11 health may occur.

12 This report presents an introduction to aquatic and terrestrial acidification, followed by
13 reviews of different approaches to estimating base cation weathering and detailed methodologies
14 that could be used to estimate base cation weathering for aquatic and terrestrial critical load
15 calculations.

16 **2. OVERVIEW OF ACIDIFICATION**

17 **2.1 EPA's Integrated Science Assessment and Risk and Exposure Assessment**

18 Deposition of SO_x, NO_x, and NH_x can lead to ecosystem exposure to acidification. The
19 *Integrated Science Assessment (ISA) for Oxides of Nitrogen and Sulfur—Ecological Criteria*
20 *(Final Report)* (ISA) (U.S. EPA, 2008) reports that acidifying deposition has altered major
21 biogeochemical processes in the United States by increasing the sulfur and nitrogen content of
22 soils, accelerating sulfate (SO₄²⁻) and nitrate (NO₃⁻) leaching from soil to drainage water,
23 depleting soil exchangeable base cations (especially calcium [Ca²⁺] and magnesium [Mg²⁺])
24 from soils, and increasing the mobility of aluminum (Al) within the soil (U.S. EPA, 2008,
25 Section 3.2.1)

26 The extent of soil acidification is a critical factor that regulates virtually all acidification-
27 related ecosystem effects from sulfur and nitrogen deposition. Soil acidification occurs in
28 response to both natural factors and acidifying deposition (U.S. EPA, 2008, Section 3.2.1).
29 Under conditions of low atmospheric deposition of nitrogen and sulfur, the naturally produced

1 bicarbonate anion is often the dominant mobile anion, with SO_4^{2-} and NO_3^- playing a limited role
2 with respect to cation leaching. Increased atmospheric deposition of sulfur and nitrogen can
3 result in marked increases in SO_4^{2-} and NO_3^- soil fluxes resulting in the concomitant leaching of
4 base cations (Ca^{2+} , Mg^{2+}) and toxic cations (Al^{n+} and H^+).

5 Acidification can impact the health of terrestrial and aquatic ecosystems. One of the
6 effects of soil acidification is the increased mobility of dissolved inorganic Al, which is toxic to
7 tree roots, fish, algae, and aquatic invertebrates (U.S. EPA, 2008, Sections 3.2.1.5, 3.2.2.1, and
8 3.2.3).

9 The changes in major biogeochemical processes and soil conditions caused by acidifying
10 deposition have significant ramifications for the water chemistry and biological functioning of
11 associated surface waters. Surface water chemistry indicates the negative effects of acidification
12 on the biotic integrity of freshwater ecosystems. Surface water chemistry integrates the sum of
13 terrestrial and aquatic processes that occur upstream within a watershed. Important terrestrial
14 processes include nitrogen saturation, forest decline, and soil acidification (Stoddard et al.,
15 2003). Thus, water chemistry integrates and reflects changes in soil and vegetative properties and
16 biogeochemical processes (U.S. EPA, 2008, Section 3.2.3.1).

17 Ecological effects occur at four levels of biological organization: (1) the individual; (2)
18 the population, which is composed of a single species of individuals; (3) the biological
19 community, which is composed of many species; and (4) the ecosystem. Low ANC
20 concentrations are linked with negative effects on aquatic systems at all four of these biological
21 levels. For the individual level, impacts are assessed in terms of fitness (i.e., growth,
22 development, and reproduction) or sublethal effects on condition. Surface water with low ANC
23 concentrations can directly influence aquatic organism fitness or mortality by disrupting ion
24 regulation and can mobilize dissolved inorganic aluminum, which is highly toxic to fish under
25 acidic conditions (i.e., $\text{pH} < 6$ and $\text{ANC} < 50 \mu\text{eq/L}$). For example, research showed that as the pH
26 of surface waters decreased to < 6 , many aquatic species, including fish, invertebrates,
27 zooplankton, and diatoms, tended to decline sharply causing species richness to decline
28 (Schindler, 1988). Van Sickle and colleagues (1996) also found that blacknose dace (*Rhinichthy*
29 spp.) were highly sensitive to low pH and could not tolerate inorganic Al concentrations greater
30 than about 3.7 micromolar (μM) for extended periods of time. For example, they found that after

1 6 days of exposure to high inorganic Al, blacknose dace mortality increased rapidly to nearly
2 100%.

3 At the community level, species richness and community structure can be used to
4 evaluate the effects of acidification. Species composition refers to the mix of species that are
5 represented in a particular ecosystem, whereas species richness refers to the total number of
6 species in a stream or lake. Acidification alters species composition and richness in aquatic
7 ecosystems. There are a number of species common to many oligotrophic waterbodies that are
8 sensitive to acidification and cannot survive, compete, or reproduce in acidic waters. In response
9 to small to moderate changes in acidity, acid-sensitive species are often replaced by other more
10 acid-tolerant species, resulting in changes in community composition and richness, but with little
11 or no change in total community biomass. The effects of acidification are continuous, with more
12 species being affected at higher degrees of acidification. At a point, typically a pH <4.5 and an
13 ANC <0 µeq/L, complete to near-complete loss of many classes of organisms occur, including
14 fish and aquatic insect populations, whereas others are reduced to only a few acidophilic forms.
15 These changes in species integrity are because energy cost in maintaining physiological
16 homeostasis, growth, and reproduction is high at low ANC levels (Schreck, 1981, 1982;
17 Wedemeyer et al., 1990).

18 In EPA's *Risk and Exposure Assessment for Review of the Secondary National Ambient*
19 *Air Quality Standards for Oxides of Nitrogen and Sulfur* (U.S. EPA, 2009), the negative impacts
20 of acidifying deposition were assessed by conducting case studies of 1) aquatic acidification in
21 Adirondack Mountains lakes and Shenandoah Mountains streams, and 2) terrestrial acidification
22 in red spruce and sugar maple forests in the White Mountains of New Hampshire and in
23 Pennsylvania, respectively. The results of these case studies revealed the significance of base
24 cation weathering in predicting aquatic and terrestrial acidification impacts. The results further
25 highlighted the need to select weathering methodologies that can be applied across geologically
26 diverse ecosystems in the United States. This report uses the information from the Risk and
27 Exposure Assessment as a starting point to identify and evaluate approaches to predicting
28 weathering at other locations and larger scales in the United States. In this report, RTI
29 recommends methodologies (including computer models) for application in the United States,
30 assesses the availability of input data for those methodologies, identifies potential remedies to

1 limited data availability, and describes uncertainties with the methodologies in predicting
2 acidification impacts.

3 **2.2 Aquatic Acidification and Critical Acid Loads**

4 Surface water chemistry is a primary indicator of acidification and the resulting negative
5 effects on the biotic integrity of freshwater ecosystems. Chemical parameters can be used to
6 assess effects of acidifying deposition on lake or stream acid-base chemistry. These receptors
7 include surface water pH and concentrations of SO_4^{2-} , NO_3^- , Al, and Ca^{2+} ; the sum of base
8 cations; and the recently developed base cation surplus. Another widely used water chemistry
9 indicator for both atmospheric deposition sensitivity and effects is acid neutralizing capacity
10 (ANC). The utility of the ANC criterion lies in the association between ANC and the surface
11 water constituents that directly contribute to or ameliorate acidity-related stress, in particular pH,
12 Ca^{2+} , and Al. ANC is also used because it integrates overall acid status and because surface
13 water acidification models do a better job projecting ANC than they do for projecting pH and
14 dissolved inorganic Al concentrations.

15 For the purpose of this study, ANC of surface waters is simply measured as the total
16 amount of strong base ions minus the total amount of strong acid anions:

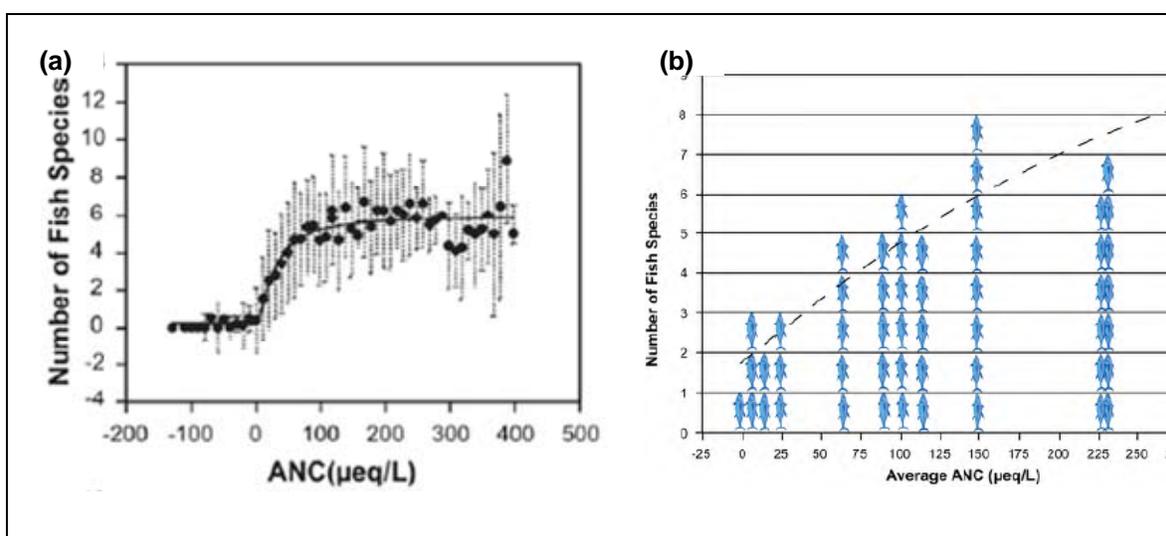
$$17 \quad \text{ANC} = (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+ + \text{Na}^+ + \text{NH}_4) - (\text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^-) \quad (2-1)$$

18 The unit of ANC is usually microequivalents per liter ($\mu\text{eq/L}$). If the sum of the
19 equivalent concentrations of the base cations exceeds those of the strong acid anions, then the
20 ANC of a waterbody will be positive. To the extent that the base cation sum exceeds the strong
21 acid anion sum, the ANC will be higher. Higher ANC is generally associated with high pH and
22 Ca^{2+} concentrations; lower ANC is generally associated with low pH and Al^{3+} concentrations and
23 a greater likelihood of toxicity to biota.

24 Low ANC coincides with effects on aquatic systems (e.g., individual species fitness loss
25 or death, reduced species richness, altered community structure). At the community level,
26 species richness is positively correlated with pH and ANC (Kretser et al., 1989; Rago and
27 Wiener, 1986) because energy cost in maintaining physiological homeostasis, growth, and
28 reproduction is high at low ANC levels (Schreck, 1981, 1982; Wedemeyer et al., 1990). For
29 example, Sullivan and colleagues (2006) found a logistic relationship between fish species
30 richness and ANC class for Adirondack Case Study Area lakes (**Figure 2-1a**) that indicates the

1 probability of occurrence of an organism for a given value of ANC. In the Shenandoah Case
 2 Study Area, a statistically robust relationship between acid-base status of streams and fish
 3 species richness was also documented (**Figure 2-1b**). In fact, ANC has been found in various
 4 studies to be the best single indicator of the biological response and health of aquatic
 5 communities in acid-sensitive systems (Lien et al., 1992; Sullivan et al., 2006).

6 Biota are generally not harmed when ANC values are >100 microequivalents per liter
 7 ($\mu\text{eq/L}$). The number of fish species also peaks at ANC values >100 $\mu\text{eq/L}$ (Bulger et al., 1999;
 8 Driscoll et al., 2001; Kretser et al., 1989; Sullivan et al., 2006). Below 100 $\mu\text{eq/L}$, ANC fish
 9 fitness and community diversity begin to decline (**Figure 2-1**). At ANC levels between 100 and
 10 50 $\mu\text{eq/L}$, the fitness of sensitive species (e.g., brook trout, zooplankton) also begins to decline.
 11 When ANC concentrations are <50 $\mu\text{eq/L}$, they are generally associated with death or loss of
 12 fitness of biota that are sensitive to acidification (Kretser et al., 1989; Dennis and Bulger, 1995).



13
 14 **Figure 2-1.** (a) Number of fish species per lake or stream versus acidity, expressed as
 15 acid neutralizing capacity for Adirondack Case Study Area lakes (Sullivan et al., 2006).
 16 (b) Number of fish species among 13 streams in Shenandoah National Park. Values of
 17 acid neutralizing capacity are means based on quarterly measurements from 1987 to
 18 1994. The regression analysis shows a highly significant relationship ($p < .0001$) between
 19 mean stream acid neutralizing capacity and the number of fish species.

20 When ANC levels drop to <20 $\mu\text{eq/L}$, all biota exhibit some level of negative effects.
 21 Fish and plankton diversity and the structure of the communities continue to decline sharply to
 22 levels where acid-tolerant species begin to outnumber all other species (Matuszek and Beggs,
 23 1988; Driscoll et al., 2001). Stoddard and colleagues (2003) showed that to protect biota from
 24 episodic acidification in the springtime, base flow ANC levels need to have an ANC of at least

1 30–40 $\mu\text{eq/L}$. Complete loss of fish populations and extremely low diversity of planktonic
 2 communities occur when ANC levels stay $<0 \mu\text{eq/L}$. Only acidophilic species are present, but
 3 their population numbers are sharply reduced (Sullivan et al., 2006).

4 The critical load approach can be used to connect current deposition of nitrogen and
 5 sulfur to the acid-base condition and biological risk to biota of lakes and streams in the study
 6 through the defined ANC thresholds. Calculating critical load exceedances (i.e., the amount of
 7 deposition above the critical load) allows the determination of whether current deposition poses a
 8 risk of acidification to a given group of waterbodies. Low critical load values (i.e., less than 50
 9 $\text{meq/m}^2\text{yr}$) mean that the watershed has a limited ability to neutralize the addition of acidic
 10 anions, and hence, it is susceptible to acidification. The greater the critical load value, the greater
 11 the ability of the watershed to neutralize the additional acidic anions and protect aquatic life.
 12 This approach also allows for the comparison of different levels of ANC thresholds (e.g., 0
 13 $\mu\text{eq/L}$ (acidic), 20 $\mu\text{eq/L}$ (minimal protection), 50 $\mu\text{eq/L}$ (moderate protection), and 100 $\mu\text{eq/L}$
 14 (full protection)) and their associated risk to the biological community. **Table 2-1** provides a
 15 summary of the biological effects experienced at each of these limits.

Table 2-1. Aquatic Status Categories

Category Label ANC Levels* Expected Ecological Effects		
Acute Concern	<0 micro equivalent per Liter ($\mu\text{eq/L}$)	Near complete loss of fish populations is expected. Planktonic communities have extremely low diversity and are dominated by acidophilic forms. The number of individuals in plankton species that are present is greatly reduced.
Severe Concern	0–20 $\mu\text{eq/L}$	Highly sensitive to episodic acidification. During episodes of high acidifying deposition, brook trout populations may experience lethal effects. Diversity and distribution of zooplankton communities decline sharply.
Elevated Concern	20–50 $\mu\text{eq/L}$	Fish species richness is greatly reduced (i.e., more than half of expected species can be missing). On average, brook trout populations experience sublethal effects, including loss of health, reproduction capacity, and fitness. Diversity and distribution of zooplankton communities decline.
Moderate Concern	50–100 $\mu\text{eq/L}$	Fish species richness begins to decline (i.e., sensitive species are lost from lakes). Brook trout populations are sensitive and variable, with possible sublethal effects. Diversity and distribution of zooplankton communities also begin to decline as species that are sensitive to acidifying deposition are affected.

Category Label ANC Levels* Expected Ecological Effects		
Low Concern	>100 µeq/L	Fish species richness may be unaffected. Reproducing brook trout populations are expected where habitat is suitable. Zooplankton communities are unaffected and exhibit expected diversity and distribution.

1 There are numerous methods and models that can be used to calculate critical loads for
2 acidity. Drawing on the peer-reviewed scientific literature (Dupont et al., 2005), this study will
3 use a steady-state critical load model that uses surface water chemistry as the base for calculating
4 the critical load. A combination of the Steady-State Surface Water Chemistry (SSWC) and First-
5 Order Acidity Balance (FAB) models were used to calculate the critical load. Both the SSWC
6 model and FAB are based on the principle that excess base-cation production within a catchment
7 area should be equal to or greater than the acid anion input, thereby maintaining the ANC above
8 a preselected level (Reynolds and Norris, 2001; Posch et al., 1997). These models assume
9 steady-state conditions and assume that all SO_4^{2-} in runoff originates from sea salt spray and
10 anthropogenic deposition. Given a critical ANC protection level, the critical load of acidity is
11 simply the input flux of acid anions from atmospheric deposition (i.e., natural and
12 anthropogenic) subtracted from the natural (i.e., preindustrial) inputs of base cations in the
13 surface water.

14 Critical loads for nitrogen and sulfur (CL(N) + CL(S)) or critical load of acidity CL(A)
15 are calculated for each waterbody from the principle that the acid load should not exceed the
16 nonmarine, nonanthropogenic base cation input and sources and sinks in the catchment minus a
17 neutralizing to protect selected biota from being damaged:

$$18 \quad \text{CL(N) + CL(S) or CL(A) = BC}_{\text{dep}}^* + \text{BC}_w - \text{Bc}_u - \text{AN} - \text{ANC}_{\text{limit}} \quad (2-2)$$

19 where

20 BC_{dep}^* = nonanthropogenic deposition flux of base cations
21 (BC*=Ca*+Mg*+K*+Na*)

22 BC_w = the average weathering flux, producing base cations

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

1 AN = the net long-term average uptake, denitrification, and immobilization of
2 nitrogen anions (e.g. NO_3^-) and uptake of SO_4^-

3 $\text{ANC}_{\text{limit}}$ = the lowest ANC-flux that protects the biological communities.

4 In order to estimate a critical load from water quality data alone, a relation to the
5 preacidification nonmarine flux of base cations for each lake or stream, BC_0^* , is used.

$$6 \quad \text{BC}_0^* = \text{BC}_{\text{dep}}^* + \text{BC}_w - \text{BC}_u \quad (2-3)$$

7 Thus, the critical load for acidity can be rewritten as

$$8 \quad \text{CL}(\text{N}) + \text{CL}(\text{S}) = \text{BC}_0^* - \text{AN} - \text{ANC}_{\text{limit}} = Q([\text{BC}^*]_0 - [\text{AN}] - [\text{ANC}]_{\text{limit}}) \quad (2-4)$$

9 where the second identity expresses the critical load for acidity in terms of catchment runoff (Q)
10 m/yr and concentration ($[\text{x}] = \text{X}/\text{Q}$). In cases where data are available, the FAB model is applied
11 to quantify the [AN] term of the critical load calculation (derivation provided in Appendix 4,
12 Attachment A of U.S. EPA, 2009). Where data are not available the contribution of nitrogen
13 anions to acidification was assumed to be equal to the nitrogen leaching rate into the surface
14 water. The flux of acid anions in the surface water is assumed to represent the amount of
15 nitrogen that is not retained by the catchment, which is determined from the sum of measured
16 concentration of NO_3^- and ammonia in the stream chemistry. This case describes the SSWC
17 model and the critical load for acidity is

$$18 \quad \text{CL}(\text{A}) = Q([\text{BC}^*]_0 - [\text{ANC}]_{\text{limit}}) \quad (2-5)$$

19 where the contribution of acid anions is considered as part of the exceedances calculation. With
20 this approach several major assumptions are made: (1) steady-state conditions exist, (2) the effect
21 of nutrient cycling between plants and soil is negligible, (3) there are no significant nitrogen
22 inputs from sources other than atmospheric deposition, (4) ammonium leaching is negligible
23 because any inputs are either taken up by biota or adsorbed onto soils or nitrate compounds, and
24 (5) long-term sinks of sulfate in the catchment soils are negligible.

25 To determine a value for BC_0^* with the SSWC method, estimates of BC_{dep} are available
26 from previous works including the recent REA (U.S. EPA, 2009). Assumptions or estimates for
27 BC_u and AN can be made based on attributes of the area of study, including vegetation

1 characteristics. But the average flux of base cations weathered in a catchment and reaching the
2 lake or streams (BC_w) is difficult to measure or compute from available information (Henriksen
3 and Posch, 2001; Henriksen et al., 2002; Langan et al., 2001). In the previous work for the Risk
4 and Exposure Assessment case studies (U.S. EPA, 2009) the average flux of base cations and the
5 resulting critical load estimation were derived from water quality data (Henriksen and Posch,
6 2001; Henriksen et al., 1992; Sverdrup et al., 1990). Weighted annual mean water chemistry
7 values were used to estimate average base cation fluxes, which were calculated from water
8 chemistry data collected from several national and regional monitoring programs. For a national
9 assessment, however, new methods must be developed to estimate the BC_w flux, which is critical
10 to the critical load calculation, through consistent, nationally-applicable means.

11 **2.1.2 Terrestrial Acidification and Critical Acid Loads**

12 Due to the impact of acidifying nitrogen and sulfur deposition on soil solution base cation
13 (Bc) and aluminum concentrations, the Bc/Al ratio in the soil solution is often used as the
14 chemical or critical indicator of terrestrial acidification. It was recently used as an indicator in the
15 U.S. EPA's Risk and Exposure Assessment for oxides of nitrogen and oxides of sulfur (U.S.
16 EPA, 2009). This Bc/Al ratio links acidifying deposition to biological responses or end points,
17 such as reduced plant or tree growth, within an ecosystem. In a meta-analysis of studies that
18 explored the relationship between Bc/Al ratio in soil solution and tree growth, Sverdrup and
19 Warfvinge (1993a) reported the Bc/Al ratios at which growth was reduced by 20% relative to
20 control trees. This 20% reduction in tree growth was selected as the critical value because it was
21 thought to represent a significant reduction in growth (H. Sverdrup *personal communication*,
22 2009b) and approximates the Bc/Al value that would result in a 10% reduction in normal tree
23 growth under field conditions (Sverdrup and Warfvinge, 1993a). **Figure 2-2** presents the
24 findings of Sverdrup and Warfvinge (1993a) based on 46 of the tree species (native and
25 introduced) that grow in North America. This summary indicates that there is a 50% chance of
26 negative tree response (i.e., >20% reduced growth) at a soil solution Bc/Al ratio of 1.2 and a
27 75% chance at a Bc/Al ratio of 0.6. These findings clearly demonstrate a relationship between
28 Bc/Al ratio and tree health; as the Bc/Al is reduced, there is a greater likelihood of a negative
29 impact on tree health.

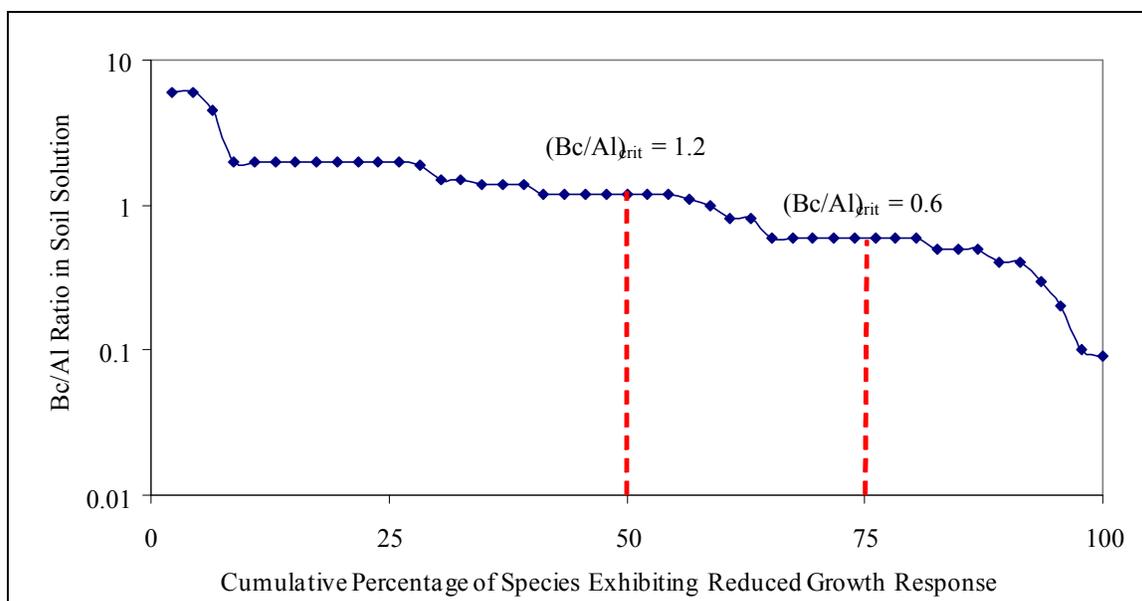


Figure 2-2. The relationship between the Bc/Al ratio in soil solution and the percentage of tree species (found growing in North America – native and introduced species) exhibiting a 20% reduction in growth relative to controls (after Sverdrup and Warfvinge, 1993).

