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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON D.C. 20460

OFFICE OF THE ADMINISTRATOR  
SCIENCE ADVISORY BOARD

[Insert date]

Honorable Stephen L. Johnson  
Administrator  
U.S. Environmental Protection Agency  
1200 Pennsylvania Avenue, NW  
Washington, DC 20460

Subject: Review of EPA's *Risk and Exposure Assessment to Support the Review of the Secondary National Ambient Air Quality Standard for Oxides of Nitrogen and Sulfur: First Draft*

Dear Administrator Johnson:

The Clean Air Scientific Advisory Committee (CASAC or Committee) NO<sub>x</sub> & SO<sub>x</sub> Secondary National Ambient Air Quality Standards (NAAQS) Review Panel (Panel) met on October 1-2, 2008 to review held a public meeting on October 1-2, 2008 to review EPA's *Risk and Exposure Assessment to Support the Review of the Secondary National Ambient Air Quality Standard for Oxides of Nitrogen and Sulfur: First Draft* (see Enclosure 1 for the Panel roster). The Panel's draft report was completed during a November 19, 2008 public teleconference. **(To be inserted pending review/approval by CASAC: "The Chartered CASAC held a public teleconference on XXXX to review and approve the report.")**

Overall, the CASAC NO<sub>x</sub>-SO<sub>x</sub> Secondary Panel found the first draft of the Risk and Exposure document (REA) to be a credible beginning in the development of the assessments needed to subsequently support rule-making, though also note that much of the analyses have yet to be completed (e.g., Chapter X, discussing the risk assessment approach associated with nutrient enrichment). The Panel has many suggestions for strengthening the document in response to the Agency's charge questions. Individual comments from the CASAC Panel members are provided in Enclosure 2.

The Panel strongly supports the up-front inclusion of an interpretation of each of the key findings in the Integrated Science Assessment (ISA) from a policy-making perspective, possibly as part of an Executive Summary, as well as in the applicable sections of the REA. As discussed in our prior reviews of the ISA and Scope and Methods documents, attention must be paid to all forms of reactive nitrogen (Nr, which includes oxidized, reduced and organic nitrogen) deposition as they can contribute to acidification and nutrient enrichment, and the

1 science would suggest that effects could be ameliorated by decreasing deposition of any of those  
2 forms. From a scientific standpoint, this intricate relationship indicates that a NAAQS standard  
3 should address total N deposition. It is dually noted that the current REA focuses on standards  
4 for nitrogen and sulfur oxides because of legal and statutory constraints. The Panel recommends  
5 that the EPA move forward with establishing scientifically founded standards which effectively  
6 protect the environment, recognizing the current constraints.

### 7 8 **Scope of the Review**

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

16  
17 Chapters 1 and 2 of the REA do, in general, satisfy the goals of providing a clear and  
18 correct framing of the issues, providing a coherent method for reaching conclusions required in  
19 the NAAQS process, summarizing the relevant policy questions and building on the ISA. The  
20 correct effects are considered and the correct relationships of effects to atmospheric and ecologic  
21 variables are outlined, at least conceptually.

22  
23 The figures used throughout the two chapters are useful in organizing the thinking of the  
24 reader. It would be helpful if Figure 1.4-1 were accompanied by text that explains how well each  
25 of the steps shown can be executed, where the major uncertainties are likely to lie, and where  
26 each component is addressed in the later parts of the REA. This modification would help guide  
27 the reader. A paragraph on the central position of loading in the calculations would also be  
28 helpful as it becomes a pivotal point in all of the calculations. The same can be said of N  
29 saturation, which plays a role later in the document but receives no mention in the opening  
30 chapters. It also is suggested that there be greater coherence between the text, figures and  
31 policy statements with respect to reduced forms of N. These reduced forms are mentioned both  
32 here and in the ISA, and probably are important contributors to the effects being seen in  
33 ecosystems, but the chemistry figures are essentially all for oxidized forms and the policy  
34 questions read this way as well.

35  
36 The uncertainty discussion is quite generic and qualitative, and it is not clear when  
37 uncertainty is being discussed and when variability is the real issue. This issue rises again in  
38 talking about the monitoring network. The existing network introduces quite a bit of uncertainty  
39 into the calculations, and so either Chapters 1 or 2 should confront this issue and explain the  
40 implications of the identified uncertainties on the ability of EPA to perform the assessments in  
41 Chapters 7 and 8. The problem of uncertainty extends to the discussion of climate change, where  
42 there are both benefits and adverse effects of atmospheric Nr deposition and it is not well stated  
43 how this clouds the issue of how a change in the secondary NAAQS will have a climate change  
44 impact (and in what direction).

1 We realize that including a discussion of the future potential primary NO<sub>x</sub> and SO<sub>x</sub>  
2 standards is premature at present, but future draft REAs should include such a discussion with a  
3 perspective towards how the primary standards would or would not be protective of the  
4 environment.

