

30 September 2008 Preliminary Review Comments from CASAC NO_x & SO_x Secondary NAAQS Review Panel on EPA's Risk and Exposure Assessment for Review of the Secondary National Ambient Air Quality Standards for Oxides of Nitrogen and Oxides of Sulfur: First Draft

Comments received:

Dr. Praveen Amar	2
Dr. Andrzej Bytnerowicz.....	4
Ms. Lauraine Chestnut.....	7
Dr. Ellis Cowling	8
Dr. Charles T. Driscoll.....	15
Dr. Paul J. Hanson	25
Dr. Dale W. Johnson.....	34
Dr. Donna Kenski.....	39
Dr. Naresh Kumar	46
Mr. Richard Poirot	49
Mr. David Shaw	53
Continuing Acidification of Organic Soils across the Northeastern U.S.A.: 1984 – 2001....	57

Dr. Praveen Amar

The specific charge is to respond to Questions #2 and 3 related to air quality analyses. Specifically, the two questions are reproduced here:

Question # 2 : Section 3.2.1 describes an approach for evaluating the spatial and temporal patterns for nitrogen and sulfur deposition and associated ambient concentrations in the case study locations. This draft document includes the analysis for the Adirondacks Case Study. Does the Panel agree with this approach and should it be applied to the other Case- Study Areas?

Question # 3 : Section 3.2.2 describes the relative contributions of ambient emissions of nitrogen and ammonia to nitrogen deposition for the case-study areas. To what extent is the approach taken technically sound, clearly communicated, and appropriately characterized?

Question # 2 Response:

The approach outlined in Section 3.2.1 should prove to be useful in that it does propose to do a complete analysis of spatial and temporal patterns of concentrations and deposition of sulfur and nitrogen compounds (dry oxidized nitrogen, dry reduced nitrogen, wet oxidized nitrogen, wet reduced nitrogen, dry sulfur deposition and wet sulfur deposition). However, the analyses at the present time are based only on CMAQ predictions (text says “CMAQ data”; “CMAQ predictions” is more appropriate) are only for one year (2002), and for just one case-study location (Adirondacks).

1. At a minimum, before one can answer the question “Does the Panel agree with this approach and should it be applied to other case-study areas?” with a reasonable level of confidence, the proposed approach needs to include an independent as well as corroborative (by comparing it to model-predicted results) analysis that is based on measured data for this case-study region (as well as the remaining case-study regions). It appears that modeled CMAQ results are reasonable, but it will increase the confidence in this approach if the measured data from NADP and CASTNet (and other networks in the Adirondacks region and other regions) corroborate the modeled predictions.
2. It is also important that before this approach is applied to other case-study areas, that the placeholders on Page 3-53 and 3-54 be completed. I would recommend that the analysis of inter-annual variation in N and S (for the years 2002-2006) deposition as well as uncertainty analysis (Section 3.2.1.5) be first completed for Adirondacks region before similar analyses are done for the other four case-study regions.
3. Once the measured deposition data analyses are completed, Section 3.2.1 should include a brief evaluation/comparison of CMAQ predictions for the four nitrogen and two sulfur components. As a part of this evaluation, the measured precipitation data and modeled (from MM5?) precipitation data (amounts and spatial patterns) should be compared. This is important since the modeled results in Section 3.2.1 indicate strong correlations between amount of precipitation and wet deposition.

4. A general comment on presentation of results on dry deposition of N and S: This section needs to be more clear and explicit that we only *estimate* dry deposition (whereas we measure wet deposition) and therefore conclusions on total deposition (wet and dry) and on the relative contribution of each pathway have a level of uncertainty that is hard to determine, but needs to be acknowledged (for example, in Section 3.2.1.5 on Uncertainty).

Question # 3 Response:

This question involves the description of relative contributions of ambient emissions of NO_x and ammonia to deposition of nitrogen (total nitrogen deposition (TND), oxidized nitrogen deposition (OND), and reduced nitrogen deposition (RND)) for the eight case-study regions. It asks if the approach used is technically sound, clearly communicated, and appropriately characterized. Here are some comments:

1. The “model of the model” or the RSM (Response-Surface Model) applied to CMAQ needs a more friendly description on how it works. On Page 3-55, the text makes an effort but does not succeed in explaining what (and how) exactly RSM does. It appears that RSM is like an “instrumented CMAQ” model in that it “represents the outputs of the CMAQ model using statistical predictions.” It is not clear to me what exactly these statistical predictions are. It might be useful to compare the “workings” of RSM with, say, Direct Decoupled Method (DDM) or other “process” models (that evaluate the relative contribution of various processes embedded in the model on model predictions). Has the RSM approach been applied by the general scientific and policy/regulatory communities outside the US EPA?
2. To the extent RSM is essentially based on the “brute-force” approach of “zeroing out” NO_x or ammonia emissions (recognizing there are some residual emissions for NO_x that include international sources and lightning, and, for NH₃, they include international, non-anthropogenic and point source emissions), I am not sure this is the right approach to accurately answer Question # 3. Are there more appropriate approaches that do not “unduly stress” the CMAQ model that can better address this question of relative contributions?
3. It is not clear to me how the twelve “emission control factors” on Page 3-56 were actually applied in the model. Were the emissions zeroed out only for the case-study region or for the whole modeling domain?

Dr. Andrzej Bytnerowicz

Question 2 – Current progress on evaluation the effects of aquatic acidification in the Adirondacks and Shenandoah. To what extent is the approach taken technically sound, clearly communicated, and appropriately characterized?

Selection of the Adirondack Mountains and Shenandoah National Park for estimation of ecological effects and risks caused by acidifying deposition of N and S is well justified. The two areas experience high levels of deposition, are characterized by a high density of anthropogenically acidified lakes and streams, and there is a well documented record of chemical and biological changes from many studies with their results published in peer-reviewed literature.

The proposed approach is logically organized and technically sound. The wet deposition data comes from the NADP/NTN networks operational in the Adirondacks since 1978 and in the Shenandoah since 1980. Current conditions were evaluated by a 3 step process that assessed trends in surface water SO_4^{2-} , NO_3^- and ANC concentrations; the percent of watershed bodies that have different degree of acidity; and the percent of water bodies receiving N & S deposition above the harmful levels (exceedance of critical loads). Biological effects of acidity caused by atmospheric N & S deposition are measured at the individual level as fitness and at the community level as species richness and community structure. ANC has been selected as a metric to quantify the current acidic conditions and biological impacts because in many studies it was found to be the best single indicator of the biological response of aquatic communities in the acid-sensitive ecosystems. Relationship between ANC and number of fish species showed that at the ANC values of 50-100 ueq/L, species richness begins to decline. Based on the ANC values and fish populations responses, five classes of biological responses (acute, severe, elevated, moderate and low concerns) have been developed and can be used for evaluation of risk assessment using the critical loads concept.

It will be interesting to see complete results of the planned evaluations.

Specific comments:

Page 32, Figure 5.1-2. why there is such a high difference in the “severe” category between the observed and MAGIC modeled outputs?

Page 33, Figure 5.1-3 – change ANC units to ueq/L. In the same figure – why not to use more conservative value of 100 ueq/L instead of 50 ueq/L as the threshold of protection?

Question 5 – Current progress on evaluating the effects of terrestrial nutrient enrichment for Coastal Sage Scrub and mixed conifer forests of California. To what extent is the approach taken technically sound, clearly communicated, and appropriately characterized?

Selection of coastal sage scrub (CSS) and mixed conifer forest ecosystems is appropriate because: (a) these ecosystems have high geographic coverage and are located in the important

wildland–urban interface in highly populated areas, (b) they encompass a strong gradient of N deposition from the low, background levels up to the highest levels recorded in the US, (c) these ecosystems have been investigated for a long time from a perspective of interactive effects of atmospheric deposition, climate change fire and other stressors, (d) results of these investigations are well documented in the peer-reviewed literature.

If the goal of this chapter was to review the current state of science for these two case studies, than the approach taken was technically sound and findings have been clearly communicated. However, if results of these two case studies were supposed to show how the relationships between the observed chemical and biological changes and N atmospheric deposition (possibly expressed as critical loads) could be linked to the concentration-based NO_x/SO_x standards, then the used approach was not inadequate and should be revised.

The chapter provides a comprehensive review of the existing scientific knowledge for these two case studies. GIS maps show modeled N deposition in portion of California encompassing the two selected ecosystems, CSS threat from fire, and the presence of acidophyte lichens. Three-dimensional maps illustrating loss of CSS in relation to different levels of fire threats or N deposition could greatly help in developing a probabilistic approach to the evaluation of N deposition risks to important California ecosystems.

For development of CL for CSS, in addition to biodiversity changes, or changes in lichen communities, accumulation of biomass (critical level for occurrence of catastrophic fires) could be considered (see Richard Minnich, UC Riverside for further information). For the mixed conifer forests, on the low end of CL estimates changes in lichen communities and on the high end of deposition, nitrate leaching to surface water are good end points. Other, such as possible changes in understory biodiversity changes could also be considered and explored.

Data on N deposition levels was obtained from the NADP and CASTNET networks and modeled N deposition distribution from the CMAQ model runs for 2002, which were based on the 12 km grids. As the authors of this analysis suggest, results from the 4 km grid would greatly improve accuracy of predicted relationships between N deposition and the biological effects. Improvement of the CMAQ model performance is needed to develop more narrow brackets for N deposition at its high end. Ranges 11.53 – 18.32, and especially 18.33 – 70.04 kg N/ha/yr are too coarse.

More data for the main drivers of N dry deposition in southern California and southern Sierra Nevada, HNO₃ and NH₃, will soon be available from the passive sampler monitoring campaigns of 2002-2008 (USFS PSW Research Station, Andrzej Bytnerowicz , unpublished).

Specific comments:

Page 13, 1st paragraph – also high levels of NH₃ and NH₄⁺ are deposited to CSS of southern California.

Page 29, Figure 3.1-1. Scale for N deposition is too coarse – a bracket 6.83-70.04 kg N/ha/yr is not acceptable.

Page 33, 1st paragraph – bark beetle should be added as important stressor in the mixed conifer forest ecosystem.

Page 44 and 45, section 5.2 – for the mixed conifer forest also changes of species composition of the under story vascular plants should be considered.

Page 45, list of questions – in regard to responses of lichens to N deposition, effects of oxidized vs. reduced N should be considered. This may be of interest because there is a potential shift towards less reduced N due to the movement of dairy farms from the Los Angeles Basin to California Central Valley.

Ms. Lauraine Chestnut

Charge question 1: Scope of the review

There seems to be some ambiguity in wording regarding use of the term “sensitive.” It sometimes seems to mean an ecosystem that is vulnerable but not necessarily harmed at current exposures, and other times it seems to mean that harm is occurring at current exposures. To me, the word sensitive fits better for the former than for the latter. For there to be harmful effects it would seem to require both sensitivity and exposure. Thus, the selected case studies are not just sensitive, they are examples of ecosystems currently harmed by N or S deposition exposure.

Use of the critical loads concept as an organizing approach for the REA makes sense, but this does not eliminate the need to define and describe the significance of the effects on ecosystem function and services at current levels of exposure. The secondary standard probably requires more than a determination of a “safe” level. The critical load needs to be defined in relation to the harm that is prevented if this load is not exceeded. The case study analyses seem to be headed in this direction.

Pages 2-7 to 2.8

Descriptions of ecosystem services reduced or degraded as a result of harmful effects on ecosystem functions are not only important inputs into economic valuation and cost-benefit analysis, they are important in helping policy makers and the public understand the significance of the effects on the ecosystems.

It is important to recognize that economic valuation needs to be in relation to an alternative. In figure 2.3-2 it is unclear what an economic value to “maintain” an ecosystem would be without specifying what would happen if some action were not taken. There may be a value to prevent a degradation or a value to obtain an improvement, but the value to simply “maintain” is ambiguous.

Page 2-13

This discussion of uncertainty is pretty weak. One important note is that variability is not the same thing as uncertainty. There may be a lot of variability in how different ecosystems respond to the same amount of N/S deposition and we may be able to specify this variability with a great deal of certainty.

It is important to acknowledge uncertainty, but a critical thing here is how to determine when there is enough known to be able to set reasonable standards.

Dr. Ellis Cowling

Specific Comments on the First Draft Risk and Exposure Assessment for Review of the Secondary National Ambient Air Quality Standards for Oxides of Nitrogen and Oxides of Sulfur

Charge Questions from OAQPS

My individual comments are organized below in response to each of the several Charge Questions posed in Lydia Wegman's memoranda to Kyndall Barry dated August 28, 2008 and September 23, 2008 in preparation for the October 1-2, 2008 CASAC meeting. As you will see, somewhat more detailed attention has been given to the five Charge Questions on Case Study Analyses and the recently received Chapters 7 and 8 than to other parts of this Risk and Exposure Assessment as requested by Chairman Ted Russell.

Scope of the Review

- 1. Chapters 1 and 2 provide the background, history, and framework for this review, including a discussion of our focus on the four key ecological effect areas (aquatic acidification, terrestrial acidification, aquatic nutrient enrichment, terrestrial nutrient enrichment). Is this review appropriately focused in terms of characterizing the important atmospheric and ecologic variables that influence the deposition and, ultimately, the ecologic impacts of nitrogen and sulfur? Does the Panel have any further suggested refinements at this time?**

My most serious reservation about the analysis framework for Chapters 1 and 2 is that chemically reduced forms of nitrogen (NH_x), organic forms of nitrogen (NC_x), and total reactive nitrogen (Nr) all are not included in the specific wording of any of the 20 policy-relevant questions that are said to constitute the framework for this review on the effects of nitrogen and sulfur pollution on acidification and nutrient enrichment of aquatic and terrestrial ecosystems in the US.

The October 31, 2007 *Resolution* from the Science Advisory Board's Integrated Nitrogen Committee makes the strong assertion from this Committee's examination of much of the same body of evidence reviewed in the ISA:

"The current air pollution indicator for oxides of nitrogen, NO_x, is an inadequate measure of reactive nitrogen in the atmospheric environment. The SAB's Integrated Nitrogen Committee recommends that inorganic reduced nitrogen (ammonia plus ammonium) and total oxidized nitrogen, NO_y, be monitored as indicators of total chemically reactive nitrogen."

Furthermore, the conclusion statements written in **bold-type** in Chapter 4 of the ISA indicate that:

"The evidence is sufficient to infer a causal relationship between "acidifying deposition" (which includes NH_x, and NC_x, as well as NO_x) and the following adverse acidification effects:

- a) “changes in biogeochemistry related to terrestrial ecosystems,”
- b) “changes in terrestrial biota,”
- c) “changes in biogeochemistry related to aquatic ecosystems,”
- d) “changes in aquatic biota.”

Also, “The evidence is sufficient to infer a causal relationship between Nr (reactive nitrogen) deposition (which also includes NH_x, NC_x, and NO_x) and the following additional ecologically adverse nutrient- enrichment effects:

- e) “alteration of biogeochemical cycling of N in terrestrial ecosystems,”
- f) “alteration of biogeochemical cycling of C in terrestrial ecosystems,”
- g) “alteration of biogeochemical flux of N₂O in terrestrial ecosystems,”
- h) “alteration of biogeochemical flux of CH₄ in terrestrial ecosystems,”
- i) “alteration of species richness, species composition and biodiversity in terrestrial ecosystems,”
- j) “alteration of the biogeochemical cycling of N,”
- k) “alteration of the biogeochemical cycling of C,”
- l) “alteration of N₂O flux in wetland ecosystems,”
- m) “alteration of CH₄ flux in wetland ecosystems,”
- n) “alteration of species richness, species composition and biodiversity in wetland ecosystems,”
- o) “alteration of biogeochemical cycling of C in freshwater aquatic ecosystems,”
- p) “alteration of species richness, species composition and biodiversity in freshwater aquatic ecosystems,”
- q) “alteration of the biogeochemical cycling of N in estuarine aquatic ecosystems,”
- r) “alteration of the biogeochemical cycling of C in estuarine aquatic ecosystems,”
- s) “alteration of species richness, species composition and biodiversity in estuarine aquatic ecosystems,”

“The evidence is sufficient to infer a causal relationship between:

- t) “exposure to NO, NO₂, and PAN and injury to vegetation” and
- s) “exposure to HNO₃ and changes to vegetation.”

On the basis of this substantial body of accumulated evidence, I recommend that a schematic diagram similar to Figure 1.3-1 be included in Chapter 1 to illustrate the “cycle of reactive, chemically **reduced** nitrogen species. I also recommend that:

- a) Chemically reduced (NH_x) and also organic forms (NC_x) be included among the nitrogen pollutants of concern in many of the 20 policy-relevant questions listed in Section 1.4 on pages 1-17 through I-20 in Chapter 1, and \
- b) Appropriated answers about chemically reduced (NH_x) forms and if possible also organic forms (NC_x) of reactive Nitrogen (Nr) be presented in REA Chapters 2, 3, and 4.

Air Quality Analyses

1. **To what extent are air quality characterizations and analyses presented in Chapter 3 technically sound, clearly communicated, appropriately characterized, and relevant to the review of the secondary NAAQS for NO_x and SO_x?**

With the exception of the reservations stated in answer to the Charge Questions about the Scope of the Review, I believe that the analyses presented in Chapter 3 are technically sound, clearly communicated, and appropriately characterized.

- 2. Section 3.2.1 describes an approach for evaluating the spatial and temporal patterns for nitrogen and sulfur deposition and associated ambient concentrations in the case study locations. This draft document includes the analysis for the Adirondacks case study. Does the Panel agree with this approach and should it be applied to the other Case Study Areas?**

The approach used for evaluating the spatial and temporal patterns for of N and S deposition and associated ambient concentration seems very reasonable to me. This approach proved to be useful in the Adirondacks Case study and I expect it to be reasonable for other case studies as well.

- 3. Section 3.2.2 describes the relative contributions of ambient emissions of nitrogen and ammonia to nitrogen deposition for the case study areas. To what extent is the approach taken technically sound, clearly communicated, and appropriately characterized?**

I presume from examining the figures and associated text for the data presented on pages 3-63 through 3-112 that this question should have read:

” Section 3.2.2 described the relative contributions of chemically oxidized and chemically reduced forms to total reactive nitrogen for the Case Study areas. To what extent is the approach taken technically sound, ...etc.”

On the assumption that my presumption is correct, I consider this combination of modeling and measurement approaches to be reasonable. But I must confess that it took me a very long time to finally understand the rationale behind the statement on lines 10-12 on page 3-13 that “In order to calculate total nitrogen (by which I suppose the author meant deposition of total reactive nitrogen) the two chemical species from the NADP (i.e., NO₃⁻ and NH₄⁺) were added together and then added to the total dry (deposition?) nitrogen-estimated values from CMAQ.

It also took me a very long time to understand what was meant by the term “zero-out of NO_x emissions” as used in most of the figure captions on pages 3-63 through 3-112) and periodically in the associated text.

With regard to the questions of “clearly communicated and appropriately characterized” I offer the following comments:

- 1) What a delight it was to find the following firm statement on lines 15-20 on page 3-70:

“Figures 3.2-42 examines the relative impact of emissions on NH₃ of the deposition of total reactive nitrogen. Figure 3.2-42 shows that NH₃ emissions represent a significant contribution to total reactive nitrogen in most case study areas, although the impact varies by season and by area. The smallest impact of NH₃, 10% occurs in the Potomac case study area in February. The largest impact of NH₃, 73% occurs in the Neuse Case study in July. The Neuse case study has the largest overall impact of from NH₃ of any of the case study areas, across all four seasons.”

- 2) On lines 6 and 7 also on page 3-63 (and another case on lines 9 and 10 on page 3-71) we find three very confusing sentences that reveal clearly why EPA’s constant use of the terms “reduce,” “reducing” and “reduction” is so often confusing and ambiguous:

“One possibility is that reducing NO_x reduces HNO₃, which limits ammonium nitrate (NH₄NO₃) formation (and for existing aerosol, a reduction in HNO₃ shifts the equilibrium towards the gas phase), thereby increasing the lifetime of NH₃. A net increase in NH₃/NH₄ results. Because the deposit velocity of NH₃ is much higher than the deposition of NH₄⁺ aerosol, dry deposition of NH_x increases.

The terms “reduce,” “reducing” and “reduction” have both chemical and numerical meanings. Fortunately we have the unambiguous terms “decrease” and “decreasing” which have only a single (always numerical) meaning. So why not use the unambiguous term “decrease” instead of the word “reduce” when our intended meaning is numerical and thus reserve the term “reduce” for its chemical meaning?