The tree species most commonly studied in North America to assess the impacts of acidification due to total nitrogen and sulfur deposition are red spruce (i.e., *Picea Rubens*) and sugar maple (i.e., *Acer saccharum*). Both species are found in the eastern United States, and soil acidification is widespread throughout this area (Warby et al., 2009). Based on the results from a compilation of laboratory studies, red spruce growth can be reduced by 20% at a Bc/Al soil solution ratio of approximately 1.2, and a similar reduction in growth may be experienced by sugar maple at a Bc/Al ratio of 0.6 (Sverdrup and Warfvinge 1993a).

Red spruce is found scattered throughout high-elevation sites in the Appalachian Mountains, including the southern peaks. Noticeable fractions of the canopy red spruce died within the Adirondack, Green, and White mountains in the 1970s and 1980s. Although a variety of conditions, such as changes in climate and exposure to ozone, may impact the growth of red spruce (Fincher et al., 1989; Johnson et al., 1988), acidifying deposition has been implicated as one of the main factors causing this decline. Based on the research conducted to date, acidifying deposition can cause a depletion of base cations in upper soil horizons, Al toxicity to tree roots, and accelerated leaching of base cations from foliage (U.S. EPA, 2008, Section 3.2.2.3). Such nutrient imbalances and deficiencies can reduce the ability of trees to respond to stresses, such as insect defoliation, drought, and cold weather damage (DeHayes et al., 1999; Driscoll et al.,

2001), thereby decreasing tree health and increasing mortality. Additional linkages between acidifying deposition and red spruce physiological responses are indicated in **Table 4.3-1**. Within the southeastern United States, periods of red spruce decline slowed after the 1980s, when a corresponding decrease in SO₂ emissions, and therefore acidic deposition, was recorded (Webster et al., 2004).

Sugar maple is found throughout the northeastern United States and the central Appalachian Mountain region. This species has been declining in the eastern United States since the 1950s. Studies on sugar maple have found that one source of this decline in growth is related to both acidifying deposition and base-poor soils on geologies dominated by sandstone or other base-poor substrates (Bailey et al., 2004; Horsley et al., 2000). These site conditions are representative of the conditions expected to be most susceptible to impacts of acidifying deposition because of probable low initial base cation pools and high base cation leaching losses (U.S. EPA, 2008, Section 3.2.2.3). The probability of a decrease in crown vigor or an increase in tree mortality has been noted to increase at sites with low Ca²⁺ and Mg²⁺ as a result of leaching caused by acidifying deposition (Drohan and Sharpe, 1997). Low levels of Ca²⁺ in leaves and soils have been shown to be related to lower rates of photosynthesis and higher antioxidant enzyme activity in sugar maple stands in Pennsylvania (St. Clair et al., 2005). In addition, plots of sugar maples in decline were found to have Ca²⁺/Al ratios less than 1, as well as lower base cation concentrations and pH values compared with plots of healthy sugar maples (Drohan et al., 2002). Sugar maple regeneration has also been noted to be restricted under conditions of low soil Ca²⁺ levels (Juice et al., 2006). These indicators have all been shown to be related to the deposition of atmospheric nitrogen and sulfur. Additional linkages between acidifying deposition and sugar maple physiological responses are indicated in **Table 2-2**.

Table 2-2. Summary of Linkages between Acidifying Deposition, Biogeochemical Processes That Affect Ca²⁺, Physiological Processes That Are Influenced by Ca²⁺, and Effect on Forest Function

Biogeochemical Response to Acidifying deposition	Physiological Response	Effect on Forest Function
Leach Ca ²⁺ from leaf membrane	Decrease the cold tolerance of needles in red spruce	Loss of current-year needles in red spruce
Reduce the ratio of Ca ²⁺ /Al in soil and soil solutions	Dysfunction in fine roots of red spruce blocks uptake of Ca ²⁺	Decreased growth and increased susceptibility to stress in red spruce

Biogeochemical Response to Acidifying deposition	Physiological Response	Effect on Forest Function
Reduce the ratio of Ca^{2+}/Al in soil and soil solutions	More energy is used to acquire Ca^{2+} in soils with low Ca^{2+}/Al ratios	Decreased growth and increased photosynthetic allocation to red spruce roots
Reduce the availability of nutrient cations in marginal soils	Sugar maples on drought-prone or nutrient-poor soils are less able to withstand stresses	Episodic dieback and growth impairment in sugar maple

Source: Fenn and colleagues, 2006.

1 Although the main focus of the Terrestrial Acidification Case Study outlined in the *Risk*
2 *and Exposure Assessment for Review of the Secondary National Ambient Air Quality Standards*
3 *for Oxides of Nitrogen and Sulfur* (U.S. EPA, 2009) was an evaluation of the negative impacts of
4 nitrogen and sulfur deposition on soil acidification and tree health, it should be recognized that
5 under certain conditions, nitrogen and sulfur deposition can have a positive impact on tree health.
6 Nitrogen limits the growth of many forests (Chapin et al., 1993; Killam, 1994; Miller, 1988), and
7 therefore, in such forests, nitrogen deposition may act as a fertilizer and stimulate growth.
8 Forests where critical acid loads are not exceeded by nitrogen and sulfur deposition could
9 potentially be included within this group of forests that respond positively to deposition. These
10 potential positive growth impacts of nitrogen and sulfur deposition are discussed further, and the
11 results of case study analyses are presented in Attachment A of Appendix 5 of the *Risk and*
12 *Exposure Assessment* (U.S. EPA, 2009).

13 In summary, among potential influencing factors, including elevated ozone levels and
14 changes in climate, the acidification of soils is one of the factors that can negatively impact the
15 health of red spruce and sugar maple. Mortality and susceptibility to disease and injury can be
16 increased and growth decreased with acidifying deposition. Therefore, the health of sugar maple
17 and red spruce was used as the endpoints (ecological responses) to evaluate acidification in
18 terrestrial systems. “Health” in the context of the Risk and Exposure Assessment terrestrial
19 acidification case study was defined as the physiological condition of a tree that impacts growth
20 and/or mortality.

21 The Simple Mass Balance (SMB) model was used to estimate critical loads of acidity in
22 the Risk and Exposure Assessment case study (Equation 2-1). The full derivation of this equation
23 is detailed in the ICP Mapping and Modeling Manual (UNECE, 2004).

$$1 \quad \quad \quad CL(S + N) = BC_{dep} - Cl_{dep} + BC_w - Bc_u + N_i + N_u + N_{de} - ANC_{le,crit} \quad (2-1)$$

2 where

3 $CL(S+N)$ = forest soil critical load for combined nitrogen and sulfur acidifying
4 deposition $((N+S)_{comb})$

5 BC_{dep} = base cation ($Ca^{2+} + K^+ + Mg^{2+} + Na^+$) deposition¹

6 Cl_{dep} = chloride deposition

7 BC_w = base cation ($Ca^{2+} + K^+ + Mg^{2+} + Na^+$) weathering

8 Bc_u = uptake of base cations ($Ca^{2+} + K^+ + Mg^{2+}$) by trees

9 N_i = nitrogen immobilization

10 N_u = uptake of nitrogen by trees

11 N_{de} = denitrification

12 $ANC_{le,crit}$ = forest soil acid neutralizing capacity of critical load leaching

13 Some of these parameters had defined or selected input values (BC_{dep} , Cl_{dep} , N_i , N_u and N_{de}),
14 while four of these parameters, including BC_w , Bc_u , N_u and $ANC_{le,crit}$, required calculation.

15 For the Risk and Exposure Assessment's terrestrial acidification case study, three values
16 of the indicator of critical load, expressed as $(Bc/Al)_{crit}$ soil solution ratio, were selected to
17 represent different levels of tree protection associated with total nitrogen and sulfur deposition:
18 0.6, 1.2, and 10 (**Table 2-3**). The $(Bc/Al)_{crit}$ ratio of 0.6 represents the highest level of impact
19 (lowest level of protection) to tree health and growth and was selected because 75% of species
20 found growing in North America experience reduced growth at this Bc/Al ratio. In addition, a
21 soil solution Bc/Al ratio of 0.6 has been linked to a 20% and 35% reduction in sugar maple and
22 red spruce growth, respectively. The $(Bc/Al)_{crit}$ ratio of 1.2 is considered to represent a moderate
23 level of impact, as the growth of 50% of tree species (found growing in North America) was
24 negatively impacted at this soil solution ratio. The $(Bc/Al)_{crit}$ ratio of 10.0 represents the lowest
25 level of impact (greatest level of protection) to tree growth; it is the most conservative value used
26 in studies that have calculated critical loads in the United States and Canada (Canada (McNulty
27 et al., 2007; NEG/ECP, 2001; Watmough et al., 2004).

¹ The ICP Mapping and Modeling Manual (UNECE, 2004) recommends that wet deposition be corrected for sea salt on sites within 70 km of the coast. Both the HBEF and KEF case study areas are greater than 70 km from the coast, so this correction was not used.

Table 2-3. The Three Indicator $(Bc/AI)_{crit}$ Soil Solution Ratios and Corresponding Levels of Protection to Tree Health and Critical Loads

Indicator $(Bc/AI)_{crit}$ Soil Solution Ratio	Level of Protection to Tree Health	Critical Load
0.6	Low	High
1.2	Intermediate	Intermediate
10.0	High	Low

1 The prediction of tree protection achieved using each of these three indicator ratios of
2 0.6, 1.2, and 10.0 includes an important estimation of base cation weathering as shown in
3 Equation 2-1, above. The purpose of this report is to describe the methodologies, data
4 requirements, data availability, and uncertainties associated with estimating base cation
5 weathering.

6 **3. AQUATIC BASE CATION WEATHERING METHODOLOGY**

7 The ISA (US EPA, 2008) reports that the principal factor governing the sensitivity of
8 terrestrial and aquatic ecosystems to acidification from sulfur and nitrogen deposition is geology
9 (particularly surficial geology). Geologic formations having low base cation supply generally
10 underlie the watersheds of acid-sensitive lakes and streams. Other factors that contribute to the
11 sensitivity of soils and surface waters to acidifying deposition include topography, soil
12 chemistry, land use, and hydrologic flowpath. Surface waters in the same setting can have
13 different sensitivities to acidification, depending on the relative contributions of near-surface
14 drainage water and deeper groundwater (Chen et al., 1984; Driscoll et al., 1991; Eilers et al.,
15 1983). Lakes and streams in the United States that are sensitive to episodic and chronic
16 acidification in response to SO_x , and to a lesser extent NO_x , deposition tend to occur at relatively
17 high elevation in areas that have base-poor bedrock, high relief, and shallow soils (U.S. EPA,
18 2008, Section 3.2.4.1).

19 **3.1 Aquatic Base Cation Weathering**

20 Base cation weathering for aquatic acidification critical loads must be representative of
21 the catchment around the waterbody of interest. This aspect of quantification of the weathering
22 rate provides the difference when calculating weathering rates for aquatic versus terrestrial
23 analysis purposes. The process of weathering itself provides the only natural in-soil source of
24 alkalinity that is available to neutralize acidity inputs to the system over the long term. Chemical
25 weathering of the mineral matrix within soils supplies base cations that are removed from soil

1 due to acid inputs. Therefore, the rate of weathering of the soils within a catchment is dependent
 2 on the chemical and physical properties of the soil (Sverdrup et al., 1992; Whitfield et al., 2006).
 3 As indicated in Section 2.2, the average flux of base cations weathered in a catchment and
 4 reaching the lake or streams (BC_w) is difficult to measure or compute from available information
 5 (Henriksen and Posch, 2001; Henriksen et al., 2002; Langan et al., 2001). Approaches also differ
 6 based on whether the weathering rate needs to account for only in-soil processes (profile
 7 measurements and models) or whether it needs to account for the flux of base cations to surface
 8 water (spatially integrated catchment data and models) (Langan et al., 2001).

9 In the Aquatic Acidification case study in the REA Report (U.S. EPA, 2009), BC_w rates
 10 were not directly calculated. Instead, the F-factor approach was used to calculate the pre-
 11 acidification, non-marine flux of base cations (BC^*_0) for each lake or stream. An F-factor
 12 (explained in Section 3.2.2) is a ratio of the change in non-marine base cation concentration due
 13 to changes in strong acid anion concentrations (Henriksen, 1984; Brakke et al., 1990), as shown
 14 in the following equations:

$$15 \quad BC^*_0 = BC^*_t - F (SO^*_{4,t} - SO^*_{4,0} + NO^*_{3,t} - NO^*_{3,0}) \quad (3-1)$$

$$16 \quad F = ([BC^*_t] - [BC^*_0]) / ([SO^*_4]_t - [SO^*_4]_0 + [NO^*_3]_t - [NO^*_3]_0) \quad (3-2)$$

17 where the subscripts t and 0 refer to present and pre-acidification conditions, respectively. The
 18 pre-acidification NO_3^- concentration, $NO^*_{3,0}$, was assumed to be zero. Several attempts have
 19 been made to create empirical relations for the F-factor and the pre-acidification SO_4^*
 20 concentration. Although the Aquatic Acidification case study relied on two of these relations, it
 21 must be noted that they were developed for areas outside of the U.S. and, therefore, cannot be
 22 applied to the conditions found within U.S. soils and climates without introducing a source of
 23 uncertainty (Henriksen and Posch, 2001; Henriksen et al., 2002; Brakke et al., 1989; Posch et al.,
 24 1997). Notwithstanding the lack of U.S.-based empirical relations, the F-factor can be used to
 25 derive BC_w estimates. Assuming that all atmospheric deposition of base cations that falls within
 26 a catchment passes through to the surface water and that one can accurately estimate the uptake
 27 of base cations within the catchment, the BC_w could ultimately be backed out of these
 28 relationships. However, both of these assumptions are likely to introduce an additional amount of
 29 uncertainty into the BC_w estimates.

1 For a national aquatic acidification assessment, different methods must be employed to
2 estimate BC_w rates. In some studies, simple assumptions for the BC_w are utilized. For instance, in
3 a study by Dupont and colleagues (2005) using the SSWC, the authors assumed that weathering
4 rates were time-independent and did not affect critical load estimates. In more advanced process
5 modeling applications, such as ones using the Model of Acidification of Groundwater in
6 Catchments (MAGIC), weathering rates can be adjusted during calibration and allowed to vary
7 over ranges like 0 and 5 times the observed watershed base cation export for base cation
8 weathering (Sullivan et al., 2004). There are several different approaches to estimating the
9 weathering rate of a soil or a catchment, ranging from empirical relations to mass balance
10 methods to calibrated process models. According to Whitfield and colleagues (2006) “to date no
11 method has proven to be superior in application to different soil types and differing levels of soil
12 acidification.” The remainder of this section is intended to examine the BC_w estimation methods
13 that would be applicable to a national aquatic acidification critical loads analysis giving
14 consideration to the limitations of the method and the possible data and processing requirements
15 for the analysis.

16 **3.2 Methodologies for Determining Base Cation Weathering Values in the United States**

17 **3.2.1 Difficulties in estimating base cation weathering**

18 Consideration must be given to several factors in the estimation of base cation weathering
19 fluxes for aquatic acidification (Sverdrup et al., 1992; Whitfield et al., 2006; Rapp and Bishop,
20 2009; Henriksen and Posch, 2001; Henriksen et al., 2002):

- 21 1. The weathering contribution of the entire catchment must be understood and not
22 simply the weathering contribution of certain soil profiles within the catchment.
23 Additionally, the various types of land use (e.g. agriculture or forest) within a
24 catchment may all affect weathering rates differently.
- 25 2. When utilizing soil profile weathering methods, the characteristics of the entire soil
26 profile must be considered and weighted according to catchment composition as
27 opposed to only the rooting zone in individual profiles as used in determining
28 weathering for terrestrial acidification purposes.
- 29 3. Based on the critical load method chosen, it is often necessary to assume that the BC_w
30 remains constant over the length of the analysis. While this simplifies the estimation
31 of BC_w , it introduces uncertainty into any analysis. The length of the analysis

1 scenario must be sufficiently long and have supporting data in order to provide a
2 long-term average, which is not subjected to short-term variations.

- 3 4. The data requirements for a national assessment necessitate using similar data sources
4 for all applications so that assumptions and methods can remain constant across the
5 nation.
- 6 5. The application of any empirical relations for calculation of BC_w or intermediate
7 component of BC_w (e.g., the F-factor) must be validated against the geographic region
8 in which they will be applied. Given that most empirical relations developed to date
9 were based on data from European nations, these relations need to be recalibrated to
10 data from the U.S.

11 Given all of these factors, estimation of BC_w for a national application poses a significant
12 challenge. The methods detailed in the following section seek to balance the limitations and
13 benefits of each approach to estimation of BC_w .

14 **3.2.2 Approaches to estimating BC_w for Aquatic Acidification**

15 Work presented in the scientific literature over the last two decades provides several
16 different approaches researchers have taken to estimate the BC_w rates for aquatic effects. These
17 approaches do not always differentiate between the actual weathering processes in-soil and the
18 other ion exchange processes taking place (Langan et al., 2001). Approaches to estimating BC_w
19 also vary between terrestrial and aquatic studies. Aquatic studies of acidification must capture
20 the weathering rates of all soil horizons which contribute base cations and not solely the rooting
21 zone as specified in terrestrial acidification studies (Whitfield et al., 2006).

22 Four general categories of approaches are outlined for determining BC_w for aquatic
23 acidification critical loads calculations using the SSWC.

- 24 1. Budgets studies of catchments or watersheds;
- 25 2. Historical weathering rate determinations;
- 26 3. Empirical relations; and
- 27 4. Process-based models.

28 In the case of empirical data relations and process-based models, specific methods are
29 provided. The strengths and weaknesses of either the general category or specific approach in
30 terms of both utilization in aquatic acidification critical loads calculations and estimation of BC_w
31 are examined in the following paragraphs and **Table 3-1**.

1 Budget Studies – Budget studies are simple means of determining fluxes within a system
2 by balancing the masses coming into and going out of a system. In determining the BC_w , a mass
3 balance would be performed around the base cations fluxes within a watershed, where
4 atmospheric deposition constitutes the main source input and streamflow the main output. Within
5 the balance, base cation retention is also accounted for through uptake by biomass and
6 immobilization in the soil. The BC_w developed from budget studies represent integrated values
7 for the whole watershed as desired for aquatic acidification estimates as opposed to only
8 weathering from the rooting zone as desired for terrestrial acidification (Sverdrup and Warfvinge
9 1988; Miller, 2001). Depending on how the balance is set up, the balance can be a single
10 equation around the total base cation flux or a series of equations for each individual cation. The
11 setup of the equations leads to the primary limitation of the method in that while it is a relatively
12 simple concept, the individual fluxes within the balance are not easily measured or known
13 (Bricker et al., 2003).

14 Most mass balance calculations require an assumption of steady-state behavior. This
15 assumption is easily justifiable over long periods of record. Additional limitations of the method
16 evolve from the number of unknown fluxes (e.g. weathering rate of individual minerals) within
17 the equations defining the balance. Researchers have utilized a variety of techniques to overcome
18 this limitation, including applying simplifying assumptions or adding additional equations.
19 However, with each assumption or additional equation, a greater amount of uncertainty that must
20 be quantified is added into the analysis. Data sources for a mass balance can also be variable
21 depending on the complexity of the relationships defined within the balance. While databases
22 and studies may exist for major elements at a variety of sites, comparable data for trace or more
23 complex elements may be lacking (Velbel and Price, 2007).

24 Historical Rate Determinations – This approach is detailed in Section 4 for terrestrial
25 acidification approaches. Because the BC_w flux required for aquatic acidification approaches
26 requires characterization of the whole soil profile averaged across a catchment or watershed, this
27 approach can become computationally intensive for aquatic purposes. While it is possible to
28 conduct such an approach on a small scale for an aquatic acidification assessment, it is more
29 likely suited to terrestrial applications and so explanation is provided in those sections of the
30 document.

1 Empirical Relations – A number of empirical relationships have been developed to
2 calculate BC_w , or related factors, from water quality data alone. Empirical relationships are only
3 as strong as the data on which they are based and are only applicable to the geographic regions
4 from which the calibration data is obtained.

5 F-Factor: The F-factor is defined as the ratio of change in non-marine base cation concentrations
6 due to changes in strong acid anion concentrations (Henriksen, 1984; Brakke et al., 1990). (See
7 Section 3.1.) A situation where $F = 1$ indicates that only soil acidification occurs within the
8 catchment, i.e. all incoming protons are neutralized in the catchment. When $F = 0$, then only
9 water acidification is occurring and none of the incoming protons are neutralized in the
10 catchment. Using historical data from Norway, Sweden, U.S.A. and Canada, the F-factor was
11 estimated empirically to be in the range 0.2–0.4 (Henriksen, 1984). Several empirical
12 relationships have been developed in order to calculate the F-factor based on current base cation
13 concentrations using data from Norway (Brakke et al., 1990) or on pre-acidification base cation
14 concentration using data from Finland (Posch et al., 1993).

15 There are several limitations to using the F-factor. While it is simple to apply anywhere the data
16 is available to satisfy the empirical relations, these relations are really only valid in Norway,
17 Finland, or wherever the specific relation was derived. In several instances, researchers have
18 applied the Norway- or Finland-based relations to Canadian (Watmough et al., 2005) and U.S.
19 study locations (Henriksen et al., 2002; Dupont et al., 2005; U.S. EPA, 2009) with the assumption
20 that the empirical equations provide adequate characterization of the relationship between base
21 cation concentrations and the F-factor.

22 A second major limitation in utilizing the F-factor is that this derived factor does not specifically
23 quantify the BC_w flux. Instead it provides calculation of the base cations leached from the soil,
24 which includes BC_w and base cations derived through deposition inputs to the system, or
25 removed by harvesting (Henriksen et al., 2002; Rapp and Bishop, 2009). Although the SSWC is
26 most often used with the F-factor, in a national application where we seek to specifically quantify
27 the BC_w , an alternative method should be used.

28 Indicator element in conjunction with weathering ratios: Chen et al., 2004: “Weathering rates at
29 Arbutus watershed could also be obtained using sodium as indicator element, as described by
30 Gbondo-Tugbawa et al. (2001). The weathering inputs of the indicator element (sodium) could be
31 derived using a mass balance approach, and the derived sodium weathering rate was used in
32 conjunction with base cation weathering ratios reported by Johnson and Lindberg (1992) for the
33 HF to derive weathering rates of other base cations. Using this method, the weathering rates of
34 sodium and calcium derived for Arbutus watershed are very similar to values derived through
35 calibration, whereas rates of magnesium and potassium derived using these two methods showed
36 some discrepancies (Table II).”

37 Weathering rates vs. Stream chemistry or landscape variables: This approach begins with a set of
38 BC_w for a specific set of water bodies. The values of BC_w are then regressed against the stream
39 chemistry parameters, such as ANC, in order to find a correlation relationship. These regression
40 relationships are then applied to stream chemistry of other water bodies within a defined region of
41 interest to find the BC_w for the water bodies. In areas where stream chemistry is not available,
42 landscape variables can be used in place to find correlations with the BC_w .

43 The limitation with this approach is that a statistically significant number of BC_w values must be
44 available from which to create a regression relationship. Also, the region in which the
45 extrapolation is valid must be defined. In work by Sullivan and colleagues (2004), extrapolation

1 of modeled BC_w values was completed using groupings of physiographic region and ANC class.
2 The value of this approach is that it can specifically be applied to BC_w and can be based on
3 modeled, monitored, or estimated BC_w values as long as there are a sufficient number of values
4 for extrapolation. Other works have extrapolated ANC values based on chemistry and landscape
5 variables in a similar manner with a high level of success (Sullivan et al., 2007b, Nanus et al.,
6 2009).

7 Process-based Models – Mineral weathering terms within modeling simulations can be a
8 large source of uncertainty as the weathering term utilized in most process models, in attempts to
9 represent reality, impacts the loss of base cations to surface waters. Therefore, when little is
10 known about the true weathering rate or the constraints on its values, models must utilize
11 calibration procedures against in-stream water chemistry data to arrive at a likely weathering rate
12 (Chen et al., 2004; Sullivan et al., 2004).

13 Process-based models vary greatly in their range of processes represented, complexity of
14 representations, time step, and required data inputs. Overall, there is no perfect model but the
15 best candidate for a task can be chosen provided the available data, the area of concern, and the
16 goals of the analysis. In this case, we would seek to use all available data resources in order to
17 derive a range of spatially-explicit BC_w values across the nation.

18 Descriptions of the four candidate process models available for use across the country for
19 determining BC_w are provided below. In order to provide as concise a description as possible,
20 these model summaries are taken directly from the scientific literature. Summation of the
21 strengths and weaknesses of each model is provided after the model description.

22 DayCent-Chem: “DayCent-Chem links together two widely accepted and tested models—(1) a
23 daily time-step nutrient cycling and soil hydrology model, version 5 of the DayCent model
24 [Parton et al., 1998], and (2) PHREEQC, an aqueous geochemical equilibrium model [Parkhurst
25 and Appelo, 1999]—to form a model that simulates N, P, S, and carbon (C) ecosystem dynamics
26 and soil and stream water acid-base chemistry (fig. 1.2). DayCent-Chem computes atmospheric
27 deposition, soil water fluxes, snowpack and stream dynamics, plant production and uptake, soil
28 organic matter decomposition, mineralization, nitrification, and denitrification (left side of fig.
29 1.2) while utilizing PHREEQC’s low-temperature aqueous geochemical equilibrium calculations,
30 including CO_2 dissolution, mineral denudation, and cation exchange, to compute soil water and
31 stream chemistry (right side of figure). DayCent-Chem’s daily soil solution and stream water
32 chemistry calculations make it possible to use the model to investigate the potential for episodic
33 acidification” (Hartman et al., 2009).