5  
6 **Air Quality Analyses**  
7

- 8 1. *To what extent are air quality characterizations and analyses presented in Chapter 3*  
9 *technically sound, clearly communicated, appropriately characterized, and relevant to*  
10 *the review of the secondary NAAQS for NO<sub>x</sub> and SO<sub>x</sub>?*  
11  
12 2. *Section 3.2.1 describes an approach for evaluating the spatial and temporal patterns for*  
13 *nitrogen and sulfur deposition and associated ambient concentrations in the case study*  
14 *locations. This draft document includes the analysis for the Adirondacks case study.*  
15 *Does the Panel agree with this approach and should it be applied to the other Case Study*  
16 *Areas?*  
17  
18 3. *Section 3.2.2 describes the relative contributions of ambient emissions of nitrogen and*  
19 *ammonia to nitrogen deposition for the case study areas. To what extent is the approach*  
20 *taken technically sound, clearly communicated, and appropriately characterized?*  
21

22 Assuming the many and important missing “placeholder” sections are filled in, the air  
23 quality characterizations and analyses presented in Chapter 3 appear to provide a reasonably  
24 sound and clearly communicated characterization of the estimated deposition of reactive nitrogen  
25 and acidifying species relevant to the specific case study areas and to potential revisions to the  
26 current secondary NAAQS for NO<sub>x</sub> and SO<sub>x</sub>.  
27

28 Given that most of Chapter 3 is devoted to presentation of modeled results from the  
29 Community Multiscale Air Quality (CMAQ) and response-surface model (RSM), a major  
30 limitation of the current chapter is the absence of any evaluation of model performance for the  
31 various forms and phases of sulfur and reactive nitrogen species for which these models are  
32 applied. Filling in the placeholders that relate to model/measurement comparisons and the  
33 characterizations of uncertainty in model results is critical. As per the panel’s previous  
34 recommendations on the ISA, much of the needed evaluation of the CMAQ model should be  
35 included in the ISA. There is also a need – either in the ISA or here in the REA – for a more  
36 detailed description of the RSM, and evaluation of its performance for the S and N species.  
37

38 Given the relatively extensive sets of air quality, deposition and environmental  
39 measurements available for the Adirondacks, this may be a good place to evaluate model  
40 performance, prior to extending this case study approach to other areas. Considering the  
41 complex terrain in sections of the Adirondacks also raises concerns over the (12-km) spatial  
42 resolution of the modeled deposition compared to the spatial patterns in actual deposition  
43 (including orographic precipitation increases and cloud water deposition) vs. the spatial patterns  
44 in sensitive environmental species or ecosystems. Possibly a sensitivity analysis on variations  
45 within selected Adirondack model grid cells could help evaluate the importance of this spatial  
46 variability.

1 The panel was pleased to note the staff efforts to link the atmospheric models relating  
2 emissions to deposition, with watershed or landscape models relating deposition to  
3 environmental effects. A major issue here is a temporal disconnect in the time scales of the  
4 different models, with the atmospheric models like CMAQ typically run for much more limited  
5 time scales such as a single meteorological year. To the extent possible, it would be helpful if  
6 CMAQ could be run for a number of recent years (2002-2006), varying both meteorology and  
7 emissions, to provide a better sense of inter-annual variability and longer term spatial patterns, as  
8 well as to provide a more robust basis for model/measurement comparisons.

9  
10 Assuming the model performance evaluations indicate reasonable performance for most  
11 species of concern here, the panel also recommends that the model results (for both sulfur and  
12 reactive nitrogen species) be used to generate a number of maps that illustrate:

- 13  
14 • emissions (preferably interpolated to better illustrate high-emitting regions),  
15 • atmospheric concentrations (gaseous and aerosol and combined species),  
16 • deposition (wet, dry, total S, total N, oxidized N, reduced N, etc.),  
17 • ratios of deposition to atmospheric concentrations and deposition to emissions

18  
19 In addition to these map illustrations, scatter plots of gridded model results would also  
20 help illustrate the key relationships between the deposition metrics most relevant to  
21 environmental effects and alternative air quality metrics upon which the secondary NAAQS  
22 might be based.

### 23 24 Case Study Analyses

25

26 The proposed use of ecological indicators that can be linked to varying levels of effects  
27 (and related losses in ecosystem services) goes beyond the idea of estimating critical loads at  
28 which ecosystems experience no effects. An important consideration that has to be made as these  
29 indicators are selected is their ability to be linked to effects of varying severity rather than  
30 defining simply a "no effects" threshold because this will be important information for the  
31 eventual assessment of what effects are adverse. Possibly a separate section is needed to discuss  
32 the various levels of ANC, for example, and its application to evaluating acidity, as well as the  
33 implications for moving beyond the critical load 'no-threshold' approach to a range of effects  
34 that offer varying degrees of ecosystem protection within specified levels of probability.

35 The modeling approaches used to develop critical loads for these case studies are very  
36 different. Evaluating these different approaches could be very instructive. In particular, a  
37 discussion of the relative merits of dynamic models vs. steady state models in these specific  
38 applications is needed. For example, MAGIC does not effectively simulate watershed nitrogen  
39 dynamics, so if this is an important component of the critical load there will undoubtedly be  
40 some errors. Is it a good idea to use a dynamic model for the aquatic assessment and a  
41 steady-state model for the terrestrial assessment? Forest ecosystems are losing exchangeable  
42 cations and accumulating S and N, so by definition they are not steady state systems. Applying  
43 a steady state model to such systems is problematic as a critical loads assessment tool.

44 In these case study chapters, the discussions of varying levels of ANC and their  
45 associated effects on ecosystem function differ from what is presented in other sections of the

1 document. A more consistent approach is needed for setting the ANC limits of concern with  
2 respect to sensitivity to acidification and recovery from acidification. The panel suggests that full  
3 protection of fish species (set at 100 µeq/L) should be considered in the case study scenarios.