Is this what was meant by the sentence quoted above?:

“One possibility is that **decreasing** emissions of NO_x **decreases** air concentrations of HNO₃, which limits ammonium nitrate (NH₄NO₃) formation (and for existing aerosol, a **decrease** in HNO₃ emissions shifts the equilibrium towards the gas phase), thereby increasing the atmospheric lifetime of gaseous NH₃. A net increase in the ratio of gaseous NH₃ to NH₄⁺ aerosol in the atmosphere results. Because the deposit velocity of gaseous NH₃ is much larger than the deposition velocity of NH₄⁺ aerosol, dry deposition of NH_x increases.

Case Study Analyses

- 1. Attachment 2 presents a GIS analysis to define geographical areas that are sensitive to acidification and nutrient enrichment. Are the national geospatial data sets chosen adequate to identify sensitive areas? Are there other data sets that have not identified by this analysis that we should consider? Does the Panel agree with approach or can they suggest alternatives?**

I have only limited experience with the several data bases that were used in the GIS analysis used in an attempt to define geographic areas that are sensitive to acidification. Thus I have only limited professional experience on which to base a detailed judgment in response to this question.

Nevertheless, my general impression derived from study of the summary map on page 18 of Attachment 2, and my general awareness of soil, vegetation, surface and ground waters, and the topographical, meteorological, and climatic factors that are relevant to acidification and nutrient enrichment, lead me to conclude that the GIS approach used was generally sound. I know of no additional data sets that should be included in this analysis.

- 2. Attachment 3 presents our current progress on evaluating the effect of aquatic acidification in the Adirondacks. It describes the use of the MAGIC model to evaluate ANC levels in selected lakes and streams in the Adirondacks and Shenandoah. To what extent is the approach taken technically sound, clearly communicated, and appropriately characterized?**

I have no direct experience on which to base an informed judgment in response to this question. However, several of my colleagues tell me that the MAGIC model is very appropriate for these kinds of analyses.

- 3. Attachment 4 presents our current progress on evaluating the effect of terrestrial acidification. It outlines a plan to use the Simple Mass Balance Model to evaluate current deposition levels on forest soil ANC for sugar maple in the Kane Experimental Forest and**

red spruce in the Hubbard Brook Experimental Forest. To what extent is the approach taken technically sound, clearly communicated, and appropriately characterized?

I have studied Attachment 4 with considerable care and consider that the approach taken so far (since this is still a work in progress) is technically sound, clearly communicated, and appropriately characterized.

- 4. Attachment 5 presents our current progress on evaluating the effect of aquatic nutrient enrichment. It outlines a plan to evaluate how changes in nitrogen deposition affect the eutrophication index in two estuaries: the Chesapeake Bay and Pamlico Sound. The analysis will model one stream reach (Potomac River and Neuse River) to determine the impact on the eutrophication index for the estuary. To what extent is the approach taken technically sound, clearly communicated, and appropriately characterized?**

I have studied attachment 5 with reasonable care and conclude that the approach taken in this case also is technically sound, clearly communicated, and appropriately characterized.

- 5. Attachment 6 presents our current progress on evaluating the effects of terrestrial nutrient enrichment. It describes an approach to evaluate the effects of nitrogen deposition on the Coast Sage Scrub community in California and in mixed conifer forests in the San Bernardino and Sierra Nevada Mountains. To what extent is the approach taken technically sound, clearly communicated, and appropriately characterized?**

I have no experience with any of the western state ecosystems that are discussed in Attachment 6. Thus I have no professional experience on which to base an informed response to this question.

Additional Effects

- 1. In this chapter, we have presented results from some initial qualitative analyses for additional effects including the impact of sulfur deposition on mercury methylation, the impact of nitrous oxide on climate change, and the impact of nitrogen deposition on carbon sequestration. Are these effects sufficiently addressed in light of the focus of this review on the other targeted effects in terms of available data to analyze them?**

Chapter 6 provides a useful overview of the impact of sulfur deposition on methylation of mercury which seems to me to be very worthy of consideration with regard to setting appropriate limits on the amount of air emission of sulfur oxides that should be permitted in various regions of the US. I see little reason for worry about nutrient enrichment or acidification effects of carbon sequestration. I do believe, however, that nitrous oxide emissions should be incorporated in EPA's review of the NAAQS for nitrogen pollution and its effects on terrestrial and aquatic ecosystems.

Synthesis and Integration of Case Study Results into the Standard Setting Process (Chapter 7)

- 1. The purpose of Chapter 7 is to summarize the Case Study results and characterize the relationship between levels of an ecological indicator and the associated degree of ecologically adverse effects. To what extent is this approach technically sound, clearly communicated and appropriately characterized at this point of the review? Does the Panel have any further suggested refinements at this time?**

I believe that the attempt being made in Chapter 7 to building a scientifically sound linkage between carefully selected ecological indicators and the extent and magnitude of ecologically adverse effects is a very complicated but very desirable goal.

In the development of Chapter 7, and even more in Chapter 8, it appears that EPA is deliberately trying to build a case for making some modest decrease in emissions of nitrogen oxides (NO_x -- which is already recognized as a Criteria Pollutant) –and of course would help decrease the adverse acidification and nutrient enrichment effects of total acidifying deposition and of total reactive nitrogen -- without also having to decrease the amounts of chemically reduced and organic forms of nitrogen that can be emitted into the air.

I believe that the extent of decrease in reactive nitrogen pollution loads that are needed to protect sensitive terrestrial and aquatic ecosystems of this country cannot be achieved without taking steps to also include significant decreases in the amounts of chemically reduced and perhaps also organic forms of total reactive nitrogen.

Considerations in the structure of the NO_x/SO_x Secondary Standard (Chapter 8)

- 2. Chapter 8 begins to explore how a secondary NAAQS might be structured to address the targeted ecological effects discussed in the assessment. The next draft of this document will include one or more examples of how this structure might be used to relate specific levels of air quality indicators with a corresponding ecological indicator for a given location and/or scenario. To What extent is the described approach technically sound, clearly communicated and appropriately characterized at this point of the review? Does the Panel have any further suggested refinements at this time?**

In Section 8.1 – *Possible Structure of a Secondary Standard* – the diagram in Figure 8.1-1 was especially informative of the approach that is currently being considered. The example given was based on the ecological indicator ANC (acid neutralizing capacity) and assumed that the pollutants of concern were only the chemically oxides form of reactive nitrogen (NO_x) and sulfur (SO_x) , and not also the chemically reduced forms of reactive nitrogen (NH_x).

Even though I was disappointed that only oxidized form of reactive nitrogen were considered in this illustration, I believe this diagram provides a very rational basis for considering various aspects of a secondary standard for total reactive nitrogen and sulfur.

The opening sentences of the first two paragraphs of Chapter 8 illustrate why it appears that EPA is deliberately trying to build a case for dealing exclusively with oxides of nitrogen and oxides of sulfur (which are already identified as Criteria Pollutants) rather than having also to deal with the chemically reduced and organic forms of reactive nitrogen) which also contribute to the many adverse acidification and nutrient enrichment effects of nitrogen and sulfur pollution (but are not yet recognized as Criteria Pollutants).

The two lead sentences read as follows:

Paragraph 1: “

“The previous chapters have provided an understanding of the risks associated with current deposition of nitrogen and sulfur associated with ambient atmospheric concentrations of NO_x and SO_x.”

In this sentence, please note especially the words “current (not anticipated future) deposition” and “ambient (not anticipated future) concentrations” and “NO_x and SO_x” rather than “total total reactive nitrogen (Nr), or” total acidifying deposition” or “NO_x, NH_x, and SO_x.”

Paragraph 2:

“In this chapter, we discuss constructing a standard based on achieving a uniform level of ecosystem protection. We explore a framework by which ambient atmospheric concentrations of NO_x and SO_x can be translated into a measure of ecosystem effects, using then transformation functions described below.”

In this sentence, please note once again the words “ambient (not anticipated future) concentrations” and “NO_x and SO_x” rather than “total total reactive nitrogen (Nr), or” total acidifying deposition” or “NO_x, NH_x, and SO_x,” and the words “uniform (not regional, local, or ecosystem-specific) level of ecosystem protection.”

A glimmer of hope with regard to consideration of both chemically reduced and oxidized form of reactive nitrogen is contained in the sentence on lines 20-23 on page 8.5:

“While [chemically] reduced species of nitrogen do contribute to the overall loadings of N, as will be demonstrated in a future version of Section 8.4, it may not be possible to focus solely on NO_x contributions to loadings while recognizing that there are impacts from reduced forms of nitrogen that must be taken into account.”

Dr. Charles T. Driscoll

The document “Risk and Exposure Assessment for Review of Secondary National Ambient Air Quality Standards for Oxides of Nitrogen and Oxides of Sulfur” is an effort by U.S. EPA staff to provide and discuss a framework for establishing secondary standards of nitrogen oxides (NO_x) and sulfur dioxide (SO₂). Overall, I found the framework thought provoking and an interesting path forward in the establishment of secondary standards. While I enjoyed reviewing the document, there were several general technical issues that I am concerned about. There are several wording and grammatical problems in the text that should be addressed before the document is more widely circulated. Finally, there are numerous small technical and wording problems in the document. I have organized my comments around these three issues.

Unfortunately, the document is not complete. Major sections are missing or partially complete. It is really a waste of time to conduct a review of such a large and complex document when the document is incomplete.

Technical Issues:

1. *Case studies and modeling approach.* I think the approach of using case studies to address the framework for secondary standards is a good and appropriate one. I also generally think the specific case studies that are advanced in the REA are appropriate and helpful. I generally endorse the approach used. There are a few general comments/issues I would like to address.

The case studies for aquatic effects in the Adirondacks and the Shenandoah Park regions, terrestrial effects on red spruce and sugar maple in the East and terrestrial effects on coastal sage scrub and conifer forests in California seem appropriate. I also like the two estuarine sites to evaluate coastal effects. I do have some concerns with the estuarine studies. First, it appears that the entire estuary watershed will not be evaluated (i.e., Chesapeake-Potomac; Pamlico; Neuse). Will this be a problem or is the scope of doing the entire watershed just too great for this assessment? More problematic is conducting analysis for two watersheds that are in fairly close proximity? Although there is considerable information for Chesapeake Bay and Pamlico Sound, wouldn't it make more sense to conduct one of these case studies at a site with more contrasting features, with different land cover, climatic or N sources? I would think interest's would be best served by either selecting a northern estuary (e.g., Gulf of Maine, Long Island Sound) or a Gulf estuary as a second site.

The other general technical comment is that the approaches used to develop critical loads for these case studies are very different. Evaluating these different approaches could be very instructive but also problematic. I like the approach proposed of using a dynamic acidification model for the Adirondack and Shenandoah case studies. Note, however, that MAGIC does not effectively simulate watershed nitrogen dynamics. So if this is an important component of the critical load, there will undoubtedly be some errors. I find it disconcerting that for the terrestrial acidification assessment a steady-state model is being

used. First, is it a good idea to use a dynamic model for the aquatic assessment and a steady-state model for the terrestrial assessment? While I agree with the authors that critical loads are a steady-state phenomenon, ecosystems are not. Forest ecosystems are losing exchangeable cations and presumably accumulating sulfur and nitrogen. This makes these systems by definition not a steady-state and increasingly sensitive to inputs of acidic deposition. While the application of a steady-state model is easy, it would seem to be problematic as an assessment tool. There are clear limitations in using a steady-state model for critical loads assessments. Finally, I don't understand how the critical loads will be determined for the coastal and terrestrial nutrient case studies. SPARROW is a statistical model and it is not clear how this can be used to evaluate greater and lower N loads.

2. *Nitrogen saturation.* Throughout the text, N saturation is referred to. However, I could not find any discussion of this phenomenon in the introductory sections. It is discussed in the ISA but not (that I could find) in the REA. A brief summary of N saturation might be helpful.
3. *Time scale disconnect.* There appears to be a disconnect between the time scales used for the atmospheric modeling and the effects assessments. Ecosystem effects of air pollutants are largely manifested over decades to multiple decades. Certainly the simulations conducted by MAGIC are conducted with what I believe to be the appropriate temporal perspective. I believe the time-scale for nutrient effects on ecosystems similarly have a long-term perspective. In contrast, the deposition/CMAQ analysis seems to be largely focused on a short-term or seasonal perspective. Why? There seems to be a complete disconnect in the atmospheric and effects modeling concerning time-scale of analysis. Isn't the primary concern here ecological effects? Do seasonal or monthly patterns in air concentration or deposition have any relevance for this long-term analysis of ecosystem effects?
4. *Climate.* I am a bit surprised that no discussion is given to changing climate. The framework to be developed is examining effects that will play out over the next decades. It is projected that climate will also change substantially over the same period. Climate change will affect hydrology and ecosystem response to air pollution. Climate change should be mentioned and needs to be addressed in future assessments.
5. *Establishing standards around ambient air concentrations.* In Chapter 8, limited discussion was advanced in establishing ecosystem effects around ambient air concentrations. While I can see that this might be a desirable objective, as we currently have primary standards and some quasi secondary standards based on ambient air concentrations. However, for ecosystem effects, I do not see this approach as workable. I think the standard needs to be based ultimately on total sulfur and total nitrogen deposition. There are many species of sulfur and nitrogen all which contribute to ecological effects but having different residence times in the atmosphere. These residence times vary in time and space. The key driver of ecological effects is long-term total deposition. Establishing standards around ambient air concentrations would seem to be intractable.

6. *Spatial variability in sensitivity.* I'm not sure if this consideration is relevant for the nutrient case studies, however, the acidification case studies will exhibit considerable spatial variability in sensitivity to acidic deposition. There is a range of ecosystem sensitivity to acidification from highly sensitive to highly insensitive. How will this range of ecosystem response to acidic deposition be addressed when establishing the critical load? Will all ecosystems be protected? 90%, 50%. Some discussion of this consideration would be helpful.

Written Document Considerations:

1. *Written perspective.* The document is written from the "we" perspective (i.e., we did this..., we analyzed that...). I find this approach somewhat disconcerting. The reason being it is not clear who owns the document. Is this EPA's document or the contractor's document? Who are we? I would like to see the document altered.
2. *Typos, errors, writing mistakes.* As with the last draft of the ISA, the REA (and the 2nd draft of the ISA) is filled with mistakes and typos. I point out many of these in my specific comments (see below). However, these are by no means all the mistakes. This document needs to be carefully read, proofread and edited for consistency and to eliminate the mistakes.
3. *Redundancy.* There are many redundant sections in the document. This makes a very long document, longer than it needs to be. The document should be edited to eliminate the redundant text.
4. *Tense.* The REA switches back and forth from the past to present tenses. I can see writing in either tense. However, the document should be edited so it is written in a consistent tense.

Specific comments:

- | | |
|--------------------|---|
| Page 1-2, line 16 | Units of ANC $\mu\text{eq/L}$? |
| Page 1-11, line 24 | I don't agree with the statement. Most published studies document inputs of oxidized and reduced N. A few don't, but most do. |
| Page 1-12, line 10 | Space missing. |
| Page 1-12, line 13 | I would change the wording. Acidification is an environmental effect due primarily to sulfur and secondarily nitrogen in most environments. |
| Page 1-13, line 12 | As above, need to define N saturation. |
| Page 1-13, line 19 | Change air to atmosphere. |

Page 1-15, line 22	alpine
Page 1-16, line 12	It is incorrect to state that watersheds conducive to methylation are found in the northeastern U.S. and southeastern Canada. They are found all over. See Figure 6.1-3.
Page 2-2, table 2.1-2	Under aquatic acidification also include hydrologic flow paths under sensitivity variable.
Page 2-4, line 15	Eliminate comma
Page 3-7	I would like to see this section expanded to include a section of background (pre Industrial Revolution) deposition, including sulfate, nitrate, ammonium and basic cation deposition.
Page 3-8	I would like to see a brief description of organic N deposition, including sources.
Page 3-9, thru 12	There is a summary of spatial deposition patterns. The discussion of how these maps are produced is in the section that follows (3-12). The methods section should be moved in front of the maps. Also, the maps are generated for 2002. Some discussion should be given as how representative this year is, given year-to-year variability in deposition. Moreover, it is critical to clarify on the deposition maps the units of mass (e.g., Kg N/ha-yr or kg NO ₃ /ha-yr).
Page 3-12, line 10	data are ...
Page 3-13, line 1	data were...
Page 3-13, line 6	Change to... kg/ha-yr.
Page 3-13, line 7	data were...
Page 3-16, line 5	Need to clarify the time interval kg/ha-yr?
Page 3-16, table 3.2-2	It is not clear what this table is. Some additional text is necessary.
Page 3-19	It would be helpful to put the Adirondack Park and the Shenandoah National Park boundaries and the Chesapeake and Pamlico watershed areas on the map so the reader can understand the scope of the analysis relative to the total resource.
Page 3-25, line 7,8	Change to... kg N-ha/yr.

- Page 3-35, line 12 Change to... fairly uniform.
- Page 3-36, figure 3.2-14 Why show figures of both monthly and seasonal deposition? Isn't this redundant?
- Page 3-38, figure 3.2-16, 17, 18, 19
 These figures are difficult to read and are they really helpful?
- Page 3-40, line 4 Change to... generally uniform...
- Page 3-50, lines 3, 17 and Page 3-51, line 6
 Change...drop to decrease
- Page 3-50, figure 3.2-28 and elsewhere
 Aren't the monthly patterns in wet deposition strongly driven by the quantity of precipitation? Wouldn't patterns for a different year with different precipitation patterns be different? As a result, this temporal section is misleading because it is strongly affected by the meteorology for that year. If true, why include all this analysis? As a minimum, this fact should be clarified and some data provided on 2002 as a reference year.
- Page 6-1, line 3-4 Rephrase. Every wetland has sulfate. The production of methyl mercury is largely mediated by sulfate reducing bacteria.
- Page 6-1, line 22 Also phosphorus (or N) can be important as it regulates aquatic productivity and therefore mercury concentrations in aquatic organisms (Driscoll et al. 2007).
- Page 6-2, line 4 Change to...Industrial Revolution.
- Page 6-2, line 28 This sentence needs to be clarified. Ionic mercury can be reduced and evaded and separately methylated. Methyl mercury is not reduced. Where does this 1-2% come from? The extent of methylation is highly variable from ecosystem to ecosystem.
- Page 6-4, line 14-16 Why is methane needed? Why do you need HgS in the equation? Define MeHg⁺.
- Page 6-4, line 20 Also anoxic conditions.
- Page 6-4, last paragraph There are other studies that probably should be cited (Branfireun et al. 1999), (Jeremiason et al. 2006).
- Page 6-5, line 12 Change to...methylation can occur within.

Page 6-5, figure 6.1-2	Hg can also be supplied from sediments.
Page 6-6, line 3	Change to... anoxia, sulfate).
Page 6-6, line 5	Change to... response, hydrology, nutrient loading, limnology).
Page 6-10, line 4	Is this really true? I do not believe it. % methyl mercury is highly variable. Need to correct.
Page 6-12, line 5	Change to... oxidizing NH_4^+ .
Page A3-1, line 15	Subscript 2.
Page A3-1, line 20	hydrogen ion, and Al^{n+} .
Page A3-1, line 20 and throughout the document	I don't think the writers of this document understand the concept of buffering capacity. Buffering capacity is the resistance of a system to changes in pH. I would recommend eliminate using the term here and elsewhere or change the phrasing to use it correctly. An alternative could be acid neutralizing capacity or acid-base status.
Page A3-2, 1 st paragraph	I suggest adding a sentence or two about immobilization/mobilization of SO_4^{2-} and NO_3^- by plants/soil organic matter.
Page A3-2, line 10	There are numerous chemical indicators.
Page A3-2, line 12	NO_3^- , Al^{n+}
Page A3-2, line 12	Change to... of base cations; and ANC.
Page A3-2, line 27	Change to... precipitation enters the soil and soil water to emerge...
Page A3-2, line 30	$\text{K}^+ + \text{Na}^+ + \text{NH}_4^+ - (\text{SO}_4^{2-} + \text{NO}_3^- + \dots)$ in ($\mu\text{eq/L}$)
Page A3-3, line 5	Change to... low pH.
Page A3-3, line 6	Change to... This is the acid neutralizing capacity (ANC), or the ...
Page A3-5, line 4	acidic surface waters (14%; $\text{ANC} < 0 \mu\text{eq/L}$).