34 DayCent-Chem was recently applied to eight different mountain watersheds from the west to the
35 east with success in certain capacities, therefore, making it a suitable candidate for a national
36 analysis. These applications did highlight difficulties in determining realistic weathering rates in
37 certain areas. With DayCent-Chem, a user must specify an initial value for weathering, which
38 may be adjusted during calibration. In several instances, this value was first set to measured or
39 estimated values for the area of interest and then modified largely during calibration (Hartman et
40 al., 2009). While the daily time step and biotic processes represented by the model provide a

1 more complex view of the environment, they also add a complexity to the model that appears to
2 greatly impact the estimation of the key parameter for this analysis.

3 MAGIC: “MAGIC is a lumped-parameter model of intermediate complexity, developed to
4 predict the long-term effects of acidic deposition on surface water chemistry [Cosby et al., 1985a,
5 1985b]. The model simulates soil solution chemistry and surface water chemistry to predict the
6 monthly and annual average concentrations of the major ions in these waters. MAGIC consists of
7 (1) a section in which the concentrations of major ions are assumed to be governed by
8 simultaneous reactions involving SO_4^{2-} adsorption, cation exchange, dissolution-precipitation-
9 speciation of Al and dissolution-speciation of inorganic C and (2) a mass balance section in
10 which the flux of major ions to and from the soil is assumed to be controlled by atmospheric
11 inputs, chemical weathering, net uptake and loss in biomass and losses to runoff. At the heart of
12 MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from
13 this pool change over time owing to changes in atmospheric deposition, the chemical equilibria
14 between soil and soil solution shift to give changes in surface water chemistry. The degree and
15 rate of change of surface water acidity thus depend both on flux factors and the inherent
16 characteristics of the affected soils” (Sullivan et al., 2004).

17 The strengths of MAGIC lie in its simplicity and ability to be applied for a large number of
18 lakes/streams in batch processes. MAGIC has been in use since the 1980s, has been widely
19 applied within the eastern portions of the country with more limited applications in the West. (See
20 Section 3.3 for further discussion.) The simplicity of MAGIC’s mass balances approach also
21 counts as one of its limitations because it may not account for all of the biotic processes that
22 affect the weathering rate. MAGIC determines the BC_w through calibration to water chemistry
23 data. The “fuzzy optimization” procedures now built into MAGIC allow for an optimized value
24 of the BC_w to be determined from a series of calibrations at each modeling location (Sullivan et
25 al., 2004).

26 PnET-BGC: “PnET-BGC is an integrated forest-soil-water model that has been used to assess the
27 effects of air pollution and land disturbances on forest and aquatic ecosystems [Gbondo-Tugbawa
28 et al., 2001]. The model was developed by linking two submodels: PnET-CN (PnET-carbon and
29 nitrogen) [Aber et al., 1997] and BGC [Gbondo-Tugbawa et al., 2001]. The main processes in the
30 model include tree photosynthesis, growth and productivity, litter production and decay,
31 mineralization of organic matter, immobilization of nitrogen, nitrification [Aber et al., 1997],
32 vegetation and organic matter interactions of major elements, abiotic soil processes, solution
33 speciation, and surface water processes [Gbondo-Tugbawa et al., 2001]... For lake simulations,
34 it is assumed that the water column is completely mixed. The model predicts monthly
35 concentrations and fluxes of major solutes in lake water, monthly concentrations and pools of
36 exchangeable cations and adsorbed sulfate in soil, and monthly fluxes of major solutes from soil
37 and forest vegetation” (Zhai et al., 2008).

38 Chen and others (2004) nicely summarize the tradeoffs associated with utilizing the PnET-BGC
39 model: “A strength of PnET-BGC over other acidification models is its ability to simulate
40 [vegetation and microbial processes]. However, this representation can also be a limitation. The
41 model depicts large element pools in soil and large fluxes through biotic processes. Any change
42 in these pools and fluxes will greatly influence the element budgets. If these simulated fluxes are
43 not accurate, then model predictions will misrepresent element dynamics.” Additionally, almost
44 all of the PnET-BGC applications to date have been completed within the eastern portions of the
45 country mostly focusing in the Adirondacks and Hubbard Brook Experimental Forest (Gbondo-
46 Tugbawa et al., 2001; Chen et al., 2004; Zhai et al., 2008). Expanding this model to western or
47 southern areas would necessitate large amounts of data gathering and processing as well as testing
48 of the representation of the biotic processes found in these differing ecosystems.

1 PROFILE: “PROFILE [Warfvinge and Sverdrup, 1992] is a steady-state soil chemical model
2 with a weathering rate sub-model that calculates weathering rates (for each base cation) explicitly
3 using independent soil properties. Mineral dissolution reactions governing the rate of weathering
4 involve many components in the liquid phase including H₂O, H⁺, OH⁻, CO₂ and organic acids.
5 These serve as the principle method for cataloguing the contribution of chemical reactions
6 between soil solution and silicate minerals to base cation release. Inhibition of the reactions
7 through increased concentrations of the products is accounted for by rate reduction factors.
8 Precipitation of secondary minerals is subtracted from the total base cation release rate. Climate
9 data, soil properties and detailed soil mineralogy are used as inputs to the model [Warfvinge and
10 Sverdrup, 1992]” (Whitfield et al., 2006).

11 The PROFILE model is more fully explained in Section 4 for the terrestrial BC_w approaches.
12 While the PROFILE model provides a highly deterministic, process-based representation of
13 mineral weathering, trying to utilize this model to determine the base cations weathering and
14 reaching surface water bodies requires the representation of all soil horizons that may contribute
15 to weathering and the summarization of BC_w calculations by catchments surrounding each water
16 body of interest. These two qualifications on top of the basic PROFILE application introduce a
17 large amount of complexity into the modeling analysis.

18
19

Table 3-1. Review of Modeling Approaches (and models) to Estimate Base Cation Weathering for Aquatic Critical Acid Load Determinations

Model Approach	Description of Method	Data Requirements	Model Complexity	Suitability for Estimating BC_w for Aquatic Critical Acid Load Determinations in The United States	Suitability for Mapping BC_w Over Large Regions in The United States	References
Budget Studies	mass balance of inputs and outputs of base cations within catchment or watershed	medium	Medium	low; BC _w estimate is often an integrated value for whole catchment or watershed	low - medium (based on data availability); may require Sr isotope ratio of stream chemistry to separate exchangeable versus weathered base cation sources	Bricker et al., 1993; Velbel and Price, 2007
Historical Rate Determinations	loss of base cations in soil profile relative to stable element (Zr, Ti, quartz or rutile)	low	Low	medium; restricted to sites with young soils of known age (eg., soils that have formed since the most recent glacial event, ~20,000 years ago)	low; restricted to sites with young soils and sites where historical rate determinations have been conducted	Sverdrup et al., 1998; Sverdrup et al., 1990
Empirical Data Relations	modeled relationships between surface water characteristics and site conditions or atmospheric deposition measures	low - high	low – high	low-medium	low-medium	
<i>F-Factor</i>	a factor that combines the effects of deposition and weathering	low - medium	Low	low; most accurately applied to sites similar to those where the model was derived; if new derivations can be completed for the U.S. the suitability of this method would increase	low; most accurately applied to sites similar to those where the model was derived; if new derivations can be completed for the U.S. the suitability of this method would increase	Brakke et al., 1990; Henriksen and Posch, 2001; Henriksen et al., 2002; Rapp and Bishop, 2009

Model Approach	Description of Method	Data Requirements	Model Complexity	Suitability for Estimating BC _w for Aquatic Critical Acid Load Determinations in The United States	Suitability for Mapping BC _w Over Large Regions in The United States	References
<i>Indicator element in conjunction with weathering ratios</i>	determine weathering rate through mass balance methods for element such as sodium (Na) then apply defined ratios to determine weathering rates of additional elements	low-medium	low	low; most accurately applied to sites similar to those where the model was derived	low; most accurately applied to sites similar to those where the model was derived	Gbond-Tugbawa et al., 2001, 2002; Chen et al., 2004
<i>Weathering rates vs. Stream chemistry or landscape variables</i>	utilize weathering rates determined by other methods and extrapolate to additional areas based on site characteristics	low - medium	low	medium; suitability will depend on the ease at which derived weathering rates can be obtained and how strong the regressions between BC _w and site characteristics are	medium; relatively good success has been had at extrapolating BC _w to additional sites based on stream chemistry; suitability will depend on data availability	Sullivan et al., 2004, 2007a, 2007b; Webb et al., 1994; Nanus et al., 2009
Process-Based Models	Steady-state and dynamic models that rely on mathematical relationships representing soil and surface water processes	medium - high	medium - high			

Model Approach	Description of Method	Data Requirements	Model Complexity	Suitability for Estimating BC _w for Aquatic Critical Acid Load Determinations in The United States	Suitability for Mapping BC _w Over Large Regions in The United States	References
<i>DayCent-Chem</i>	Mineral weathering rates are set and then calibrated within the process model; Rates are specified by mineral and not necessarily base cations alone	high	high	medium - high; provides daily time step results which can be used to estimate time to recovery or time to damage; uncertainty on how well model can simulate BC _w in some areas will impact confidence of results in these areas	medium; DayCent-Chem has had trouble in estimating mineral weathering rates in some areas of the country	Hartman et al., 2007; Hartman et al., 2009
<i>MAGIC</i>	BC _w determined through calibration to fulfill the requirements of a catchment mass balance by optimizing simulated soil and surface water chemistry to monitored values	medium - high	medium - high	medium - high; numerous applications in the east with some, but fewer in number, applications in the west; little coverage in the Midwest but these areas are less of a concern for aquatic acidification effects	medium - high; will be restricted in areas where soils data are lacking (some western areas); otherwise, highly applicable in any areas where MAGIC applications have been completed	Cosby et al., 1985a, 1985b, 1989a; Sullivan et al., 2004; Sullivan et al., 2008
<i>PnET-BGC</i>	BC _w determined through calibration and held constant throughout dynamic modeling simulations	high	medium - high	low-medium; model applications mostly completed only within northeastern U.S. vegetation and other biotic processes represented by the model would need validation to other regions of the country	low-medium; because BC _w is found through calibration alone for this model, the other model processes and input data must be validated for any application before calibration can be used for BC _w	Gbondo-Tugbawa et al., 2001; Chen et al., 2004; Zhai et al., 2008

Model Approach	Description of Method	Data Requirements	Model Complexity	Suitability for Estimating BC _w for Aquatic Critical Acid Load Determinations in The United States	Suitability for Mapping BC _w Over Large Regions in The United States	References
<i>PROFILE</i>	BC _w determined as a function of weathering of individual soil minerals and field-based soil and biotic conditions	high	high	medium - high; may have restrictions in desert regions and areas that are lacking necessary data; also must be able to characterize catchment summary values and not solely individual profiles	medium - high; may have restrictions in desert regions and areas that are lacking necessary data	Warfvinge and Sverdrup, 1992 and 1995; Sverdrup, 1990

3.3 Proposed Methodology for Estimating and Mapping Base Cation Weathering for Aquatic Critical Acid Load Calculations

In determining the proposed methodology for a national assessment, the identified strengths and weaknesses of each approach in the previous section had to be weighed against one another. Because every method required a large environmental data component, the largest deciding factor in the proposed approach became the number and spatial representation of previous applications of an approach within the United States. This decision factor immediately ruled out applying any of the empirical relationships (e.g. F-factor, relation of BC_w to stream chemistry) derived primarily with data from other countries, although it did not rule out deriving new relationships using the same methods. Ultimately, the F-factor approach was not chosen because it did not directly provide a BC_w rate. Additionally, application of an empirical relation alone provided little information on the long-term versus current state of the ecosystem. Therefore, a combination of a process-based model determination of BC_w rates with regional expansion of these rates through empirical relations is proposed at the methodology for a national assessment.

Utilizing a process-based model, which can calibrate BC_w rates to stream or lake chemistry across any number of years, provides a credible long-term estimate of the BC_w rate that can be input into the SSWC in order to obtain the system critical load. The process-based model most widely applied throughout the U.S. to date is the MAGIC model. The intermediate complexity of this model provides a balance between data inputs required to run the model and the processes involving base cations, nitrogen, and sulfur within a watershed, which is considered a requirement of providing a national assessment. Finally, because of its wide application, MAGIC has been extensively tested against independent databases providing the opportunity for iterative model testing and refinement (Sullivan, 2000).

The following steps outline the main processes of the method:

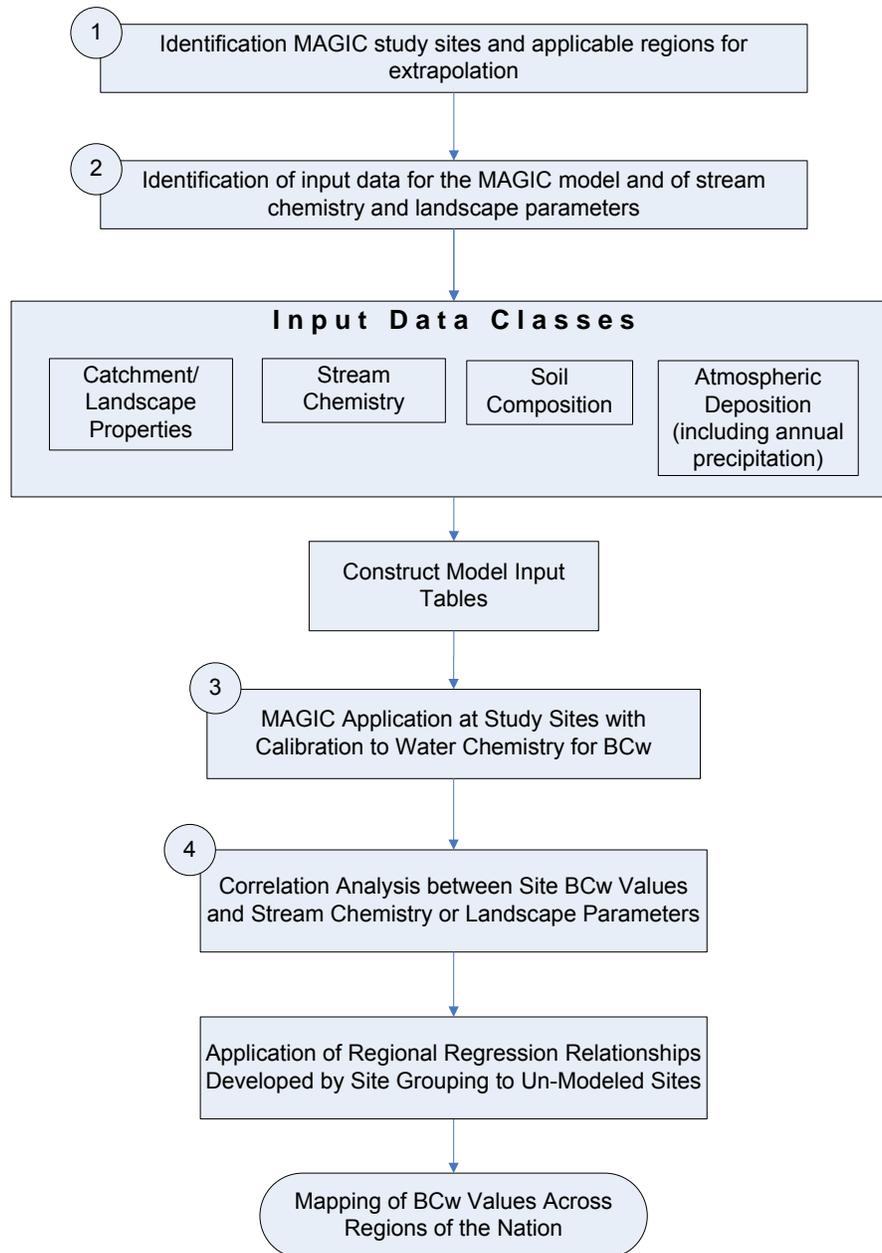
Step 1. Definition of MAGIC study sites and the regions to which each grouping of study sites may be extrapolated.

Step 2. Data gathering and processing for population of the MAGIC model for each study site with additional regional data gathering of available stream/lake chemistry and landscape parameters.

Step 3. MAGIC modeling application on selected stream/lake study sites where BC_w is arrived at through calibration against water chemistry data.

1 **Step 4. Extrapolation of BC_w for modeled streams/lakes to other waterbodies**
 2 **within the region through correlation analysis using stream chemistry data,**
 3 **where available, and landscape parameters in its absence.**

4 **Figure 3-1** provides a flow chart of these steps and their components.



5 **Figure 3-1.** Process steps for estimating BC_w using the MAGIC model with regional
 6 extrapolation
 7

Step 1. Definition of MAGIC study sites and the regions to which each grouping of study sites may be extrapolated.

MAGIC has been used to assess acidification impacts in a large number of areas across North America (**Table 3-2**). These previous applications should be utilized where possible to provide a starting point for the national analysis. Sites within the eastern United States likely provide a wide range of coverage from which initial extrapolations can begin. Within the mid-west and western areas of the country, additional sites will need to be investigated. Authors of these studies should be contacted to obtain data sources and model results. Previous model applications should be compared for the years and objectives of the analysis and input data to determine if the results already created could be utilized in an extrapolation analysis without rerunning the model.

Table 3-2. Locations of Previous MAGIC Applications within the U.S. and Canada¹

Location(s)	Reference
25 lakes in south-central Ontario, Canada	Aherne, J, P.J. Dillon, and B.J. Cosby. 2003.
2 catchments located in Nova Scotia, Canada	Dennis, I.F., T.A. Clair, and B.J. Cosby. 2005
Maryland	Ellis, H., and M. Bowman. 1994.
36 lake catchments in the Adirondack Mountains of New York	Church, M.R. and J. Van Sickle. 1999.
40 to 50 sites within each of three physiographic provinces in the eight-state southern Appalachian Mountains region	Sullivan, T.J., B.J. Cosby, A.T. Herlihy, J.R. Webb, A.J. Bulger, K.U. Snyder, P.F. Brewer, E.H. Gilbert, and D.L. Moore. 2004.
33 representative watersheds in the Adirondacks	Sinha, R., M.J. Small, P.F. Ryan, T.J. Sullivan, and B.J. Cosby. 1998.
Shenandoah National Park	Bulger, A. J; Dolloff, C. A.; Cosby, B. J.; Eshleman, K. N.; Webb, J. R., and Galloway, J. N. 1995
60 Southern Appalachian streams	Bulger AJ, Cosby BJ, Webb JR. 2000.
Joyce Kilmer And Shining Rock Wilderness Areas (North Carolina/Tennessee)	Sullivan, T.J. and B.J. Cosby. 2002
Monongahela National Forest, West Virginia	Sullivan, T.J. and B.J. Cosby. 2004
Shasta Lake, Idaho	Eilers J.M., B.J. Cosby, J.A. Bernert, T.A. Sullivan, 1998.
Libby Lake, Montana	Bernett, J.A., Eilers J.M., B.J. Cosby. 1997.
Popo Agie Wilderness, WY, and Weminuche Wilderness, CO	Sullivan, T.J., Cosby, B.J., Bernert, J.A., and Eilers, J.M. 1998.
Rocky Mountain, Grand Teton, Sequoia, and Mount Rainier National Parks	Cosby and Sullivan. 2001
The Loch, a subalpine lake in Rocky Mountain National Park in Colorado	Sullivan, T.J., B.J. Cosby, K.A. Tonnessen, and D.W. Clow. 2005.
2 locations in the Sierra Nevadas	Sullivan and Eilers, 1996

¹References from this table are presented in Appendix 2.

1 When selecting sites for MAGIC analyses that will later be used in an extrapolation
2 analysis, Sullivan and colleagues (2004) outlined two key considerations:

- 3 1. Do not select too many watersheds for modeling that occurred in the same general
4 area in order to avoid skewing the results too heavily to one portion of the region for
5 the following extrapolation step
- 6 2. Screen sites to remove those in which the water chemistry data were not internally
7 consistent or for which available data suggested the possibility of significant
8 influence from road salt, geological sulfur, land use, or insect defoliation.

9 **Step 2. Data gathering and processing for population of the MAGIC model for**
10 **each study site with additional regional data gathering of available**
11 **stream/lake chemistry and landscape parameters.**

12 The data requirements of the MAGIC model are summarized in **Table 3-3**. The table
13 includes both data inputs derived from monitoring data and constant parameters that the user
14 must set based on available data and methods suggested by previous MAGIC applications.
15 Additional information on data inputs can be found in: Cosby and colleagues, 1985a; Cosby et
16 al., 1985b; Sullivan and Cosby, 2004; Sullivan et al., 2007c.

17 Due to the wide range of water quality monitoring assessments conducted within the
18 United States, a large amount of water quality data is typically available to work from. Similarly,
19 in recent times advances and expansions of atmospheric modeling have been conducted
20 providing a large amount of deposition estimates from which to pull model input data. The area
21 of data most lacking, especially in the western United States, is the composition of soils. Sources
22 of soil data are discussed in Section 4.3.3. Given that there may be areas in which soils data are
23 not available, work by Sullivan and others used a tiered assessment of MAGIC applications to
24 overcome this obstacle. The tiers consisted of: (1) chemistry data were available from within the
25 watershed to be modeled with multiple soil sampling sites in an individual watershed aggregated
26 on an area-weighted basis; (2) soils data within the catchment were missing but were available
27 from a nearby watershed underlain by similar geology; and (3) soils data were neither available
28 from within the watershed nor from nearby watersheds on similar geology. In order to populate
29 soil characteristics for tier 2 and 3 watersheds, a surrogate approach was used meaning that these
30 watersheds were paired with a watershed for which all input data were available. In order to be
31 paired, watersheds had to have similar streamwater characteristics (ANC, sulfate, and base cation

- 1 concentrations), physical characterization (location, elevation), and bedrock geology data
- 2 (Sullivan et al., 2004).

Table 3-3. Input Data Requirements of MAGIC Model

Data Class	Data Element	Measure
Catchment	Area	
	Relative area of lake/stream	fraction
Stream Chemistry	pH	unitless
	ANC	eq/L
	Ca ²⁺	eq/L
	Mg ²⁺	eq/L
	K ⁺	eq/L
	Na ⁺	eq/L
	SO ₄ ²⁻	eq/L
	NO ₃ ⁻	eq/L
	Cl ⁻	eq/L
	Aluminum solubility constant	log ₁₀
	Slope of pH-pAl relationship	unitless
Aqueous Phase - Equilibrium Constants	Organic acid	log ₁₀
	Organic aluminum	
	Inorganic aluminum speciation	
	Inorganic carbon speciation and dissociation of water	
Solid Phase – Weathering and Exchange Constants	Cation exchange selectivity coefficients	log ₁₀
	Weathering rates (Ca ²⁺ , Mg ²⁺ , K ⁺ , NH ₄ , SO ₄ ²⁻ , Cl ⁻ , NO ₃ ⁻ , F)	eq/m ² /yr
Soil Composition	Thickness	Depth (m)
	Total cation exchange capacity	eq/kg
	Exchangeable bases (Ca ²⁺ , Mg ²⁺ , K ⁺ , and Na ⁺)	mg/kg
	Bulk Density	kg/m ³
	Porosity	fraction
	pH	unitless
	Sulfate adsorption half saturation	eq/m ³
	Aluminum solubility constant	log ₁₀
Slope of pH-pAl relationship	unitless	
Atmospheric Deposition	Annual precipitation	Volume (m/yr)
	Ca ²⁺	Total annual deposition (eq/ha/yr)
	Mg ²⁺	
	K ⁺	
	Na ⁺	
	SO ₄ ²⁻	
	NH ₄	
	NO ₃ ⁻	
Cl ⁻		

3

Step 3. MAGIC modeling application on selected stream/lake study sites where BC_w is arrived at through calibration against water chemistry data.

As was completed with the REA (U.S. EPA, 2009), batch processing of MAGIC models at a range of sites can be completed. Calibration of those sites with available data (streamwater chemistry, soil chemical and physical characteristics, and atmospheric deposition) is completed by setting values of the “fixed parameters” within the system and comparing the output of the model run to the observed values of such characteristics as stream ANC. There are eight parameters optimized through this method including the BC_w rate. The eight observations used to drive the calibration procedure include the current soil exchangeable pool size and current output flux of each of the four base cations. The model is iteratively run adjusting the “fixed parameters” from a specified range of values (representing uncertainty in knowledge of these parameters), so that the outputs match the observed parameters within an acceptable margin of error. The set of “fixed parameters” that are obtained that allow the model to meet this acceptable of margin of error become the range of calibrated parameters from which the median is chosen to represent the parameter value for the watershed. “The use of median values assures that the simulated responses approximate the most likely behavior of each watershed, given the assumptions inherent in the model and the data used to constrain and calibrate the model” (Sullivan et al., 2004). This “fuzzy optimization” procedure has been developed for use with MAGIC modeling to help quantify the uncertainties within the modeled parameters (Sullivan et al., 2004). Using these calibration procedures of each site MAGIC run will provide not only an estimate of BC_w but an expected range of values in which BC_w falls, thereby providing bounds and certainty limits for the following extrapolation step.