4 It would be useful and instructive to include an N-limited site among the case studies, for  
5 example a rapidly-growing and N-demanding Douglas-fir forest ecosystem in the Pacific  
6 Northwest or a loblolly pine stand in the Southeast.

7  
8 For better understanding of the regional effects of N deposition in the southern Sierra  
9 Nevadas, the Agency should consider a comparison of responses in mixed conifer forests (e.g.,  
10 the Kings River Project area) as compared to ANC changes in the nearby lakes of the sub-alpine  
11 and alpine zone (e.g., such as leaching of nitrate to streams, lichen species composition, and  
12 invasion of invasive grasses).

13  
14 It may also be useful to include an up front discussion of soil solution and possible  
15 surface water acidification responses to the introduction of mineral acid anions in an already acid  
16 soil (intensity effect, which can be instantaneous for both increases and recovery from  
17 acidification and requires no change in the soil itself) as opposed to an acidification effect via  
18 soil change, which can take a long time and essentially not be reversible without liming.

- 19  
20 *1. Attachment 2 presents a GIS analysis to define geographical areas that are sensitive to*  
21 *acidification and nutrient enrichment. Are the national geospatial datasets chosen*  
22 *adequate to identify sensitive areas? Are there other data sets that have not been*  
23 *identified by this analysis that we should consider? Does the panel agree with this*  
24 *approach or can they suggest alternatives?*  
25

26 The selected datasets and the general GIS approach are appropriate for this analysis, and  
27 the panel has no recommendation for additional datasets to consider. The age of several  
28 datasets (e.g., range of red spruce) and the spatial representativeness of the acidophytic lichen  
29 database are possibly significant limitations that should be noted.

- 30  
31 *2. Attachment 3 presents our current progress on evaluating the effect of aquatic*  
32 *acidification in the Adirondacks. It describes the use of the MAGIC model to evaluate*  
33 *ANC levels in selected streams and lakes in Adirondacks and Shenandoahs. To what*  
34 *extent is the approach taken technically sound, clearly communicated, and appropriately*  
35 *characterized?*  
36

37 The selection of the Adirondacks and Shenandoahs and the use of MAGIC are  
38 appropriate, however, this section needs to be edited for clarity. At present, it is generally  
39 confusing, especially the modeling approach and descriptions of MAGIC and ASTRAP.  
40 Numerous errors made it difficult to fully assess technical merits.

41 ANC has been selected as a metric to quantify the current acidic conditions and  
42 biological impacts because in many studies it was found to be the best single indicator of the  
43 biological response of aquatic communities in the acid-sensitive ecosystems. Based on the ANC  
44 values and fish populations responses, five classes of biological responses (acute, severe,  
45 elevated, moderate and low concerns) have been developed and can be used for evaluation of

1 risk assessment using the critical loads concept. EPA should consider using a more  
2 conservative value of 100 µeq/L instead of 50 µeq/L for better protection of fish species.

3 Some comparisons of these case study results with other efforts to evaluate acid  
4 deposition/biogeochemical responses in each of these sites (especially the Adirondacks) would  
5 be useful to indicate either differences from or support for these modeling efforts.

- 6 3. *Attachment 4 presents our current progress on evaluating the effect of terrestrial*  
7 *acidification. It outlines a plan to use the Simple Mass Balance Model to evaluate*  
8 *current deposition on forest soil ANC for sugar maple in Kane Experimental Forest and*  
9 *red spruce in Hubbard Brook Experimental Forest. To what extent is the approach taken*  
10 *technically sound, clearly communicated, and appropriately characterized?*

11  
12 The selection of the study area was reasonable. This chapter is highly uneven with  
13 substantial detail provided in some cases and broad generalizations in others. This makes it  
14 difficult for the reader to ascertain the salient points. This section, too, is in need of editing for  
15 clarity.

- 16  
17 4. *Attachment 5 presents our current progress on evaluating the effect of aquatic nutrient*  
18 *enrichment. It outlines a plan to evaluate how changes in nitrogen deposition affect the*  
19 *eutrophication index in two estuaries: Chesapeake Bay and Pamlico Sound. The analysis*  
20 *will model one steam reach (Potomac River and Neuse River) to determine the impact on*  
21 *the eutrophication index for the estuary. To what extent is the approach taken*  
22 *technically sound, clearly communicated, and appropriately characterized?*

23  
24 The approach is appropriately characterized. The Chesapeake Bay has been the focus of  
25 considerable efforts relating to the effects of nitrogen loading on eutrophication. There have been  
26 extensive investigations on this site and there are extensive data sets that can be used in the  
27 analyses. A drawback of this site, however, is that it is not likely that atmospheric nitrogen  
28 loading is a major component of the total nitrogen loading. Hence, the Chesapeake Bay will not  
29 be very sensitive to changes in atmospheric nitrogen inputs. Although the information on the  
30 Neuse River is less extensive, there are similar problems with the overall importance of  
31 atmospheric N loading.