Page A3-5, line 26	United States
Page A3-6, line 24	Need to define the time and mass basis of deposition (e.g., kg SO ₄ /ha-yr or kg S/ha-yr).
Page A3-7, line 12	Change to... weathering rates and limited neutralizing of acid inputs.
Page A3-8, line 5	Again need to define the time and mass basis of deposition.
Page A3-9, line 19	Al ⁿ⁺
Page A3-9, line 21	with limited leaching
Page A3-9, line 23	EPA-administered Long-Term Monitoring (LTM) program.
Page A3-15, line 12	SO ₄ ²⁻
Page A3-16, line 9	comma
Page A3-16, line 19	it's the acid neutralizing capacity of a ...
Page A3-16, line 21	The acid neutralizing capacity of a ...
Page A3-17, line 3	20 µeq/L (limited protection)
Page A3-16, line 12	This sentence makes no sense. At ANC = 0 µeq/L a water is chronically acidic.
Page A3-17, line 8	Sub and super script
Page A3-20, line 5	Units should be eq/ha-yr.
Page A3-20, line 7,8	I would eliminate the term occult deposition simply call it cloud and fog deposition.
Page A3-20, line 10	Units meq/m ² -yr
Page A3-22, line 24	This description needs to be expanded or clarified. There are more than 200 NADP sites.
Page A3-28. line 25	in the catchment
Page A3-29, line 19	400 meq/m ³

Page A3-29, line 24	The titles used for these classes should be consistent with the titles established in table 4.1-1 on A-14.
Page A3-33	There needs to be some discussion on the time and nitrogen retention assumptions used to obtain critical loads.
Page A4-1	I would change the title to Forest Acidification Case Study.
Page A4-1, line 17	hydrogen ions
Page A4-1, line 19	where strong acids
Page A4-4	Should also consider citing the recent paper by (Warby et al. (in press)) attached), which shows widespread soil acidification in the Northeast.
Page A4-5, line 14	This statement needs to be reworded. Al mobilization occurs under low % base saturation and high concentrations of acid anions. The statement as it stands is incorrect.
Page A4-9, line 18	Should be (Driscoll et al. 2001).
Page A4-10	It would be helpful to cite the study by (St. Clair et al. 2005) which shows decreases in foliar antioxidant enzymes in sugar maple in response to lower foliar and soil Ca ²⁺ in Pennsylvania.
Page A4-19, line 1	Again need to specify the mass and time basis of deposition.
Page A4-28, line 10	acidity input neutralized by
Page A4-28, line 18	parties
Page A4-49	Need to indicate the units of the figure.
Page A4 References	Should be BioScience.
Page A5-18, 1 st paragraph	Need to use metric units.
Page A5-26, line 6	Need to define Nr.
Page A5-30	SPARROW is a steady-state model. Will need to demonstrate how you can use it.
Page A5-55, line 7	were from

Page A5-58, line 6, 8	Does the SAV coverage really have this level of significant figures?
Page A6-10, line 1	Change to... Mediterranean climate. This climate is...\
Page A6-25, line 16	result of long-term elevated N deposition rather than pulses
Page A6-42, line 7	data are
Page 7-3, line 12	Change to... where strong acids are
Page 7-11, line 2	catchment to neutralized acid anion deposition is known as acid neutralizing capacity.
Page 8-1, line 14	There cannot possibly be a uniform level of ecosystem protection due to the inherent variability in ecosystem sensitivity.
Page 8-4, figure 8.1-1	Add climate as a variable/fixed factor.
Page 8-5, line 2	What is meant by the point of deposition?
Page 8-8, line 14	What about forest acidification?
Page 8-8, line 14	How can you say whether precipitation occurs or not. Is there a location where precipitation does not occur? Rewrite sentence.
Page 8-10, line 24.	Do you mean deposition is expressed on an equivalence basis? Please clarify.
Page 8-11, line 4	This sentence makes no sense and should be rewritten.
Page 8-14, line 1	data are
Page 8-14, line 20	Do you mean equivalence ratio?

References:

- Branfireun, B. A., N. T. Roulet, C. A. Kelly, and J. W. M. Rudd. 1999. In situ sulphate stimulation of mercury methylation in a boreal peatland: Toward a link between acid rain and methylmercury contamination in remote environments. *Global Biogeochemical Cycles* **13**:743-750.
- Driscoll, C. T., Y.-J. Han, C. Y. Chen, D. C. Evers, K. F. Lambert, T. M. Holsen, N. C. Kamman, and R. K. Munson. 2007. Mercury contamination in forest and freshwater ecosystems in the Northeastern United States. *BioScience* **57**:17-28.

- Driscoll, C. T., G. B. Lawrence, A. J. Bulger, T. J. Butler, C. S. Cronan, C. Eagar, K. F. Lambert, G. E. Likens, J. L. Stoddard, and K. C. Weathers. 2001. Acidic deposition in the northeastern United States: Sources and inputs, ecosystem effects, and management strategies. *BioScience* **51**:180-198.
- Jeremiason, J. D., D. R. Engstrom, E. B. Swain, E. A. Nater, B. M. Johnson, J. E. Almendinger, B. A. Monson, and R. K. Kolka. 2006. Sulfate addition increases methylmercury production in an experimental wetland. *Environmental Science and Technology* **40**:3800-3806.
- St. Clair, S. B., J. E. Carlson, and J. P. Lynch. 2005. Evidence for oxidative stress in sugar maple stands growing on acidic, nutrient imbalanced forest soils. *Oecologia* **145**:258-269.
- Warby, R. A. F., C. E. Johnson, and C. T. Driscoll. (in press). Continuing acidification of organic soils across the northeastern USA: 1984 - 2001. *Soil Science Society of America Journal*.

Dr. Paul J. Hanson

The Risk and Exposure Assessment (REA) ... represents a good beginning, but many sections are not yet complete or only partially complete making it difficult to judge the full intent or appropriateness of the document.

Specific comments and suggested edits:

Front matter:

Page xii: Should the definition of ecological dose be limited to toxicants that inhibit *microbe-mediated ecological processes*? I would think that the term should apply to all biological organisms. It may be that it is a term that dominates microbial studies.

Top of Page xiii: The most common example of an ecosystem benefit would probably be an increase in productivity. Why isn't this an example?

Page xiii: The difference between elasticity and sensitivity (page xv) isn't clear. Is there a reference for the use of the term elasticity that might be placed here?

Page xv: The precipitation range for semi-arid regions should probably be 250 to 500 mm. It certainly shouldn't be the same as the definition for arid systems.

Chapter 1

Page 1-3 line 8: I recommend the following wording change "...both ambient air and surface deposited species of NO_x and SO_x...

Page 1-10 line 23: N₂O is nitrous oxide not nitrogen dioxide.

Page 1-12 line 9: For parallel structure I would add the spelled out version of sulfur dioxide.

Page 1-13 line 5: Remove the semicolon.

Page 1-13 line 13: I would change "direct effects" to 'direct adverse effects'. There is some evidence for localized N uptake.

Page 1-14 line 11: The text must be changed to "...detail on how acidification affects sensitive ecosystems....." Don't leave the reader with the impression that acidification is having effects on all ecosystems.

Page 1-14 line 17: I don't understand "re-acidification". This concept needs to be further developed.

Page 1-14 line 31: Add 'productivity' to the list of changes driven by N deposition.

Page 1-15 line 14: This threshold for N saturation is only relevant for some, but not all eastern forests. Those levels of N deposition would be easily assimilated by much of the upland oak forests throughout the eastern United States growing on deep soils with ample base saturation. Page 3-186 of the ISA states "there is currently no published national assessment of empirical critical loads for N in the U.S....."

Table 3-25 is a nice summary of what is known. The REA needs to reflect the limited amount of data available for developing quantifiable thresholds, and appropriately characterize those ecosystems for which it might appropriately be applied. Avoid inappropriate extrapolations. Lines 14 to 19 on page 4-16 of the ISA include good statements that should be used within the REA to qualify the nature of ecosystem sensitivity.

Page 1-15 lines 21 and 22: Similarly, the wording may need to be changed here to suggest if these levels represent an appropriate threshold for all or just some sensitive grasslands.

Page 1-15 line 30: Add a reference for the sentence ending on this line.

Figure 1.3-3 still doesn't show the productivity enhancement effect of N, which is clearly a dominant process in the N cycle.

Bottom of page 1-17: Should some mention be made at this point to N standards for water pollution? It isn't necessary, but might be a useful connection. Section 3.3.6 of the ISA and the associated annex might be cited.

Figure 1.4-1 doesn't adequately capture the integrated nature of NO_x and SO_x pollution that is being attempted in this document. Are they truly intertwined all along this process or do they only come together after deposition takes place?

Chapter 2

In Table 2.1-1 ANC should be defined, productivity should be added as an ecosystem service where appropriate, and N leaching might be added as an indicator of terrestrial nutrient enrichment. The characteristics of sensitivity for terrestrial nutrient enrichment might be updated.

Sections of Table 2.3-1 still need to be filled in.

Chapter 3

Page 3-4 lines 6 and 7: Check the wording. 30 to 70% of the animal wastes can't be emitted as NH₃. Should it read 30 to 70% of the N losses from animal wastes?

Page 3-5 lines 10 to 15: Are there not any natural sulfur emissions in and around Yellowstone or in other hot springs areas of the country? I realize they may be inconsequential....

Pages 3-10 to 3-11: Question: Have all of the emissions reductions resulting from past clean air legislation been realized? Will new standards for ozone impact the likely deposition rates for N in the future? Should such a discussion be included someplace in this document?

Chapter 3 doesn't include much on temporal changes in deference to the maps of recent conditions. Those are fine, but I think some discussion of where we have been and where we are going should be included in the REA. Figures 2-59 or 2-103 from the ISA might be considered.

Page 3-12: Super and subscripts for charge are missing for SO₄⁻², NO₃⁻, and NH₄⁺.

Question: Do the QMAC estimates of deposition to terrestrial systems include foliar uptake of NO or NO₂ near urban areas or along major roadways where air concentrations are high enough to drive this pathway?

Table 3.2-2 is not well defined. It needs references.

I was disappointed by how much information was still not added to the document (especially in this Chapter). We are being asked to provide comment on a document that has a lot missing from it.

Captions to Figure 3.2-12, -13, and -14 need to be reworded to "...nitrogen deposition by source and quarter.... The most interesting data in many cases has to do with the source of N forms rather than the season of the year.

Figures 3.2-22, -23, -24, and -25 lack units (presumably kg/ha as for N).

Captions to Figure 3.2-27 and -28 need to be reworded to "...sulfur deposition by source and quarter....

Page 3-54: Again...we don't have much to review yet.

Page 3-54 line 14: Reword as...."Public welfare effects associated with direct exposure to NO_x and SO_x do not occur for current ambient concentrations."

Page 3-54 line 23: The discussion on pages 1-10 and 1-11 seems to disagree with this statement. The REA has already been defined to deal with total reactive N.

The discussion of Data and Tools (Section 3.2.2.2) should probably be presented earlier within Chapter 3 (perhaps around page 3-17).

Figures 3.2-35 and -36: Adding pixels for actual forest cover within these maps would be useful to better reflect the actual extent of the forest types. The coastal sage map (Figure 3.2-37) appears to be drawn this way.

The text for Figures 3.2-39, -40, -41, -42, -43, and -44 is way too small and the figure captions are inadequate. Please revise.

Page 3-70: At this point of the discussion it occurred to me that a case study for an area dominated by NH₃ deposition (i.e., Iowa, Minnesota, Illinois) should probably be added to the REA. It wouldn't necessarily show adverse effects, but it would complete the picture of total reactive N deposition across the US. Page 3-103 of the ISA provides some rationale for not including such a case study since agricultural areas are overwhelmed by fertilizer additions. However, limited natural areas (forests, prairies) are embedded within areas dominated by agriculture.

Chapter 4: Incomplete and not reviewed.

Chapter 5: Incomplete and not reviewed.

Chapter 6

Figure 6.1-4: SRB should be defined in the figure caption.

Page 6-16 line 13: Remove the word "often". Fungi should probably also be recognized as an important contributor to decomposition.

Increased nitrogen does affect the N content of green leaves. Is this pattern well established for litterfall

as well? Does the pattern differ by vegetation type (i.e., trees, grasses, crops...)?

Page 6-17: Some of this material might be better left to the ISA document. Lines 24 to 28 are not needed here.

Page 6-19: How the contribution of atmospheric deposition to upland watersheds actually finds its way into waterways isn't clear. The 'filtering' effect of upland vegetation will vary tremendously from location-to-location. This concept needs to be made clear in the document.

Chapter 6 seems to lack summary conclusions:

What terrestrial systems are at risk? What percent of US land area?

What aquatic systems are at risk? What percent of US freshwater area?

Chapter 7

Page 7-5 line 4: Replace "ecosystem health" with another term. It isn't and perhaps can't be defined.

Page 7-5. Line 7: Change to "this is hypothesized to change...." Or provide the references that show proof.

Page 7-5 line 21: Spell out CSS.

Page 7-7 Table 7.1-1: Replace "tree health" with a more meaningful term or terms such as rate of growth, survival....

Page 7-8: The deposition levels proposed are appropriate for 'sensitive' ecosystem, but not all ecosystems. This concept of one size does not fit all will need to be worked into the conclusions of the REA. While protection of sensitive systems may be a justification for a new standard and level, it shouldn't be interpreted as having the same effect on all areas of the US. That is, lowering inputs to areas currently unaffected will not help them. Pages 3-78 and 3-79 of the ISA include text that might be useful in clarifying this point.

Chapter 7 ends abruptly and seems incomplete.

Chapter 8

Page 8-1 lines 14 and 15: The concept of achieving a standard based on a "uniform level of ecosystem protection" seems at odds with the REA document. The REA clearly states that the impacts of N and S deposition are localized throughout the US and subject to the correct combinations of deposition and susceptibility of the target terrestrial and aquatic ecosystems.

Page 8-4 Figure 8.1-1: An air quality based estimate of total N and S form deposition may not be sufficient information to judge impacts on acid neutralizing capacity. A data layer on extant edaphic conditions is needed. The deposition metric should probably also be enhanced to allow for the estimation of biological immobilization (i.e., plant and microbial uptake of some fraction of the total deposition).

Page 8-5 lines 1 to 3: Plant uptake needs to be included in this list.

Page 8-28 lines 2 to 9: I don't agree with the assumption that annual accumulation of N inputs into wood increment can be ignored in this analysis. Except for low or no productivity ecosystems this is a significant sink for atmospheric N deposition that must be included in the calculation of N available for

other soil interactions.

Section 8. 4 is incomplete. More material is needed.

Attachment 3

Page 1 line 16: The phrase “a host of biogeochemical processes” is too vague. Please expand this concept.

Attachment 4

Pages 2 and 3: Table 1.1-1 is not filled in. The term forest health should be replaced.

Pages 12 and 13: Table 1.2-2 is not complete.

Page 31: The authors conclude that the simple mass balance method would be used in the REA. What caused the authors to exclude the dynamic model method? Lack of input data? Lack of validation?

Page 32: All evapotranspiration does not occur at the surface of the soil profile. Did the authors mean to imply evaporation alone?

Page 42 line 17: Is the nitrogen immobilization mentioned here microbe and plant or just microbe?

Figure 3.1-2 is missing units.

Page 53: The conclusions need work. The imbalances for Ca, Mg, and Al suggested for forest soils are for localized sensitive systems. As worded, the conclusions would be taken as a broad generalization for all US ecosystems.

Attachment 5: No comment

Attachment 6

Page 6: Table 1.2-2 is missing too much information to be fully evaluated.

The studies cited and discussed for the CSS system should be closely evaluated to determine which were based on manipulative studies capable of determining cause-and-effect relationships versus those that represent correlation studies for which relationships between known variables and measured responses were assumed to be viable explanations for adverse responses.

Studies highlighted in the ISA within Tables 3-15, 3-17, 3-18, and 3-19 might have a larger presence within the REA.

Figure 5.1-1 and -2: In my opinion the change in CSS seen in Figure -1 doesn't correlate very well with the dominant deposition patterns in -2. How well does N deposition really correlate with change? How much does land use change through time get in the way of the interpretation of N deposition cause and effects in this case study?

Page 46 lines 4 versus line 15: The conclusion of “compelling evidence” on line 4 does not seem to agree with the authors conclusion about the research still underway on line 15. A word change seems in order.

Page 47 line 5: Is a modification of a valued ecosystem an adverse effect?

Dale W. Johnson
24 Sept 2008

As has been my recurring theme in previous reviews, I am sorry to say that this document is unbalanced with respect to the effects of nitrogen deposition. It all boils down to a very simple set of facts: 1) most terrestrial ecosystems in the USA are nitrogen-deficient; therefore 2) increased inputs of N are likely to cause growth increases; 3) growth increases will almost certainly result in increases in carbon (C) sequestration, which in turn may have inadvertent benefits for the CO₂ / climate problem. This is not to diminish any statements about the negative effects of N deposition, it is simply to add balance to this document, which I believe it lacks. I am still sensing great resistance to any acknowledgement of these simple facts, and I believe that is a major mistake to ignore them in this and related documents. Specifically, it will provide an open invitation to those who want no pollution controls to claim bias and dismiss the true concerns over N-saturation and associated soil and water acidification as well as undesirable species changes such as described for the California Coastal Ecosystems in the Terrestrial Case Study section. Not to mention the basic scientific mandate we all have to treat this and all other subjects scientific in a completely objective manner.

Below are some specific comments, some editorial in nature, some technical in nature, and some where I see this lack of objectivity and balance. Following that I will address the specific questions assigned to me.

Specific comments:

p. 1-13, lines 4-7: This is a balanced statement – the review of effects should really flow from this approach, considering both increased productivity (which may be beneficial in some cases, detrimental in others) and increased soil acidity and eutrophication.

p. 1-15, line 14: 5.6 to 10 kg ha⁻¹ yr⁻¹? Can you really narrow this down to one decimal point?

p. 1-15, line 17: should include “and carbon sequestration” after “carbon cycling”.

0. 1-17, line 13: From a soils point of view, the effects of NO_x really cannot be readily distinguished from the effects due to total reactive nitrogen – both are transformed in the soil rather extensively.

p. 2-5, line 25: should add “timber production and carbon sequestration” after “water”. I note that timber production is mentioned page 2-7, lines 19-20, but only in the context of how soil acidification might negatively affect it. Soil acidification may well negatively affect timber production, and the latter statement should stay as it is, but increased N deposition will probably also increase timber production and this needs to be acknowledged. This is the kind of bias that is common in the document.

p. 2-9, line 27: should add “timber production and carbon sequestration” after “water quality”

Attachment 1, p. 3: I see Carbon Sequestration is listed as a potential section 6.3 – this is a good thing. Looking forward to seeing it.

Attachment 3, p. 1, lines 17-26: There needs to be a discussion of the effects of mineral acid anions on soil solution (what Reuss calls intensity effects, which can happen very quickly) in addition to the discussion of how they affect soils (capacity effects, which take a long time to occur). Reuss points out in his 1983 paper (Reuss, 1983) and in our small book (Reuss and Johnson, 1985), both of which are cited later in the Terrestrial Case Study, that Al^{3+} increases to the 3/2 power of Ca^{2+} , for example, as total mineral acid anion (e.g., nitrate and sulfate) concentrations increase, and this happens even if there is NO CHANGE IN THE SOIL AT ALL. Thus, if the soil is already acid, the introduction of mineral acid anions will cause the immediate mobilization of Al and acidification of soil solutions and probably surface waters long before any change in the soil takes place. Conversely, if the mineral acid anion concentrations are reduced, one should see a very rapid recovery. In short, the soil solution can change very quickly and almost independently of the soil, and this has major implications for the effects of N and S deposition on aquatic ecosystems.

Attachment 4, p. 1. lines 16-29: Same exact comment above applies here and in this case, our small book is cited as a source but only part of the story (the soil part, not the soil solution part) is reviewed. This is an important point – please include it in the next draft.

Attachment 4, p. 5, lines 10-17: Same comment as above here. It is not necessarily true that “inorganic Al does not become mobilized until after soil Ca is depleted” if the soil is already acidic, as many unpolluted soils indeed are.

Question 4 Response: The revisions have improved the characterization of adverse ecological effects, but I see no real consideration of the potential positive effects of N deposition as yet. Timber production is mentioned, but only in a negative context and I see little or nothing on C sequestration. The one pager for section 5 refers to case studies and gives no indication that this approach will be changed.

Question 4b: I see no discussion on effects on carbon budgeting as yet – have I missed something? I do see Carbon Sequestration is listed as a potential section 6.3 – this is a good thing. Looking forward to seeing it.

Review of “The Risk and Exposure Assessment for Review of the Secondary National Ambient Air Quality Standards for Oxides of Nitrogen and Oxides of Sulfur, First Draft”

Chapters 7 and 8 (Sent 19 Sept 2008)

Chapter 7: We are asked if the approach is technically sound to consider “ecologically adverse effects”. For the most part, yes, it is. However, once again, I note that this section focuses entirely on negative effects of N. Once again, this document should also consider cases where increased production could be a positive effect – such as on timber production and C sequestration.

p. 7-1, lines 21-27: This is a real mouthful. Can it be simplified and broken into at least two sentences?

p. 7-3, line 12: Why “inorganic and mineral acids”? They are basically the same thing.