Step 4. Extrapolation of BC_w for modeled streams/lakes to other waterbodies within the region through correlation analysis using stream chemistry data, where available, and landscape parameters in its absence.

Regionalization of MAGIC modeling results can be completed through either “binning” sites based on characteristics like physiographic region and ANC concentration (Sullivan et al., 2004) or creating regional regressions to relate site characteristics (chemistry or landscape) to a parameter of interest (e.g., ANC; Sullivan et al., 2007a). In order to provide some measure of “goodness of fit” to the extrapolations, we have chosen to proceed with creating regression relationships between the BC_w determined through calibration of the MAGIC model and either

1 water chemistry or landscape parameters. In previous studies, the landscape variables considered
2 for regression relationships with ANC have included elevation, watershed area, ecoregion,
3 lithology, forest type and geological sensitivity class (Sullivan et al., 2007b). We expect to
4 follow similar methods to create the relations with BC_w (i.e., the response variable). Within each
5 region of extrapolation landscape variables appropriate to the region will be selected. For
6 example, the types of forest selected for inclusion may vary between an extrapolation in the
7 Southern Appalachians as opposed to the Rocky Mountains. In all instances, there must be
8 adequate representation of the variable within all modeled and non-modeled watersheds or it will
9 be eliminated from the pool of candidate variables available for regression analysis.

10 Sullivan and others (2007b) relied on the corrected Aikake's Information Criteria (AIC)
11 to evaluate all possible correlation relations. The corrected version of the evaluation criteria was
12 used because of the relatively small sample sizes available from which to build the regressions.
13 Additional evaluation criteria can easily be applied for choosing the best-fitting and most
14 meaningful regressions for extrapolation from a set of individual modeled sites to a larger set of
15 regional sites. Potential criteria for evaluating individual variables within correlation models
16 include partial F tests, t-values, and variance inflation factors. To evaluate the model as a whole
17 statistics such as PRESS, coefficient of determination, adjusted coefficient of determination,
18 Mallows' C_p , and root mean square error of the model can all be utilized (Helsel and Hirsch,
19 1992). If a commercial statistical package, such as SAS, is chosen to complete this portion of the
20 analysis the predefined routines and groupings of evaluation statistics can be employed with
21 relative ease.

22 **3.3.1 Potential limitations of proposed methodology**

23 The limitations with the proposed methodology can be divided into five distinct
24 categories:

- 25 1. MAGIC is an intermediate level model that does not take into account biotic
26 processes which may affect the calculation of BC_w rates within a watershed.
- 27 2. While MAGIC is the most widely applied acidification model within the U.S. it still
28 faces the challenge of having limited applications in the Midwest and western states.
- 29 3. As an extension of the bias in eastern applications, processing and organization of the
30 data required for input into the MAGIC model in the East far exceeds that of the
31 West. Additionally, there is an indication that soils data are more incomplete or hard

1 to obtain in the West. Note that the terrestrial acidification national assessment faces
2 even greater demands in terms of soil composition data needs. As such, there can be a
3 combined effort in obtaining new data that will benefit both assessments.

- 4 4. The population and calibration of specific site applications of MAGIC across the
5 country constitutes a major modeling effort. However, it may be possible to leverage
6 previous applications.
- 7 5. The proposed approach calls for the creation of several different regional
8 extrapolations of BC_w rates based on sets of individual MAGIC applications. The
9 success of these extrapolations remains to be seen and will depend upon the
10 limitations mentioned above in even applying the MAGIC model at a multitude of
11 locations and upon the availability of a statistically significant number of model
12 outcomes on which to base the regressions for each regional analysis.

13 While these limitations may seem extensive, there are many possibilities for overcoming
14 the limitations. For example, criteria on model application years can be relaxed to include more
15 of the previously completed MAGIC applications in lieu of updating and rerunning models at the
16 same sites. And, joint data collection between the aquatic and terrestrial acidification
17 assessments can allow the most efficient use of resources and demands on other agencies.

18 **3.3.2 Uncertainty analyses**

19 As typical with any process based model, the major uncertainties in MAGIC include
20 input data variability, model calibration uncertainty, and the ability of the mathematical model
21 processes to represent reality. Within this national analysis, there will also be uncertainty
22 associated with regional extrapolation of modeling results from individual watersheds to the
23 region. However, Sullivan and colleagues (2004) state that these “errors and uncertainties are not
24 additive, but rather would be expected to some extent to cancel each other out.”

25 Several research projects have undertaken attempts to quantify the relative magnitude of
26 the effects of sources of uncertainty for regional, long-term MAGIC simulations using Monte
27 Carlo methods (Cosby et al., 1989b, 1989c, 1990; Hornberger et al., 1989, 1990). While the
28 results of these studies indicated that the different sources of uncertainty can have varying levels
29 of impacts on the outputs of the MAGIC model, the development of the “fuzzy optimization”
30 technique for calibration was designed to reduce these impacts of uncertainty. With “fuzzy
31 optimization” there is an explicit accounting within different uncertainty categories and a

1 resulting time-variable measure of overall simulation uncertainty for each state variable. One
2 way the optimization procedure reduces uncertainty is in its selection of parameter and variable
3 values for the “fixed parameters” from distributions of possible values rather than having a user
4 select a single value during a single calibration (Sullivan et al., 2004).

5 Outside of the operation and calibration of the MAGIC model, the parameterization of
6 the input data provides another source of uncertainty. As identified in previous sections, the soils
7 composition data are expected to be the greatest source of uncertainty. If a tiered approach to
8 populating soils data for watersheds lacking in data is used, uncertainty with the method can be
9 examined by calibrating selected tier 1 watersheds twice, once using the appropriate site-specific
10 soils data, and a second time using borrowed soils data from an alternate site, using either tier 2
11 or tier 3 protocols. A comparison between the results from each of the scenarios can then be
12 made to determine the magnitude of difference in output parameters. If this analysis can be done
13 at multiple sites, than a sensitivity analysis can be performed over the results to determine if
14 there is a consistent bias in results from modeling analyses utilizing tier 2 or 3 procedures
15 (Sullivan et al., 2004).

16 **4. TERRESTRIAL BASE CATION WEATHERING METHODOLOGY**

17 **4.1 Introduction**

18 Geology is one of the most important factors in determining the potential sensitivity of an
19 area to terrestrial acidification (U.S. EPA, 2008, Section 3.2.4). In particular, the characteristics
20 of the soils and the upper portion of the bedrock can impact the acid-neutralizing ability of the
21 soils in a particular area. Acid-sensitive soils are those which contain low levels of exchangeable
22 base cations and low base saturation (U.S. EPA, 2008, Section 3.2.4). Bedrock composition and
23 soil pH are two characteristics that are directly related to the ability of a system to neutralize
24 acid. Soils overlying bedrock, such as calcium carbonate (e.g., limestone), which is reactive with
25 acid, are more likely to successfully neutralize acidifying deposition than soils overlying
26 nonreactive bedrock. In addition, soils with higher pH (i.e., more alkaline) have a greater
27 capacity to neutralize acidifying deposition.

28 This section reviews the effect of acidification known as base cation weathering,
29 describes its significance in estimating critical acid loads, and identifies methodologies for
30 estimating base cation weathering. Further, this report recommends a methodology for potential

1 use in the review of the NO_x and SO_x secondary National Ambient Air Quality Standards and
2 describes the steps and information resources needed to apply that methodology across the
3 United States.

4 **4.2 Terrestrial Base Cation Weathering**

5 In the calculation of terrestrial critical acid loads using the simple mass balance (SMB)
6 methodology, **base cation weathering** (BC_w)² is defined as “the release of base cations from
7 minerals in the soil matrix due to chemical dissolution” (UNECE, 2004), and this weathering
8 occurs in the rooting zone of the soil profile and consists of the release of calcium (Ca²⁺),
9 magnesium (Mg²⁺), potassium (K⁺) and sodium (Na⁺). It does not include the removal of base
10 cations from soil ion exchange complexes (cation exchange sites) or the degradation of soil
11 organic matter. Base cations from these sources have already been released through the
12 weathering process. Base cation weathering is often a dominant source of base cations in soils,
13 replacing Ca²⁺, Mg²⁺, K⁺ and Na⁺ that are lost through leaching and uptake by plant (Langan et
14 al., 1995; Langan et al., 1996; Ouimet, 2008). Therefore, BC_w plays an important role in
15 determining the sensitivity of a site to acidifying nitrogen and sulfur deposition (Hodson and
16 Langan 1999a). The BC_w term is also one of the most influential parameters in the SMB
17 calculations of terrestrial critical acid loads. Li and McNulty (2007) determined that 49% of the
18 variability in critical load estimates was due to this term. Sverdrup and colleagues (1995)
19 (reference in Langan et al., 1996) determined that BC_w can account for 90% of the variation in
20 critical loads.

21 For the Terrestrial Acidification case study in the Risk and Exposure Assessment (U.S.
22 EPA, 2009), BC_w rates were calculated using the clay-substrate method (McNulty et al., 2007).
23 This method was selected for the Risk and Exposure Assessment because it is one of the most
24 commonly used methods to estimate BC_w for critical load analyses in North America (Ouimet et
25 al., 2006; Watmough et al., 2006; McNulty et al., 2007; Pardo and Duarte, 2007), and has been
26 used to map critical loads across the United States (McNulty et al., 2007). However, the
27 applicability of the clay-substrate method is most likely limited because it is an empirical model
28 that appears to be based on a modification of the soil type – texture approximation method that
29 was developed on a restricted number sites in northern Europe that were glaciated during the last

² Within the SMB equation, Bc_w refers to the weathering of Ca²⁺, Mg²⁺ and K⁺.

1 glacial advance (CLAD, 2009; H. Sverdrup *personal communication*, 2009a, UNECE, 2004). It
 2 relies on a classification of the acidity of soil parent material and soil clay content and consists of
 3 three equations (equations 4-1 – 4-34).

$$4 \quad \text{Acid Substrate: } BC_e = (56.7 \times \% \text{clay}) - (0.32 \times (\% \text{clay})^2) \quad (4-1)$$

$$5 \quad \text{Intermediate Substrate: } BC_e = 500 + (53.6 \times \% \text{clay}) - (0.18 \times (\% \text{clay})^2) \quad (4-2)$$

$$6 \quad \text{Basic Substrate: } BC_e = 500 + (59.2 \times \% \text{clay}) \quad (4-3)$$

7 where

8 BC_e = empirical soil base cation ($Ca^{2+} + K^+ + Mg^{2+} + Na^+$) weathering rate
 9 (eq/ha/yr)

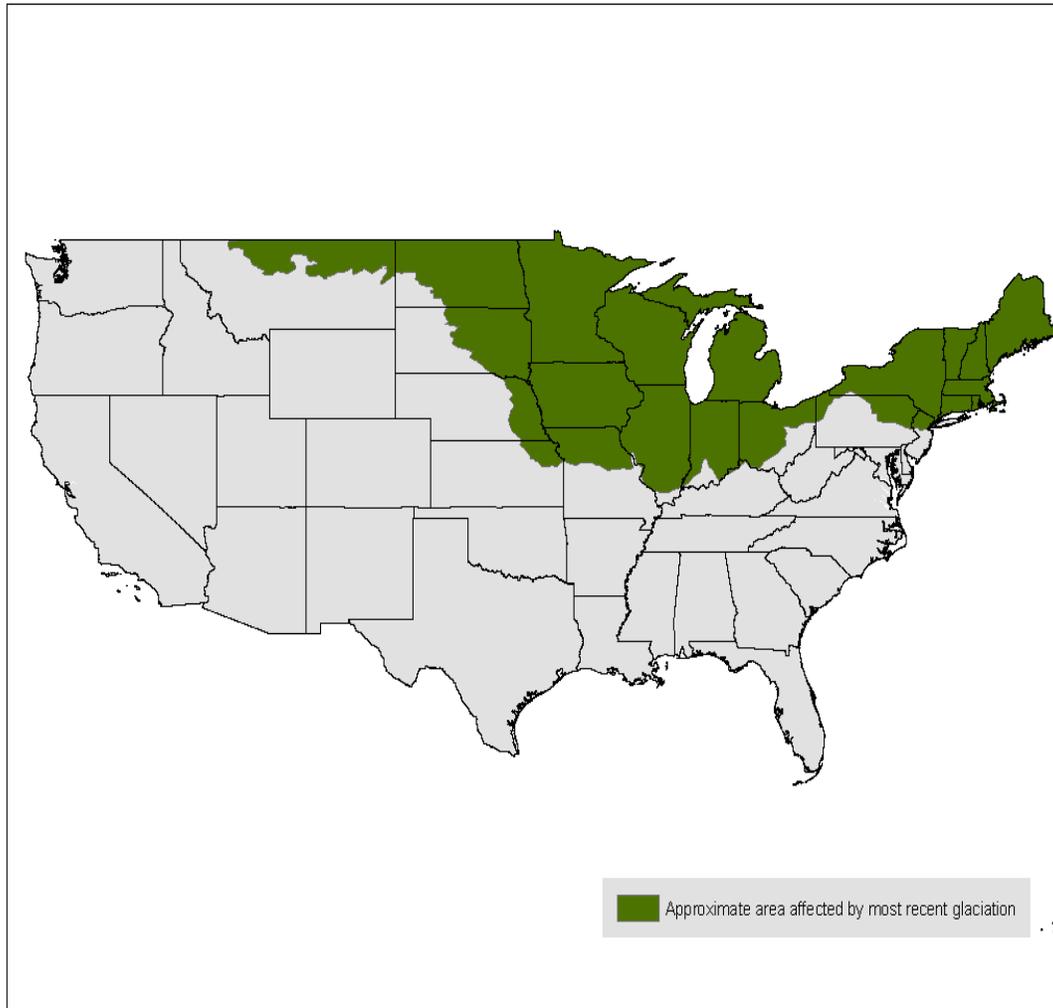
10 % clay = the percentage of clay (determined by particle size) within the rooting zone
 11 of soil profile.

12 Critical load experts from both the United States and Canada have commented that the clay-
 13 substrate model, in general, appears to perform well in young soils that have formed since the
 14 last glaciations (approximately 20,000 years before present). However, the model may not be
 15 suitable or provide accurate estimates on older, more weathered soils that were not impacted by
 16 the last glaciation (P. Arp *personal communication*, 2009). These soils have undergone
 17 weathering for a longer period of time and the relationships between clay particle size and base
 18 cation release may not be as strong as in younger soils (H. Sverdrup *personal communication*,
 19 2009a). To our knowledge, however, there have been no published studies that have tested this
 20 hypothesis and compared BC_w estimates generated with the clay-substrate model and other
 21 methods on sites underlain by old, more weathered and recently glaciated soils. At least one
 22 study has compared the clay-substrate BC_w method with estimates from other models on
 23 glaciated soils in Canada and found that the rate estimates were similar within the area of
 24 assessment (Whitfield et al., 2006).

25 Results from the Risk and Exposure Assessment (U.S. EPA, 2009) appear to support the
 26 distinction between the suitability of applying the clay-substrate model to glaciated versus older,
 27 non-glaciated soil environments. As outlined in Appendix 5 of the Risk and Exposure

1 Assessment, the regression analysis assessing the relationship between the growth of sugar
2 maple (*Acer saccharum*) and critical acid load exceedance was not significant ($p=0.38$) when all
3 plots were included in the analysis. However, when the analyses were restricted to sites located
4 on younger, glaciated soils, which resulted in the removal of 25% of the data from the analyses,
5 the linear regression relationship was significant at the $p=0.10$ level. Improvements in the
6 significance of the relationship may, in part, have been due to the greater accuracy of the BC_w
7 estimates in the critical load calculations for the plots north of the glaciations line.

8 The majority of the conterminous United States was not directly impacted by the most
9 recent glacial advance (**Figure 4-1**) and some of the soils in these areas have not been influenced
10 by glaciations in at least 700,000 years (Sverdrup et al., 1992). Only ten states had their full land
11 area impacted by glaciers during the glacial advance 20,000 years ago. Therefore, if the concerns
12 and supportive results regarding the suitability of the clay-substrate model for the estimation of
13 BC_w on older, non-recently-glaciated soils are correct, the model may not be an appropriate
14 method to estimate BC_w for a large portion of the United States. Given that the BC_w parameter is
15 one of the most influential variables within the SMB calculations to estimate critical acid loads,
16 it is particularly important to use a method that provides accurate and defensible estimates of
17 BC_w . Therefore, any and all future work focused on estimating and mapping terrestrial critical
18 acid loads in the United States, should acknowledge the potential limitations of the clay-substrate
19 model and consider the adoption of a BC_w modeling approach that is transferable and can be
20 applied to multiple locations and different soil conditions and soil ages.



1
2 **Figure 4-1.** Areas of continental U.S. that were covered during the last glacial event
3 (Reed and Bush, 2005).

4 **4.3 Methodologies for Determining Base Cation Weathering Values in the United States**

5 **4.3.1 Difficulties in estimating base cation weathering**

6 Base cation weathering is one of the most difficult parameters to estimate (Sverdrup et
7 al., 1990; Ouimet and Duchesne, 2005; Langan et al., 1996), as it is a function of a time, soil
8 mineralogy, and a variety of other environmental biotic and abiotic factors. Weathering occurs
9 over centuries and millenia and results in the chemical and physical alterations of parent material
10 and minerals. Minerals that are present in the soil may no longer resemble the original bedrock
11 parent material (C. Smith *personal communication*, 2009). In addition, the soil may be derived
12 from parent material that was transported to its current location and does not resemble the
13 underlying bedrock. Abiotic factors including temperature and moisture and location on the

1 landscape and biotic factors including vegetation and soil microbes can also impact base cation
2 weathering through removal of base cations and chemical weathering of minerals (Brady and
3 Weil, 2002). Combined, these factors pose many challenges to determining BC_w in the soil
4 profile for terrestrial critical acid load estimations. As a result, a variety of BC_w methods and
5 approaches have been developed (Sverdrup et al., 1990).

6 **4.3.2 Approaches to estimating BC_w :**

7 Methods and models that have been developed to estimate BC_w for critical acid load
8 determinations differ significantly in the approaches used to generate weathering estimates
9 (Langan et al., 1995; Sverdrup et al., 1990; UNECE, 2004). For the purposes of this work
10 assignment, BC_w methods and models are grouped into three main approaches:

- 11 1. budget studies of catchments or watersheds;
- 12 2. historical weathering rate determinations; and
- 13 3. empirical and mathematical models.

14 Each of these approaches vary in complexity, data intensity and scalability, thereby offering
15 different strengths and weaknesses to estimating BC_w . In addition, these approaches differ in
16 their abilities to map BC_w over regional and larger land areas. **Table 4-1** provides a summary of
17 the approaches to BC_w , critical load models that use the approaches, the strengths and
18 weaknesses of the different models, and the suitability of the approaches and models to map BC_w
19 and therefore critical loads over large areas. For a model to be suitable for large-scale mapping, it
20 must be quick to apply, supported by existing databases, not require extensive and costly
21 analyses, and be transferable to sites with varying conditions and geological histories (Sverdrup
22 et al., 1990).

23 *Budget Studies* - The budget study approach, also referred to as input-output balances
24 (Kolka et al., 1996; Langan et al., 1996; Starr et al., 1998), estimates BC_w as a component of the
25 mass balance input and output of cations within a catchment or watershed (Langan et al., 1996;
26 Sverdrup et al., 1990; Sverdrup et al., 1998). In most catchments, the main source of input is
27 atmospheric deposition and output is streamflow, and base cation retention is accounted for
28 through uptake by biomass and immobilization in the soil. Base cation weathering is therefore
29 determined through mass balance differences between these different input, output and storage
30 pools. The main strengths of this method are that it only requires a moderate amount of input
31 data and relies on data collected from the catchment or watershed. In addition, it offers the

1 potential for mapping multiple catchments, if the necessary input data is available. However,
2 several of the drawbacks to this method include an assumption that the catchment is in a steady-
3 state condition and the cation exchange capacity does not change over time (Langan et al., 1996;
4 Miller, 2001; Sverdrup et al., 1998). In addition, it is often difficult to determine BC_w within the
5 rooting zone of individual soil profiles because the BC_w estimates from budget studies represent
6 integrated values for the whole watershed, the full soil profile, bedrock weathering and all soil
7 processes (Sverdrup and Warfvinge 1988; Miller, 2001). It is also difficult to separate
8 contributions of base cations from exchange sites versus mineral weathering and chemical
9 dissolution (Sverdrup et al., 1990; Miller, 2001). Therefore, it is challenging, and potentially
10 erroneous, to use budget studies of catchments to estimate BC_w for terrestrial critical acid loads.
11 It may be possible to modify the budget study approach and evaluate base cation input and
12 output in the rooting zone of individual soil profiles (Kolka et al., 1996), and to separate base
13 cations from exchanges soil pool versus weathering sources using techniques such as the analysis
14 of strontium (Sr) isotope ratios (Miller et al., 1993). However, the soil profile approach would
15 require lysimeter measurements of soil solution chemistry at each site and the soil solution would
16 also need to be analyzed for Sr isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$). Both of these analyses would be very
17 time intensive and would not be practical over large areas.

18 *Historical Rate Determinations* – The historical weathering rate approach, also
19 sometimes referred to as element depletion (Langan et al., 1996; Miller, 2001) or pedological
20 mass balance (PMB) (Ouimet and Duchesne, 2005; Ouimet, 2008), estimates BC_w by
21 determining the relative depletion of base cations to the depletion of a stable element as a
22 function of the age of the soil profile (Langan et al., 1996). Zirconium (Zr), titanium (Ti), rutile
23 and sometimes quartz are typically selected as the stable soil elements for this method (Langan et
24 al., 1996; Sverdrup et al., 1998) because they are very resistant to weathering (Starr et al., 1998).
25 This technique is commonly applied to soils that were formed since the last glaciation, and
26 characterizes the ratio of base cations to the stable element in the upper weathered soil horizons
27 and the unweathered C horizon. It assumes that post glaciation, the mineral matrix of the soil
28 consisted of freshly ground material that was not previously exposed to weathering (Sverdrup et
29 al., 1998), the lowermost soil is representative of the parent material and the stable element is
30 found in a constant proportion throughout the soil profile (Langan et al., 1996; Starr et al., 1998).
31 Over time, base cations are weathered and lost from the profile through uptake and leaching, but

1 the concentration of the stable element remains constant due to resistance to weathering (Starr et
2 al., 1998). Main strengths of this approach are that it is a good technique to estimate weathering
3 in young soils, does not require a large amount of data and BC_w is relatively easy to calculate.
4 However, this approach also presents some major weaknesses. It estimates the historic BC_w rate
5 which may be differ from the current weathering rate. Historic weathering rates may
6 underestimate current BC_w because the historical weathering occurred under more neutral
7 conditions with less acidifying deposition (Sverdrup et al., 1990). Conversely, historic
8 weathering rates may be higher than current BC_w if the original post glaciations soil contained a
9 significant proportion of easily weathered material that have since been depleted (Miller, 2001).
10 Studies have indicated that the initial phase of weathering lasts a few hundred to several
11 thousand years and can deplete a maximum of 25% of the mass during this period (Sverdrup et
12 al., 1998). In addition, the historic rate approach is not suitable for older, more weathered soils.
13 In such soils, it is often difficult to determine the amount of time since the last glacial or mass
14 disturbance event that caused the formation of newly ground material (H. Sverdrup *personal*
15 *communication*, 2009b). Therefore, this method cannot be applied to all locations and it is often
16 difficult or impossible to extrapolate results to larger geographical areas. Since a large proportion
17 of the soils in the United States were not influenced by the most recent glaciation, the historic
18 rate approach to estimate BC_w for terrestrial critical acid load estimates could only be applied to
19 a fraction of the land area.

20 *Empirical and Mathematical Models* – Empirical and mathematical models estimate BC_w
21 based on laboratory- and field-based relationships between soil, abiotic and biotic factors. Over
22 the past several decades, a large number of BC_w models have been developed for terrestrial
23 critical acid load determinations. Initial models were developed from a limited number of sites
24 and data. More recent models incorporate a larger number of factors and are more complex and
25 data intensive. One of the first BC_w models was the Skokloster Assignment which is a semi-
26 empirical method that was devised during the Critical Load Workshop in Skokloster, Sweden in
27 1988 (UNECE, 2004). It divides minerals into 5-6 mineral classes based on the dominant
28 weatherable soil minerals and assigns a range of critical acid loads to each. This method was
29 later expanded to include a larger range of minerals and to estimate BC_w based on the relative
30 abundance of fast versus slow weathering minerals. The Skokloster Assignment was originally
31 based on soils with density, moisture content, clay content and pH conditions similar to the soils

1 in the three Gårdsjön catchments in Sweden, and was validated against a preliminary version of
2 the PROFILE model, described further below (Hodson and Langan 1999b; H. Sverdrup *personal*
3 *communication*, 2009b).