- 32  
33 5. *Attachment 6 presents our current progress on evaluating the effects of terrestrial*  
34 *nutrient enrichment. It describes an approach to evaluate the effects of N deposition on*  
35 *the Coastal Sage Scrub community in California and mixed conifer forests in San*  
36 *Bernardino and Sierra Nevada Mountains. To what extent is the approach taken*  
37 *technically sound, clearly communicated, and appropriately characterized?*

38  
39 The selection of coastal sage scrub (CSS) and mixed conifer forest ecosystems is  
40 appropriate. The chapter provides a comprehensive review of the existing scientific knowledge  
41 for these two ecosystems. For development of critical loads for CSS, accumulation of biomass of  
42 invasive grasses (critical level for occurrence of catastrophic fires) could be considered (see  
43 Richard Minnich, UC Riverside, for further information). For the mixed conifer forests, change  
44 in lichen communities is a good endpoint at the low end and nitrate leaching to surface water is a  
45 good endpoint at the high end of deposition.

1 This chapter accurately summarizes the current state of science for these two ecosystems  
2 and the findings have been clearly communicated. However, the REA still needs to show how  
3 the results of these two case studies (specifically, the relationships between the observed  
4 chemical and biological changes and N atmospheric deposition, possibly expressed as critical  
5 loads) could be linked to the concentration-based NO<sub>x</sub>/SO<sub>x</sub> standards. It is imperative that this  
6 additional linkage information is incorporated in the next draft of Chapter 8.

7  
8 **Additional Effects**

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

14 These descriptions and level of detail seem adequate, but certainly the issues go beyond  
15 those associated with carbon sequestration, mercury methylation and increasing nitrous oxide  
16 emissions. The chapter could be improved by a short summary that describes those terrestrial and  
17 aquatic ecosystems for which these deleterious impacts are expected. Additional information is  
18 needed as to the effect of changes in pH on mercury concentrations in fish and other organisms.  
19 This summary should also indicate the importance of these ecosystems to individual regions and  
20 the entire United States with respect to the overall deleterious environmental impacts. In  
21 considering the impacts of nitrogen on carbon sequestration the positive (e.g., increased timber  
22 production) and the negative impacts need to be considered and presented in a balanced fashion.

23  
24 **Synthesis and Integration of the Case Study Results into the Standard Setting Process**

- 25 *1. The purpose of Chapter 7 is to summarize the Case Study results and characterize the*  
26 *relationship between levels of an ecological indicator and the associated degree of*  
27 *ecologically adverse effects. To what extent is this approach characterized at this point*  
28 *of the review? Does the Panel have any further suggested refinements at this time?*  
29

30 Chapter 7 remains in the early stage of development, thus it is difficult to provide  
31 summary comments on the overall content and direction of the Chapter. The Chapter ends  
32 abruptly and seems incomplete.  
33

34 In general terms, the outline and material included in the Chapter are appropriate to the  
35 intended summary. Table 7.1 will be very important in its final form and the EPA should  
36 carefully consider panel comments on its content. The initial statement used to begin Section 7.2  
37 strikes the right balance between important effects while recognizing their localized nature. As  
38 appropriate throughout this section, the wording should be scrutinized so that the reader is clear  
39 when NO<sub>x</sub> and SO<sub>x</sub> versus total S or N deposition are the real drivers for the effects under  
40 discussion. In the summarized cases key metric is total deposition irrespective of the original  
41 atmospheric forms of S or N inputs.  
42  
43

1 **Considerations in the Structure of the NOx/SOx Secondary Standard**

- 2 1. *Chapter 8 begins to explore how a secondary NAAQS might be structured to address the*  
3 *targeted ecological effects discussed in the risk assessment. The next draft of this*  
4 *document will include one or more examples of how this structure might be used to relate*  
5 *specific levels of air quality indicators with a corresponding ecological indicator for a*  
6 *given location and/or scenario. To what extent is the described approach technically*  
7 *sound, clearly communicated and appropriately characterized at this point of the review?*  
8 *Does the Panel have any further suggested refinements at this time?*  
9

10  
11 As noted before, the Panel views that, scientifically, a standard developed to protect  
12 ecological systems should focus on total acidifying deposition and excess nutrient enrichment,  
13 both of which include chemically-reduced nitrogen deposition. However, we also recognize the  
14 statutory and time constraints. This has led to EPA staff to focus on developing a combined  
15 standard for only sulfur and nitrogen oxides. The approach is scientifically-founded in that it is  
16 designed to lead to deposition rates that would protect the target ecosystems, as measured by  
17 specific ecosystem-based indicators (e.g., ANC). While it does not, directly, include deposition  
18 of reduced or organic forms of nitrogen, the approach does consider reduced and organic  
19 nitrogen deposition impacts, and could lead to control programs that would decrease  
20 chemically-reduced and organic N deposition. The approach is innovative and environmentally  
21 relevant. The description should be more clear and should provide more detail on how the  
22 approach would promote controlling chemically-reduced nitrogen deposition as a means to  
23 decreasing ecological acidification and nutrient enrichment. Currently, the discussion in  
24 Chapter 8 on establishing the linkage between ambient air concentrations and ecosystem effects,  
25 and the importance of spatial and temporal scales, is limited. Further, the Chapter should show  
26 how the approach directly addresses the Panel's concerns that, from a scientific perspective, the  
27 resulting environmentally-focused standard would include all reactive N deposition. Further,  
28 the Panel has concerns as to how readily that a standard based on this approach could be  
29 implemented. There are a number of complications that need to be addressed so as to fully  
30 inform policy-makers and the development of an ANPR. Critical questions that need to be  
31 elaborated upon include identifying the appropriate spatial scales and what level of protection is  
32 being provided to various ecosystems.  
33