Section 7.1.4:

Chapter 8: Many questions are posed to the panel here and I will not repeat them. I had problems with the conceptual framework for the calculations, as noted below.

Section 8.3.3: I had a very difficult time following this section and do feel like I ought to be able to. It would help a great deal if units could be specified in the various equations and the assumptions were clearly spelled out in the beginning. For example, is it assumed that base cation concentrations will remain at pre-industrial levels? The equations would suggest so, as would the statement on p. 8-29, lines 13-15. I cannot really agree with the assumption state here that “pre-industrial base cation concentrations effectively set the long-term capacity of the catchment to neutralize acidic deposition because it represents the only source of base cation input that is sustainable over the long-term”. For one thing, soils in humid regions always naturally acidify and therefore there is no long-term steady state base cation flux until soils become extremely acidic– it is always slowly decreasing. I also think that the implicit assumption here that base cation concentrations in streams will not increase over the long-term in response to acidic inputs is flawed – some soils have a very large exchangeable base cation pool and could buffer such inputs for a much longer term than the typical attention span of scientists and policy makers, let alone the public.

p. 8-29, lines 18-19: This statement makes no sense. At steady state, the leaching rate of base cations is, by definition, equal to weathering inputs, not “at lesser or greater rates”.

Dr. Dale W. Johnson

This draft is an improvement in some ways but I believe that it remains biased against showing any possibility of beneficial effects of N deposition and I continue to believe that this is a grave mistake. It now contains detailed descriptions of N and S cycles and recognized the fact that nitrogen (but not sulfur) is often a limiting nutrient. It now considers the potential for N deposition to enhance production and C sequestration specifically within the body of the text – and then summarily dismisses such a possibility and mentions nothing of it in summary statements. The authors clearly do not accept the possibility that N deposition can have any beneficial effects and I cannot force them to do so – I am a reviewer, not a censor. However, I will continue to voice my disagreement when asked for a review.

Curiously, it appears that the treatment of the potential benefits of sulfur are discussed much more extensively than those for nitrogen (although I fully recognize that N deposition is probably not important for crop systems, given how much they are fertilized).

Specific comments:

p. 3-7, lines 1-3: In addition to these studies, are the very detailed studies of Richter and Markewitz (2001) which show long-term soil acidification due to both tree uptake and atmospheric deposition. The fourth resampling of Walker Branch Watershed will also soon be published (Johnson et al., 2008) and I will send a copy. It documents continued declines in exchangeable Ca^{2+} and Mg^{2+} with the exception of cases where decomposing logs enrich Ca^{2+} . The Ca declines are attributed mostly to uptake where the Mg^{2+} declines attributed mostly to leaching, augmented by acid deposition.

p. 3-12: I do not think the study by Bailey et al is by any means the most thorough resampling study in the US. The Richer and Markewitz study is much more comprehensive and detailed, and fully deals with the causes of soil change in a quantitative manner, which the Bailey study does not. As noted in my last review, while Bailey did evaluate the role of uptake in causing the soil changes they observed, they have grossly overestimated the potential role of acidic deposition in the soil changes they observed – it would have taken a prolonged S deposition rate of something like $200 \text{ kg ha}^{-1} \text{ yr}^{-1}$ for many decades, for example, to produce such changes as they saw in some cases. It is simply not logical to blame acidic deposition for that magnitude of change. I wrote a letter to the editor on this (Johnson, D.W. 2006. Comments on “Thirty years of change in forest soils of the Allegheny Plateau, Pennsylvania.” *Soil Sci. Soc. Amer. J.* 69: 2077.), to which they responded, which the authors of this document should look at if they intend to highlight the Bailey studies as hallmark studies showing soil acidification by acid deposition. I noted this in my last review of this document, but this comment was apparently overlooked. The authors may choose to dismiss my letter and accept Bailey’s conclusions, but they should at least acknowledge the controversy.

p. 3-13, line 33 to p. 3-14, line 1: Once acidified, it is unlikely that Al levels in soils will decline again unless the soils are limed.

p. 3-26, lines 6-12: What about the effects of N on N-deficient systems?

p. 3-43, line 5: The base cation decline could be explained as a simple consequence of charge balance.

p. 3-75, lines 1-17: This is amazing. So we do not even know if our forests are growing at a faster or a slower rate. A fundamental piece of knowledge that is missing while we speculate about all these negative effects.

p. 3-104, lines 17-23: The beginning of this paragraph acknowledges that N can be both beneficial and detrimental – so I would add to the end of it something like the following: “ or on the other hand, improved forest health by alleviation of N deficiency, increased productivity and C sequestration”.

p. 3-115: Good segment on disturbance – there are also many other references on the effects of fire, including effects on water quality – see references below.

p. 3-131, lines 1-11: It is very common in commercial fertilizer studies as well as pollution N addition studies for trees to take up only a fraction of applied N unless it is applied to foliage. Even so, as noted on lines 9-11, growth increases to this uptake are common.

p. 3-133, lines 1-8: This paragraph, in my view, is biased. Of course when you add a limiting nutrient you will run up against the next limiting nutrient – this is very well known. Is this then a wholly bad thing or was the addition of the limiting nutrient “good” to start with? This seems like a blind focus on the negative to me. Why is that.

p. 3-133, lines 9-12 through p. 3-133, lines 1-10: Again, I see unnecessary bias here. By my reading, there were 6 positive responses to N listed in Table 3-15, and some were at the “moderate to high” levels of N addition. I count three negative responses, including the one by McNulty which is so prominently highlighted, and three which showed both positive and negative responses, depending on time and which species was being looked at. AND, I will wager that if you included fertilization studies in commercial, fast-growing forests, you would find a very high proportion of positive growth responses indeed.

p. 3-135, Regional Trends.... It is a shame that we do not have the data to know whether forest growth has increased, decreased, or stayed the same from the forest inventory system. The Europeans have this, yet we seem not to. That being the case, apparently, I do not find this segment particularly illuminating, although it may be the best we can do.

p. 3-136, lines 3-17: I am glad that the authors included a discussion of the Magnini paper – even though they do dismiss it rather easily. I am not sure I agree with that – nitrogen is, as is acknowledged in this document – a limiting nutrient and it seems highly probable that adding it will cause increased growth. I do not understand why there is such resistance to this concept, but the authors opinions obviously differ from mine. At least it was discussed.

p. 3-162, Trees: Again, the view here is that there is nothing good about “altered growth rates”. Can’t altered growth rates be a “good” thing if they are in the positive direction and in, for example, commercial forests? Does this not bear even the slightest mention?

3-163 to 3-175: A very good review of N effects from the pollutant point of view. Do traditional forest fertilization studies tell us anything more?

3-164 Grasslands: It would be good to mention the cheatgrass issue in the Great Basin here. Cheatgrass is a nitrophile and increased N deposition will undoubtedly facilitate the spread of this noxious species also.

p. 3-191, line 13: I would add “increased growth” after “sensitive”

p. 3-206, lines 4 and 8-18: “forest yields” is mention in the headlines, but no mention of increased timber yield is mentioned in the following paragraph – all is negative. Why is this.

p. 3-212 to 3-218: A very good, thorough and objective treatment of sulfur.

General References

Johnson, D.W., D.E. Todd, C.F. Trettin, and P.J. Mulholland. 2008. Changes in Soil Exchangeable K^+ , Ca^{2+} , and Mg^{2+} in Forests of Walker Branch Watershed, 1972-2004. *Soil Sci. Soc. Amer. J.* (in press)

Richter, D.D., and D. Markewitz. 2001. *Understanding Soil Change: Soil Sustainability over Millennia, Centuries, and Decades.* Cambridge University Press. 255p

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Trettin, C.A., D.W. Johnson, and D.E. Todd, Jr. 1999. Forest nutrient and carbon pools: a 21-year assessment. *Soil Sci. Soc. Amer. J.* 63: 1436-1448.

References on the effects of fire:

Adams, M.A., Iser, J., Keleher, A.D., and D.C. Cheal. 1994. Nitrogen and phosphorus availability and the role of fire in heathlands at Wilsons Promontory. *Aust. J. Bot.* 42:269-281.

- Baird, M., Zabowski, D., and R.L. Everett. 1999. Wildfire effects on carbon and nitrogen in inland coniferous forests. *Plant Soil* 209:233-243.
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- Knight, H. 1966. Loss of nitrogen from the forest floor by burning. *For. Chron.* 42(2):149-152.
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- Raison, R.J. and J.W. McGarity. 1980. Some effects of plant ash on the chemical properties of soils and aqueous suspensions. *Plant Soil* 55:339-352.
- Rashid, G.H. 1987. Effects of fire on soil carbon and nitrogen in a Mediterranean oak forest of Algeria. *Plant Soil* 103:89-93.

Trabaud, L. 1994. The effect of fire on nutrient losses and cycling in a *Quercus coccifera* garrigue (southern France). *Oecologia*, 99: 379-386.

Williams, M.R. and J.M. Melack. 1997. Effects of prescribed burning and drought on the solute chemistry of mixed-conifer forest streams of the Sierra Nevada, California. *Biogeochem.* 225-253.

Dr. Donna Kenski

Overarching concerns: EPA staff have clearly made a great effort in pulling this document (and its companion ISA) together, and should be commended for the high-quality (and quantity) produced thus far. Nevertheless its current incomplete status and the pressing schedule make it hard to see how all the remaining tasks can be completed, and reviewed, in sufficient time to meet the predetermined deadlines. Staff and contractors to EPA need to be realistic in judging how much can really be done in the remaining months. If it is time to set priorities, perhaps that is something that can be discussed at this meeting.

The CAA requirement that the secondary standard be in the form of a concentration standard is going to require us to tolerate a much higher level of uncertainty than usual in the standard setting process, because of the need to employ multiple models to characterize the concentration-deposition-ecological effect-ecological indicator linkage. The REA in general needs to be much more comprehensive and transparent in describing the levels of uncertainty encountered at each of these steps and their impacts on overall uncertainty. For example, so much hinges on the CMAQ estimates of deposition, and yet there is little information given in the REA or the ISA on CMAQ performance. It seems from the ISA that CMAQ has really only been evaluated in terms of its annual estimates of aerosol deposition, and those are accurate to within a factor of 2. No CMAQ performance evaluation is given for deposition to specific locations, particularly locations that share characteristics of the sensitive areas focused on in this analysis. Likewise, none is given for measurements with a shorter time frame than annually.

Scope of the Review

- 1. Is the review appropriately focused in terms of the targeted effect variables and in terms of characterizing the important atmospheric and ecologic variables that influence deposition and ultimately the ecologic impacts of nitrogen and sulfur? Does the Panel have any further suggested refinements at this time?*

Generally, the review seemed to focus on appropriate variables, although as noted above, the complete scope may be too broad to accomplish before the court's deadline. The policy-relevant questions posed in Sec. 1.4 weren't actually addressed directly (perhaps it's still too soon, given the incomplete case studies) but I did note that questions 3 and 4 of that list (i.e., to what extent do receptor surfaces influence dry deposition, and can effects of NO_x be distinguished from effects due to total reactive nitrogen) did not seem to be discussed or addressed by any of the case studies Attachments 3-6, although Chap. 3 did present a nice graphical characterization of the areas and their relative proportions of NO_x vs total and other forms of N nitrogen. However, most of that was modeled data and little comparison to measured values was presented for comparison. Perhaps more of that is coming in the second draft, since there were lots of missing sections to Chap. 3.

Similarly, the list of issues on p. 1-20 should include evaluating the impacts of atmospheric deposition relative to other paths (nitrogen runoff from agricultural lands, for example). This might be what is meant by the last bullet, but it wasn't clear; perhaps it could be made more explicit.

Air Quality Analyses (Chapter 3)

1. *To what extent are the air quality characterizations and analyses presented in Chapter 3 technically sound, clearly communicated, appropriately characterized and relevant to the review of the NAAQS?*

The analyses in Chap. 3 could more accurately be described as modeled estimates of air quality, rather than air quality characterizations, which I think of as based on measured data. While the graphs were useful and logically presented, there was very little measured data given for comparison, so it is not possible to judge their 'soundness'. Combined with the lack of CMAQ validation discussion (mentioned above), it becomes more important to see these in the context of measured data as well. But this may be premature if the next draft is meant to include such comparisons.

I would have liked more discussion of the monthly patterns of deposition shown for example in Figs 3.2-14 through 3.2-19. Clearly wet deposition is driven largely by precipitation, but what drives the other components of deposition? Are these emission patterns or meteorological patterns or biological activity patterns? A minor complaint on the communication of the results: the color scheme for Figures like 3.2-6 etc. is not intuitive. The scheme used was almost a rainbow-like scale, which is easy to interpret and would have been fine, but instead green was sandwiched between yellow and orange, breaking the natural progression of colors (red -> orange -> yellow) that most of us have internalized and making it harder to visually establish a continuous gradient of concentration changes.

2. *Section 3.2.1 describes an approach for evaluating the spatial and temporal patterns for N and S deposition and associated ambient concentrations in the case study locations. This document includes the analysis for the Adirondacks case study. Does the Panel agree with this approach and should it be applied to the other case study areas?*

I do think it was a sound approach and a useful exercise that may give as clear a picture of deposition as we're likely to get. With the additions/changes noted above, I would welcome this analysis for the other areas.

3. *Section 3.2.2 describes the relative contributions of ambient emissions of nitrogen and ammonia to nitrogen deposition for the case study areas. To what extent is the approach taken technically sound, clearly communicated, and appropriately characterized?*

This was an interesting exercise that was very useful in establishing the relative importance of NO_x and NH₃ emissions to overall N deposition and the relative responsiveness of deposition to changes in emissions. It was very helpful to establish this kind of personal internal calibration in a strong visual way. Given the lack of spatial and temporal variability in the contributions of NO_x to oxidized N and NH₃ to reduced N, those maps probably don't need to be shown, just described instead. The results look perfectly logical and convincing, although I resist accepting these results completely until seeing further documentation of CMAQ's performance. The REA notes that the RSM has been validated for PM and O₃, but it's not clear whether that validation translates to deposition parameters as well. Presumably the missing section 3.2.2.5 on

uncertainty will address some of these issues. Again, as above, the color scale on all these plots is counterintuitive. Using the color red to depict no impact and green for 100% impact is contrary to general mapping conventions and at least in my case, caused me to continually misinterpret the plots.

Case Study Analyses (Attachments 2-6)

1. *Att. 2: Are the national geospatial datasets chosen adequate to identify sensitive areas? Are there other data sets that have not been identified by this analysis that we should consider? Does the panel agree with this approach or can they suggest alternatives?*

I have no knowledge of other datasets that could be useful to this effort. Some of the data were quite old (1971 for the range of red spruce) and caused me to wonder whether the range could have changed significantly in the intervening 37 years. Perhaps the authors could comment on the issues that might be affected by such old observations. Similarly, the dataset on acidophytic lichens was clearly not complete, or at least spatially representative, and impacts the results. One can't protect lichens that haven't been identified as sensitive, and the current map, which shows clusters of lichens within some states but none in neighboring states, strongly implies that some species have not been identified in those neighboring states.

2. *Att. 3: re MAGIC model to evaluate ANC levels in selected streams and lakes in Adirondacks and Shenandoahs. To what extent is the approach taken technically sound, clearly communicated, and appropriately characterized?*

This section was poorly written and extremely confusing, especially the modeling approach and description of MAGIC and ASTRAP. I think the dates given for scaling the historic data to deposition are wrong in several places, but the text was too convoluted to tell for sure. Also it would have been nice to see a map or at least a better description of how the ASTRAP sites are connected to the MAGIC sites. The classes and descriptions of ANC limits kept changing within the text and figures and should be made consistent. The discussions of critical load frequently mixed up the concepts of greater than-less than and above-below, adding to the confusion. It was very difficult to wade through the errors and try to make sense of what was really being accomplished here. The approach may be sound, but can't be assessed on the basis of what was presented. It was certainly not communicated or characterized in a satisfactory way.

3. *Att. 4: use of SMB model to evaluate current deposition on forest soil ANC for sugar maple in Kane Experimental Forest and red spruce in Hubbard Brook Experimental Forest. To what extent is the approach taken technically sound, clearly communicated, and appropriately characterized?*

The selection of the study area was reasonable and the description of the method was clear. Without results it's not possible to say too much more. The Table 3.1-2 had some numbers that need to be explained further, however. The range of critical N loads vary by a factor of 10 over the 3 study periods shown, and each of the methods gives very different results. Why the big difference? The text mentions biomass changes; is this the sole reason? Is this magnitude of change in biomass typical? How comparable are the methods? The text in Section 1.1.1 was unnecessarily repetitive and could be tightened up; no need to quote the ISA at such length.

4. *Att. 5: Aquatic nutrient enrichment—evaluate how changes in N deposition affect the eutrophication index in two estuaries: Chesapeake Bay and Pamlico Sound. To what extent is the approach taken technically sound, clearly communicated, and appropriately characterized?*
5. *Att. 6: Terrestrial nutrient enrichment—evaluate effects of N deposition on CSS community in California and mixed conifer forests in San Bernardino and Sierra Nevada Mountains. To what extent is the approach taken technically sound, clearly communicated, and appropriately characterized?*

Additional Effects (Chap. 6)

1. *Impacts of S deposition on Hg methylation, impacts of NO on climate change, and impact of N deposition on C sequestration. Are these effects sufficiently addressed in light of the focus of this review on the other targeted effects and in terms of the data available to analyze them?*

This seemed like an adequate review of these effects. The focus appropriately belongs on acidification and enrichment effects.

Synthesis and Integration of Case Study Results into the Standard Setting Process (Chap 7)

1. *Purpose is to summarize the case study results and characterize the relationship between levels of an ecological indicator and the associated degree of ecologically adverse effects. To what extent is the approach taken technically sound, clearly communicated, and appropriately characterized? Does the Panel have suggested refinements?*

I'm still uncertain about exactly how the case studies ultimately are used. Are they merely for scientific support and justification, or do the model results from them get incorporated eventually into a quantitative relationship that can be plugged into the framework presented in Chapter 8? I think my confusion stems from the incomplete nature of this chapter. When it is fleshed out in the next version with real data, the application of the case study results will be obvious.

Considerations in the Structure of the NO_x/Sox Secondary Standard (Chap 8)

1. *Is the suggested overall structural framework for a secondary standard technically sound and logically presented?*

The recently added Chapter 8 was very lucid and well written, presenting a helpful blueprint for how to move from ambient concentrations to possible secondary standard. I found no technical or logical fault in it.

2. *Is the description and development of the deposition transformation function (Fig 8.1.1) between air quality indicators and the deposition metric clear and technically sound?*
3. *Is the description and development of the ecological effect function (Fig. 8.1.1) between the deposition metric and the ecological indicator clear and technically sound?*

4. *Does the discussion adequately capture the potential use of categorical variables versus continuous variables when accounting for the variability of atmospheric, landscape, and ecological factors?*

These were all fine.

5. *Are there any key elements missing from the framework?*

There needs to be a more complete discussion of how a standard can accommodate geographic variation; i.e., how to equitably control NO_x and SO_x to adequately protect sensitive areas without overcontrolling in areas that are far less sensitive to acid deposition. Section 8.3.1 made reference to varying factors within the transformation function by location, and the fact that deposition loads will vary by location, but it was not clear from the text how this translates to variation in the standard. It seems that the standard must account for different concentrations in different regions, but how that is specified is still pretty fuzzy.

Another big piece that is missing is the discussion of CMAQ (or other model) uncertainties. It was interesting that this is the first place in the REA (Sec. 8.3.2.1.2) where CMAQ performance evaluation (or the lack thereof) is mentioned. Given the very heavy reliance of the REA analyses on CMAQ (a necessary reliance, admittedly), it is critical to have its performance characterized as thoroughly as possible so that the Administrator and others can assess a proposed standard's potential for success.

Section 8.3.2.2.2 leaves aggregation methodology as an open research issue. Does this mean it will be resolved in the next draft by work the staff is doing? If not what are the implications of leaving this issue unresolved?

6. *Does the framework need to be expanded or revised to accommodate the appropriate consideration of ecological indicators besides ANC when developing a secondary NAAQS for NO_x and SO_x*

Isn't that the point of the case studies? It seems premature to answer this question until those results are complete. ANC seems adequate for acidification effects.

7. *Does the panel have any further suggested refinements at this time?*

Section 8.3.2.4 needs additional attention. It mentions possible work on MCIP and CMAQ to incorporate measurements, which would be great and I highly encourage. But is it really possible to produce results and incorporate them into the next draft?