4 A second model, the Soil Type – Texture Approximation assigns weathering rate classes
5 to soils based on soil texture and parent material acidity classes. It was developed for European
6 forest soils (UNECE, 2004). As described earlier, it is believed that the clay-substrate model that
7 is used extensively throughout North America was derived from the Soil Type – Texture
8 Approximation.

9 A third model, the Total Base Cation Content Correlation was developed using $Zr(SiO_4)$
10 and historical rate approach applied to eleven sites in Sweden (UNECE, 2004). Correlation
11 between historical BC_w rates and the total content of base cations in the undisturbed bottom soil,
12 corrected for temperature, were used to develop equations to estimate the weathering of Ca^{2+} , K^+
13 and Mg^{+2} (Olsson et al., 1993). For a more complete review and description of these three
14 empirical models see Hodson and Langan (1999) and UNECE (2004). In general, the main
15 benefits of these models are the minimal data requirements, transferability, and the potential to
16 be applied to multiple sites. Therefore, such models offer good options for mapping of BC_w for
17 critical acid load determinations. However, these models also have several key weaknesses
18 which limit their utility for estimating BC_w in many locations, including a large proportion of the
19 United States. All of the models were determined using data from a limited number of sites
20 within Sweden and other regions of Europe and are based on average or generalized
21 relationships. Therefore, similar to the clay-substrate model, these models may do a reasonable
22 job of estimating BC_w on sites that were recently glaciated and/or have similar conditions to the
23 Swedish sites. However, they should not be applied everywhere, as they may poorly estimate
24 BC_w on sites with older, more weathered soils. As stated for Total Base Cation Content
25 Correlation, the method is only applicable to granitic soils (Hodson and Langan, 1999) and
26 should be used with caution because the relationships are based on Nordic geological history
27 (UNECE, 2004).

28 A fourth model that supported the creation of some of the aforementioned empirical BC_w
29 models, and is currently in its 5th version is PROFILE (Warfvinge and Sverdrup 1992 and 1995;
30 Sverdrup, 1990). PROFILE (version 5.0) is a mechanistic, mathematical, steady-state, kinetics
31 model that calculates the weathering of Ca^{2+} , Mg^{2+} , and K^+ in each horizon of a soil profile

1 (Akselsson et al., 2005). It is unique and differs from other empirical models in that it calculates
 2 BC_w rates for soil from independently measured geochemistry and soil conditions (Jönsson et al.,
 3 1995; Ouimet and Duschene 2005). It combines laboratory-based evaluations of mineral-
 4 specific chemical dissolution with field-based conditions and other soil measurements to
 5 estimate individual weathering rates of Ca^{2+} , Mg^{2+} , and K^+ (Langan et al., 1996). The model
 6 includes 14 of the most common primary and secondary soil minerals (**Table 4-2**)³, and their
 7 release of base cations in five separate reactions (Sverdrup et al., 1990; Hodson et al., 1997;
 8 Sverdrup et al., 1998):

- 9 i) Reaction with hydrogen ion (H^+) and dissolved aluminum (Al)
- 10 ii) Reaction with water and dissolved Al
- 11 iii) Reaction with hydroxyl ion (OH^-) and dissolved Al
- 12 iv) Reaction with carbon dioxide (CO_2)
- 13 v) Reaction with strongly complexing polydentate organic acids

14 The reaction rates are calculated using constants contained within the model and data input by
 15 the user, and the total base cation release rate by chemical weathering is calculated as the sum of
 16 all parallel simultaneous process rates minus the rate of precipitation of secondary solid phases
 17 (Sverdrup et al., 1998). The rate equation (Equation 4-4) for the weathering of all minerals
 18 within the rooting zone of the soil profile is defined as:

$$19 \quad RW = \sum_{(\text{horizons})} \sum_{(\text{minerals})} r_i \cdot A_{exp} \cdot x_i \cdot \theta \cdot z \quad (4-4)$$

20 where

21 r_i = dissolution rate of mineral i ($kmol_c/m^2/s$) – sum of the 5 separate reactions

22 A_{exp} = exposed surface of mineral matrix (m^2/m^3)

23 θ = soil moisture saturation (m^3/m^3)

³ Thirteen additional minerals can be added to PROFILE, as necessary (H. Sverdrup *personal communication*).

1 x_i = fraction of mineral i in the mineral matrix of the soil horizon

2 z = soil layer thickness (m)

3 The weathering rate is either increased or reduced by different soil and biotic and abiotic
4 conditions, many of which are entered as input data by the user. Input data includes site climatic
5 and deposition attributes, soil physical and chemical characteristics and biological components
6 that influence the soil chemistry and BC_w (input data required by PROFILE discussed further in
7 Section 4.3.3). As summarized by Jönsson and colleagues (1995), “The weathering rate is
8 increased by a high H^+ concentration, a high soil moisture (water) content, and a high CO_2
9 pressure. Weathering reactions are product inhibited, i.e., decrease by high concentrations of
10 reaction products in the soil solution such as inorganic aluminum and base cations. The surface
11 activity is calculated as dependent on the mineral surface area, temperature and soil moisture
12 saturation. The soil temperature impact on the weathering rate is expressed as an Arrhenius
13 equation, as dependent on the activation energy. The soil moisture saturation is important for the
14 reaction rate as the reactions will only take place on wetted surfaces. The degree of surface
15 wetting, and thus surface activity, is considered to be a function of the soil moisture saturation.
16 This is calculated from soil bulk density, the solid particle density and the volumetric water
17 content.” For a more detailed description of the theory and calculations behind PROFILE, see
18 Sverdrup (1990), Sverdrup and Warfvinge (1992, 1993a, 1995).

19 A main weakness of the PROFILE model is that it is data intensive and complex, and can
20 be difficult to parameterize. However, PROFILE does offer some significant benefits that set it
21 apart from the other models. As described, it determines current BC_w rates from laboratory-
22 derived weathering rates of individual minerals and therefore is not bound to data from a specific
23 location or region. Therefore, it can be used to determine and map BC_w over large areas (Miller
24 et al., 1993). Although it was developed in Sweden, it has been successfully applied to the
25 mapping of BC_w and critical loads in the Northeastern United States, Maryland, Minnesota,
26 Pennsylvania, Thailand, China, Argentina, and Greece (Duan et al., 2002; Miller, 2001; Sverdrup
27 et al., 1992; H. Sverdrup *personal communication*, 2009b).

Table 4-1. Review of modeling approaches (and models) to estimate base cation weathering for terrestrial critical acid load determinations.

Model Approach	Description of Method	Data Requirements	Model Complexity	Suitability for Estimating BC_w for Terrestrial Critical Acid Load Determinations in The United States	Suitability for Mapping BC_w Over Large Regions in The United States	References
Budget Studies	mass balance of inputs and outputs of base cations within catchment, watershed or soil profile	medium	medium	low; BC _w estimate is often an integrated value for whole catchment or watershed	low - medium (based on data availability); may require Sr isotope ratio of stream chemistry to separate exchangeable versus weathered base cation sources	Sverdrup et al., 1998; Sverdrup et al., 1990
Historical Rate Determinations	loss of base cations in soil profile relative to stable element (Zr, Ti, quartz or rutile)	low	low	medium; restricted to sites with young soils of known age (e.g., soils that have formed since the most recent glacial event, ~20,000 years ago)	low; restricted to sites with young soils and sites where historical rate determinations have been conducted	Sverdrup et al., 1998; Sverdrup et al., 1990
Empirical Models	modeled relationships between soil attributes and abiotic and biotic site conditions	low - high	low - high	low - high	low - high	

Model Approach	Description of Method	Data Requirements	Model Complexity	Suitability for Estimating BC _w for Terrestrial Critical Acid Load Determinations in The United States	Suitability for Mapping BC _w Over Large Regions in The United States	References
<i>Skokloster Assignment</i>	BC _w rate categorically determined by relative abundance of minerals grouped into 5-6 weathering rate classes; originally developed for soils similar to those found in the 3 Gårdsjön catchments in Sweden	low	low	low; most accurately applied to sites similar to those where the model was derived	low; most accurately applied to sites similar to those where the model was derived	UNECE, 2004; Hodson and Langan, 1999
<i>Soil Type - Texture Approximation</i>	BC _w categorically determined as a function of parent material acidity and soil texture, modified by temperature; developed from data from European forest soils	low	low	low - medium; most accurately applied to sites similar to those where the model was derived	low - medium; most accurately applied to sites similar to those where the model was derived	UNECE, 2004; Hodson and Langan, 1999

Model Approach	Description of Method	Data Requirements	Model Complexity	Suitability for Estimating BC _w for Terrestrial Critical Acid Load Determinations in The United States	Suitability for Mapping BC _w Over Large Regions in The United States	References
<i>Total Base Cation Content Correlation</i>	BC _w determined by correlations between historical rate determinations (Zr) and total content of base cations in the undisturbed bottom soil, corrected for temperature; based on data from eleven sites in Sweden	low	low	low; restricted to sites with granitic soils and Nordic geological histories	low; restricted to sites with granitic soils and Nordic geological histories	UNECE, 2004; Hodson and Langan, 1999
<i>Clay-Substrate Model</i>	BC _w determined by one of three equations based on parent material acidity and % clay content; most likely a modification of the Soil Type - Texture Approximation	low	low	low - medium; most accurately applied to sites similar to those where the model was derived (most likely young soils formed since the last glaciation)	low - medium; most accurately applied to sites similar to those where the model was derived (most likely young soils formed since the last glaciation)	original source unknown; Ouimet et al., 2006; Watmough et al., 2006; McNulty et al., 2007; Pardo and Duarte, 2007

Model Approach	Description of Method	Data Requirements	Model Complexity	Suitability for Estimating BC _w for Terrestrial Critical Acid Load Determinations in The United States	Suitability for Mapping BC _w Over Large Regions in The United States	References
<i>PROFILE</i>	BC _w determined as a function of weathering of individual soil minerals and field-based soil and biotic conditions	high	high	medium - high; may have restrictions in desert regions and areas that are lacking necessary data	medium - high; may have restrictions in desert regions and areas that are lacking necessary data	Warfvinge and Sverdrup, 1992 and 1995; Sverdrup, 1990

Table 4-2. The fourteen dominant minerals modeled within PROFILE.

Dominant Minerals
K-Feldspar
Plagioclase
Albite
Hornblende
Pyroxene
Epidote
Garnet
Biotite
Muscovite
Fe-Chlorite
Mg-Vermiculite
Apatite
Kaolinite
Calcite

1

2 **4.3.3 Proposed methodology for estimating and mapping base cation weathering for** 3 **terrestrial critical acid load calculations**

4 As has been outlined in the above review, there are multiple approaches to estimate BC_w
5 for terrestrial critical acid loads. However, not all are suitable for both calculating and mapping
6 terrestrial critical acid loads throughout the United States. Such an approach has to be quick and
7 easy to apply, be supported by available data and be easily and accurately transferable to sites
8 within the United States that differ in soil, biotic and abiotic properties and conditions. In
9 addition, as stated by Miller (2001), “the most promising approach for a logically consistent
10 estimation of the present-day weathering rate over broad regions is the application of model(s)
11 that predict the weathering rate from first principles, given detailed measurements of the soil
12 environment and laboratory-derived rate constants for specific mineral weathering reactions.”
13 Therefore, an approach that is based on soil mineralogy and weathering of individual minerals is
14 preferable. Of all the models that are currently available for determining BC_w for terrestrial
15 critical acid load determinations, PROFILE meets these requirements and appears to be the most
16 suitable. Methodologically, it has few location restrictions and models BC_w based on site-
17 specific mineralogy and soil and site conditions. In addition, it has already been successfully
18 applied in both glaciated and non-glaciated regions of the United States to estimate and map BC_w

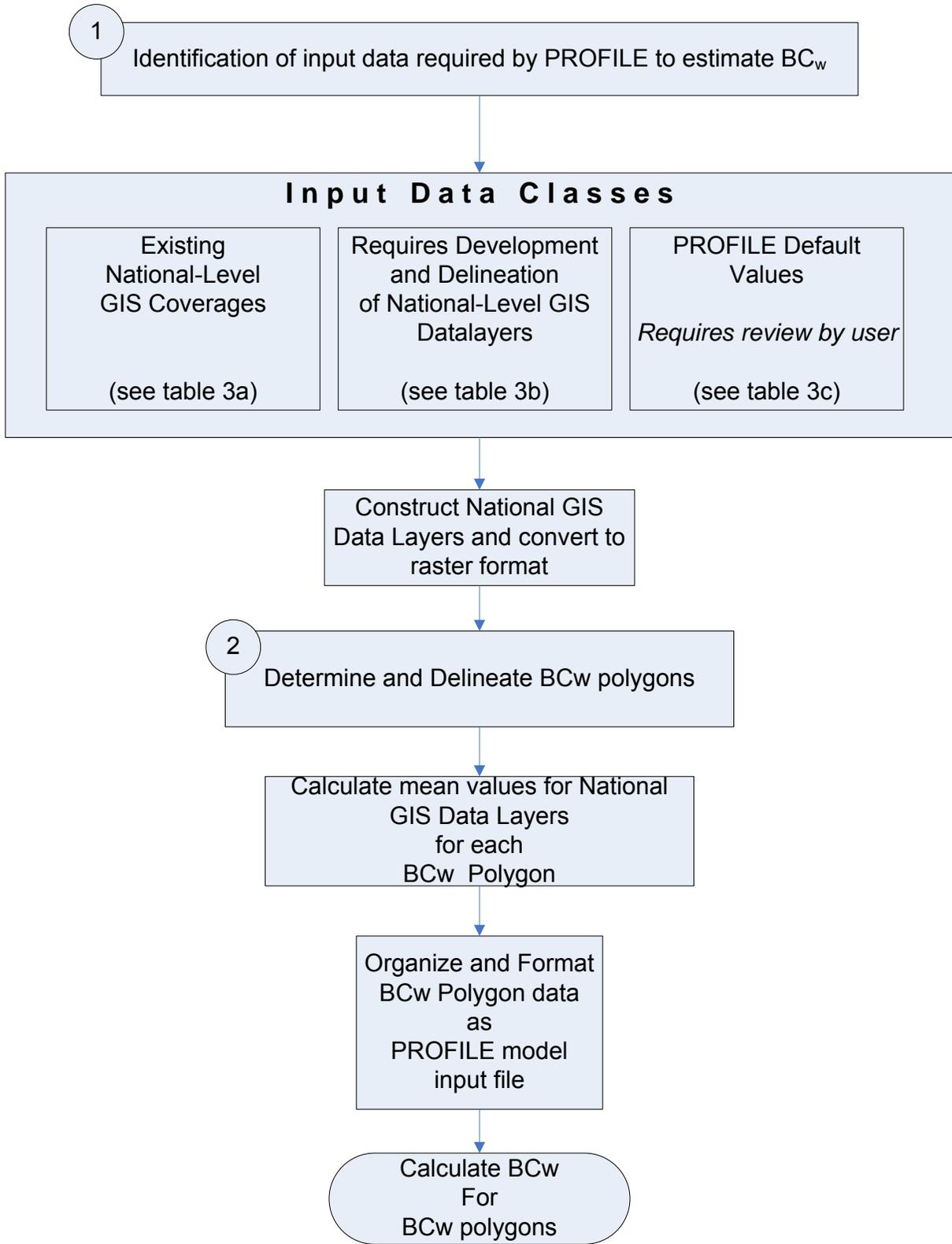
1 and critical acid loads (Miller et al., 1993; Sverdrup et al., 1992; H. Sverdrup *personal*
2 *communication*, 2009b). Although, as with all models, PROFILE does have some weaknesses
3 and limitations (discussed further in Section 4.3.5) that need to be acknowledged and addressed
4 prior to application, critical load experts, in general, agree that PROFILE is the best model to
5 date for estimating and mapping BC_w rates for terrestrial critical acid load determinations in the
6 United States (J. Aherne *personal communication*, 2009, J. Cosby *personal communication*,
7 2009, J. Lynch *personal communication*, 2009, R. Ouimet *personal communication*, 2009, H.
8 Sverdrup *personal communication*, 2009b).

9 There are two forms of PROFILE (version 5.0) that can be used for estimating BC_w : the
10 single site application which estimates BC_w for a single location or soil profile, and the regional
11 application which PROFILE can be run for a region or conterminous areas (C. Akselsson
12 *personal communication*, 2009). For mapping BC_w in the conterminous United States, the
13 regional application of the model would be applied, and the estimation and mapping of BC_w
14 would involve two main steps:

15 **Step 1. Identification of input data required by PROFILE and development of**
16 **spatial data layers, national databases and default values for each data**
17 **element within the model**

18 **Step 2. Determination of polygon layer to spatially define the BC_w rates and**
19 **development of continuous coverage map of calculated BC_w values.**

20 These process steps are further illustrated in the flowchart presented in **Figure 4-2**.



1
2

Figure 4-2. Process Steps for Estimating BC_w Using the PROFILE Regional Model

Step 1. Identification of input data required by PROFILE and development of spatial data layers, national databases and default values for each data element within the model

PROFILE (version 5.0) is data intensive and requires the user to provide or review a total of 26 soil, climatic and biological input data (**Table 4-3a-c**). In addition, to run the regional application of PROFILE, it would be necessary to have each of these data parameters available as continuous coverages. A large proportion of these variables are already included in existing databases in the United States and could be easily converted into continuous coverage data layers for the conterminous United States, if not currently available in continuous coverage format. Others, such as soil mineralogy, would need to be modeled or constructed from other data. Still others may need to be represented by default values from the literature, until more unique, spatially site-specific values are determined.

Table 4-3a. Data required to estimate BC_w with the regional PROFILE model (version 5.0). The data in this table must be input by the user and are currently available as a continuous coverage layers for at least a portion of the conterminous United States.

PARAMETER	UNITS	DESCRIPTION
precipitation	m/yr	30-year long-term average
cation deposition	kEq/ha/yr	ammonium (NH_4^+), Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Al - wet and dry deposition
anion deposition	kEq/ha/yr	sulphate (SO_4^{2-}), chloride (Cl^-) and nitrate (NO_3^-) - wet and dry deposition
number of soil layers	#	up to 5 layers (with the forest floor/organic layer being the first horizon)
soil layer height	m	by layer
temperature	°C	mean annual soil temperature by layer
dry soil bulk density	kg/m ³	by layer
run-off	m/yr	number between 0 and the precipitation rates. If there is no lateral flow, runoff rate should equal the precipitation rate times the % of precipitation leaving the last soil layer.

13

Table 4-3b. Data required to estimate BC_w with the regional PROFILE model (version 5.0). The data in this table must be input by the user and are not currently available as a continuous coverage layers for at least a portion of the conterminous United States (will require development of national coverage layer).

PARAMETER	UNITS	DESCRIPTION
net uptake	kEq/ha/yr	nitrogen (N), Ca^{2+} , Mg^{2+} , K^+ - only applied if biomass removed through harvesting or fire
cation uptake	%	% of total soil profile (all soil layers combined should sum to 100%). Can be estimated using root distribution
nitrogen uptake	%	% of total soil profile (all soil layers combined should sum to 100%). Can be estimated using root distribution
litterfall	kEq/ha/yr	N, Ca^{2+} , Mg^{2+} and K^+ - input to forest floor
soil water content	m ³ /m ³	by layer
surface area	m ² /m ³	soil surface area by layer

PARAMETER	UNITS	DESCRIPTION
logKgibbsite	-	by layer
dissolved organic carbon (DOC)	mg/L	by layer
mineralogy	%	% abundance of 14 dominant mineral groups (K-Feldspar, Plagioclase, Albite, Hornblende, Pyroxene, Epidote, Garnet, Biotite, Muscovite, Fe-Chlorite, Mg-Vermiculite, Apatite, Kaolinite, Calcite)

1

Table 4-3c. Data required to estimate BC_w with the regional PROFILE model (version 5.0). The data in this table are used to support calculations within the model and should be reviewed by the user.

PARAMETER	UNITS	DESCRIPTION
forest canopy	kEq/ha/yr	N, Ca^{2+} , Mg^{2+} , K^+ - nutrients removed by or leached from canopy
net mineralization	kEq/ha/yr	N, Ca^{2+} , Mg^{2+} , K^+ - net accumulation of soil organic matter
precipitation entering soil horizon	%	expressed as % of precipitation. If no lateral flow, % leaving top layer should be same as % entering underlying layer
precipitation leaving soil horizon	%	expressed as % of precipitation. If no lateral flow, % leaving top layer should be same as % entering underlying layer
CO ₂ pressure	x atm	entered as multiple of atmospheric pressure; typically ranges from 5 in the organic horizons to 40 in the mineral soil layers
immobilization	-	nitrogen immobilization - constant
nitrification	-	constant
denitrification	-	constant
nutrient uptake kinetics	-	coupled vs. uncoupled uptake of N and base cations / uptake mechanism (unspecific, vanselow and none)

2 A total of eight parameters including climate, deposition, run-off and many of the soil
3 variables have data available as continuous coverages for the conterminous the United States
4 (**Table 4-4**), and for most of these variables, data exist for all 48 states. However, some of these
5 databases are missing variables and/or data or may need to be modified. Currently, there is no
6 data that describes wet and dry Al deposition. This data, however, is not available in most
7 locations where PROFILE is applied, and this parameter is typically left blank within model (H.
8 Sverdrup *personal communication*, 2009b). Therefore, the absence of this datalayer in the United
9 States should not pose a problem for the BC_w estimates. The soil temperature parameter within
10 the SSURGO database is poorly populated and data only exists for seventeen states. However,
11 mean annual air temperature is often used as a surrogate for soil temperature within PROFILE
12 because the two temperature measures are similar in some of regions (Miller, 2001). In some
13 cases, models describing the relationship between air and soil temperature are also available
14 (e.g., Yin and Arp, 1993). Therefore, the use of air temperature instead of soil temperature or
15 modeled soil temperature could be explored with the application of PROFILE in the United
16 States, if necessary.

Table 4-4. Available datasets and databases for the conterminous United States that could be used to estimate BC_w with the regional application of the PROFILE model (version 5.0).

DATA	SOURCE URL or REFERENCE	DATE(S) OF AVAILABLE DATA	UNITS	RESOLUTION	STATES WITH COVERAGE
Total annual precipitation	http://prism.oregonstate.edu/products/matrix.phtml?vartype=ppt&view=maps	1971-2000	in/yr	0.64 km ²	all
Average maximum air temperature	http://prism.oregonstate.edu/products/matrix.phtml?vartype=ppt&view=maps	1971-2000	°F	0.64 km ²	all
Average minimum air Temperature	http://prism.oregonstate.edu/products/matrix.phtml?vartype=ppt&view=maps	1971-2000	°F	0.64 km ²	all
Run-off	http://pubs.er.usgs.gov/djvu/HA/ha_710_plt.djvu	1951-1980	in/yr	1:2,000,000	all
Dry cation deposition (NH ₄ ⁺ , Ca ²⁺ , Mg ²⁺ , K ⁺ , Na ⁺)	http://www.epa.gov/castnet/data.html	1987-2008	kg/ha	86 stations in the 48 conterminous states	all (except: ID, SD, NE, NM, and TX) Extrapolated 400 km from each station
Wet cation deposition (NH ₄ ⁺ , Ca ²⁺ , Mg ²⁺ , K ⁺ , Na ⁺)	http://www.epa.gov/castnet/data.html , http://nadp.sws.uiuc.edu/maplib/grids/2008/	1987-2008, 1994-2006	kg/ha	86 stations in the 48 conterminous states, 6.25 km ²	all (except ID, SD, NE, NM, and TX) Extrapolated 400 km from each station
Dry anion deposition (SO ₄ ²⁻ , Cl ⁻ , NO ₃ ⁻)	http://www.epa.gov/castnet/data.html	1987-2008	kg/ha	86 stations in the 48 conterminous states	all (except ID, SD, NE, NM, and TX) Extrapolated 400 km from each station
Wet anion deposition (SO ₄ ²⁻ , Cl ⁻ , NO ₃ ⁻)	http://www.epa.gov/castnet/data.html , http://nadp.sws.uiuc.edu/maplib/grids/2008/	1987-2008, 1994-2006	kg/ha	86 stations in the 48 conterminous states, 6.25 km ²	all (except ID, SD, NE, NM, and TX) Extrapolated 400 km from each station
NH ₄ ⁺ and NO ₃ ⁻ wet and dry deposition	Community Multiscale Air Quality (CMAQ) - http://www.epa.gov/AMD/CMAQ/	2002	kg/ha	12 km ²	all
Soil horizon depth	HZDEPT_R field of chorizon table (http://soildatamart.nrcs.usda.gov/documents/SURGOMetadataTableColumnDescriptions.pdf)	1987-2008, 1994-2006	cm	1:12,000 - 1:63,360	all
Soil bulk density	DB3BAR_R field of CHORIZON table (http://soildatamart.nrcs.usda.gov/documents/SURGOMetadataTableColumnDescriptions.pdf)	N/A	g/cm ³	1:12,000 - 1:63,360	all

DATA	SOURCE URL or REFERENCE	DATE(S) OF AVAILABLE DATA	UNITS	RESOLUTION	STATES WITH COVERAGE
Soil texture (% sand, silt, and clay)	SANDTOT_R, SILTTOT_R, and CLAYTOT_R fields of CHORIZON table (http://soildatamart.nrcs.usda.gov/documents/SURGOMetadataTableColumnDescriptions.pdf)	N/A	%	1:12,000 - 1:63,360	all
Soil stoniness (% of soil with particles >2mm)	FRAGVOL_R in CHFRAGS table (http://soildatamart.nrcs.usda.gov/documents/SURGOMetadataTableColumnDescriptions.pdf)	N/A	%	1:12,000 - 1:63,360	all
Soil temperature	SOITEMPMM field of the COSOILTEMP table (http://soildatamart.nrcs.usda.gov/documents/SURGOMetadataTableColumnDescriptions.pdf)	N/A	°C (average by month)	1:12,000 - 1:63,360	AK,CA,CO,GA,ID,KS,MI,MN,MO,MT,NC,NE,NM,OR,PR, TX,VA

1 Although a portion of the input data to estimate BC_w with PROFILE are already available
2 as national data coverages, there are nine additional input parameters that are not currently
3 described by nationwide datasets, and nine parameters that are built into the regional application
4 of the model and may require review and adjustment prior to applying PROFILE in the United
5 States. The nine input parameters that would require the development of national GIS coverages
6 or datasets that could be applied throughout the United States include: net uptake, % base cation
7 and nitrogen uptake, litterfall, soil water content, surface area, $\log K_{gibbsite}$, mineralogy, and
8 dissolved organic carbon (DOC).