34 In summary, the CASAC Panel was pleased to review this first draft of the Risk and  
35 Exposure Assessment to Support the Review of the Secondary National Ambient Air Quality  
36 Standard for Oxides of Nitrogen and Sulfur. The Agency's venture into new territory in the  
37 consideration of multi-pollutant standards is laudable. Shifting to standards which focus on  
38 ecological effects and employ metrics that are specifically relevant to ecosystems will have some  
39 inherent difficulties, and the Panel looks forward to the evolution of suggested approaches  
40 between now and the next draft of the REA.  
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Sincerely,

Dr. Armistead (Ted) Russell, Chair  
CASAC NO<sub>x</sub> & SO<sub>x</sub> Secondary  
NAAQS Review Panel

Dr. Jonathan M. Samet, Chair  
Clean Air Scientific Advisory Committee

**Enclosures**

1 Enclosure 1: Roster of CASAC NO<sub>x</sub> & SO<sub>x</sub> Secondary NAAQS Review Panel

2  
3 **U.S. Environmental Protection Agency**  
4 **Clean Air Scientific Advisory Committee**  
5 **NO<sub>x</sub> & SO<sub>x</sub> Secondary NAAQS Review Panel**  
6

7 **CHAIR**  
8

9 **Dr. Jonathan M. Samet**, Professor and Chair, Department of Preventive Medicine, University  
10 of Southern California, Los Angeles, CA  
11

12 **CASAC MEMBERS**  
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14 **Dr. Joseph Brain**, Philip Drinker Professor of Environmental Physiology, Department of  
15 Environmental Health, Harvard School of Public Health, Harvard University, Boston, MA  
16

17 **Dr. Ellis B. Cowling**, University Distinguished Professor At-Large Emeritus, Colleges of  
18 Natural Resources and Agriculture and Life Sciences, North Carolina State University, Raleigh,  
19 NC  
20

21 **Dr. James Crapo**, Professor of Medicine, Department of Medicine , National Jewish Medical  
22 and Research Center, Denver, CO  
23

24 **Dr. H. Christopher Frey**, Professor, Department of Civil, Construction and Environmental  
25 Engineering, College of Engineering, North Carolina State University, Raleigh, NC, USA  
26

27 **Dr. Donna Kenski**, Data Analysis Director, Lake Michigan Air Directors Consortium,  
28 Rosemont, IL  
29

30 **Dr. Armistead (Ted) Russell** (*Panel Chair*), Professor, Department of Civil and Environmental  
31 Engineering , Georgia Institute of Technology, Atlanta, GA  
32

33 **PANEL MEMBERS**  
34

35 **Dr. Praveen Amar**, Director, Science and Policy, NESCAUM, Boston, MA  
36

37 **Dr. Andrzej Bytnerowicz**, Senior Scientist, Pacific Southwest Research Station, USDA Forest  
38 Service, Riverside, CA  
39

40 **Ms. Lauraine Chestnut**, Managing Economist, Stratus Consulting Inc., Boulder, CO  
41

42 **Dr. Douglas Crawford-Brown**, Professor Emeritus, Department of Environmental Sciences and  
43 Engineering, University of North Carolina at Chapel Hill, Chapel Hill, NC

1 **Dr. Charles T. Driscoll, Jr.**, Professor, Environmental Systems Engineering, College of  
2 Engineering and Computer Science, Syracuse University, Syracuse, NY

3  
4 **Dr. Paul J. Hanson**, Distinguished R&D Staff Member, Environmental Sciences Division, Oak  
5 Ridge National Laboratory, Oak Ridge, TN

6  
7 **Dr. Rudolf Husar**, Professor and Director, Mechanical Engineering, Engineering and Applied  
8 Science, Center for Air Pollution Impact & Trend Analysis (CAPITA), Washington University,  
9 St. Louis, MO

10  
11 **Dr. Dale Johnson**, Professor, Department of Environmental and Resource Sciences, College of  
12 Agriculture, University of Nevada, Reno, NV

13  
14 **Dr. Naresh Kumar**, Senior Program Manager, Environment Division, Electric Power Research  
15 Institute, Palo Alto, CA

16  
17 **Dr. Myron Mitchell**, Distinguished Professor and Director, College of Environmental and  
18 Forestry, Council on Hydrologic Systems Science, State University of New York, Syracuse, NY

19  
20 **Mr. Richard L. Poirot**, Environmental Analyst, Air Pollution Control Division, Department of  
21 Environmental Conservation, Vermont Agency of Natural Resources, Waterbury, VT

22  
23 **Mr. David J. Shaw**, Director, Division of Air Resources, New York State Department of  
24 Environmental Conservation, Albany, NY

25  
26 **Dr. Kathleen Weathers**, Senior Scientist, Institute of Ecosystem Studies, Millbrook, NY

27  
28 **SCIENCE ADVISORY BOARD STAFF**

29  
30 **Ms. Kyndall Barry**, Designated Federal Officer, 1200 Pennsylvania Avenue, NW  
31 1400F, Washington, DC, Phone: 202-343-9868, Fax: 202-233-0643, (barry.kyndall@epa.gov)

32  
33 **Dr. Holly Stallworth**, Designated Federal Officer, 1200 Pennsylvania Avenue, NW,  
34 Washington, DC, Phone: 202-343-9867, Fax: 202-233-0643, (stallworth.holly@epa.gov)

1 Enclosure 2: Compilation of Individual Panel Member Comments on EPA’s *Risk and Exposure*  
2 *Assessment to Support the Review of the Secondary National Ambient Air Quality Standard*  
3 *for Oxides of Nitrogen and Sulfur: First Draft*  
4