Section 8.3.3 on the deposition-indicator links could benefit from a discussion of how influential the various parameters are on the outcome, at least in a qualitative sense. It would help the reader (and presumably the Administrator) evaluate which are the critical parameters controlling the relationship.

Specific comments, typos, etc.:

p. 3-3, Fig 3.1.2 (also Fig 3.1-5) Avoid use of pie charts, as they make it difficult to make quantitative comparisons. Bar charts are almost always preferable. The use of 3-D unnecessarily complicates these figures and also makes it more difficult to visually compare the slices of the pies.

p. 3-4, lines 12-13: Fig. 3.1-4 actually shows facilities, not annual emissions by state.

p. 3-6, lines 14-16: Is the NEI fire inventory error corrected here? If not, a statement about the correct magnitude of fire emissions should be added.

p. 3-8, line 9: Figure 3.1-6 shows total N deposition in Ohio and Pennsylvania of >20 kg/ha/yr, definitely much more than the 9.2-9.6 kg/ha/yr cited here. Which is correct? This and the following figs 3.1-7,8,and 9 are nice but the colors are difficult to distinguish in the printed version.

p. 3-50, line 1: ARD -> ADR

p. 3-57, line 10: remove question mark

p. 6-7 caption to Fig. 6.1-3: watershed should be plural

p. 6-18, line 6: Not clear what 'further stabilizing soil carbon compounds' actually means. Do they then have longer lifetimes?

p. 6-23, line 12: Onondagal ->Onondaga

p. 7-1, line 28: area should be plural

p. 8-14: Equation numbers don't follow the text

Attachment 2, p. 2, line 14: remove 'is'

Attachment 2, p. 3, line 19: is this really 51 inches, or should it be cm, as 4.1.11 says about this same dataset?

Attachment 2, p. 7, line 17: remove 'Sulfur Containing'

Attachment 2, p. 7, line 26: remove 'Nitrogen Containing Chemical Species'

Attachment 2, p. 8, line 9: remove 'deposited'

Attachment 2, p. 11, line 8: remove 'Nitrogen Containing Chemical Species'

Attachment 2, p. 11, line 18: Containing -> Including

Attachment 2, p. 16, line 4: remove meter

Attachment 3: fix the subscripts and superscripts throughout. Too many grammar errors and typos to enumerate here – this whole section needs careful editing.

Attachment 3, p. 6, line 24: deposition is more like 17 and 13 kg/ha according to the Figure 3.1-1, not 15 and 10.

Attachment 3, p. 8, line 4: deposition is more like 18 and 11 kg/ha according to Fig. 3.2-1. This makes me distrust the % declines in these species, here and on p. 6, but I didn't recalculate them.

Attachment 3, p. 12, Fig. caption: 12 streams are shown, not 13. Lots of other typos in this caption.

Attachment 3, p. 16, line 26: >50 should be <50

Attachment 3, p. 17, lines 6-8: Fig. 4.1-2 doesn't imply that biota are not often harmed below and ANC of 100, only that the harm is less severe than for lower ANC

Attachment 3, p. 17, line 12: It doesn't make sense to say that an ANC of 0 protects surface waters from becoming acidic. waterbody

Attachment 3, p. 17, line 17: change 'deposition – critical load' to 'deposition less than critical load'

Attachment 4, p. 1, line 6: should be 'sulfur loads *to* and effects *on* a chosen...'

Attachment 4, p. 10, line 4: on -> at

Attachment 4, p. 11, line 16: not clear, reword

Attachment 4, p. 11, lines 21-22: not clear, reword

Attachment 4, p. 23, line 22: HBEF

Attachment 4, p. 25, line 8: litterfall

Attachment 4, p. 33, line 17: put weathering on its own line

Attachment 4, p. 38, line 13: Arrhenius

Attachment 4, p. 48 and 49: It would be helpful for these figures to include the HBEF as well; its very hard to place it accurately given the map on p. 21

Dr. Naresh Kumar

SECTION 6.1 SULFUR AND MERCURY METHYLATION

GENERAL COMMENTS

The section begins with a segment on the chemistry and physics of mercury atmospheric transport, fate, and deposition, followed by a more detailed segment discussing the chemical determinants of mercury methylation.

The two segments of the section differ greatly in their accuracy, completeness, and understanding of mercury chemistry and environmental behavior. While the second part, on mercury methylation specifically, is generally complete and accurate, the first, background, segment has a number of factual errors, misinterpretations, and erroneous conclusions in it.

As two examples, the first segment presents an erroneous picture of the behavior of elemental mercury (or Hg^0) in the environment, and of “methylmercury” (dimethylmercuric salts) in organisms. In the first case, Hg^0 is presented as being “reduced” in surface ecosystems to become methylmercury; in reality, Hg^0 is the reduced form, and plays no part in methylation, which occurs through bacterial action on the oxidized form, divalent mercury (or Hg^{+2} in the text). In the second case, methylmercury is openly stated to be “lipophilic,” or preferentially attached to fatty tissues in fauna, when in fact methylmercury is lipophobic and associated with protein sulfhydryl groups, in muscle tissue.

The entire section need to be thoroughly reviewed and rewritten from the beginning to more accurately reflect our basic understanding of mercury chemistry, transport, and fate in the environment. Specific comments on the text follow.

SPECIFIC COMMENTS

- To date, there has been *no* unequivocal demonstration of sulfate limitation in US or global waterways such that natural sulfate addition or subtraction alone has produced a change in methylation rates or mercury in fish. Such demonstrations have occurred only in experimental manipulations of microcosm ecosystems. Since fish take up only a fraction of the methylmercury in the water column and biota of lower trophic levels, there is always an excess of MeHg in studied water bodies. And downtrends in sulfate addition have always been matched by downtrends in divalent mercury deposition, so that it is not possible to separate sulfate availability from divalent mercury burden.
- It is mentioned that “*Mercury concentrations have increased approximately 2 to 5 times since the onset of the industrial revolution and appear in even the most remote locations on the Earth (Munthe et al., 2007; U.S. EPA, 2006).*” The accepted global average ratio of atmospheric mercury mass now compared to the period prior to the Industrial

Revolution is in the range of 2 to 3, not 2 to 5. Ratios higher than 3 can be found in local, single-instance measurements of concentrations in, e.g., an ice core, but these are characteristic of individual locations and not the global balance of mercury.

- It is stated in the text that “*In the United States, the primary source of mercury to ecosystems is atmospheric deposition due to coal combustion (e.g., coal-fired electric utilities). Other sources include municipal waste combustion, medical waste incineration, chlor-alkali plants, and industrial boilers.*” This sentence appears to propagate the common misconception that mercury emissions (anywhere) are proportioned exactly the same as mercury deposition (anywhere else). This is obviously incorrect, since both total and wet deposition of mercury at any location on earth (or in the United States) is made up of contributions from hundreds of sources at widely varying distances upwind, and is not linearly proportional to the fraction of total emissions each source, or source type, makes up. Therefore, it should be noted that a significant amount of mercury depositing within the United States originates in other countries, primarily mainland Asia. The sources of mercury depositing to U.S. ecosystems varies widely, both geographically and by source, depending on the proximity of U.S. sources and the precipitation climatology of the setting.
- It is mentioned that, “*Depending on the particulate association and oxidation state, atmospheric mercury particles can remain suspended in the atmosphere for more than 2 years (Evers et al., 2007; U.S. EPA, 2006).*” This sentence should be rewritten or *deleted*. There is no relation between “particulate association” (an unexplained term) and oxidation state for mercury; most of the mercury bound to particles is divalent mercury (or “ Hg^{+2} ” as used in the report). But the statement that such particle-bound mercury has an atmospheric lifetime of more than 2 years is not true; due to gravitational settling, coagulation, etc., Hg_p has an average lifetime in the atmosphere of several days to about two weeks, no more. And no source of mercury emissions to the atmosphere issues more than about 3% of mercury mass in the form of particle-bound mercury, in any case. It is suggested inserting something like this: “*There are three primary forms of mercury in atmospheric sources of the substance: elemental mercury, reactive gaseous mercury, and particle-bound mercury. Once emitted, the three forms behave very differently in the atmosphere and deposit over very different geographic patterns. It generally takes hundreds or thousands of miles for half of the emitted gaseous elemental mercury to deposit to ground level, while half of the reactive gaseous mercury will deposit within about 150 miles of the source. Particulate-bound mercury, generally 3 percent or less of the emitted mercury mass, deposits in intermediate patterns (M. Cohen, 2004).*”
- The text states that, “*When deposited into terrestrial and aquatic ecosystems, elemental mercury is oxidized to reactive mercury (Hg^{+2}) (Ambrose et al., 2005; U.S. EPA, 2006).*” A number of statements need to be corrected or nuanced in this passage. Any “deposition”

of elemental mercury occurs by gas-phase transfer at ground level from regions of higher concentration (that is, the atmosphere) to regions of lower concentration (to plant stomata, soil pores, interstitial spaces, etc.), basically a down-gradient mass transfer. There is nearly no oxidation of elemental mercury to the divalent form occurring at the ground surface; more likely is removal of elemental mercury back to the atmosphere by revolatilization, or evasion. There may also be a net output of elemental mercury from the surface by insolation (solar radiation) producing photoreduction of divalent mercury, or demethylation and photoreduction of monomethylmercuric halides.

- The entire sentence where methylmercury is stated to be “lipophilic” needs to be corrected. First, mercury cannot be “reduced and methylated to methylmercury”; the reduced form of mercury is the insoluble elemental mercury, Hg^0 ; because of its insolubility in water, it is unavailable to sulfate-reducing bacteria for the methylation process. Of the “deposited mercury pool,” typically half or more is (wet-deposited) divalent mercury, most of the remainder dry-deposited elemental mercury; of the amount of divalent mercury dissolving in water bodies, between 1% and 10% may be methylated and dissolved in the water column. Of this 1% to 10% (depending on the particular water chemistry; higher fractions for more anoxic waterways), perhaps 10% of that (or 0.1% to 1% of the dissolved divalent mercury) may be taken up into the food web. Second, mercury is most certainly *NOT* lipophilic, but rather *lipophobic*: it attaches to protein-based sulfhydryl groups and resides primarily in muscle and nerve tissue (“fish flesh”). This distinction is important because it is the root of the finding that cooking fish which may be mercury-laden will in fact not decrease, but increase, the concentration of the mercury in the cooked product. Any fat that is cooked off is mercury-free, and the lower weight cooked fish remaining has the same mass of mercury as prior to cooking, but in a lower-weight portion of fish (with some fat and water mass cooked off), hence higher net mercury concentration.
- There seems to be a faulty reference in the sentence “*The majority of U.S. waters are sulfate-limited (Harmon et al., 2007); therefore, decreases in sulfate are likely to promote decreases in methylmercury.*” Harmon et al., 2007, “Using Sulfate-Amended Sediment Slurry Batch Reactors to Evaluate Mercury Methylation,” *Arch. Environ. Contam. Toxicol.* 52, 326–331 (2007); [DOI: 10.1007/s00244-006-0071-x] does not have a single word to say about sulfate-limited waterways. The term “-limited,” in fact, occurs only once in the document, in the introduction, with no reference to the state of U.S. waters.

Mr. Richard Poirot

These comments pertain primarily to REA Chapter 3 (Sources, Ambient Concentrations, and Deposition), for which the following charge questions were provided.

Question 1: To What Extent are the air quality characterizations and analyses presented in chapter 3 technically sound, clearly communicated, appropriately characterized, and relevant to the secondary NAAQS for NO_x and SO_x?

Question 2: Section 3.2.1 describes an approach for evaluating the spatial and temporal patterns for nitrogen and sulfur deposition and associated ambient concentrations in the case study locations. This draft document includes the analysis for the Adirondacks Case Study. Does the Panel agree with this approach and should it be applied to the other Case- Study Areas?

Question 3: Section 3.2.2 describes the relative contributions of ambient emissions of nitrogen and ammonia to nitrogen deposition for the case-study areas. To what extent is the approach taken technically sound, clearly communicated, and appropriately characterized?

Assuming the many and important missing “placeholder” sections are filled in, I think the air quality characterizations and analyses presented in chapter 3 will provide a technically sound, clearly communicated, appropriately characterized, and relevant to the secondary NAAQS for NO_x and SO_x (although it still remains unclear to me what kind of 2ndary standards are being contemplated). Many of these placeholders refer to evaluations of model performance, and since the majority of the chapter consists of presentation of intensively graphical model results, filling the placeholders will be key to providing confidence in the model results. The technical approach appears to be reasonable, but without a better sense of model performance (including both CMAQ and the RSM meta-model), the technical soundness and relevance to NAAQS can't really be evaluated.

The presentation of the information is clear (even beautiful), but there is minimal discussion or interpretation of the graphical results, which makes it difficult to maintain interest in looking so many pictures. Conversely, it might be informative to poll the model results in ways that might provide a better understanding of relationships among the various metrics of air quality, deposition and environmental effects. For example: what would the maps look like that show the ratios of S deposition to S emissions; N (oxidized) deposition to N (oxidized) emissions; N (reduced) deposition to N (reduced) emissions. What would maps look like that show ratios of S (or N) deposition to ambient SO₂ (or NO₂) concentrations? What if modeled S emissions were rolled back to show alternate lower maximum levels of SO₂ (and/or NO₂) – what would be the subsequent changes in S (and/or N) deposition in sensitive downwind areas? If sections of the Adirondacks were considered to be experiencing adverse levels of acidifying deposition, how could the models be used to determine the “significant contributing area” – or perhaps some combination of emission size, and frequency upwind – such that a non-attainment area might be defined to better include the contributing emissions? A possible approach for an improved

secondary SO_x or NO_x NAAQS might consider (much) lower levels but averaged over larger areas or longer averaging times.

With the caveat that the model performance needs to be more clearly examined and documented, I think the more detailed approach applied here for the Adirondack case study is reasonable, and could be applied to other case study areas. One possible concern – possibly more relevant to the Adirondacks than to most of the other case study areas – is whether the 12 km gridding might be coarse relative to the spatial variability in deposition, terrestrial & aquatic ecosystems and associated effects. Potentially the larger grid cells may fail to adequately capture orographic increases in precip volume & deposition and the additional increases from occult deposition at highest elevations (or in certain coastal areas) – in comparison with variations in sensitive terrestrial and aquatic biota within these grid cells. See for example: Miller, E.K. et al. 1993. Atmospheric deposition to forests along an elevational gradient at Whiteface Mountain, NY USA. *Atmos. Environ.* 27A:2121-2136.

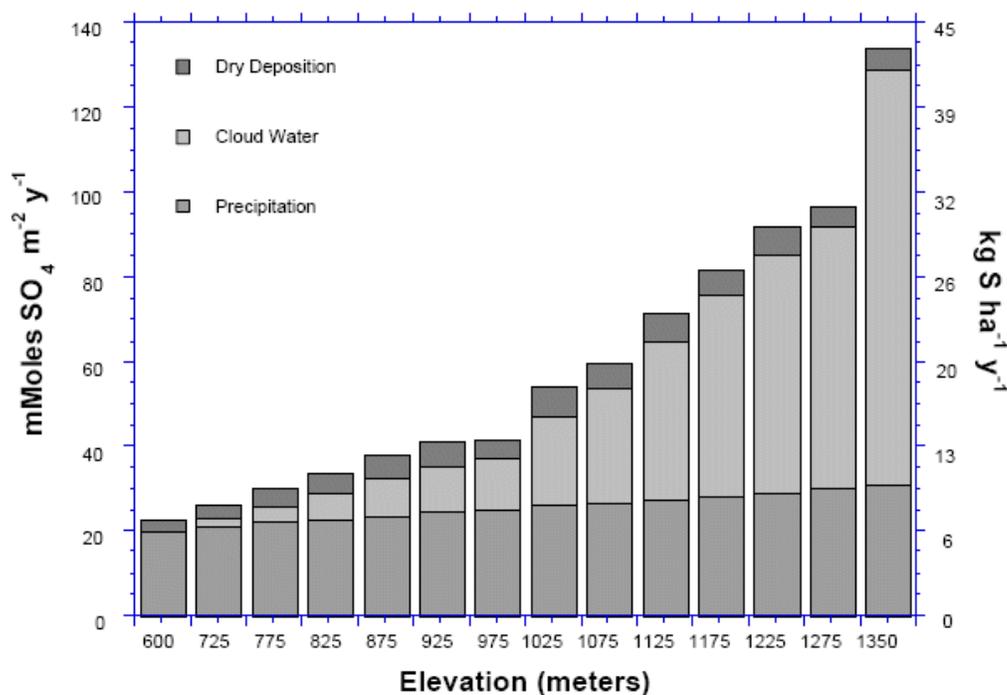


Figure 1. Variation in wet, dry, cloud, and total sulfur deposition over ~2km ground distance as a function of elevation on Whiteface Mt., NY, 1986-1989 (from Miller et al. 1993).

Possibly this influence of occasionally large terrain, deposition and species variations within the relatively large grid cells could be evaluated by conducting a higher resolution sensitivity analyses within selected grid cells in the Adirondacks case study area. Alternatively, it might at least be possible to disaggregate the coarser modeled dry dep. estimates to combine with the higher resolution wet dep. estimates from the Grimm & Lynch approach. Arguably the dry dep totals and variability may be less important than wet dep at more remote receptor locations. Possibly also a terrain-based cloud deposition model could be added to provide added detail for higher elevations or in coastal areas.

Regarding the soundness of the technical modeling approach to estimate the relative contributions of ambient emissions of oxidized and reduced nitrogen to nitrogen deposition for the case-study areas – the approach seems sound but again there is a need to evaluate the performance of the models (CMAQ + RSM). Trust but verify. This evaluation could/should extend where possible to subcomponents of the models such as emissions inputs and space/time patterns of modeled estimates of wet oxidized N and wet reduced N deposition.

That being said, I do like the approach of directly linking the estimates of changes in Nr deposition to changes in specific emission sources. I would think a similar approach could also be taken to zero out and otherwise reduce SOx emissions from different source categories. Down the road, this may allow a bundling & comparing of projected “optional” future emission controls (small, medium, large, etc.) to desired reductions in deposition in sensitive areas, in comparison to the associated concentrations in atmospheric NOx & SOx concentrations (in the event the layers say we have to stick with the traditional indicators). What new NAAQS limits of these indicators (perhaps averaged over larger - or much larger - areas than single monitors) would be necessary to achieve the desired reductions of Nr and/or S deposition in sensitive areas?

In addition, if you were to add various levels of SOx (and NOx) emission reductions to your modeled scenarios, it would be a snap to calculate and display the resulting changes in sulfate and nitrate aerosols (and in their visibility effects) that would result from any changes in S & N emissions or deposition or SO₂ & NO₂ concentrations. This would allow you to (a) consider a more complete set of welfare benefits that would result from any revised NAAQS based on deposition effects and/or (b) might lead to and help justify alternative ambient air indicators – for example the sum of total atmospheric oxidized S and N compounds (sum in ug/m³ of S from SO₂ and pSO₄ and N from NO, NO₂, HNO₃, and pNO₃ or somesuch) – that might not be considered if only deposition-related effects are considered, but which might, set at the right levels, result in large deposition-related benefits.