9 Net Uptake

10 A national dataset of net uptake of nutrients by forest systems could be developed using
11 the approach outlined by McNulty and colleagues (1997). Briefly, the United States Forest
12 Service (USFS) and United States Geological Survey (USGS) dataset describing the 21 different
13 forest types would be used to map forest cover in the 48 states, and nitrogen and base cation
14 (Ca^{2+} , Mg^{2+} , K^+) uptake by each forest type would be determined using the average values
15 presented in **Table 4-5**. These values were calculated by McNulty and colleagues (2007) and
16 incorporate annual volume growth by region from the USFS Forest Inventory and Analysis
17 (FIA) database and nitrogen and base cation contents by tree species and tree component from
18 the Tree Chemistry Database (Pardo et al., 2004). Net uptake would only be necessary for sites
19 that are actively managed and experience removal of biomass through logging and/or fire.
20 Therefore, based on the assumption that only wilderness and conservation areas are not harvested
21 or managed, these nitrogen and base cation uptake estimates would only be applied to forest
22 areas that are not designated as wilderness by the National Wilderness Preservation System of
23 the United States (McNulty et al., 2007).

24

Table 4-5. Nitrogen and base cation uptake by forest type
(from McNulty et al., 2007).

FOREST COVER TYPE	NITROGEN UPTAKE (eq/ha/yr)	BASE CATION UPTAKE (eq/ha/yr)
white-red-jack pine	59.07	77.14
spruce fir	54.27	83.72
longleaf slash pine	154.74	227.22
loblolly shortleaf pine	140.41	208.58
oak pine	129.71	213.75
oak hickory	102.56	254.87
oak-gum-cypress	124.18	235.68
elm-ash-cottonwood	79.74	156.3
maple-beech-birch	101.76	190.51
aspen-birch	81.69	125.46
douglas-fir	109.89	179.03
hemlock-sitka-spruce	98.88	161.12
ponderosa pine	75.29	174.39
western white pine	40.69	37.11
lodgepole pine	40.19	61.25
Larch	65.1	77.14
fir-spruce	94.65	146
Redwood	100.92	156.62
Chaparral	106.6	201.61
pinyon-juniper	40.87	58.21
western hardwoods	135.21	263.33

1

2

Soil Surface Area

3 Soil surface area is commonly determined in the laboratory using the Brunauer-Emmett-
4 Teller (BET) nitrogen absorption technique (Hodson et al., 1997). However, data from such
5 analyses are not available for all soils in the United States. Therefore, it would be necessary to
6 estimate surface area from other soil data. Within the PROFILE model, surface area is calculated
7 with soil texture and particle size distribution data (Equation 4-5) (Alveteg et al., 2004), and
8 Sverdrup and colleagues (1992), used this equation in their study of critical acid loads in
9 Maryland. This same approach could be used for mapping soil surface areas in the United States.
10 Soil texture is part of the U.S. Department of Agriculture- Natural Resources Conservation
11 Service (USDA-NRCS) Soil Survey Geographic (SSURGO) database (Table 4.0). Therefore, it

1 would be possible to produce a continuous coverage map of soil surface areas in the United
2 States.

$$3 \quad Aw = (8.0x_{\text{clay}} + 2.2x_{\text{silt}} + 0.3x_{\text{sand}}) p / 1000 \quad (4-5)$$

4 where

$$5 \quad Aw = \text{total exposed surface area (m}^2\text{/m}^3\text{)}$$

$$6 \quad x = \text{weight fraction of clay, silt and sand when } x_{\text{clay}} + x_{\text{silt}} + x_{\text{sand}} = 1;$$

$$7 \quad p = \text{soil density in kg/m}^3$$

8 **Soil Mineralogy**

9 Soil mineralogy is one of the most important and influential variables within PROFILE.
10 However, it is also a very time intensive and expensive measurement. Therefore, soil mineralogy
11 data in the United States is sparse, and a continuous coverage layer of soil mineralogy does not
12 exist. In most regional applications of PROFILE in Europe and other regions, the mineralogy
13 input data are based on a combination of data from soil geochemical and mineralogy analyses
14 and mineralogical composition based on output from a model such as the Analysis to Mineral
15 (A2M) model (Posch and Kurz, 2007). The A2M model estimates all possible mineral
16 compositions from total chemical analyses (Ca²⁺, Mg²⁺, K⁺, Na⁺, Ti, Al, phosphorus (P), silicon
17 (Si), iron (Fe)) of the soil and a pre-specified set of minerals that are likely to be present in the
18 soil. The highest probability mineral composition is an output of the arithmetic mean of all
19 extreme mineral modes. The resulting mineralogies are then mapped to “geological provinces”
20 (Sverdrup et al., 1990) that have the same parent material bedrock but may differ in soil
21 mineralogy in a consistent pattern (Sverdrup et al., 1990). Alternatively, the mineralogies can be
22 mapped to “mineralogy polygons” that are delineated based on probable similarities in mineral
23 compositions of the soils. Typically, the spatial borders of mineralogy polygons are determined
24 by underlying parent material geology and/or soil type groupings that are likely to have the same
25 mineralogies (H. Sverdrup *personal communication*, 2009b). In areas where the soils have
26 formed from transported materials, such as glacial till, it is sometimes necessary to consider the
27 surficial geology and model the origin and transport of materials to determine the parent material
28 geology (McKenzie and Ryan, 1999).

1 Due to the diverse geological history of the United States, it may be necessary to include
2 a variety of variables and databases in the characterization and mapping of mineralogy. Parent
3 materials underlying soils in the conterminous United States vary extremely. These materials
4 include not only bedrock beneath young soils, but also a variety of young and old regolith
5 materials that include both residuum formed in place and all varieties of transported sediments.
6 In addition, the soils are old and highly weathered in a large portion of the United States, and
7 therefore, no longer resembles the mineral composition of the parent material. For example, the
8 mineralogy of soils atop ancient residuum of the Appalachian region will vary significantly from
9 the mineralogy of younger residuum of the Western mountain ranges. Also, the mineralogy of
10 soil developed on the older loessal plain in the Mississippi basin will vary from the younger
11 glacial deposits along the northern regions of the United States. Therefore, determination of soil
12 mineralogy in the United States would require an approach that is able to recognize the varied
13 geological histories, different parent material origins, and soil mineralogies that differ from the
14 original parent material sources. Such an approach would involve the following steps be
15 conducted simultaneously:

- 16 1. Delineation of mineralogy polygons based on soil classification at a level supported
17 by available data
- 18 2. Determination of mineralogy and geochemical data availability for each mineralogy
19 polygon
- 20 3. Comparison of mineralogy polygons with underlying bedrock and surficial geology
- 21 4. Testing modeled mineralogy against actual mineralogy measurements

22 *Delineation of mineralogy polygons based on soil classification at a level supported by*
23 *available data* - Mapping and creation of a national GIS coverage of mineralogy in the
24 conterminous United States would require the delineation of “mineralogy polygons”.
25 “Mineralogy polygons” are spatially-defined polygons that are delineated based on probable
26 similarities in mineral compositions of the soils. These polygons would need to be large enough
27 in scale to be adequately covered by available mineralogy and soil analysis data, yet small
28 enough to only represent single assemblages of soil minerals. Ideally, each mineralogy polygon
29 should have at least one data point or soil profile analysis that describes the total analysis (Ca^{2+} ,
30 Mg^{2+} , K^+ , Na^+ , Ti, Al, P, Si, and Fe) and/or mineralogy of the soil layers. Where data are
31 missing, it would be necessary to interpolate data from other locations using correlations with

1 surrounding and adjacent known data and other supporting criteria indicative of similar
 2 mineralogies and weathering patterns (e.g., geologic and physiographic regions, bedrock geology
 3 data, climatic regions, and others).

4 Within the United States, one of the most suitable coverages for the delineation of the soil
 5 mineralogy polygons is the SSURGO soils database (**Table 4-6**). The smallest unit within this
 6 database is the soil mapping unit which can consist of up to five individual soil series. A soil
 7 series is defined as “soils that are similar in all major profile characteristics (Brady and Weil,
 8 2002), and soils within the same series have been influenced by similar climate, topographic
 9 location, biota, parent material and pedological time frame. Therefore, the soil within a series,
 10 regardless of location would be expected to have identical or sufficiently similar mineralogies
 11 (C. Smith *personal communication*, 2009). The soil groupings within the higher levels of soil
 12 taxonomy may also be based on characteristics such as soil mineralogy. For example, soil orders
 13 are largely classified by the degree of weathering and soil development, with Entisols
 14 representing the youngest, least weathered soils, and Ultisols and Spodosols being more highly
 15 weathered. Therefore, it may be possible to group the soil mapping units at a higher level of
 16 taxonomy, such as the great group, family or order, as the “mineralogy polygons”. However,
 17 since soils are classified based on multiple formative factors, the “mineralogy polygons” could
 18 be a mixture of groupings based on different levels of soil taxonomy, with all groupings based on
 19 factors indicative of similar mineral assemblages in the soil.

20 Detailed soil delineations have been completed for more than 80% of the conterminous
 21 United States and are used in the NRCS Soil Survey Geographic (SSURGO) dataset (**Figure 4-**
 22 **3**). Data are missing for many public land areas (e.g., national forest lands), and there are
 23 approximately 21,000 soil series delineations within the conterminous United States.

Table 4-6 Datasets with Geochemical and Mineralogy Data for U.S. Soils

DATA	SOURCE	RESOLUTION	INCLUDED DATA
Soil Survey Geographic Database (SSURGO)	http://soils.usda.gov/survey/geography/ssurgo/	1:12,000 to 1:63,360	SSURGO is linked to a National Soil Information System (NASIS) attribute database. The attribute database gives the proportionate extent of the component soils (i.e., u soil series) and their properties for each map unit. The SSURGO map units consist of 1 to 3 components each. There are approximately 15,000 and 20,000 soil series polygons delineated across the United States

DATA	SOURCE	RESOLUTION	INCLUDED DATA
U.S. General Soil Map (STATSGO II)	http://soils.usda.gov/survey/geography/statsgo/	1:250,000	The tabular data contain estimated ranges (low, high, and representative values) of physical and chemical soil properties, soil interpretations depicting the range for the geographic extent of the map unit. Soil map units are linked to attributes in the tabular data, which give the proportionate extent of the component soils and their properties.
Surficial Geology of the United States (1977) (also Map of Surficial Deposits and Materials in the Eastern and Central United States (East of 102° West Longitude))	http://tin.er.usgs.gov/geology/state/ or http://water.usgs.gov/GIS/metadata/usgswrd/XML/ofr99-77_geol75m.xml also http://pubs.usgs.gov/imap/i-2789/	1:7,500,000 (E of 102° W Longitude: 1:2,000,000)	Provides approximate areal extent of about 45 categories of regolith types across the conterminous United States. Compilation East of 102° West Longitude has further classified deposits generally within original polygons.
Element Concentrations in Soils and Other Surficial Materials of the Conterminous United States (Shacklette Data, 1977)	USGS, Denver Federal Center Offices	Sampling density: 1 sample per 6,000 km ² ; equivalent to the collection of samples on a 75-km grid.	Ultra-low-density geochemical baseline data from 1,323 samples locations characterizing soils and other surficial materials in the conterminous United States. Elements analyzed included: Ag, Al, Ba, Be, B, Ca, Ce, Cr, Co, Cu, Ga, Ge, Hg, Fe, La, Li, Pb, Mg, Mn, Mo, Na, Nd, Ni, Nb, P, K, Rb, S, Sc, Se, Sr, Th, Ti, U, V, Yb, Y, Zn, Zr, and total carbon.
The National Geochemical Survey – Database and Documentation (Version 5.0, on-going)	http://tin.er.usgs.gov/geochem/doc/home.htm and http://tin.er.usgs.gov/geochem/	Nominal grid spacing of 17 by 17 kilometers (i.e., minimum sample density of 1 sample per 289 km ² in all land areas of the country)	Stream-sediment-based geochemical survey for the United States; Analytical methods include a 40-element ICP package plus single-element determinations of As, Se, and Hg by atomic absorption for every sample. about 60,000 stream-sediment samples that have been analyzed. Digital data files are presented in 6 categories. In total there are 43 individual data files for the United States. Some of the data has also been processed into vector data to produce maps showing the elemental concentration of As, Se, Hg, Pb, Zn, Cu, Al, Na, Mg, P, Ca, Ti, Mn, and Fe at the county level. Database contains 287 attributes (77,212 records).
Integrated Geologic Map Databases for the United States (1998-2007)	http://gsa.confex.com/gsa/2006AM/finalprogram/abstract_110914.htm and http://tin.er.usgs.gov/geology/state/	1:100,000	Seamless national-scale geologic spatial data-layer and database to support national and regional level projects, including mineral resource and geoenvironmental assessments. Data include general geologic unit age, dominant lithology (rocktype1 must be >50% of unit) and second most dominant lithology (rocktype2).

DATA	SOURCE	RESOLUTION	INCLUDED DATA
Soil Pedon Pit Data (on-going)	USDA NRCS	Area covered by a pedon varies from 10 - 100 square feet; approximately 30,000 soil pits/pedons in the NRCS database	Geochemical elements: Al, Ca, Fe, K, Mg, Mn, Na, P, Si, Sr, Ti, and Zr. X-ray diffraction for clay mineralogy by horizon; optical mineralogy analysis is performed on the dominant sand fractions of the soil from the A-horizon, B-horizon, and C-horizon, or the most dominant horizon. More than 60 fields describing the minerals are listed in the database. The dataset is not uniform in that elemental analyses were routinely done through the 1970's but then these analyses were suspended through the 1980's. Elemental analyses were resumed during the early 1990's. It is estimated that as much as one third of the 30,000 soil pedons have geochemical data. Likewise, optical mineralogy is not performed for all pedons and the NRCS staff estimate that approximately as many as one third of the 30,000 soil pits have optical analysis results. Even though the number of pedons with data are similar for geochemical and optical analysis results, the data are not necessarily associated with the same set of pedons or even soil series.
Physiographic Regions of the United States (Fenneman, 1946)	http://water.usgs.gov/GIS/dsd/l/physio.e00.gz	1:7,000,000	Geomorphic / physiographic broad-scale subdivisions based on terrain texture, rock type, and geologic structure and history. Nevin Fenneman's (1946) three-tiered classification of the United States - by division, province, and section.

1

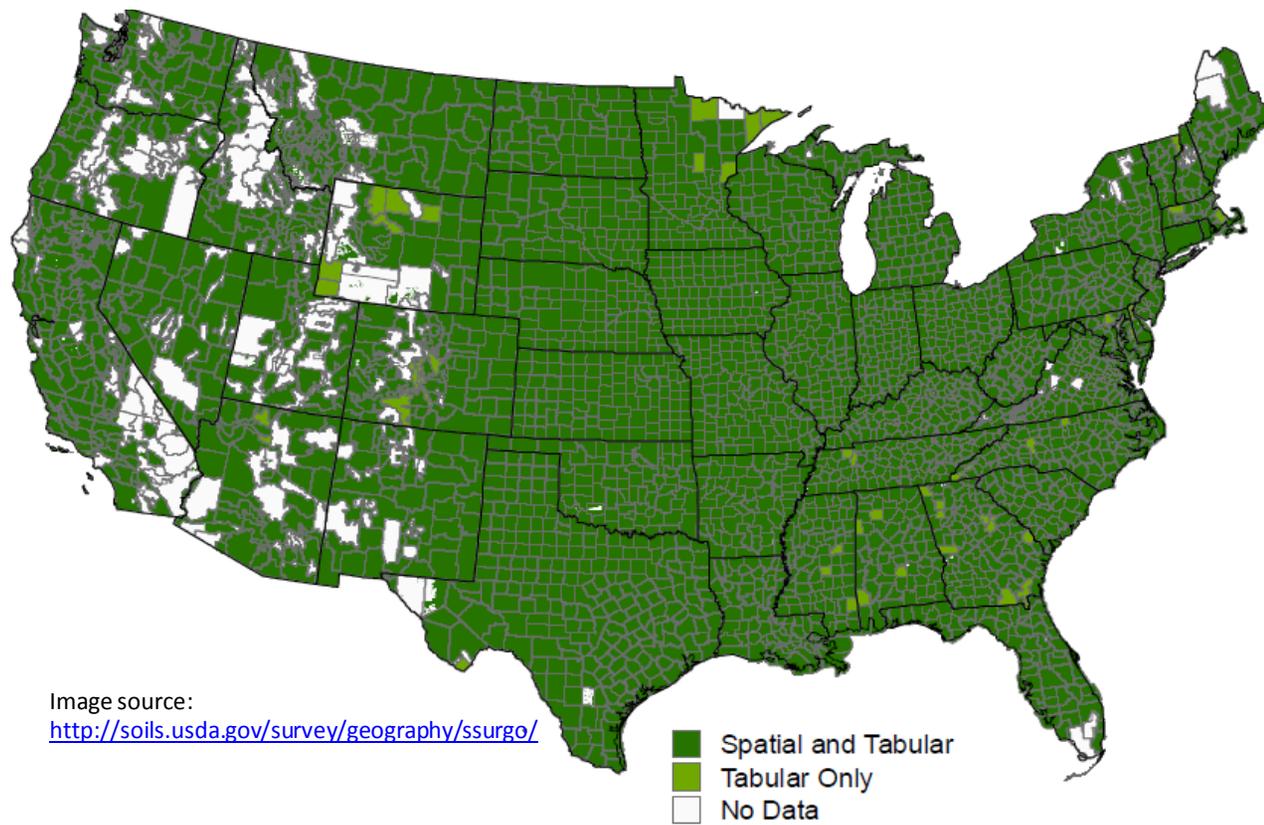


Figure 4-3. Map Showing the Distribution and Status of SSURGO Data

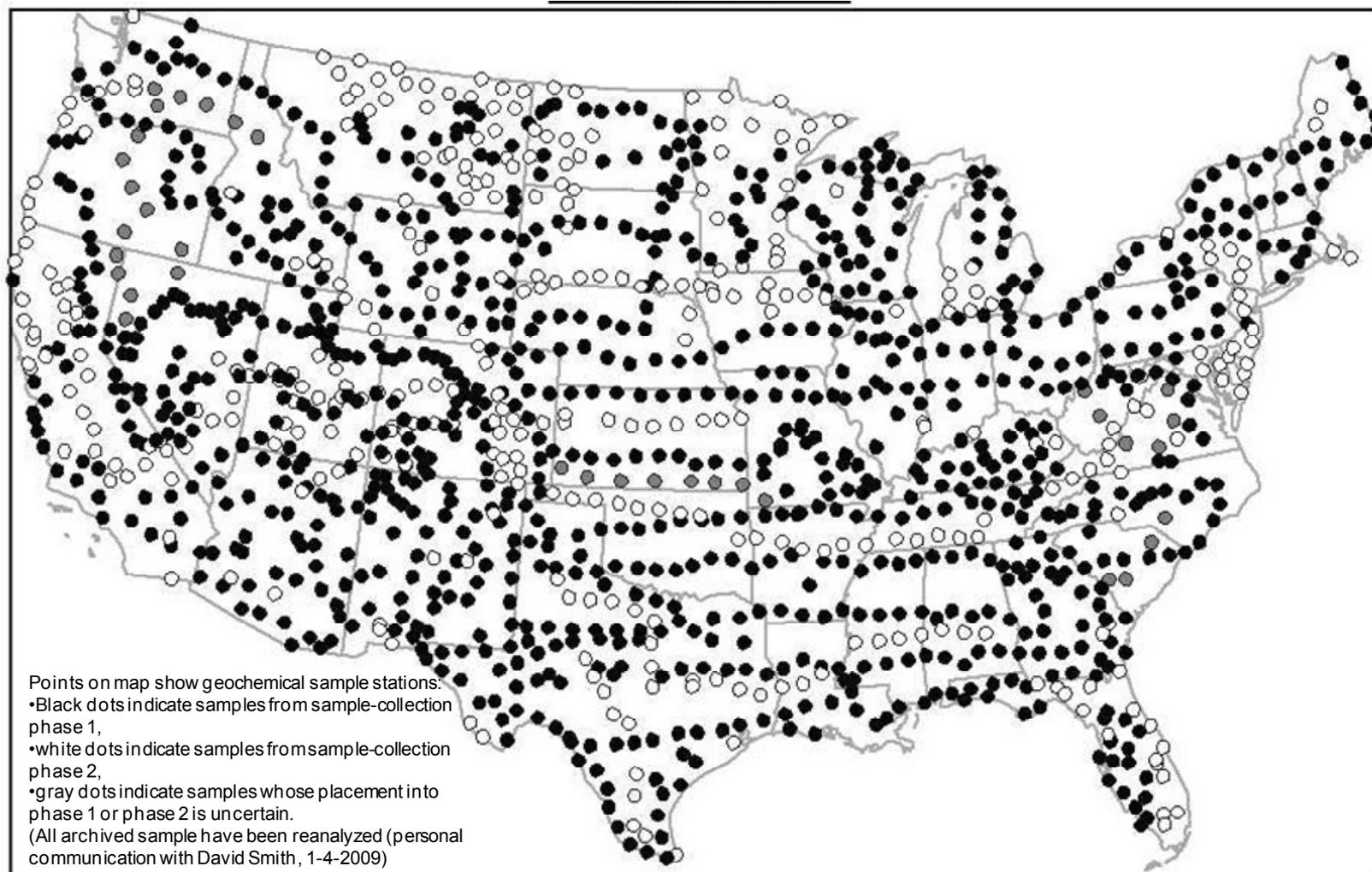
1 Determination of mineralogy and total analysis data availability for each mineralogy
2 polygon - The soils for each spatially-defined “mineralogy polygon” would require %
3 mineralogy to determine BC_w with the PROFILE model. The relative abundances of 14
4 dominant minerals are required as model input, and this % mineralogy can be based on direct
5 measurements of soil mineralogy or can be determined with the A2M model. As outlined earlier,
6 the A2M model is able to estimate the most probable % mineral composition, or proportion of
7 mineral phases, of a soil based on total analysis data and the identification of the minerals that
8 are likely to be present in the soil. Therefore, it would be necessary to determine the availability
9 of such data for each of the “mineralogy polygons” in the conterminous United States.

10 Currently, there are potentially three consistent national-scale datasets that contain
11 various levels of mineralogy and total analysis data to serve as inputs for the A2M and PROFILE
12 models. These include:

- 13 • *Chemical Analyses of Soils and other Surficial Materials of the Conterminous United*
14 *States* (Shacklette dataset) and accompanying *Geochemical Landscapes Project* data,
- 15 • the more recent *National Geochemical Survey* data, and
- 16 • the *United States Department of Agriculture (USDA) NRCS pedon soil pit dataset*.