5 Comments received:  
6

7 Dr. Praveen Amar ..... 13  
8 Dr. Andrzej Bytnerowicz ..... 15  
9 Ms. Lauraine Chestnut ..... 18  
10 Dr. Ellis B. Cowling..... 20  
11 Dr. Douglas Crawford-Brown ..... 27  
12 Dr.Charles T. Driscoll..... 30  
13 Dr. Paul J. Hanson ..... 40  
14 Dr. Rudolf Husar..... 46  
15 Dr. Dale W. Johnson..... 49  
16 Dr. Donna Kenski ..... 52  
17 Dr. Naresh Kumar..... 59  
18 Dr. Myron J. Mitchell ..... 62  
19 Mr. Richard Poirot ..... 81  
20 Mr. David Shaw ..... 86

21

1 **Dr. Praveen Amar**

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

6  
7 Question # 2 : Section 3.2.1 describes an approach for evaluating the spatial and temporal  
8 patterns for nitrogen and sulfur deposition and associated ambient concentrations in the case  
9 study locations. This draft document includes the analysis for the Adirondacks Case Study. Does  
10 the Panel agree with this approach and should it be applied to the other Case- Study Areas?

11  
12 Question # 3 : Section 3.2.2 describes the relative contributions of ambient emissions of nitrogen  
13 and ammonia to nitrogen deposition for the case-study areas. To what extent is the approach  
14 taken technically sound, clearly communicated, and appropriately characterized?

15  
16 **Question # 2 Response:**

17  
18 The approach outlined in Section 3.2.1 should prove to be useful in that it does propose to do a  
19 complete analysis of spatial and temporal patterns of concentrations and deposition of sulfur and  
20 nitrogen compounds (dry oxidized nitrogen, dry reduced nitrogen, wet oxidized nitrogen, wet  
21 reduced nitrogen, dry sulfur deposition and wet sulfur deposition). However, the analyses at the  
22 present time are based only on CMAQ predictions (text says “CMAQ data”; “CMAQ  
23 predictions” is more appropriate) are only for one year (2002), and for just one case-study  
24 location (Adirondacks).

- 25  
26 1. At a minimum, before one can answer the question “Does the Panel agree with this approach  
27 and should it be applied to other case-study areas?” with a reasonable level of confidence,  
28 the proposed approach needs to include an independent as well as corroborative (by  
29 comparing it to model-predicted results) analysis that is based on measured data for this  
30 case-study region (as well as the remaining case-study regions). It appears that modeled  
31 CMAQ results are reasonable, but it will increase the confidence in this approach if the  
32 measured data from NADP and CASTNet (and other networks in the Adirondacks region  
33 and other regions) corroborate the modeled predictions.
- 34  
35 2. It is also important that before this approach is applied to other case-study areas, that the  
36 placeholders on Page 3-53 and 3-54 be completed. I would recommend that the analysis  
37 of inter-annual variation in N and S (for the years 2002-2006) deposition as well as  
38 uncertainty analysis (Section 3.2.1.5) be first completed for Adirondacks region before  
39 similar analyses are done for the other four case-study regions.
- 40  
41  
42 3. Once the measured deposition data analyses are completed, Section 3.2.1 should include  
43 a brief evaluation/comparison of CMAQ predictions for the four nitrogen and two sulfur  
44 components. As a part of this evaluation, the measured precipitation data and modeled  
45 (from MM5?) precipitation data (amounts and spatial patterns) should be compared.

1 This is important since the modeled results in Section 3.2.1 indicate strong correlations  
2 between amount of precipitation and wet deposition.  
3

- 4
- 5 4. A general comment on presentation of results on dry deposition of N and S: This section  
6 needs to be more clear and explicit that we only *estimate* dry deposition (whereas we  
7 measure wet deposition) and therefore conclusions on total deposition (wet and dry) and  
8 on the relative contribution of each pathway have a level of uncertainty that is hard to  
9 determine, but needs to be acknowledged (for example, in Section 3.2.1.5 on  
10 Uncertainty).  
11

### 12 **Question # 3 Response:**

13  
14 This question involves the description of relative contributions of ambient emissions of NO<sub>x</sub>  
15 and ammonia to deposition of nitrogen (total nitrogen deposition (TND), oxidized nitrogen  
16 deposition (OND), and reduced nitrogen deposition (RND)) for the eight case-study regions. It  
17 asks if the approach used is technically sound, clearly communicated, and appropriately  
18 characterized. Here are some comments:  
19

- 20 1. The “model of the model” or the RSM (Response-Surface Model) applied to CMAQ  
21 needs a more friendly description on how it works. On Page 3-55, the text makes an  
22 effort but does not succeed in explaining what (and how) exactly RSM does. It appears  
23 that RSM is like an “instrumented CMAQ” model in that it “represents the outputs of the  
24 CMAQ model using statistical predictions.” It is not clear to me what exactly these  
25 statistical predictions are. It might be useful to compare the “workings” of RSM with,  
26 say, Direct Decoupled Method (DDM) or other “process” models (that evaluate the  
27 relative contribution of various processes embedded in the model on model predictions).  
28 Has the RSM approach been applied by the general scientific and policy/regulatory  
29 communities outside the US EPA?  
30
- 31 2. To the extent RSM is essentially based on the “brute-force” approach of “zeroing out”  
32 NO<sub>x</sub> or ammonia emissions (recognizing there are some residual emissions for NO<sub>x</sub> that  
33 include international sources and lightning, and, for NH<sub>3</sub>, they include international,  
34 non-anthropogenic and point source emissions), I am not sure this is the right approach to  
35 accurately answer Question # 3. Are there more appropriate approaches that do not  
36 “unduly stress” the CMAQ model that can better address this question of relative  
37 contributions?  
38
- 39 3. It is not clear to me how the twelve “emission control factors” on Page 3-56 were actually  
40 applied in the model. Were the emissions zeroed out only for the case-study region or for  
41 the whole modeling domain?  
42  
43

**Dr. Andrzej Bytnerowicz**

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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 logical 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?