Other Minor Comments:

p. 3-1 lines 16-23: This is a good example of what seems like an intentional sense of vagueness regarding which pollutants and secondary transformation products are or are not the subject of this review, and/or available as potential indicators for secondary NAAQS. Why are nitric acid and PNO₃ considered part of “NOx”, while SOx includes only gaseous SO₂?

p. 3-4, Figure 3.1-3: This figure just doesn’t look right – and seems inconsistent with the reduced nitrogen deposition map in Figure 3.1-8 on p. 3-11.

p. 3-4, lines 3-5: Does confined feeding really increase animal wastes, or does it just increase atmospheric emissions from them?

p. 3-4, line 12: Figure 3.1-4 does not show annual 2002 SO₂ emissions “by state”.

p. 3-5, line 4: I would change “Industrial” to “Anthropogenic”.

p. 3-5, lines 10-15: Should marine DMS emissions be mentioned here?

p. 3-6, lines 14-16: Can you provide any quantitative indication of how large these fire SO₂ emission underestimates are?

p. 3-8, lines 5-7: Does this increased deposition of reduced nitrogen also pertain over the 100-year period of the preceding sentence. Can you say something more precise about trends over the past several decades?

p. 3-12, lines 10-14: This description relates to how NADP interpolates its wet deposition data. However, later you indicate using the precip-volume-enhanced estimates from Grimm & Lynch (2004). So which was it? One general concern is that the 12 km gridding may overly smooth some of the more extreme orographic increases in precip – and you seem to exclude cloud water deposition. Possibly this could be handled by conducting some sensitivity analyses for grid cells containing higher elevation terrain – especially for the Adirondack and Shenandoah case studies.

p. 3-16, line 11: Why not also describe CASTNet (& AIRMoN dry) data for HNO₃, NO₃, NH₄, SO₄?

p. 3-23, lines 4&5 and lines 11&12: say roughly the same thing twice.

p. 3-23, line 7: “(25% wet vs. 6% dry)” and 69% what?

p. 3-23, line 12: Change “does” to “do”.

p. 3-54, line 17: You could add “current and historical” before “atmospheric deposition”.

p. 3-55, lines 20-21: Can you provide any indication of if and how well the RSM technique (and for that matter the underlying CMAQ model) works for all the SO_x, NO_x and reduced N species you will use it for?

p. 3-57, line 5: Am I missing something or did you only use a couple (zero-outs) of these 210 control runs? So what was the purpose of the other runs?

p. 3-71, line 8: Delete one “deposition” in “greater deposition of oxidized nitrogen deposition”.

p. 3-71, lines 8-15: I would think formation of aerosol NH₄NO₃ would tend to increase the transport distance, but would not lead to any net decrease or increase in Nr deposition. It all gets deposited eventually. An exception might be if aerosols persist long enough to transport out of the (US or North American) domain.

p. 3-73: I must have blinked somewhere, because I didn’t expect to see this large, international “sugar maple case study” area discussed npreviously. Its not listed as a “Case Study Location” in Table 2.1-1 on page 2-2&3. It reminds me to ask for a clearer “up-front” description (& map) of all the intended case study areas.

Mr. David Shaw

General Comments

Thank you for addressing the outcome of this REA. I believe that this makes the document more focused.

I still feel that a specific goal of this assessment should be to identify and report sensitive areas which do not have adequate monitoring. Adopting this longer view in this analysis will enable the next review process to start from a stronger point. In identifying areas without adequate monitoring data, we may be able to start the process of getting a stronger data record of results for future analysis. It is my hope that this will lead to better modeling due to better data.

While there are certainly areas that are deficient in monitoring data, there definitely are areas of strong monitoring data with analysis. I still feel that the areas of certainty do not receive equal treatment as uncertainty. I feel we must be clear that we do understand causes, effects and variability in our ecosystem response.

On this note, the analyses presented in Chapter 3 of the REA rely heavily on modeling and don't always reinforce where the measurements are the strongest. It is important to emphasize where we have the most confidence (e.g. wet deposition, ANC measurements in case study areas) and the least confidence (e.g. air concentrations and dry deposition of NO_x/SO_x, where measurements are lacking). Much of the information on dry deposition will come from CMAQ, and the measured data from CASTNet and other special studies could be used to assess the model at selected locations.

Charge Questions

Scope of the Review – Question 1

Chapters 1 and 2 provide the background, history, and the framework for this review, including a discussion of our focus on the four key ecological effect areas (aquatic acidification, terrestrial acidification, aquatic nutrient enrichment, terrestrial nutrient enrichment). Is this review appropriately focused in terms of the targeted areas and in terms of characterizing the important atmospheric and ecologic variables that influence the deposition and, ultimately, the ecologic impacts of nitrogen and sulfur? Does the Panel have any further suggested refinements at this time?

Pages 1- 1 to 1-10:

I feel that this gives good overall information on the Rational, Background and History. It might also be a good place to address other pollutants associated with NO_x and SO_x analyzing the whole set of problems associated with these pollutants.

Page 1-8 lines 3-5:

Lines 3-5 state that 'in spite of the complexities and uncertainties....' it became clear that a program to address acid rain was needed. In actuality, it was the evidence of a preponderance of the scientific data of the NAPAP effort which made it clear that an acid rain program was

needed. This builds on one of my general comments regarding an emphasis on uncertainty rather than giving equal treatment to those areas where certainty exists.

Page 1-16:

I would recommend adding a discussion on critical loads as the organizing principle of this RAE assessment. Include the current understanding of ecological indicators and how levels of the proposed standard will be integrated.

Page 1-20:

It would be helpful to explain how the existing monitoring data will be used to evaluate the success of the proposed standard? How and when will the existing monitoring networks be evaluated for adequacy of measuring ecosystem response?

Page 2-10:

I appreciate the effort in adding sulfur and mercury methylation. The fact that it will be addressed will make this a stronger analysis.

Page 2-11, Table 2.3-1:

I feel that it would be beneficial to add to Cultural Services “chemical and biological degradation of Constitutionally (federal and states) protected Wilderness areas”. This would apply to several if not all Targeted Effect Areas. The point being that the ADK case study area, for example, represents a 6 million acre region, 43% of which is protected by the NYS Constitution as ‘forever wild’ Forest Preserve. Here, tree cutting is not allowed, yet atmospheric deposition damages forests and diminishes aquatic ecosystems within these forests. The remaining 57% is devoted principally to forestry, agriculture, and open-space recreation, a portion of which is sensitive to negative effects of atmospheric deposition. This landscape holds an additional cultural value to New Yorkers especially, and to others from the US and around the world.

Pg 2-12:

In the box where “provisioning services” and “cultural services” for Sulfur and Mercury Methylation are provided, fish kills is listed as an ecological impact. From the literature that I am familiar with, fish kills or declines in fish populations are not a good indicator of MeHg, however, declines in the success of species higher in the food web such as loons and humans occur because of MeHg neuron toxic effects and bio accumulation.

Air Quality Analysis

Question 1

To what extent are the air quality characterizations and analyses presented in Chapter 3 technically sound, clearly communicated, appropriately characterized, and relevant to the review of the secondary NAAQS for NO_x and SO_x?

Sections 3.1.4 and 3.2:

It seems as if the dataset discussion (Section 3.2) would be more beneficial if it appeared before the composite deposition maps (Section 3.1.4). These composite maps consist of modeled dry and measured/interpolated wet deposition. For these maps, are the units actually kg ha⁻¹ y⁻¹, or

are they $\text{kg N ha}^{-1} \text{y}^{-1}$ and $\text{kg S ha}^{-1} \text{y}^{-1}$? Some mention should be made that the dry deposition estimates are generally consistent with whatever measurements (e.g. CASTNet) are available, that one year of modeling is adequate to capture the seasonal/spatial variability in the predictions (i.e. this is not an atypical year), and that other photochemical models are capable of estimating dry deposition and could be used to perform such an analysis.

Section 3.2.1.2:

I am interested to know why SO_2 and NO_2 from SLAMS/NAMS monitors are not included in the measured database? While there may not be many NO_2 monitors in rural areas, there should still be some measurements of SO_2 in the case study areas.

Page 3-21 ADK case study area:

There are several questions regarding the selection of this study that would be of interest to note in the REA:

How were the 44 lakes and ponds selected?

How was the subset of 15 lake sites selected for geographic variation in deposition assessment?

How representative are these sites of the whole region?

Is there an elevational stratification?

Are any of the intensive study sites part of the current Adirondack monitoring programs (e.g., ALTM, TIME, AEAP)?

Have any or will any of the model results be compared with existing long term monitoring data?

Some important facts to point out regarding this region is that 22% of it is above 600 m where the sensitive spruce fir forest community becomes dominant. Further up above 900 m are key signature mountain peak ecosystems containing over 100,000 acres.

Monitors are not measuring any deposition data above 610 m in NYS, with the exception of the top of Whiteface Mountain.

Pages 3-35 through 3-37, and 3-50 through 3-53:

It may not be necessary to include the additional information on a monthly basis. The form of the annual NAAQS looks to be seasonal or annual, so presenting deposition on a seasonal basis seems to be adequate to capture the variation over the course of a year.

Figures 3.2-29 through 3.2-44:

I would recommend that the metrics for these figures are clearly stated. Also, it would be helpful to confirm that the “whiskers” are the minimum and maximum and that the boxes are 25th/75th percentiles.

Figures 3.2-45 onward:

It might help the reader to reverse the color scheme, that is display the smallest impacts in green and the largest impacts in red.

Misc.

In the introduction there are many references to "...noted *below* in Section 1.x...." I would recommend removing the word "below" in each of these references.

Page 1-3 line 19, "Chapter 2" should be bold.

Continuing Acidification of Organic Soils across the Northeastern U.S.A.: 1984 – 2001

1 Continuing Acidification of Organic Soils across the
2 Northeastern U.S.A.: 1984 – 2001

3

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6

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14 **Continuing Acidification of Organic Soils across the**
15 **Northeastern U.S.A.: 1984 – 2001**

16 **Abstract**

17 We conducted a resurvey of the O horizon in 2001 in watersheds previously sampled in 1984
18 under the Direct/Delayed Response Program (DDRP) to evaluate the effects of reductions in
19 acidic deposition in the northeastern USA. In this 17-year interval, median base saturation in the
20 Oa-horizon decreased from 56.2% in 1984 to 33.0% in 2001. Effective cation exchange capacity,
21 normalized to soil carbon concentration, showed no significant change between 1984 and 2001.
22 The change in base saturation was the result of almost equivalent changes in carbon-normalized
23 exchangeable calcium (Ca_N) and exchangeable aluminum (Al_N). The median Ca_N declined by
24 more than 50%, from 23.5 to 10.6 $\text{cmol}_c \text{ kgC}^{-1}$, while median Al_N more than doubled, from 8.8 to
25 21.3 $\text{cmol}_c \text{ kgC}^{-1}$. We observed the greatest change in soil acid-base properties in the montane
26 regions of Central New England and Maine, where base saturation decreased by more than 50%
27 and median soil pH_s (0.01M CaCl_2) decreased from 3.19 to 2.97. Changes in median
28 concentrations of other exchangeable cations were either statistically insignificant (Mg_N , K_N) or
29 very small (Na_N). We observed no significant change in the median values of either total soil
30 carbon content (%C) or total soil nitrogen content (%N) over the 17-year interval. The
31 acidification of the Oa-horizon between 1984 and 2001 occurred despite substantial reductions in
32 atmospheric acidic deposition. Our results may help to explain the surprisingly slow rate of
33 recovery of surface waters.

34
35 **List of abbreviations:** AA - atomic absorption; ADR - Adirondacks; Al_N - exchangeable
36 aluminum normalized to soil carbon concentration; ANC - acid neutralizing capacity; BBWM -

37 Bear Brook Watershed in Maine; Ca_N - exchangeable calcium normalized to soil carbon
38 concentration; CAAA - Clean Air Act Amendments; CATPOC - Catskills and Poconos; CEC -
39 cation exchange capacity; CEC_e - effective cation exchange capacity, CEC_{eN} - effective cation
40 exchange capacity normalized to soil carbon concentration; CNE - Central New England; DDRP
41 - Direct Delayed Response Project; ELS - Eastern Lake Survey; EPA - Environmental Protection
42 Agency; ICPMS - Inductively Coupled Plasma Mass Spectrometer; K_N - exchangeable
43 potassium normalized to soil carbon concentration; Mg_N - exchangeable magnesium normalized
44 to soil carbon concentration; Na_N - exchangeable sodium normalized to soil carbon
45 concentration; NAPAP - National Acid Precipitation Assessment Program; SNE - Southern New
46 England.

47

48 **INTRODUCTION**

49 The effects of acidic deposition on soils include the depletion of base cations, decreasing base
50 saturation and possibly cation exchange capacity (CEC_e), increased mobilization of Al, Mn, and
51 H^+ , and the accumulation of N and S (Blake et al., 1999; Driscoll et al., 2001). These effects
52 have been studied in laboratories, in whole watershed manipulations, and at intensive study sites.
53 Laboratory experiments have shown that strong acid additions to soils result in increased base
54 cation leaching, which returns to pre-acidification levels once acid additions are ended (Dahlgren
55 et al., 1990). Studies at the Bear Brook Watershed in Maine (BBWM) (Fernandez et al., 2003;
56 Norton et al., 2004), using paired catchments, have concluded that a watershed treated with bi-
57 monthly additions of ammonium sulfate ($1800 \text{ eq ha}^{-1} \text{ yr}^{-1}$) had lower exchangeable Ca and Mg
58 in all horizons, and that there was increased export of base cations from the watershed over the
59 nine-year study period. A similar study by Edwards et al. (2002) in West Virginia came to

60 similar conclusions. Rustad et al. (1996) treated Typic Haplorthods at BBWM with H₂SO₄ and a
61 combined H₂SO₄-HNO₃ mix (2000-4000 mol_c/ha/yr) for four years (1988-1991), then allowed a
62 two-year recovery period. They found that after the recovery period, the soil and soil solution
63 chemistry remained mostly unchanged. They concluded that this particular hardwood forest soil
64 was not permanently altered by the acid additions and could recover quickly.

65

66 The mandates of the 1970 and the 1990 Clean Air Act Amendments (CAAA) in the United
67 States, and similar legislation in Canada and Europe, have resulted in ubiquitous decreases in the
68 wet deposition of sulfate (SO₄²⁻) and hydrogen ion (H⁺) across these regions (Stoddard et al.,
69 1999; Driscoll et al., 2003; Kahl et al., 2004). Consequently, since the late 1980s, research at
70 both intensive study sites and on regional scales has focused to the recovery of these aquatic
71 ecosystems following reduced acidic deposition (e.g., Driscoll et al., 1989; Likens et al., 1996;
72 Stoddard et al., 1999; Evans et al., 2001; Skjelkvale et al., 2001; Clair et al., 2002; Jefferies et al.,
73 2003; Warby et al., 2005), and to a lesser extent, the response of watershed soils. Most of the
74 studies on soil acidification and subsequent recovery from acidic deposition in North America
75 and Europe have been conducted at intensive study sites (Mulder et al., 1991; Markewitz et al.,
76 1998; Alewell et al., 2000; Huntington et al., 2000). A number of studies have shown that soils in
77 acid-impacted areas, despite reduced acidic deposition, are still acidifying. Matschullat et al.
78 (1992) reported that soils in the Lake Söse watershed in the Harz Mountains in Germany
79 acidified from the soil surface down, and currently show no signs of recovery. At Solling,
80 Germany, Wesselink et al. (1995) studied long-term changes (1969-1991) in bulk precipitation
81 chemistry, throughfall water, soil water, and exchangeable base cations in beech and spruce
82 forests. They found that despite significant decreases in the deposition of sulfate, soil

83 acidification continued to occur in the spruce forest, while some recovery of base status of soils
84 in the beech forest was observed.

85
86 Very few studies have been conducted to investigate how changes in acidic deposition have
87 affected soils, over time, on a regional scale. Johnson et al. (1994) resampled 48 sites in the
88 Adirondacks in 1984 that had previously been sampled between 1930 and 1932. They found that
89 moderately acidic organic horizons ($\text{pH} > 4.0$) showed significant decreases in pH and
90 extractable Ca, while strongly acidic organic horizons ($\text{pH} < 4.0$) showed similar decreases in
91 extractable Ca without any significant change in pH. They also observed that the E horizon
92 appeared to lose extractable Ca, while the B and C horizons showed no evidence of acidification.
93 Bailey et al. (2005) reported substantial decreases in the base status of forest soils on the
94 Allegheny Plateau in Pennsylvania between 1967 and 1997. In that period, exchangeable Ca in
95 Oa and A horizons declined by an average of 77%, while exchangeable Al nearly doubled at the
96 four sites under investigation. Lapenis et al. (2004) studied archived soils at three sites across
97 Russia over a period of about 100 years, and also observed marked decreases in soil pH and Ca,
98 and increases in Al.

99
100 Exchangeable Ca has been the primary topic of much of the research focused on the effects of
101 acid deposition on soil properties. Many studies have suggested that the depletion of pools of
102 exchangeable base cations, especially Ca, due to acidic deposition, has resulted in the delayed
103 recovery of surface water acid neutralizing capacity (ANC) following reduced inputs of acidic
104 deposition (e.g., Bailey et al., 1996; Lawrence et al., 1999; Likens et al., 1996; Alewell et al.,
105 2000; Huntington et al., 2000). Calcium is also a macronutrient for plants, making it very

106 important for forest growth and productivity (Likens et al., 1996). Research by many groups has
107 concluded that forest ecosystems have been negatively impacted by declines in soil Ca and
108 associated decreases in soil base status (e.g., Bondietti et al., 1990; Lawrence et al., 1997; Shortle
109 et al., 1997; DeHayes et al., 1999; Bullen and Bailey, 2005). Decreased productivity of sugar
110 maple (*Acer saccharum* Marsh.) and increased freezing injury in red spruce (*Picea rubens* Sarg.)
111 have been the most widely studied soil-related impacts of acid precipitation on forest
112 productivity in the northeastern U.S. (e.g., Shortle et al., 1997; DeHayes et al., 1999; Drohan et
113 al., 1999; Driscoll et al., 2001; Bailey et al., 2004; Schaberg et al., 2006).

114
115 The future rate of recovery of watersheds following reduced inputs of acidic deposition is still
116 not well understood and the extent to which soil pools of base cations will recover is uncertain
117 (Stoddard et al., 1998). To date, far less work has been done on the recovery of soils following
118 reduced acidic deposition than has been done on surface water recovery. Modeling studies
119 suggest that significant recovery of soils in the northeastern U.S. will take a very long time, and
120 that some sites may show little or no improvement, regardless of future rates of acidic
121 deposition. For example, Chen and Driscoll (2005a) applied an integrated biogeochemical model
122 (PnET-BGC) to 37 forest watersheds in the Adirondacks to assess the response of surface waters
123 and soils to changes in acidic deposition. They found that even under aggressive future emission
124 scenarios (75% reduction in sulfur dioxide, and 30% in nitrogen oxide, relative to 1990 values)
125 most lake watersheds would still have soil % base saturation (%BS) below 20% in 2050. A
126 similar result was observed by Chen and Driscoll (2005b) for 60 watersheds in Northern New
127 England and Maine.

128 The objective of this study was to examine the changes in the chemical properties of the O
129 horizon in the northeastern U.S. between 1984 and 2001. To accomplish this objective, we
130 resampled soils in watersheds used for the Direct/Delayed Response Program (DDRP). We
131 focused on the Oa horizon because: (1) it is an important cation reservoir in acid forest soils; (2)
132 it is near the soil surface, making it potentially more responsive to changes in atmospheric
133 deposition chemistry; and (3) the Oa Horizon is not diagnostic of any soil types or classes and
134 hence comparisons can be made across soil types and classes. This horizon is the first to
135 experience acidification (Johnson et al., 1994; Matschullat et al., 1992), and is therefore likely to
136 be the first to show signs of recovery following reduced acidic deposition.

137

138 **METHODS**

139 In 1984 the Direct/Delayed Response Program (DDRP) was initiated at the request of the
140 Administrator of the U.S. Environmental Protection Agency (EPA) (Church et al., 1989). The
141 DDRP was conducted under the National Acid Precipitation Assessment Program (NAPAP) and
142 was designed to assess the then-current and future effects of acidic deposition on surface waters
143 in three regions of the eastern U.S. (Lee et al., 1989a). The central question that the DDRP was
144 designed to address was: How many surface waters would become acidic due to the then-current
145 or altered levels of acidic sulfur deposition, and on what time scales would these changes occur
146 (Lee, et al., 1989b)?

147

148 The DDRP watershed selection process was designed to allow results to be extrapolated to the
149 population of lakes studied in the earlier Eastern Lakes Survey (ELS) (Church et al., 1989).
150 Using preliminary results from the ELS, lakes were divided into three ANC classes. A random

151 sample of 50 lakes was selected from each ANC class. Refusal of access and other factors
152 ultimately reduced the total to 145 lake watersheds in the northeastern U.S. region.

153

154 **Soil Sampling**

155 The DDRP identified about 600 soil-mapping units on the 145 watersheds in the northeastern
156 U.S. (Church et al., 1989; Lee et al., 1989a). The soils were grouped into 38 sampling classes
157 based on how they might respond to acidic deposition (Lee et al., 1989b). In total, approximately
158 280 pedons and 1400 horizons were sampled by the DDRP (Adams et al., 1992). The DDRP
159 used a three-part scheme for randomly selecting sites for each of the sampling classes: 1) they
160 randomly selected a watershed in which the soil class of interest occurred; 2) they randomly
161 selected a potential location in that watershed using soil maps; and 3) they randomly selected a
162 direction in which to move if the field crew found that the sampling class did not occur within 5
163 m of the potential sampling site (Church et al., 1989). Because of this site selection scheme,
164 some watersheds were not sampled at all, while others were the site of multiple pits. In the
165 Northeast region, the DDRP sampled all horizons thicker than 3 cm down to bedrock or to 1.5 m,
166 the samples were cooled to 4°C within 12h, and transported to laboratories for further analysis
167 (Church et al., 1989).