17 A summary of these datasets is outlined in Table 4-6.

18 *Chemical Analyses of Soils and other Surficial Materials of the Conterminous United*
19 *States (Shacklette Data)* and the *Geochemical Landscapes Project* datasets provide geochemical
20 baseline data for soils and other surficial materials in the conterminous United States. The
21 original Shacklette dataset contains geochemical data from soils and other regolith collected and
22 analyzed by Hans Shacklette and colleagues beginning in 1958 and continuing until about 1976.
23 This dataset has approximately 1,323 samples, at a sampling density of approximately 1 sample
24 per 6,000 square kilometers (**Figure 4-4**). The soil samples within this dataset were analyzed for
25 a large number of elements, including Ca, Fe, Mg, Na, P, K, and Ti (Gustavsson et al., 2001),
26 that are required by the A2M model. However, assessments of mineralogy were not included in
27 these original analyses. An additional drawback with the data set is its extremely low numbers of
28 samples for the entire conterminous United States. However, more recent high-resolution studies
29 (e.g., Smith et al., 2005) for select elements (e.g., Calcium) have illustrated that the regional
30 patterns established by the Shacklette data are generally maintained except where areas have
31 been affected by anthropogenic factors (Smith, 2006).



Shacklette, Hansford T., and Josephine G. Boerngen, 1984

Figure 4-4. Soil Sampling Locations Included in the USGS Shacklette Dataset

The *Geochemical Landscapes Project* was begun in 1998 with most work occurring after 2002. The purpose of the data collection is to increase the density of the *Shacklette* data locations to produce a high resolution geochemical dataset for North American soils of 6,000 data points (D. Smith *personal communication*, 2009). This is an on-going collaborative effort by the USGS, USDA Natural Resource Conservation Service, other federal agencies, and academia to build a national-scale soil geochemical survey. The project has just completed a third year of continental-sampling and completed sample collection for approximately 80% of the conterminous United States (D. Smith *personal communication*, 2009). The USGS anticipates that sampling may be completed for the conterminous United States in 2010; or 2011 at the latest. Both total and mineralogy analyses are being performed on these samples. Mineralogy analyses include x-ray diffraction on the clay fraction and optical analyses on the fine sands and silts. In addition, the original Shacklette data have been re-analyzed for mineralogy.

The *National Geochemical Survey (NGS)* dataset is being built by on-going efforts by the USGS to produce a new stream-sediment-based geochemical survey for the United States at a spacing of 17 by 17 kilometers (i.e., minimum sample density of 1 sample per 289 km² in all land areas of the country) (**Figure 4-5**). The project has sought to capitalize on existing datasets and archived samples. For this reason the NGS is based primarily on analyses of stream sediments to build on the massive archives of data and samples from DOE's National Uranium Evaluation (NURE) program. Much of the survey has entailed reanalysis of approximately 35,000 archival samples from the NURE program. Where NURE samples do not exist, USGS has been working with cooperators to obtain new samples. In total, the project is expecting to have more than 60,000 samples. Most or all of the sampling has been completed for the conterminous United States and only few analyses are left to complete (D. Smith *personal communication*, 2009). The samples are being analyzed for 40 elements, including all of the elements which are necessary input for the A2M model. In addition, for a select number of samples mineralogy analyses (x-ray diffraction of clay fraction and optimal analyses of fine sands and silts) are also being conducted.

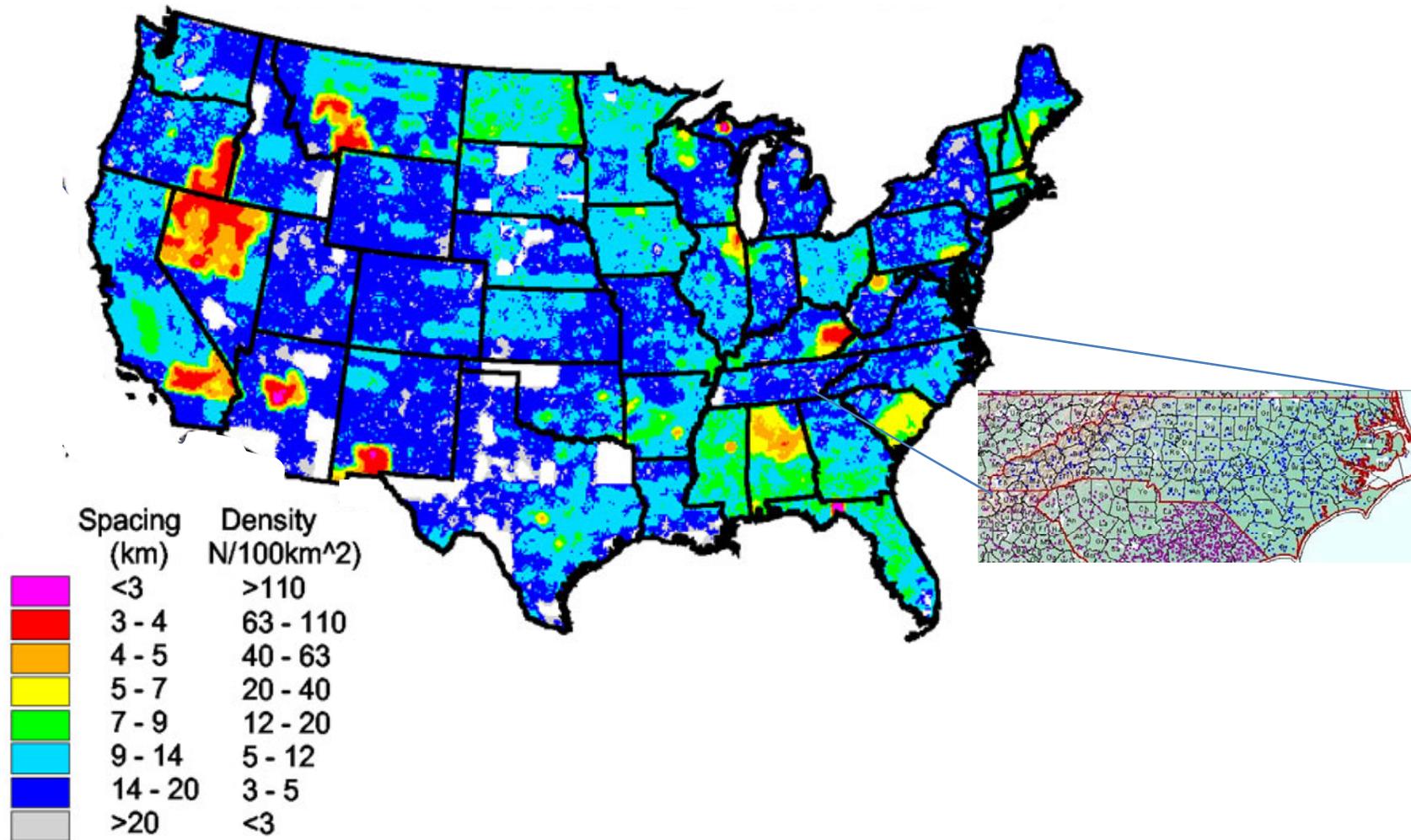
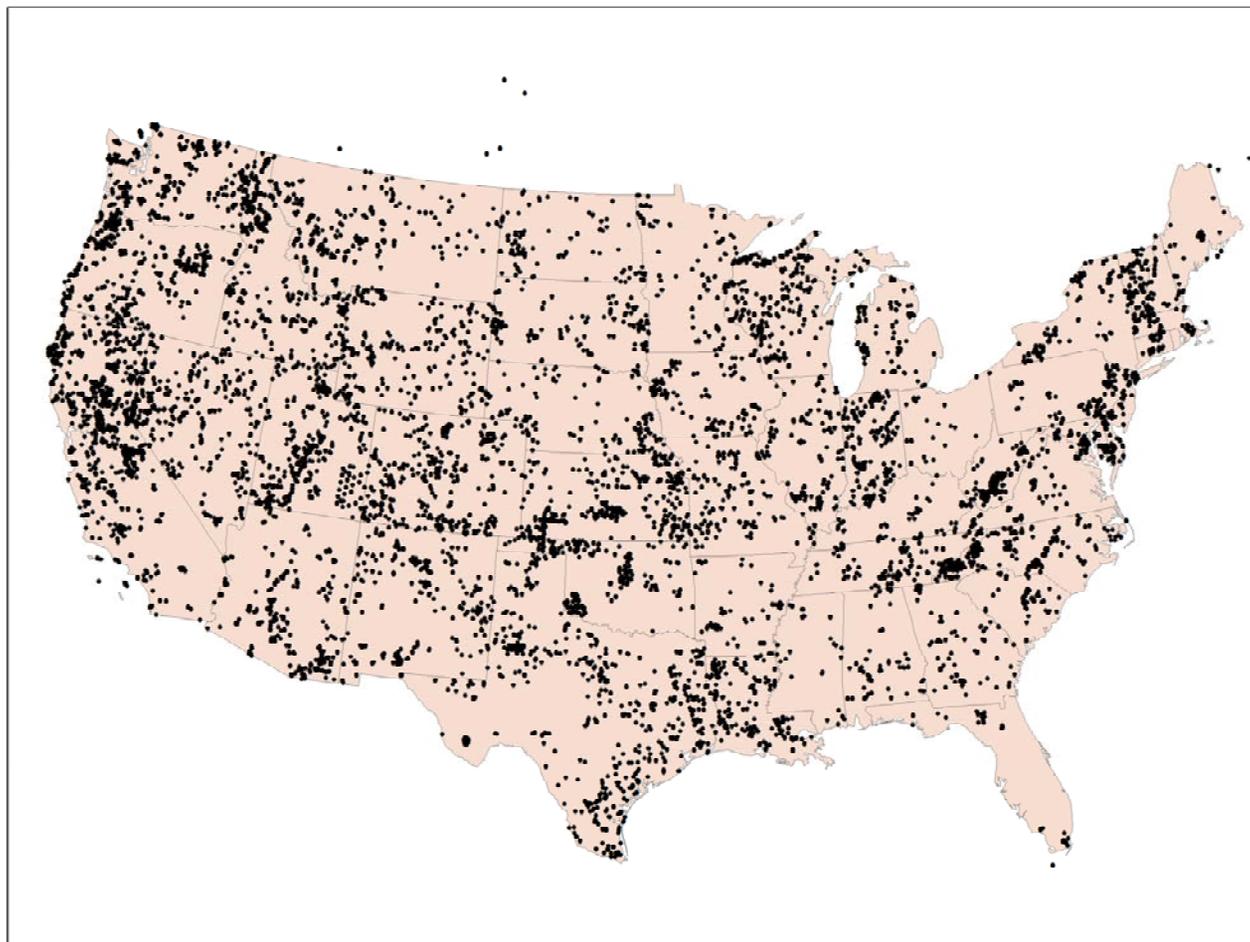


Image source: <http://tin.er.usgs.gov/geochem/doc/status.htm>

Figure 4-5. Sample Density of USGS National Geochemical Survey

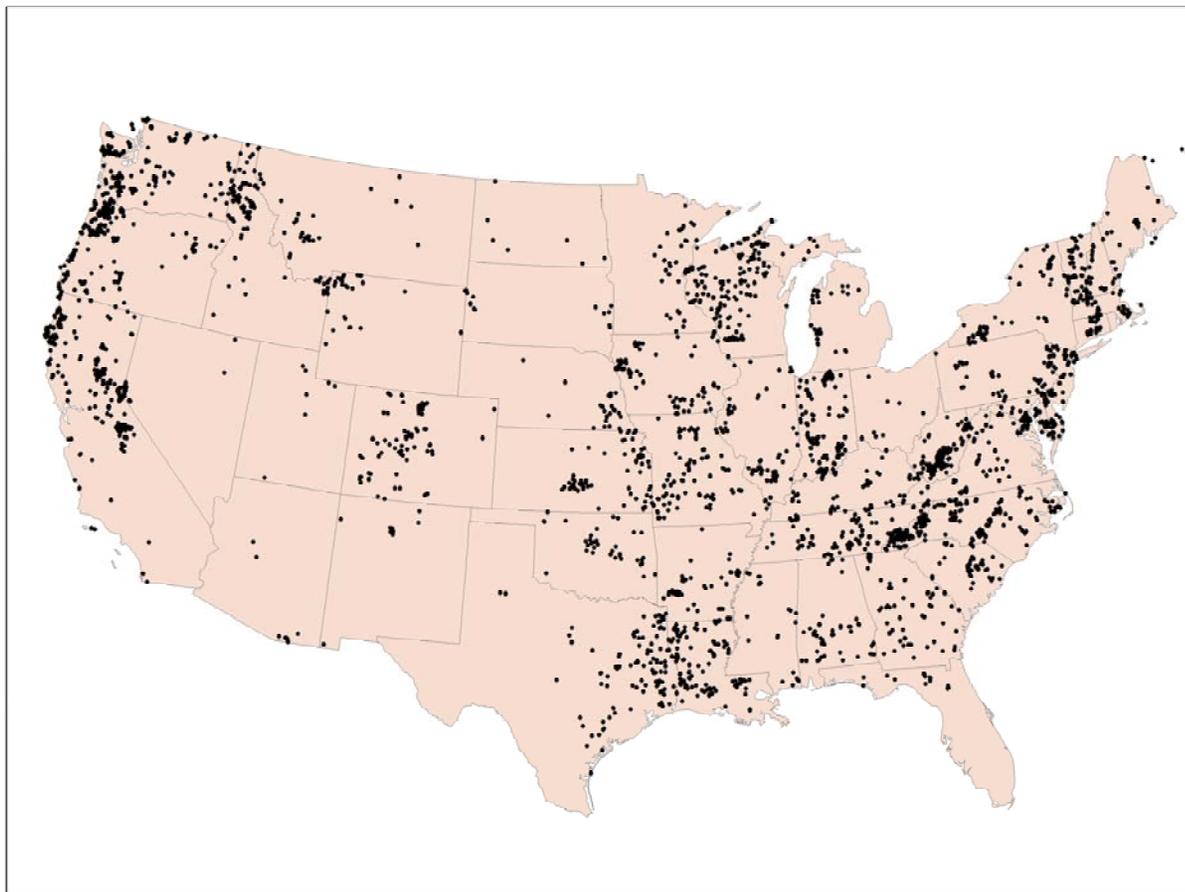
1 *USDA NRCS Soil Pedon Pit Data* were collected by the USDA NRCS for data required
2 for delineation of soil series, map units, and associated attributes. The data are contained in the
3 NRCS USSOILS database that provides data for the SSURGO database. There are currently
4 approximately 30,000 soil pits/pedons in the NRCS database, and soil samples from these pits or
5 pedons have been analyzed for a large variety of physical and chemical properties. These
6 analyses include total chemical analysis, which includes elements required by A2M (e.g., Al, Ca,
7 Fe, K, Mg, Na, P, Si, Ti). In addition, mineralogy has been characterized through two analyses:
8 x-ray diffraction, which identifies clay mineralogy, and optical mineralogy which determines the
9 mineral composition of the fine sand and silt fractions of the soil (C. Smith *personal*
10 *communication*, 2009). However, these three analyses have not been conducted on all soils. Only
11 11,747 of the 30,000 soil pits have been analyzed for at least one of the three parameters (**Figure**
12 **4-6**), and only 4,710 soils have been analyzed for all three (**Figure 4-7**).



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Figure 4-6. NRCS Soil Pedon Sample Pit Locations (30,000 total)

(Image created by RTI using data provided by NRCS on 12/2009)



1

2

Figure 4-7. NRCS Soil Pedon Pit Sample Locations with Geochemical and Mineralogy Data

3

(Image created by RTI using data provided by NRCS on 12/2009)

1 In summary, three main datasets have been identified that could provide the necessary
2 total analyses and mineralogy data for each “mineralogy polygon.” These datasets would be
3 combined into a single database and overlaid on top of the “mineralogy polygon” datalayer to
4 determine the degree to which each polygon is covered by mineralogy and total analysis data. At
5 the scale of a nationwide analysis, the data from each of these datasets is considered comparable
6 given the sampling and analysis protocols that have been used (D. Smith *personal*
7 *communication*, 2009). Although the combined database would be large and offer over 75,000
8 data points, it is not likely that data would be available for all “mineralogy polygons.” In such
9 cases, it would be necessary to determine the mineralogy through alternate methods. Potentially,
10 interpolation between data points could be conducted using numerical probabilistic methods. In
11 addition, it may be possible to determine probable mineralogy based on underlying bedrock or
12 surficial geology (described further in next session). Methods involving professional judgment
13 could also be used to interpret patterns and assign reasonable and appropriate values to express
14 the apparent condition. If such an approach were taken, it would be necessary to work with soils
15 experts who are familiar with the SSURGO database (e.g., NRCS Regional Staff) to make such
16 judgments.

17 *Comparison of mineral polygons with underlying bedrock and surficial geology* - In
18 many locations in the United States, soils have developed from the underlying bedrock or
19 surficial materials. Therefore, it may be possible to validate, support or identify the mineralogies
20 of each of the “mineralogy polygons” through a comparison with the physiographic regions of
21 the United States and the underlying bedrock and surficial geology. The physiographic provinces
22 are based on geology and topography. Therefore, these provinces relate geology and geological
23 history with expected soil characteristics, and the locations of “mineralogy polygons” should
24 broadly follow the patterns within these province boundaries. Similarly, the “mineralogy
25 polygons” could be compared against the underlying geologies to determine the accuracy of the
26 soil taxonomy groupings that were used to delineate the polygons. In addition, overlays of the
27 “mineralogy polygon” datalayer and bedrock or surficial geology could support the estimation
28 of probable mineralogies and percent compositions for “mineralogy polygons” that are missing
29 soil mineralogy and or total analysis data.

30 The USGS 1:100,000 scale bedrock geology GIS cover would be first used for the
31 comparison between the “mineralogy polygons” and bedrock geology (Table 6.0). Most rock

1 types are typically characterized by less than 4 mineral types. Correlating the “mineralogy
2 polygons” with the bedrock type can be used to obtain a gross approximation of mineral phases
3 that would be expected in the residual parent materials and the corresponding soils. This would
4 be a particularly useful protocol to apply to areas where the soils have formed in place from the
5 weathering of the bedrock. For example, this approach could be used in unglaciated regions
6 where Entisols or residuum predominant.

7 The 1:7,500,000 scale USGS surficial geology layer could be used as the source for
8 comparison between “mineralogy polygon” and surficial geology (refer to Table 6.0). The
9 surficial geology layer would identify the type of regolith on which the soil has developed.
10 Regolith is defined here as any unconsolidated materials on top of bedrock, and consists of
11 residuum which has formed in place and transported materials that have been deposited by
12 gravity, wind, water or ice. Therefore, this layer will indicate the type of parent material that
13 supported the development of the soil and will provide an indication of the potential mineral
14 composition of the soil. Specific correlation of mineral types can be more difficult for
15 transported deposits. However, an association is still possible as correlated with general up-grade
16 areas that relate the likely origin, or areas of parent material, for the transported deposit. Even
17 though more generalized approaches to determining the mineralogy are suggested by the
18 available data, modeling the geologic source of parent materials by applying techniques similar
19 to soil-landscape modeling or environmental correlation modeling could be conducted
20 (McKenzie and Ryan, 1999).

21 Test modeled mineralogy against actual mineralogy measurements - To validate and test
22 the accuracy of the % mineral values assigned to the “mineralogy polygons”, comparisons
23 should be made between the “mineralogy polygon” data layer and areas with detailed mineralogy
24 soil analyses. Such sites may include the LTER sites outlined in **Table 4-7** or those detailed
25 within the scientific and geological literature. In addition, there may be locations where detailed
26 mineralogy assessments have been conducted by mining companies or research groups that could
27 be used to test the “mineralogy polygon” data layer. Comparisons would be particularly
28 important for mineralogy polygons with % mineralogy determined by the A2M model.

Table 4-7. Long-Term Ecological Research (LTER) sites that could potentially be suitable as “field test” sites to validate BC_w estimates generated with the regional application of the PROFILE model (version 5.0).

LTER STUDY	LOCATION	ADDITIONAL INFORMATION
H.J. Andrews Experimental Forest	Cascade Mountains, Oregon	http://andrewsforest.oregonstate.edu/
Coweeta LTER	Southern Appalachian mountains, North Carolina	http://www.lternet.edu/sites/cwt/
Harvard Forest	Massachusetts	http://www.lternet.edu/sites/hfr/
Hubbard Brook Experimental Forest	White Mountain National Forest, New Hampshire	http://www.lternet.edu/sites/hbr/
Kellogg Biological Station	Southwest Michigan	http://www.lternet.edu/sites/kbs/
Konza Prairie LTER	Northeastern Kansas	http://www.lternet.edu/sites/knz/
Niwot Ridge	Colorado	http://www.lternet.edu/sites/nwt/
Santa Barbara Coastal LTER	California	http://www.lternet.edu/sites/sbc/
Sevilleta LTER	New Mexico	http://www.lternet.edu/sites/sev/

1

2

PROFILE Input Parameters Assigned Default Values

3

4 Development of national datasets or default values for the % base cation and nitrogen
 5 uptake (by layer), litterfall, soil water content, logK_{gibbsite}, and DOC input parameters would
 6 most likely require the use of data from the literature and research conducted in the United
 7 States. The % base cation and nitrogen uptake by soil layer variables are a function of the
 8 distribution of fine roots, and rooting distributions are typically entered as one of four classes
 9 into PROFILE (H. Sverdrup *personal communication*, 2009b). These root distribution classes are
 10 based on data from an extensive literature search on the rooting habitats of common tree species
 11 in Europe (Sverdrup and Stjernquist, 2002). A similar literature search could be conducted for
 12 the main species within the 21 forest types in the United States, and the four root distribution
 13 classes could be adjusted accordingly.

13

14 The litterfall parameter within PROFILE characterizes the amounts of N, Ca²⁺, Mg²⁺ and
 15 K⁺ returned to the soil with the senescence of leaves, branches and stems. It is calculated as a
 16 function of the site-specific growth rates of individual tree species and the nutrient content of the
 17 different litter components. Since PROFILE is a steady-state model, the growth rates are
 18 averaged over the rotation of the stand. Litterfall values have been determined for European tree
 19 species (Sverdrup et al, 1990; Sverdrup and Stjernquist, 2002), and the same procedure could be
 used for estimating values for the main species in the 21 forest types in the United States. The

1 Tree Chemistry Database (Pardo et al., 2004) could be serve as the source of litter nutrient
2 content and the USFS FIA database could potentially supply species-specific growth rates.

3 Soil water content is highly variable. However, since PROFILE is a steady-state model, it
4 is necessary to use a single value representative of the water content throughout the year. In
5 Sweden, a default value of $0.2 \text{ m}^2/\text{m}^3$ is often used (Halveteg et al., 2004), and it would be
6 necessary to establish a similar default value or set of default values for the United States. Such
7 values could be obtained from the literature. In addition, it may be possible to estimate a set of
8 soil water content estimates based on a simple water balance model that includes the influences
9 of precipitation, run-off, soil texture and/or soil drainage classes (H. Sverdrup *personal*
10 *communication*, 2009b). Data outlined in Table 4 and soil texture and the six drainage classes
11 (Well Drained; Excessive; Moderately Well; Poorly; Somewhat Excessively; Somewhat Poorly)
12 included within the SSURGO soils database could potentially be used in this simple water
13 balance model.

14 Soil dissolved organic carbon (DOC) and the logKgibbsite coefficient would also require
15 the use of values from the literature. Currently, with the application of PROFILE within Europe,
16 DOC is entered as 20 mg/L in the organic layers but drops rapidly with depth in the mineral soil
17 horizons (Alveteg et al., 2004). These values are based on a compilation of data from European
18 field sites (H. Sverdrup *personal communication*, 2009b) and are a function of the organic matter
19 content of the soil (Sverdrup et al, 1990). Similar values and relationships would need to be
20 established for forest systems in the United States based on available data and studies outlined in
21 the literature. LogKgibbsite is a coefficient that describes the concentration of Al in the soil
22 solution. It depends on the soil solution pH and differs by soil layer. Two sets of values have
23 been developed for the application of PROFILE within Europe, with one set being used for clay
24 soils and the other for non-clay soils (Sverdrup and Stjernquist, 2002). These values and
25 grouping by soil clay content were based on data from the literature and the consistent trends in
26 the gibbsite coefficients within and between soils (H. Sverdrup *personal communication*, 2009b).
27 For the application of PROFILE within the United States, it would be necessary to review the
28 logKgibbsite values, review the literature and potentially adjust the values as necessary to be
29 representative of conditions found in the United States.

Regionally-based Built-in PROFILE Input Parameters

There are nine variables that are currently built into the calculations of BC_w for the regional application of PROFILE (version 5.0) and do not require input data from the user. The values of these variables were determined by field research in Europe, and are thought to vary minimally between sites or are calculated based on the input data. These variables include: forest canopy, net mineralization, % precipitation entering layer, % precipitation leaving layer, CO_2 pressure, immobilization, nitrification, denitrification, nutrient uptake kinetic variables (C. Akselsson *personal communication*, 2009). Prior to applying PROFILE to map BC_w throughout the United States, the values and equations used for each of these variables should be examined.