1 Selection of coastal sage scrub (CSS) and mixed conifer forest ecosystems is appropriate  
2 because: (a) these ecosystems have high geographic coverage and are located in the important  
3 wildland–urban interface in highly populated areas, (b) they encompass a strong gradient of N  
4 deposition from the low, background levels up to the highest levels recorded in the US, (c) these  
5 ecosystems have been investigated for a long time from a perspective of interactive effects of  
6 atmospheric deposition, climate change fire and other stressors, (d) results of these  
7 investigations are well documented in the peer-reviewed literature.

8  
9 If the goal of this chapter was to review the current state of science for these two case studies,  
10 than the approach taken was technically sound and findings have been clearly communicated.  
11 However, if results of these two case studies were supposed to show how the relationships  
12 between the observed chemical and biological changes and N atmospheric deposition (possibly  
13 expressed as critical loads) could be linked to the concentration-based NO<sub>x</sub>/SO<sub>x</sub> standards, then  
14 the used approach was not inadequate and should be revised.

15  
16 The chapter provides a comprehensive review of the existing scientific knowledge for these two  
17 case studies. GIS maps show modeled N deposition in portion of California encompassing the  
18 two selected ecosystems, CSS threat from fire, and the presence of acidophyte lichens.  
19 Three-dimensional maps illustrating loss of CSS in relation to different levels of fire threats or N  
20 deposition could greatly help in developing a probabilistic approach to the evaluation of N  
21 deposition risks to important California ecosystems.

22  
23 For development of CL for CSS, in addition to biodiversity changes, or changes in lichen  
24 communities, accumulation of biomass of invasive grasses (critical level for occurrence of  
25 catastrophic fires) could be considered (see Richard Minnich, UC Riverside for further  
26 information). For the mixed conifer forests, on the low end of CL estimates changes in lichen  
27 communities and on the high end of deposition, nitrate leaching to surface water are good end  
28 points. Other, such as possible changes in understory biodiversity changes could also be  
29 considered and explored.

30  
31 Data on N deposition levels was obtained from the NADP and CASTNET networks and modeled  
32 N deposition distribution from the CMAQ model runs for 2002, which were based on the 12 km  
33 grids. As the authors of this analysis suggest, results from the 4 km grid would greatly improve  
34 accuracy of predicted relationships between N deposition and the biological effects.

35  
36 Some data for the main drivers of N dry deposition in the San Bernardino Mountains, gaseous  
37 HNO<sub>3</sub> and NH<sub>3</sub> from passive samplers have already been published (Bytnerowicz et al, 2007).  
38 More results on distribution of N nitrogenous gases monitored with passive samplers in southern  
39 California and southern Sierra Nevada in currently being prepared for publication (Andrzej  
40 Bytnerowicz, unpublished).

41  
42 Suggestion: For better understanding of regional (southern Sierra Nevada) effects of N  
43 deposition, comparison of responses in mixed conifer forests (Kings River Project) such as  
44 leaching of nitrate to streams, lichen species composition, and invasion of invasive grasses, could  
45 be compared to ANC changes in the nearby lakes of the sub-alpine and alpine zone.

46

1 Specific comments:

2  
3 Page 13, 1<sup>st</sup> paragraph – also high levels of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> are deposited to CSS of southern  
4 California.

5  
6 Page 29, Figure 3.1-1. Scale for N deposition is too coarse – a bracket 6.83-70.04 kg N/ha/yr is  
7 not acceptable.

8  
9 Page 33, 1<sup>st</sup> paragraph – bark beetle should be added as important stressor in the mixed conifer  
10 forest ecosystem.

11  
12 Page 44 and 45, section 5.2 – for the mixed conifer forest also changes of species composition of  
13 the under story vascular plants should be considered.

14  
15 Page 45, list of questions – in regard to responses of lichens to N deposition, effects of oxidized  
16 vs. reduced N should be considered. This may be of interest because there is a potential shift  
17 towards less reduced N due to the movement of dairy farms from the Los Angeles Basin to  
18 California Central Valley.

19  
20 Reference:

21  
22 A. Bytnerowicz, M. Arbaugh, S. Schilling, W. Fraczek, D. Alexander, P. Dawson (2007) Air  
23 pollution distribution patterns in the San Bernardino Mountains of southern  
24 California: a 40-year perspective. *TheScientificWorldJOURNAL* **7(S1)**, 98–109. DOI  
25 10.1100/tsw.2007.57.

**Ms. Lauraine Chestnut**

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Charge question 1: Scope of the review

There seems to be some ambiguity regarding use of the term “sensitive.” It sometimes seems to mean an ecosystem that is vulnerable but not necessarily harmed at current or historic deposition rates, 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 appropriately selected as not just sensitive, but currently being affected by N and/or S deposition.