168

169 During the summer of 2001 (28th May – 4th August) we collected organic horizon samples (Oa
170 horizon) from 46 of the original 145 DDRP watersheds (Fig. 1). During the summer of 2002
171 (25th June – 15th July), a further nine watersheds, not sampled in 2001, were sampled in the
172 Adirondacks. One soil pit was excavated in each of the DDRP watersheds. Pits were not
173 excavated at exactly the same sites as the DDRP pits. Precise locations of the 1984 pits were not
174 available. Furthermore, forest soils are highly spatially variable over short distances, so even if

175 we knew the position of the 1984 sites, there is no assurance that the samples could be treated as
176 paired. Criteria for soil pit sites were: slope $< 15^\circ$; mostly within 150 m of the lake; canopy
177 composition above the pit representative of the area; and not within 2 m of any noticeable
178 disturbance. The pits were excavated to the C horizon, to bedrock, or to a depth of 1.5m,
179 whichever was shallower. If possible, approximately one-half kilogram of sample was collected
180 from each horizon using a pointed mason's trowel. The samples were placed in plastic bags and
181 transported to Syracuse University for further analysis.

182
183 The Oa horizon was chosen for the comparison between 1984 and 2001 because it is not
184 diagnostic of any particular soil type in the region. Also, conditions in the northeastern U.S.
185 allow for the development of Oa horizons at most locations. Although a C concentration of 20%
186 or greater is diagnostic for an O horizon (Golden, 2003), we included all Oa-horizon samples
187 with $C > 16\%$ by mass to account for analytical and sampling error. Consequently, some of these
188 samples may be properly classified as A horizons. One effect of this %C cutoff was the
189 exclusion of samples from the Southern New England (SNE) subregion. The 3-cm thickness
190 requirement for sampling in 1984 also resulted in a number of watersheds without sampled Oa
191 horizons. Consequently, we focused on the Adirondacks, Catskills/Poconos, and the montane
192 Central New England/Maine (CNE/Maine) subregions (Fig. 1). Note that our CNE/Maine
193 subregion is a composite of the CNE and Maine subregions in the original DDRP. Ultimately,
194 the datasets were comprised of 55 samples from 55 watersheds for the 2001 survey, and 75
195 samples from 47 watersheds for the 1984 survey. A total of 24 watersheds were sampled in both
196 1984 and 2001 surveys (Fig. 1), with 1 sample collected from each watershed in the 2001 survey
197 and 36 samples collected from the 24 watersheds in the 1984 survey.

198 **Chemical Methods**

199 The chemical analytical methods used by the DDRP are detailed by Cappo et al. (1987). In the
200 2001 survey the same methods, which are all widely used soil chemical analyses, were followed
201 as closely as possible. However, archived samples were not available for re-analysis.

202 Exchangeable base cations (Ca, Mg, K, and Na) and exchangeable acidity (Al and H) were
203 measured in extracts of neutral salts, NH₄Cl (1M) and KCl (1M), respectively. The mass to
204 volume ratio (m:v) of organic soil to volume of extractant was 2.5 g : 55 mL. All the soils were
205 extracted for approximately 14h on a mechanical vacuum extractor (Centurion International,
206 Lincoln NE). The exchangeable base cations and Al were determined by spectroscopic analysis
207 of the NH₄Cl extracts using inductively coupled plasma mass spectrometry (ICPMS: 2001
208 samples) or flame atomic absorption (Flame AA: 1984 samples). Exchangeable acidity was
209 measured by titration of the KCl extract with sodium hydroxide (0.007M) to an endpoint of pH
210 8.2, using a phenolphthalein indicator. The CEC of the soil was determined as the sum of the
211 exchangeable base cations and the exchangeable acidity. Since neutral salts were used for the
212 extractions, the pH of the extracts was near the pH of the soil, and so the CEC measured is the
213 effective CEC (CEC_e). Base saturation was determined as the fraction of the CEC_e occupied by
214 exchangeable base cations, expressed as a percentage.

215

216 Soil pH was determined in deionized water (pH_w) and 0.01M CaCl₂ (pH_s). The mass to volume
217 ratio was 5 g : 25 mL for the DDRP, and 4 g : 20 mL for the 2001 survey. The soil and solution
218 were stirred thoroughly for about 1 min, and again after 15, 30, 45, and 60 min. The suspension
219 was allowed to settle for 1 min and the pH electrode was placed in the supernatant above the

220 soil-solution interface. In this paper pH_s rather than pH_w is discussed, as the exchangeable
221 properties of the soil were measured using salt solutions.

222

223 The total %C and %N of the soils were measured by an elemental analyzer in both studies. The
224 DDRP crushed the samples to pass through a 60-mesh sieve and dried the samples for 24 h in an
225 oven at 50°C . In the 2001 survey we ground the samples as finely as possible using a mortar and
226 pestle, and dried the samples overnight in an oven at 60°C .

227

228 **Statistical Methods**

229 Yanai et al. (2005) reported that small variations in sampling depth, resulting in the inclusion of
230 more or less mineral matter in O horizons, can result in large differences in measured Ca and Al.
231 Therefore, we normalized the exchangeable Ca, Na, Mg, K, Al, exchangeable acidity, sum of
232 base cations, and CEC_e using the soil carbon content (Ca_N , Na_N , Mg_N , K_N , Al_N , Acidity_N , Sum
233 BC_N , and CEC_{eN} , units: $\text{cmol}_c \text{kgC}^{-1}$). We also analyzed the data by dividing the data into three
234 approximately equal groups based on carbon concentration - <30%, 30-40%, and >40% by mass.
235 In this paper we discuss the changes of these properties as well as the base saturation and pH_s
236 between 1984 and 2001. Since neither the 1984 nor the 2001 data were normally distributed,
237 nonparametric statistics were used. Medians rather than means were used to report central
238 tendency. Readers should note that unlike the mean, median CEC_e does not necessarily equal
239 median exchangeable acidity plus median exchangeable bases. A Mann-Whitney U test for
240 independent groups was used to determine the significance of the changes reported, with $p < 0.05$
241 indicated as significant.

242

243 **RESULTS**

244 **Exchangeable Base Cations**

245 There was a significant decrease in Ca_N in the Oa horizon across the whole region (Table 1; Fig.
246 2), and in each of the subregions (Table 2; Fig. 2). Median exchangeable Ca_N decreased across
247 the whole region from $23.5 \text{ cmol}_c \text{ kgC}^{-1}$ to $10.6 \text{ cmol}_c \text{ kgC}^{-1}$ (Table 1), with the largest decrease
248 observed in the montane regions of CNE/Maine, where median Ca_N decreased from 34.1 cmol_c
249 kgC^{-1} to $9.0 \text{ cmol}_c \text{ kgC}^{-1}$ (Table 2; Fig. 2). Exchangeable Ca_N decreased the most in soils with
250 higher C content ($\text{C} > 40\%$), which were also the soils with the highest Ca_N in 1984 (Table 3;
251 Fig. 3). In 1984 about 55% of the Oa horizons had Ca_N above $20 \text{ cmol}_c \text{ kgC}^{-1}$; by 2001 this value
252 had decreased to about 25% (Fig. 4), further illustrating the region-wide depletion of Ca_N in the
253 Oa horizon.

254

255 Exchangeable Mg_N and K_N both showed small increases across the region but these increases
256 were not significant. The $0.43 \text{ cmol}_c \text{ kgC}^{-1}$ decrease in Na_N was statistically significant, but Na
257 represents a minor fraction of CEC_e in these soils.

258

259 **Cation Exchange Capacity and Base Saturation**

260 The normalized effective cation exchange capacity (CEC_{eN}) showed no significant change
261 between 1984 and 2001 in the region as a whole or in any of the subregions (Table 2; Fig. 2,4).

262 The variability of CEC_{eN} across the region, relative to other measured properties of the organic
263 horizon, was small, ranging from a median of $\sim 56.5 \text{ cmol}_c \text{ kgC}^{-1}$ in the Adirondacks to ~ 67.5
264 $\text{cmol}_c \text{ kgC}^{-1}$ in the montane subregion of CNE/Maine.

265

266 In contrast to CEC_{eN} , median base saturation declined across the region by about 40%, from
267 56.2% in 1984 to 33.0% in 2001 (Table 1). The largest decline was observed in CNE/Maine
268 where base saturation decreased from 65.1% to 27.6%. In 1984, the CNE/Maine subregion had
269 the highest median base saturation, but by 2001 this value was the lowest of the subregions
270 studied (Table 2). Base saturation decreased in all Oa-horizons, regardless of C content (Table 3;
271 Fig. 3).

272

273 **Exchangeable Acidity and Exchangeable Aluminum**

274 Both $acidity_N$ and Al_N showed significant and ubiquitous increases between 1984 and 2001,
275 increasing by $14.5 \text{ cmol}_c \text{ kgC}^{-1}$ and $12.5 \text{ cmol}_c \text{ kgC}^{-1}$ region-wide, respectively. This increase was
276 most marked in CNE/Maine, which had the lowest median $acidity_N$ of the subregions in 1984
277 ($20.9 \text{ cmol}_c \text{ kgC}^{-1}$) and the highest in 2001 ($46.5 \text{ cmol}_c \text{ kgC}^{-1}$) (Table 2; Fig. 4). While Al_N for
278 these soils comprises about 60% of $acidity_N$, changes in Al_N accounted for most of the change in
279 $acidity_N$.

280

281 **Total Carbon, Total Nitrogen and pH_s**

282 Neither %C nor %N showed any significant change across the region. We observed a significant
283 decrease in pH_s of 0.16 pH units (Table 1). The decrease in pH_s was the greatest in CNE/Maine
284 (0.22 pH units) and it was the only subregion in which pH showed significant change (Table 2;
285 Fig. 2). The pH_s decreased the most in soils with low C content ($C < 30\%$), decreasing by 0.67 pH
286 units, while soils with higher C content ($C > 40\%$) experienced little change, though they were the
287 most acidic ($pH \sim 2.85$) (Table 3; Fig. 3). Since most of the CEC_e in organic soils in the
288 northeastern U.S. is derived from organic matter (Johnson, 2002), we investigated the

289 relationship between %C and CEC_e . We found that there was no statistically significant
290 difference ($p = 0.52$) between the regression slopes of CEC_e vs. %C for 1984 and 2001.

291

292 **Paired Watersheds**

293 The 24 watersheds that were sampled in both the 1984 and 2001 surveys exhibited similar
294 changes in pH, base saturation, and exchangeable acid/base concentrations to those changes
295 observed across the whole region and in the subregions (Table 2). Normalized exchangeable
296 calcium (Ca_N) decreased by 51% in these watersheds, similar to the decline observed region-
297 wide. Increases in exchangeable acidity and exchangeable Al in the paired watersheds were not
298 as great as the overall trend (Table 2). Base saturation exhibited a large, statistically significant
299 decrease from 52.9% to 34.5%, while pH decreased from 3.05 to 2.96 pH units. The changes in
300 the chemical concentrations observed in these 24 watersheds were the most similar to changes
301 observed in the Adirondack subregion, since approximately two-thirds of these watersheds are
302 located in this subregion.

303

304 **DISCUSSION**

305 **Changes in Soil Chemical Properties: 1984 – 2001**

306 We observed large decreases in Ca_N and base saturation in Oa horizons across the northeastern
307 United States. Median exchangeable Ca decreased by ~55% and base saturation decreased by
308 ~40% region-wide. During the period 1992-1993, Lawrence et al. (1997) sampled 12 sites across
309 the region and found that Ca ranged from 2.1 $cmol_c\ kg^{-1}$ to 21.6 $cmol_c\ kg^{-1}$ with a median of 6.6
310 $cmol_c\ kg^{-1}$ for the Oa horizon. This value lies approximately halfway between the 1984 DDRP
311 median (9.7 $cmol_c\ kg^{-1}$) and what we observed in 2001 (3.7 $cmol_c\ kg^{-1}$) (Table 1).

312 Our results are consistent with other studies of soil change in the region. Johnson et al. (1994)
313 examined changes in the chemistry of forest soils in the Adirondacks between the 1930s and
314 1984. They found that moderately acidic organic horizons ($\text{pH} > 4.0$) showed significant
315 decreases in pH and extractable Ca, while strongly acidic organic horizons ($\text{pH} < 4.0$) showed
316 similar decreases in extractable Ca without any significant change in pH. Although we did not
317 sample the same sites, our results indicate that forest soils in the Adirondacks have continued to
318 acidify after the sampling conducted by Johnson et al. (1994) in 1984 (Table 2). Bailey et al.
319 (2005) found evidence of very large changes in the acid-base chemistry of forest soils at four
320 sites in the Allegheny Plateau of Pennsylvania, between 1967 and 1997. Exchangeable Ca in the
321 Oa and A horizons at the four sites declined from a mean of $4.7 \text{ cmol}_c \text{ kg}^{-1}$ in 1967 to 1.1 cmol_c
322 kg^{-1} in 1997. Exchangeable Al increased from 3.3 to $5.9 \text{ cmol}_c \text{ kg}^{-1}$ in the same period, while
323 mean pH_s declined from 3.8 to 2.9.

324

325 Other studies of long-term soil acidification have also documented large changes in the acid-base
326 chemistry of forest soils. Markewitz et al. (1998) reported a decrease in base saturation from
327 67.7% to 8.8% in the 0 – 7.5 cm soil layer in the Calhoun Experimental Forest, South Carolina,
328 between 1962 and 1990. They also observed significant increases in exchangeable acidity and a
329 small increase in CEC_e . However, they determined that only 38% of the observed soil
330 acidification was due to acidic deposition, while 62% was attributed to internal natural
331 acidification of the watershed. Blake et al. (1999) also found decreasing trends in base saturation
332 at the Rothamsted Experimental Station, U.K., between 1883 and 1991, but observed greater
333 decreases in exchangeable Ca than increases in exchangeable Al, resulting in a significant
334 decrease in CEC_e .

335 In this study we found that the CNE/Maine subregion showed the greatest declines in
336 exchangeable base cations and base saturation. We also observed the greatest increases in
337 acidity_N and Al_N in this subregion (Table 2; Fig. 2). Based on modeled rates of acidic deposition,
338 the CNE/Maine subregion receives lower inputs of acidity than either the Adirondacks or
339 Catskills/Poconos (Ollinger et al., 1993). Thus, the high rate of soil acidification in CNE/Maine
340 is somewhat surprising. There are two possible reasons that may help explain this finding. First,
341 it is possible that the other subregions were so extensively acidified prior to the DDRP sampling
342 in 1984 that a decline of the same magnitude as observed in CNE/Maine was not possible. Our
343 data are consistent with this hypothesis, as the decline in median Ca_N in CNE/Maine (25.1 cmol_e
344 kgC⁻¹) was greater than the 1984 concentrations in both the Adirondacks and Catskills/Poconos
345 (Table 2). Emissions of sulfur dioxide peaked in 1973, and have declined substantially since
346 (e.g., Driscoll et al., 2001), so the second, related hypothesis is that the acidification of soils in
347 the CNE/Maine subregion was delayed relative to the other regions because of the strong
348 regional gradient in acidic inputs from west to east (Ollinger et al., 1993). In this case, our study
349 period (1984-2001) may have missed the period of greatest acidification in the Adirondacks and
350 Catskills/Poconos, but captured the period of greatest acidification in the CNE/ Maine subregion.
351

352 As with base cations, pH decreased the most in CNE/Maine. These soils had the highest recorded
353 pH of any subregion in 1984, and this was the only subregion to experience statistically
354 significant decrease in pH (Table 2; Fig. 2). A study by Falkengren-Grerup (1987) of 22 forest
355 soils in southern Sweden between 1949-70 and 1984 showed that the least acidic soils were most
356 impacted by acid rain, and experienced the largest declines in pH. Johnson et al. (1994) made
357 similar observations for Adirondack O horizons. Our data are consistent with this phenomenon,

358 since soils with higher pH (i.e., CNE/Maine) showed the largest declines in exchangeable Ca and
359 pH (Table 2). At lower soil pH the increased solubility of Al may have caused a shift in the soil
360 solution-exchange surface equilibrium, resulting in a greater fraction of Al on exchange sites.

361
362 Changes in pH are very important in organic soils, as most of the CEC_e in organic soils is pH-
363 dependent (Johnson, 2002). In our study we found that pH had statistically significantly
364 decreased by ~0.2 pH units between 1984 and 2001 (Table 2). We also found that pH decreased
365 with increasing %C, resulting in a greater fraction of the exchangeable acidity being comprised
366 of H^+ in higher C soils (Table 3). The CEC_{eN} showed a general decrease with increasing carbon
367 content in both the surveys (Table 3), indicating that high-carbon soils have lower CEC_e per unit
368 carbon. This may be a result of the degree to which humification has occurred in the soils. The
369 more humified soils would have lower C content, but a greater carboxylic functional group
370 content relative to the soils that have undergone less humification. This characteristic would
371 mean that the fraction of CEC_e associated with carboxylic groups would be higher in these lower
372 C content soils, resulting in higher overall CEC_{eN} .

373
374 We found that the relationship between CEC_e and %C in Oa horizons had essentially remained
375 unchanged between 1984 and 2001. This is not surprising since neither the CEC_e nor %C
376 changed significantly between the two surveys. Sullivan et al. (2006) found a stronger
377 correlation between %C and CEC_e for their study of 66 watersheds in the Adirondacks sampled
378 in 2003. The difference between the two studies could be due to the fact that our survey covered
379 a broader geographic region, encompassing more variability in soil type. Johnson (2002)

380 observed a similar pattern, with greater correlations between %C and CEC_e at intensive study
381 sites than on a regional scale.

382

383 Due to the pH-dependence of CEC derived from soil organic matter, acidifying soils may exhibit
384 a decrease in CEC_{eN} . However, in this study we found no significant change in CEC_{eN} across the
385 region, or in any of the subregions (Table 2; Fig. 2). Surprisingly, there was also little regional
386 variability of CEC_{eN} , which ranged from ~56 to ~67 $cmol_c\ kgC^{-1}$. Therefore, decreases in Ca_N
387 were approximately equivalent to increases in Al_N . The result was a region-wide decrease in base
388 saturation of ~40% (Table 2). Again, the most significant changes were in CNE/Maine, where
389 base saturation decreased by ~58% from 65.1 to 27.6%, driven by large decreases in Ca_N and
390 equivalent increases in Al_N (Table 2; Fig. 2).

391

392 In general, predictions from modeling studies are consistent with our results. Chen and Driscoll
393 (2005a) modeled 37 DDRP watershed in the Adirondacks to assess how surface waters and soils
394 would respond to changes in regional acidic deposition. Their modeling results indicate that soil
395 base saturation declined by more than 50% between 1850 and 1984. Furthermore, they predicted
396 that base saturation would continue to decline after 1984, as we observed, unless aggressive
397 emission controls were implemented. Chen and Driscoll (2005b) also conducted a similar study
398 concerning 60 DDRP watersheds in Northern New England and Maine. This study also predicted
399 that only with aggressive emission controls would soils begin to reverse the acidification that has
400 occurred in the past 150 years. These modeling results focused on mineral soils, while this study
401 focuses on the Oa horizon. It is possible that the base cations leached from organic soils adsorb
402 onto the mineral horizons, resulting in a slower rate of %BS decrease in the mineral soils. These

403 two modeling studies also suggested that continuing decreases in soil %BS would be greater in
404 NNE and ME than in the Adirondacks, which is consistent with the regional differences
405 presented in this paper.

406

407 Our data clearly show that soils in the northeastern U.S. are still experiencing acidification, with
408 decreases in exchangeable Ca, pH, and base saturation, and increases in exchangeable Al and
409 exchangeable acidity (Tables 1,2; Fig. 2). The changes that we observed have, in general, been
410 very large. The similarity in %C between 1984 and 2001 suggests that field sampling of Oa
411 horizons was done consistently. Furthermore, the patterns in soil chemistry were similar when
412 the data set was reduced to only those watersheds sampled in both years. While there may be
413 some unidentified differences in laboratory methods, the magnitude of the changes we observed
414 are far too great to be explained by minor procedural differences. It is also worth noting that the
415 DDRP specifically selected watersheds that were thought to be sensitive to acidic deposition
416 (Church et al., 1989). Thus, these watersheds are likely to be particularly responsive to changes
417 in acidic deposition. We interpret our results as showing that organic soils in acid sensitive areas
418 in the northeastern U.S. are continuing to acidify, despite reduction in acidic deposition, and are
419 showing no signs of chemical recovery.