It may be necessary to modify the model equations and/or replace the current values with those from the literature to ensure that the values within PROFILE are representative of conditions and processes in the United States (H. Sverdrup *personal communication*, 2009). Forest canopy, within PROFILE, accounts for the Ca^{2+} , Mg^{2+} , K^+ and N (as NH_4^+) that is absorbed from or leached into the precipitation that is in contact with the canopy. Potassium, Ca^{2+} , Mg^{2+} are typically leached from the foliage and NH_4^+ is absorbed. The default values within PROFILE are currently based on the results of field studies in Europe and are divided by forest type (deciduous versus non-deciduous). Net mineralization within the model is a function of soil organic matter content. Currently, net mineralization is set to “0” within PROFILE assuming that the forests are managed sustainably and net mineralization is at an equilibrium; Ca^{2+} , Mg^{2+} , K^+ and NH_4^+ released through mineralization of organic matter is taken up by the vegetation, returned as litter and remineralized. Therefore, there is no net loss or gain of nutrients through mineralization. However, the net mineralization default value of “0” can be changed if forest management is not sustainable and involves short rotations and/or practices such as whole tree harvesting which remove the foliage and a large pool of “mineralized” nutrients from the site.

The % of precipitation entering and leaving the soil layers variables within PROFILE are determined based on the fine root distribution in the soil profile. Carbon dioxide pressure in the soil is estimated from a small dataset of measurements conducted in different regions of the world. The values that are used within PROFILE are a function of soil particle size. Immobilization of nitrogen within PROFILE is currently set to range between 0.5 – 1.0 kg N/ha/yr. This range of values was determined by the amount of the amount of nitrogen that has

1 accumulated in Northern European soils since the last glaciations. Denitrification and
2 nitrification are currently determined by mathematical equations that include the influences of
3 temperature, available soil nitrogen, soil moisture and soil pH. Nutrient uptake kinetics within
4 PROFILE consists of coupled versus uncoupled uptake of nitrogen and base cations. Within
5 PROFILE, uptake is set to “coupled” as a default because the uptake of Ca, Mg and Al and K
6 and NH₄⁺ are coupled (Sverdrup et al., 1990). Uptake kinetics within the model are also
7 described as unspecified or vanselew depending on the uptake dynamics of base cations and Al
8 absorbed to the root surface. Currently, within PROFILE, deciduous species and domestic crops
9 are defaulted to vanselew kinetics and grasses, and conifers use unspecified kinetics (H.
10 Sverdrup *personal communication*, 2009). Unspecified kinetics indicates that the ion exchange
11 matrix on the root surface is indifferent to the valence of the absorbing ions (Sverdrup and
12 Warfvinge, 1993).

13 **Step 2. Determination of polygon layer to spatially define the BC_w rates and**
14 **development of continuous coverage map of calculated BC_w values.**

15 Following the establishment of continuous coverage databases and national datasets and
16 default values for the application of PROFILE (version 5.0) within the United States, it would be
17 necessary to construct a spatially-explicit continuous datalayer for mapping BC_w throughout the
18 48 states. The resolution of the datalayer should be small scale and provide the highest level of
19 detail permitted by the data. In addition, the location of individual BC_w polygons should be tied
20 to a variable or set of variables which strongly influence BC_w. Since soil attributes including
21 mineralogy, bulk density, volumetric water content and exposed surface area of minerals
22 (discussed further in Section 4.3.6) are the largest sources of variability in the BC_w calculations,
23 it may be most appropriate to map BC_w according to mineralogy, soil series or a higher level of
24 soil taxonomy. Input data and default values for the 26 PROFILE variables would then be
25 mapped to the delineated BC_w polygon layer. When multiple or sections of multiple polygons of
26 the same datalayer are present in a BC_w polygon, a weighted average value for the data would be
27 calculated. All the data for each BC_w polygon would then be formatted according to the
28 requirements of PROFILE and the PROFILE regional model would be run to produce maps of
29 BC_w.

4.3.5 Potential limitations of proposed methodology

Although PROFILE is arguably the most suitable model currently available for estimating and mapping BC_w for terrestrial critical acid load determinations in the United States, the model does have some limitations that should be acknowledged and potentially remedied prior to application. The model and algorithms contained therein were developed in Sweden using Swedish soils as the basis for the soil chemical and physical relationships (Hodson et al., 1997). The soils in Sweden are comparatively young, having formed since the last glaciations, approximately 10,000 years ago (Sverdrup and Warfvinge, 1988). Therefore, there is some concern that PROFILE may not accurately model base cation release in older soils (C. Smith *personal communication*, 2009). As discussed by Hodson and Langan (1999), PROFILE does not take into account the decreasing reactivity of minerals with duration of dissolution, and assumes that the reaction rates are constant regardless of time and duration of dissolution. In addition, the model assumes a constant versus decreasing reactive surface area as total surface area increases. According to the authors, these shortcomings were two of the main reasons that PROFILE did not show a decreased weathering rate with soil age relative to other models. However, at the same time PROFILE has been used to estimate BC_w in multiple locations with older, more weathered soils, such as Maryland, China, Thailand, Argentina and Greece, and has performed with apparent success (Duan et al., 2002; Sverdrup et al., 1992; H. Sverdrup).

PROFILE currently accounts for the weathering of 14 different minerals, with the potential to include 13 additional minerals, if necessary. Potentially, there may be minerals within the United States that are not represented within the 27 that are currently included within PROFILE. However, a total of 48 minerals have been investigated by the researchers that developed the model (H. Sverdrup *personal communication*, 2009b). Therefore, it may be possible to add additional minerals to PROFILE to ensure that it is able to address BC_w in all regions of the United States.

Additional limitations and concerns regarding the application of PROFILE to estimate BC_w rates have been identified in a thorough review by Hodson and colleagues (1997). Some of the main issues brought up by the authors include: the need for a more consistent set of constants for the weathering rate equations; inaccuracies in the mineral compositions; errors in the calculation to determine surface area; and confounding influences of soil particles greater than 2mm in size on soil bulk density. Hodson and colleagues (1997) point out the need to reexamine

1 the reaction rate coefficients associated with hornblende, tourmaline, staurolite, kaolinite, garnet,
2 augite, biotite and chlorite, arguing that coefficients assigned to these minerals are not correct.
3 Similarly, the authors claim that the compositions of the minerals used within PROFILE may be
4 incorrect in some applications and may need to be modified by the user to more accurately
5 reflect the soil being modeled. Hodson and colleagues (1997) also demonstrate the potential to
6 over and underestimate BET surface area using the soil texture equation provided within
7 PROFILE. They claim that the equation underestimated the surface area of a British soil by 65%.
8 In part, the authors attributed these inaccuracies to the development of the soil texture – surface
9 area relationship from only 92 mineral soil samples from Sweden. Lastly, Hodson and colleagues
10 (1997) point out the need to recognize soil particles greater than 2mm in size in the soil bulk
11 density estimates, as such particles can impact the density by as much as 50% for stony soils.
12 The concerns raised by Hodson and colleagues (1997) appear to be valid and should be
13 considered by users of the PROFILE model. However, the authors of the review critiqued an
14 early version of PROFILE (version 3.01) and the most recent version of PROFILE may have
15 already addressed some of these limitations. For example, the abundance of particle sizes greater
16 than 2 mm is included in the current regional model of PROFILE (version 5.0). It should also be
17 noted that Hodson and colleagues (1997) did acknowledge that despite the apparent weaknesses
18 of PROFILE, BC_w rates calculated with the model are comparable to those calculated using other
19 methods.

20 In addition to the potential limitations of PROFILE as a model, application of PROFILE
21 to map BC_w rates throughout the United States may also present some drawbacks or restrictions.
22 There may be areas of the United States where input data required by the model is not available.
23 In such situations, it would be necessary to extrapolate data from areas with similar soil, biotic or
24 abiotic conditions. Similarly, if data for specific variables are limited in many areas, it may be
25 necessary to adopt best available default values over large areas, until more data and better
26 coverage across the states is available.

27 **4.3.6 “Field Tests” of model and uncertainty analyses**

28 As outlined in the preceding sections, the proposed methodology to map BC_w throughout
29 the United States would involve the use of the regional application of PROFILE (version 5.0),
30 continuous coverage data, and in some cases, input and default values from the literature.
31 Therefore, at least a portion of the input data would not be site specific and would be entered as

1 class values or generated by sub-models or mathematical relationships. Soil water content and
2 soil mineralogy are examples of such data. It is largely unknown to what degree, if any, this
3 proposed methodology designed for mapping large areas would influence and potentially distort
4 the estimates of BC_w . Therefore, to validate the weathering estimates from the proposed mapping
5 methodology, it would be worthwhile to conduct “field tests” of the model output in different
6 regions of the United States. Such “field tests” could consist of comparing the regional estimates
7 of BC_w with those determined with the single site version of PROFILE and site-specific data.
8 (No actual on-the-ground field research required.) In addition, where available, the PROFILE-
9 generated BC_w rate estimates could be compared with weathering rates determined by other
10 methods. Both approaches would provide an indication of the quality and accuracy of estimates
11 from the mapping methodology and regional application of PROFILE. Sites within the Long-
12 Term Ecological Research (LTER) network would be good locations for the “field tests” due to
13 the large amounts of data available at many of these sites. In addition, at some sites, such as
14 Hubbard Brook, base cation weathering has been determined using methods other than the
15 PROFILE model. A list of LTER sites within the conterminous 48 states that could potentially
16 serve as “field test” sites is presented in Table 6.0. A sub-set of these sites representing different
17 regions and conditions within the United States should be selected to validate the BC_w estimates.

18 In addition to the validating the proposed methodology with “field test” site comparisons,
19 uncertainty analyses should also be conducted on the BC_w estimates that are generated with the
20 methodology. There are a total of 26 parameters within the regional application of PROFILE
21 (version 5.0) that require data entry by the user or review prior to applying the model, and each
22 of these parameters could be expected to have a level of uncertainty. Therefore, cumulatively,
23 the uncertainties associated with the BC_w estimates could be quite large. In addition, because
24 BC_w is one of the most influential terms in the calculation of terrestrial critical acid loads, and
25 critical loads can be used as a measure of the impact of acidifying nitrogen and sulfur deposition
26 on terrestrial ecosystems, it is important to gain a good understanding of the uncertainty
27 associated with the BC_w estimates. Critical acid loads could potentially be used by decision
28 makers to set policy and NO_x and SO_x emission standards within the United States. Furthermore,
29 uncertainty analyses can reveal which parameters are the most influential in the BC_w estimates,
30 thereby guiding which parameters should receive the greatest attention in the development of the
31 datasets and national coverages for the PROFILE model.

1 Earlier versions of the PROFILE model (version 3.01) have already been reviewed and
2 analyzed by researchers based on the application of the model to sites in Norway, Sweden,
3 Scotland and Wales (Jönsson et al., 1995; Hodson et al., 1996; Zak et al., 1996). Monte Carlo
4 analyses testing the uncertainty associated with user defined input variables indicated that
5 varying input parameter errors individually and simultaneously (within the range of values
6 reported in the literature) resulted in a variation in model output of +/- 40% (Jönsson et al.,
7 1995). The authors also determined that bulk density, volumetric water content and exposed
8 surface area of minerals were the largest source of variation in the output values. The least
9 sensitive parameters were soil stratification, precipitation and percolation. Similar analyses were
10 conducted by Hodson and colleagues (1996) who determined the influence of single input
11 parameters, one at a time. Based on their analyses, BC_w estimates could vary by over 100% using
12 the ranges in parameters values measured in field studies. The authors also found that some
13 minerals, such as K-feldspar, were particularly sensitive to variation in input values, and soil
14 temperature, moisture content and exposed mineral surface area caused the largest amounts of
15 variation in the BC_w estimates. These results based on an earlier version of PROFILE suggest
16 that ranges in input values can cause the BC_w estimates from the model to vary by moderate to
17 large amounts. However, the level of uncertainty associated with outputs from the most current,
18 regional application of PROFILE (version 5.0) is still unknown. In addition, there has yet to be
19 an assessment of the performance of the model in the United States and a determination of how
20 ranges in data from different regions in the country would impact the variation in model output.
21 Therefore, uncertainty analyses should be conducted as a component of the proposed
22 methodology, to provide bounds to the range of output values associated with the BC_w estimates
23 for terrestrial critical acid load calculations in the United States.

24 **5. CONCLUSIONS AND RECOMMENDATIONS**

25 The goal of this task was to inform EPA about the tools and data available to develop
26 maximum deposition loads across the United States for aquatic and terrestrial acidification. In
27 particular, this effort focused on methodologies to estimate Bc_w , a parameter that plays a crucial
28 role in predicting an ecosystem's ability to neutralize acid deposition. Based on the findings of
29 this literature review, discussions with experts, evaluation of tools, and assessment of data

1 availability, two process-based models are recommended: MAGIC for aquatic acidification (with
2 extrapolation through regional regression modeling) and PROFILE for terrestrial acidification.

3 It is clear that addressing limitations on soil data availability in the United States will
4 require considerable effort to populate both models; however, resources invested to satisfy this
5 data need can be leveraged to the benefit of both terrestrial and aquatic modeling goals. It is also
6 clear that the MAGIC and PROFILE models' application in the United States has focused on
7 select regions; however, model developers believe these models can be applied successfully in
8 other regions, particularly regions with more sensitive ecosystems. Finally, neither MAGIC nor
9 PROFILE models are readily accessible for public use. Therefore, it will not be practical to
10 assume states and regions could operate the models. Rather, it would be more manageable for the
11 models to be run at the Agency level with states and regional offices providing the needed input
12 data.

13 It is recommended that following EPA review of this report, candidate regions of the
14 United States be identified for modeling and levels of effort be estimated to prepare the MAGIC
15 and PROFILE models for operation and to collect and/or predict their input data. As part of the
16 effort, it is recommended that RTI collaborate with recognized experts in the development and
17 application of these two models.

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APPENDIX 1

Potentially Applicable National-Scale Geochemical Data

1
2
3 Currently, there are potentially three consistent national-scale data sets that are most
4 appropriate for use in this project: the *Shacklette data*, the more recent *National Geochemical*
5 *Survey* data, and the NRCS pedon soil pit (i.e., LIMS database).

6 **Chemical Analyses of Soils and other Surficial Materials of the Conterminous United** 7 **States (Shacklette Data) & the Geochemical Landscapes Project**

8 These data provide an ultra-low-density geochemical baseline for soils and other surficial
9 materials in the conterminous United States. It is the most widely cited reference for
10 geochemical background data and the data are most appropriately used to provide information on
11 background concentrations of elements in soil for areas represented by small map scales.

12 The data set contains geochemical data from soils and other regolith collected and
13 analyzed by Hans Shacklette and colleagues beginning in 1958 and continuing until about 1976.
14 Originally compiled as a paper record, the data was later included as part of the original USGS
15 PLUTO database. Approximately 1,323 samples were collected through 1976. The 1,323 sample
16 locations that comprise the Shacklette data represent a sampling density of approximately 1
17 sample per 6,000 square kilometers (metadata); equivalent to the collection of samples on a 75-
18 km grid across the country.

19 The sampling protocol called for removal of loose organic debris from the surface and
20 then collection of soil from a depth of 0-20 cm (Smith et al., 2005). Where possible, sample
21 locations were selected where surficial materials had been altered very little from their natural
22 condition as evidenced by the presence of native plants. The sample material at most sites could
23 be termed "soil" because it was a mixture of disintegrated rock and organic matter. Some of the
24 sampled deposits, however, were not soils as defined above, but were other regolith types. These
25 included desert sands, sand dunes, some loess deposits, and beach and alluvial deposits that
26 contained little or no visible organic material.

27 This national-level geochemical data set of 1,323 samples has been collected and
28 analyzed according to standardized protocols. This is considered one of the principal strengths of
29 the data set overall. The samples were chemically analyzed by various but compatible techniques
30 in the U.S. Geological Survey laboratories in Denver, CO. Geochemical point-symbol maps were
31 plotted for 40 elemental results and published as USGS. Professional Paper 1270 (Shacklette and
32 Boerngen, 1984). The original elements analyzed included: Ag, Al, Ba, Be, B, Ca, Ce, Cr, Co,
33 Cu, Ga, Ge, Hg, Fe, La, Li, Pb, Mg, Mn, Mo, Na, Nd, Ni, Nb, P, K, Rb, S, Sc, Se, Sr, Th, Ti, U,
34 V, Yb, Y, Zn, Zr, and total carbon. A newer set of national-level interpolated maps displaying
35 the geochemical distribution for 22 elements using the *Shacklette data* has since been published
36 (Gustavsson, et al, 2001). Using weighted-median and Bootstrap procedures for interpolation and

1 smoothing, full-color maps were produced for seven major elements (Al, Ca, Fe, K, Mg, Na, and
2 Ti) and 15 trace elements (As, Ba, Cr, Cu, Hg, Li, Mn, Ni, Pb, Se, Sr, V, Y, Zn, and Zr).

3 The major drawback with the data set is its extremely low numbers of samples for the
4 entire conterminous United States. However, more recent high-resolution studies (e.g., Smith et
5 al., 2005) have illustrated that the regional patterns established by the *Shacklette data* are
6 generally maintained except where areas have been affected by anthropogenic factors (Smith,
7 2006).

8 Efforts are also on-going to build upon the Shacklette data by increasing the density of
9 the sample locations and producing a high resolution geochemical data set for North America.
10 Also referred to as the *Geochemical Landscapes Project*, this is a collaborative effort by the
11 USGS, USDA Natural Resource Conservation Service, other federal agencies, and academia to
12 build a national-scale soil geochemical survey that will eventually increase the sample density of
13 the Shacklette data set. The Geochemical Landscapes project began in October 2002 in
14 collaboration with partners in Canada (Geological Survey of Canada; Agriculture and Agri-Food
15 Canada) and Mexico (Consejo de Recursos Minerales/Servicio Geológico de México; Instituto
16 Nacional de Estadística Geografía e Informática) that has as its long-term goal a soil
17 geochemical survey of North America (Smith et al., 2005). A 3-year pilot project was completed
18 in 2004. During the pilot project soil samples were collected for major- and trace-elements from
19 265 soil samples collected from two continental-scale transects in North America (Smith et al.,
20 2005). The project has just completed a third year of continental-sampling and completed sample
21 collection for approximately 60% of the conterminous United States (D. Smith *personal*
22 *communication*, 2009). The state areas that have been completed to date are: ME, NH, VT, CT,
23 RI, MA, NY, MO, AR, MS, LA, NV, UT, CO, WY, KS, NJ, MD, WV, DE, NE, FL, SC, GA,
24 AL, OK, NM, MT, ID, MN, and SD. The USGS anticipates that sampling may be completed for
25 the conterminous US in 2010; or 2011 at the latest. However, funding doesn't allow for analyses
26 to be completed for a number of samples and several hundred grams of each sample is being
27 archived for on-going and future analysis.

28 **National Geochemical Survey (NGS)**

29 Efforts are on-going by the USGS to produce a new stream-sediment-based geochemical
30 survey for the United States at a nominal spacing of 17 by 17 kilometers (i.e., minimum sample
31 density of 1 sample per 289 km² in all land areas of the country). Project mapping shows that the
32 work is either complete or nearly completed. Unlike other national geochemical data collection
33 efforts, the analytical routines and standards will be consistent throughout the survey. Analytical
34 methods include a 40-element ICP package plus single-element determinations of As, Se, and Hg
35 by atomic absorption for every sample.

36 The project has sought to capitalize on existing datasets and also achieved samples. For
37 this reason the NGS is based primarily on analyses of stream sediments to build on the massive

1 achieves of data and samples from DOE's National Uranium Evaluation (NURE) program.
2 Much of the survey has entailed reanalysis of approximately 35,000 archival samples from the
3 NURE program. Where NURE samples do not exist, USGS has been working with cooperators
4 to obtain new samples. The project website reports a total of about 50,000 stream-sediment
5 samples that have been analyzed for 42 elements, including arsenic, selenium, and mercury. Last
6 reported during 2004, only about 10,000 more samples needed to be collected and analyzed to
7 complete the national survey. Samples are generally categorized as follows:

- 8 ➤ *Inherited Data*: Much of the RASS and PLUTO data were inherited into the NGS;
- 9 ➤ *Independent Reanalyses of NURE samples*: These sample were reanalyzed by USGS
10 projects other than the NGS. Prior to the NGS, numerous USGS projects reanalyzed
11 samples from the NURE archives. Other USGS projects have continued to reanalyze
12 NURE samples in parallel with the NGS. In the majority of these cases, most or all of the
13 NURE samples in an area were reanalyzed.
- 14 ➤ *NURE-Systematic*. Systematic reanalyses of NURE samples done by the NGS. An
15 archive of stream sediment and soil samples collected by the NURE program is stored at
16 the USGS in Denver, Colo. Rules were established to select a subset of samples for
17 reanalysis that maintains the NGS coverage.
- 18 ➤ *NURE-Targeted*. Targeted reanalyses of NURE samples done by the NGS for various
19 reasons.
- 20 ➤ *USGS-Resampling*. Reanalyses of USGS archived project samples done by the NGS. The
21 archive includes most of the samples for which there are analytical data in the National
22 Geochemical Database, including those collected by USGS programs.
- 23 ➤ *Collaborative Sampling with State Programs*. Collaborative sampling programs by the
24 USGS and states.

25 Digital data files are presented in 6 categories. In total there are 43 individual data files
26 for the United States. Some of the data has also been processed into vector data to produce maps
27 showing the elemental concentration of As, Se, Hg, Pb, Zn, Cu, Al, Na, Mg, P, Ca, Ti, Mn, and
28 Fe at the county level.

29 **USDA NRCS Soil Pedon Pit Data**

30 The USDA NRCS measures soil geochemical characteristics along with performing
31 quantitative and bulk mineralogy tests and other physiochemical measurements for soil series
32 delineated across the United States. This data set and associated detail was discovered through
33 communication with NRCS staff (C. Smith *personal communication*, 2009; T. Reinsch *personal*
34 *communication*, 2009). Most of the geochemical and mineralogy data is associated with
35 individual soil pedons. The NRCS defines a pedon as the smallest unit that can be called a soil. It
36 is a three-dimensional sample that extends from the soil surface to the deepest roots or genetic
37 soil horizons. The area covered by a pedon varies from 10 - 100 square feet, depending on
38 changes in soil properties. Pits are dug to expose the pedons and the NRCS generally refers to

1 the data associated with the pedons as soil pit data. There are currently approximately 30,000 soil
2 pits/pedons in the NRCS database.

3 Groups of pedons with very similar characteristics that are closely associated in the
4 landscape are called polypedons. Polypedons that have a common set of characteristics that fall
5 within a particular range are delineated as a basic soil unit referred to as a soil series which have
6 been identified as the basic unit of the proposed data framework, as previously discussed. The
7 same soil series delineations can occur in different and distant areas (i.e., across county areas,
8 states, or regions). A variety of data are used to define a soil (e.g., geomorphic position in the
9 landscape, relationship to the water-table, supported flora, geology, number and type of horizons,
10 sediment texture, sediment color variations, etc.), and therefore geochemical and mineralogy
11 data has not been collected from every soil pedon associated with an individual series of the
12 same name since associations can be made based on a number of these other related
13 characteristics. However, geochemical and quantitative mineralogy data has been measured for a
14 significant number of pedons and soil series locations across the country.

15 Since soils of the same series name possess enough similarities to be classified as similar
16 soils it is thought that the geochemistry data can also be extrapolated to pedons of like soil series
17 (C. Smith *personal communication*, 2009). Assigning mineral phases to the soil series that do not
18 have either geochemical or mineralogy data associated with their pedons will require
19 professional judgment by researchers familiar with the soil pit data and soil taxonomy to make
20 geochemical data extrapolations with a degree of confidence. In these cases the characteristics of
21 surrounding soils would be used to extrapolate geochemistry or mineralogy, or another data set
22 could be used to aid in the characterization. GIS tools would be used to help automate these
23 determinations where necessary. NRCS staff would aid RTI in determining rules and developing
24 database relationship tables that could be used in automating any extrapolation of this data. The
25 NRCS would also aid RTI in evaluating the reasonableness of the results.

26 Since soil series are delineated across the conterminous United States the pit data could
27 potentially provide a complete geochemical and mineralogy data layer for determining
28 mineralogy. Since mineralogy is already associated with the geochemical data a more accurate
29 assignment of mineral modes may be possible using this data set. Laboratory analysis includes
30 the major geochemical elements: Al, Ca, Fe, K, Mg, Mn, Na, P, Si, Sr, Ti, and Zr. In addition, x-
31 ray diffraction is used to indentify clay mineralogy generally for each horizon of a pedon, and
32 optical mineralogy analysis is performed on the dominant sand fractions of the soil from the A-
33 horizon, B-horizon, and C-horizon, or the most dominant horizon. More than 60 fields describing
34 the minerals are listed in the database. The dataset is not uniform in that elemental analyses were
35 routinely done through the 1970's but then these analyses were suspended through the 1980's.
36 Elemental analyses were resumed during the early 1990's. It is estimated that as much as one
37 third of the 30,000 soil pedons have geochemical data. Likewise, optical mineralogy is not
38 performed for all pedons and the NRCS staff estimate that approximately as many as one third of
39 the 30,000 soil pits have optical analysis results. Even though the number of pedons with data are

1 similar for geochemical and optical analysis results the data is not necessarily associated with the
2 same set of pedons or even soil series.

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APPENDIX 2**References for Table 3-2: Applications of the MAGIC Model**

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