420

421 **Links to Observed Changes in Surface Water Chemistry**

422 Numerous studies have shown that surface waters across the northeastern U.S., southeastern
423 Canada, and Europe have experienced some chemical recovery following reduced acidic
424 deposition (e.g., Driscoll et al., 1989; Likens et al., 1996; Evans et al., 2001; Skjelkvale et al.,
425 2001; Clair et al., 2002; Jefferies et al., 2003; Stoddard et al., 2003; Warby et al., 2005).

426 However, the chemical recovery of surface water ANC has been much slower than expected,
427 when reductions of strong acid anion concentrations are considered alone. A number of
428 investigators have suggested that the recovery of surface waters has been impeded by the long-
429 term leaching of base cations from forest soils (e.g., Stoddard et al., 1998; Lawrence et al., 1999;
430 Driscoll et al., 2001; Lawrence, 2002; Warby et al., 2005). Strong acid inputs to these base
431 cation-depleted soils, even at lower concentrations, are not accompanied by a stoichiometric
432 mobilization of base cations as strong acidic anions move through the soil profile. This
433 incomplete neutralization results in the release of Al and/or H^+ to soil solutions and ultimately
434 retards the recovery of surface water ANC. Thus, the general trends of decreasing exchangeable
435 Ca in soils in this study are also seen for surface waters in the same subregions (Driscoll et al.,
436 1989; Likens et al., 1996; Stoddard et al., 2003; Warby et al., 2005).

437

438 It seems counterintuitive that soils in the northeastern United States have continued to acidify
439 during a period in which surface waters have begun to show improvements in ANC and pH.
440 Indeed, one might expect that improved soil base status is required before drainage water ANC
441 and pH can increase. However, the “recovery” phase currently underway in the region is
442 characterized by continuing acidic deposition, albeit at lower rates. Soil acidification is likely to
443 continue until acidic inputs decline to the point where soil base cation pools are sufficient to
444 neutralize them. Laboratory studies, field manipulations, and modeling exercises provide useful
445 insight into this process.

446

447 For example, Dahlgren et al. (1990) conducted an acidification experiment using a Spodosol Bs
448 horizon from BBWM. They found that synthetic throughfall additions were initially neutralized

449 by the release of base cations and adsorption of sulfate to the soil. After this initial period, high
450 concentrations of Al were observed in the leachate solutions for the duration of the acidification
451 phase of the experiment. Results from the experiment indicated that an increase in the pH of
452 throughfall from 3.66 to 3.89 would cut leachate Al concentrations by half with little change in
453 base cation concentrations. Although this represents “recovery” of the leachate solution, the soil
454 would continue to acidify due to the lack of exchangeable Ca and other base cations. When the
455 throughfall pH was increased to 4.78, however, retention of base cations by the soil was
456 observed, suggesting that at this input acidity the base status of the soil would improve.

457

458 The BBWM study is a paired watershed study (Church, 1999). The project was divided into a 2.5
459 year calibration period (1987-1989), nine years of $(\text{NH}_4)_2\text{SO}_4$ addition to the west watershed
460 (1989-1998), and a period of recovery. The east watershed served as a reference watershed.
461 Church (1999) found that the west watershed showed increased export of base cations and that
462 the neutralization of the acid additions was largely by cation desorption and the mobilization of
463 Al. Fernandez et al. (2003) reported that the treated watershed had lower contents of
464 exchangeable Ca and Mg in all horizons (27 and 66 kg ha^{-1} of Ca and Mg, respectively), but that
465 the O horizon was more depleted of base cations than the underlying mineral soils. The
466 difference in exchangeable Ca and Mg between the treated and untreated watersheds at the
467 BBWM (~59%), was similar in magnitude to the decline in Ca_N that we observed in this study
468 (~55%), over the 17 year period. This finding is consistent with our hypothesis that organic
469 horizons would be the first to experience acidification, and therefore possibly be the first to show
470 signs of recovery, following reduced acidic deposition.

471 To investigate links between the changes in organic horizons and surface waters, we further
472 analyzed the data by dividing the soils into three groups based on the ANC of the surface water
473 in the watershed from which the soils were sampled (Table 4). The three ANC classes were:
474 chronically acidic ($\text{ANC} < 0 \mu\text{eq L}^{-1}$), low ANC ($0 < \text{ANC} < 25 \mu\text{eq L}^{-1}$), and moderate ANC
475 ($\text{ANC} > 25 \mu\text{eq L}^{-1}$), based on 1984 ANC values. Chronically acidic and low ANC surface
476 waters are the most susceptible to acidic deposition, but tend to be the first to show recovery
477 (Warby et al., 2005). In this study we found that Oa-horizons showed less acidification in
478 watersheds with surface waters in the chronically acidic and low ANC classes, and the greatest
479 acidification in watersheds characterized by higher ANC surface waters (Table 4).

480

481 In the chronically acidic and low ANC class watersheds, median base saturation decreased by
482 8.1% and 3.2%, respectively, while in the moderate ANC class watersheds it decreased by
483 29.4%. Only in the chronically acidic ANC class did soils show an increase in both CEC_{eN} and
484 pH, while in the low ANC class CEC_{eN} decreased by ~8% and pH increased by 0.08 pH units.
485 Organic horizons in the moderate ANC class showed the largest increase in Al_{N} and
486 exchangeable acidity, the largest decrease in Ca_{N} , and were the only soils to experience a
487 decrease in pH_{s} . Changes in the acid-base status of soils in the moderate ANC class were also the
488 only statistically significant changes, except for CEC_{eN} where the decline between 1984 and
489 2001 was small and not statistically significant. The data clearly indicate that the changes in the
490 acid-base status of these organic soils are consistent with the “faster” recovery exhibited by
491 lower ANC surface waters, following reductions in acidic deposition. Note, however, that the
492 changes observed in Table 4 are also driven by geographic factors. In general, the lowest ANC
493 surface waters are found in the Adirondacks and ANC increases towards CNE/Maine. Therefore,

494 the trends observed when soils are grouped by ANC class are similar to the trends observed
495 when soil is grouped by geographic subregion (Table 2).

496

497 **Implications for Forest Ecosystem Health**

498 Because of their low base saturation and low natural weathering rates, many forest soils in the
499 northeastern U.S. are particularly vulnerable to acidification. Many studies have focused on the
500 depletion of base cations from these soils, Ca in particular, and how this has affected forest
501 productivity (e.g., Bondietti et al., 1990; Lawrence et al., 1997; Shortle et al., 1997; DeHayes et
502 al., 1999; Bailey et al., 2004; Bullen and Bailey, 2005; Schaberg et al., 2006). These studies have
503 suggested that forest ecosystems in the region have been negatively impacted by decreases in soil
504 base status due to acidic deposition. In particular, reduced Ca levels have been associated with
505 decreased productivity in sugar maple stands in NY, VT, and PA (Drohan et al., 1999; Driscoll et
506 al., 2001; Bailey et al., 2004; Schaberg et al., 2006), and with increased freezing injury in red
507 spruce stands (Shortle et al., 1997; DeHayes et al., 1999; Driscoll, et al., 2001). Jenkins and Keal
508 (2004) also found a greater abundance of sugar maple saplings in the northeastern Adirondacks
509 than in the southwestern Adirondacks, and concluded it was due to less acidic deposition, and
510 generally higher soil base cation concentrations in the northeastern region. Also, regeneration of
511 sugar maple improved markedly in response to an experimental addition of calcium silicate in
512 New Hampshire (Juice et al., 2006).

513

514 Some of the most compelling evidence comes from studies that show increased Ca and Mg in
515 tree stems in the 1950s and 1960s, then a steady decline thereafter (Bondietti, 1990; Likens et al.,
516 1998). This pattern corresponds in time to elevated acidic deposition and the depletion of Ca and

517 Mg in the soils. Another study by Shortle et al. (1997) showed that the concentration of
518 putrescine, a stress marker in trees, was significantly correlated to Al/Ca binding ratios of forest
519 floors. They concluded that even trees that appear healthy may be stressed due to adverse Al/Ca
520 ratios. Cronan and Grigal (1995), after an extensive literature review, showed that trees had a
521 greater than 50% probability of adverse impacts on growth when the soil solution Ca/Al ratio
522 was less than 1:1.

523

524 Despite substantial reductions in acidic inputs to forest ecosystems of the northeastern United
525 States, our data indicate that organic horizons in the region continue to lose exchangeable Ca and
526 accumulate exchangeable Al. This trend will likely continue until inputs of acidic deposition
527 decrease to a level at which weathering can fully neutralize incoming acidity. Furthermore,
528 modeling results suggest that this condition may only occur if aggressive emission controls are
529 implemented (Chen and Driscoll, 2005a,b). The continuing acidification of soils in the region
530 poses a serious threat to the health of forests, with additional declines in base status likely to
531 increase the number of sites exhibiting lower forest productivity and/or vulnerability to winter
532 injury.

533

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702 **Table 1.** Summary statistics of acid-base soil properties of organic horizons for 1984 (n=75) and
 703 2001 (n=55) from across the northeastern U.S.

704

Variable	Unit	Year	Mean					
				10	25	Median	75	90
Total N	%	2001	1.5	0.9	1.3	1.4	1.7	2.1
		1984	1.5	0.9	1.2	1.5	1.8	2.0
Total C	%	2001	34.7	23.6	26.5	34.9	41.3	46.8
		1984	37.1	19.4	27.4	38.8	47.0	49.9
Na^{**}	cmol _c /kg	2001	0.0	0.0	0.0	0.0	0.1	0.1
		1984	0.2	0.1	0.1	0.1	0.3	0.4
Na_N^{**}	cmol _c /kgC	2001	0.15	<0.1	<0.1	0.10	0.20	0.30
		1984	0.7	0.2	0.3	0.5	0.6	1.1
Mg	cmol _c /kg	2001	1.6	0.6	0.9	1.5	2.2	3.0
		1984	2.1	0.4	0.9	1.6	2.9	3.9
Mg_N	cmol _c /kgC	2001	4.8	1.9	2.7	4.6	6.4	7.6
		1984	5.9	1.6	2.6	4.4	7.1	9.9
K	cmol _c /kg	2001	0.9	0.2	0.4	0.9	1.1	1.5
		1984	0.8	0.2	0.5	0.7	1.1	1.6
K_N	cmol _c /kgC	2001	2.6	0.6	1.7	2.4	3.2	4.5
		1984	2.2	0.9	1.2	2.0	2.9	3.7
Ca^{**}	cmol _c /kg	2001	5.3	0.8	1.6	3.7	7.5	12.0
		1984	14.5	2.1	3.9	9.7	20.6	26.6
Ca_N^{**}	cmol _c /kgC	2001	15.4	2.6	5.6	10.6	20.8	35.6
		1984	41.5	6.7	12.8	23.5	48.8	84.3
Sum BC^{**}	cmol _c /kg	2001	7.8	2.2	4.7	6.2	10.8	15.6
		1984	17.6	3.2	6.3	12.9	25.3	32.0
Sum BC_N^{**}	cmol _c /kgC	2001	23.0	7.8	13.6	18.9	29.6	46.9
		1984	50.3	12.1	20.1	39.2	59.1	93.1
Acidity^{**}	cmol _c /kg	2001	12.7	7.0	9.1	11.6	15.8	20.6
		1984	9.0	2.1	5.3	9.2	12.2	15.0
Acidity_N^{**}	cmol _c /kgC	2001	39.0	18.8	24.3	38.0	49.6	62.9
		1984	25.5	5.2	15.0	23.6	34.8	47.7
Al^{**}	cmol _c /kg	2001	7.5	2.1	3.4	6.2	10.7	13.8
		1984	4.4	0.6	1.7	3.6	6.3	10.2
Al_N^{**}	cmol _c /kgC	2001	23.4	5.1	10.8	21.3	32.1	44.4
		1984	14.0	1.5	3.8	8.8	22.8	35.5
CEC_e[*]	cmol _c /kg	2001	20.5	12.0	17.0	20.6	23.7	28.9
		1984	26.7	11.5	19.9	23.0	30.2	39.4
CEC_{eN}	cmol _c /kgC	2001	62.0	39.1	50.1	60.6	71.2	82.5
		1984	75.8	44.1	51.3	62.7	74.8	108.1
Base Saturation^{**}	%	2001	36.6	15.0	22.5	33.0	47.4	66.2
		1984	57.0	22.1	38.2	56.2	79.6	90.6
pH_w	pH units	2001	3.8	3.4	3.6	3.7	3.9	4.3
		1984	3.9	3.3	3.5	3.7	4.1	5.0
pH_s[*]	pH units	2001	3.0	2.7	2.8	3.0	3.1	3.2
		1984	3.3	2.7	2.8	3.1	3.6	4.0

705

706 **Table 2.** Acid-base properties of organic horizons in the northeastern United States (whole
707 region) and subregions in 1984 and 2001. Median values are shown. Units for CEC_{eN} , Ca_N , Al_N ,
708 and $Acidity_N$ are $cmol_c kgC^{-1}$. Units for pH are pH units and BS are %. ADR: Adirondacks,
709 CATPOC: Catskills and Poconos, CNE: Central New England/Maine, and Paired Watersheds:
710 the 24 watersheds sampled in both the 1984 and 2001 surveys.

	Whole Region		ADR		CATPOC		CNE		Paired Watersheds	
	1984	2001	1984	2001	1984	2001	1984	2001	1984	2001
Number of samples	75	55	28	28	10	8	37	19	36	24
Base saturation	56.2**	33.0**	54.3*	40.0*	40.7	29.5	65.1**	27.6**	52.9**	34.5**
CEC_{eN}	62.7	60.6	57.3	56.2	58.6	58.4	67.8	67.2	62.2	59.1
$Acidity_N$	23.6**	38.0**	22.6*	30.5*	35.3	41.3	20.9**	46.5**	26.7	31.5
Ca_N	23.5**	10.6**	21.4**	13.7**	15.2	9.0	34.1**	9.0**	22.3**	11.0**
Al_N	8.8**	21.3**	10.3	16.4	23.7	32.4	5.7**	26.1**	8.9	12.8
pH_s	3.14*	2.98*	3.00	2.93	3.12	3.04	3.19*	2.97*	3.05*	2.96*

711

712 **Table 3.** Acid-base properties of organic horizons across the northeastern United States, grouped
 713 by soil carbon content. Values are medians. Units for CEC_{eN} , Ca_N , Al_N , and EA_N are $cmol_c$
 714 kgC^{-1} . Units for pH are pH units and BS are %.

	C < 30 %		C 30 - 40 %		C > 40 %	
	1984	2001	1984	2001	1984	2001
Number of Samples	19	18	20	21	36	16
Base Saturation	49.7	28.3	48.0*	33.0*	65.0*	42.0*
CEC_{eN}	68.3	77.2	66.9*	57.0*	55.2	55.7
$Acidity_N$	31.3*	49.2*	30.7	32.8	20.3	24.2
Ca_N	20.4	10.1	17.2*	9.4*	28.0*	14.0*
Al_N	19.7	30.1	18.0	19.3	6.5	6.6
pH_s	3.71*	3.04*	3.19*	2.96*	2.88	2.83

715

716 **Table 4.** Acid-base properties of organic horizons in the northeastern United States grouped by
 717 the ANC class of lakes in the watersheds from which the respective soil samples were collected.
 718 Values are medians. Units for CEC_{eN} , Ca_N , Al_N , and EA_N are $cmol_c\ kgC^{-1}$. Units for pH are pH
 719 units and BS are %.

720

	ANC < 0		0 < ANC < 25		ANC > 25	
	1984	2001	1984	2001	1984	2001
Number of Samples	10	13	14	17	51	25
Base Saturation	33.4	25.3	41.4	38.2	65.6**	36.2**
CEC_{eN}	52.4	60.5	57.3	52.9	69.2	64.4
Acidity_N	35.2	44.6	30.0	32.8	19.9**	38.0**
Ca_N	13.5	8.2	16.8	8.4	34.8**	17.1**
Al_N	18.9	27.4	13.7	17.4	6.5**	16.2**
pH_s	2.94	3.03	2.88	2.96	3.2**	3.0**

721

722 **Fig. 1.** Map of the sites sampled by the DDRP in 1984 and the sites resampled in the 2001
723 survey. Shown are the sample sites for the three subregions studied.

724

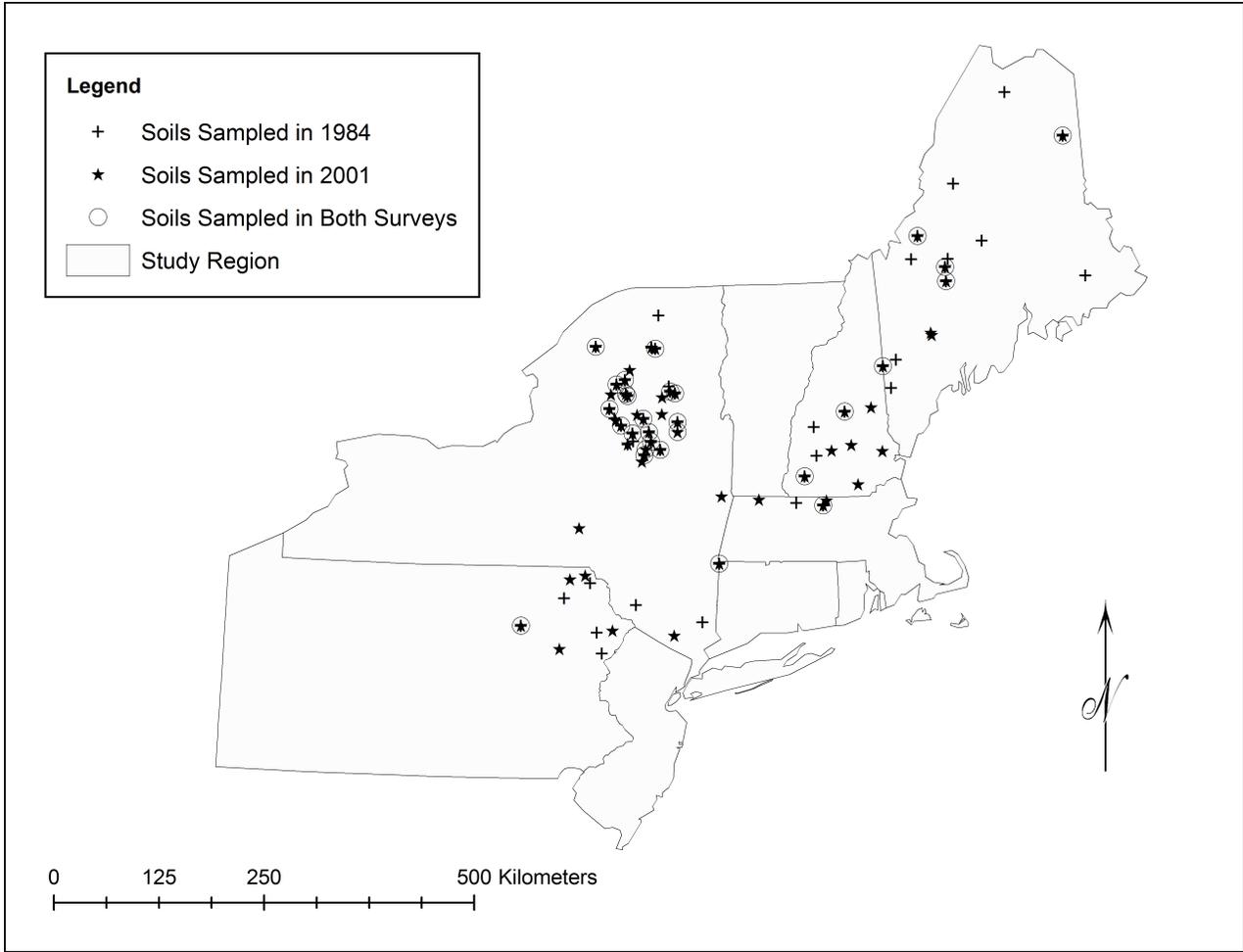
725 **Fig. 2.** Acid-base soil properties of organic horizons for the whole region and the subregions for
726 1984 and 2001. Boxes indicate the interquartile ranges; whiskers indicate the 10th and 90th
727 percentiles; median trends are indicated by the line in the box; dots indicate the 5th and 95th
728 percentiles of the outliers. Units for CEC_{eN}, Ca_N, Al_N, and EA_N are (cmol_c kgC⁻¹) and BS is %.

729

730 **Fig. 3.** Acid-base soil properties of organic horizons across the northeastern U.S. grouped by soil
731 carbon content. Values are medians for each of the carbon bins. Units for CEC_{eN}, Ca_N, Al_N, and
732 EA_N are (cmol_c kgC⁻¹). Units for pH are pH units and BS are %.

733

734 **Fig. 4.** Cumulative frequency diagrams for selected acid-base properties of organic soils across
735 the northeastern US.



736