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 is best considered relative 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 specified amount of degradation or a value to obtain a specified improvement, but the value to simply “maintain” is probably 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 but it 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. The uncertainty issue will need to be taken up again when the analysis is further along. A key question is whether there is enough confidence in the results that they are useful to assist policy decision-making. This requires more than just listing sources of uncertainty, but necessitates an assessment of the significance of the uncertainty and how it affects the results.

Case studies

The proposed use of ecological indicators that can be linked to varying levels of effects (and related losses in ecosystem services) goes beyond the idea of estimating critical loads at which ecosystems experience no effects. This does not come through in the current draft until Chapter 7, and is a missing perspective in the various case study appendices. An important consideration

1 that has to be made as these indicators are selected is their ability to be linked to effects of  
2 varying severity rather than defining simply a "no effects" threshold, because this will be  
3 important information for the eventual assessment what effects are adverse.

4  
5 The REA ultimately needs to describe the significance of the effects on ecosystem function and  
6 services at current levels of exposure and at alternative levels of exposure that might be achieved  
7 with alternative standards in the case study areas. Selecting any secondary standard probably  
8 requires more than a determination of a "safe" level because the standard needs to protect against  
9 adverse effects, not just any effects. The case study analyses seem to be headed in this direction  
10 and I look forward to seeing this further fleshed out in the second draft.

## 11 Chapter 8

12  
13  
14 An important issue is that is not yet addressed is how the analysis will deal with spatial scale in  
15 defining a potential standard. This is complicated by expected variability in ecological response  
16 to deposition in different locations even within a case study ecosystem. It is unlikely to be  
17 reasonable or even feasible to set a standard to protect the most sensitive ecosystems (or  
18 components of an ecosystem). The scale decisions can be somewhat analysis driven in that the  
19 results may show reasonable categories or groupings, such as X% of lakes in the Adirondacks  
20 that would have an ANC of 50 or 100 at various ambient co

1 **Dr. Ellis B. Cowling**  
2  
3

4 **Scope of the Review**

- 5 **2. Chapters 1 and 2 provide the background, history, and framework for this review,**  
6 **including a discussion of our focus on the four key ecological effect areas (aquatic**  
7 **acidification, terrestrial acidification, aquatic nutrient enrichment, terrestrial nutrient**  
8 **enrichment). Is this review appropriately focused in terms of characterizing the important**  
9 **atmospheric and ecologic variables that influence the deposition and, ultimately, the**  
10 **ecologic impacts of nitrogen and sulfur? Does the Panel have any further suggested**  
11 **refinements at this time?**  
12

13 My most serious reservation about the analysis framework for Chapters 1 and 2 is that chemically  
14 reduced forms of nitrogen (NH<sub>x</sub>), organic forms of nitrogen (NC<sub>x</sub>), and total reactive nitrogen  
15 (Nr) all are not included in the specific wording of any of the 20 policy-relevant questions that  
16 are said to constitute the framework for this review on the effects of nitrogen and sulfur pollution  
17 on acidification and nutrient enrichment of aquatic and terrestrial ecosystems in the US.  
18

19 The October 31, 2007 *Resolution* from the Science Advisory Board's Integrated Nitrogen  
20 Committee makes the strong assertion from this Committee's examination of much of the same  
21 body of evidence reviewed in the ISA:  
22

23 "The current air pollution indicator for oxides of nitrogen, NO<sub>x</sub>, is an  
24 inadequate measure of reactive nitrogen in the atmospheric environment.  
25 The SAB's Integrated Nitrogen Committee recommends that inorganic  
26 reduced nitrogen (ammonia plus ammonium) and total oxidized nitrogen,  
27 NO<sub>y</sub>, be monitored as indicators of total chemically reactive nitrogen."  
28

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

30 "The evidence is sufficient to infer a causal relationship between "acidifying deposition"  
31 (which includes NH<sub>x</sub>, and NC<sub>x</sub>, as well as NO<sub>x</sub> ) and the following adverse acidification  
32 effects:

- 33 a) "changes in biogeochemistry related to terrestrial ecosystems,"  
34 b) "changes in terrestrial biota,"  
35 c) "changes in biogeochemistry related to aquatic ecosystems,"  
36 d) "changes in aquatic biota."  
37

38 Also, "The evidence is sufficient to infer a causal relationship between Nr (reactive nitrogen)  
39 deposition (which also includes NH<sub>x</sub>, NC<sub>x</sub>, and NO<sub>x</sub>) and the following additional ecologically  
40 adverse nutrient- enrichment effects:

- 41 e) "alteration of biogeochemical cycling of N in terrestrial ecosystems,"  
42 f) "alteration of biogeochemical cycling of C in terrestrial ecosystems,"  
43 g) "alteration of biogeochemical flux of N<sub>2</sub>O in terrestrial ecosystems,"  
44 h) "alteration of biogeochemical flux of CH<sub>4</sub> in terrestrial ecosystems,"

- 1 i) “alteration of species richness, species composition and biodiversity in terrestrial
- 2 ecosystems,”
- 3 j) “alteration of the biogeochemical cycling of N,”
- 4 k) “alteration of the biogeochemical cycling of C,”
- 5 l) “alteration of N<sub>2</sub>O flux in wetland ecosystems,”
- 6 m) “alteration of CH<sub>4</sub> flux in wetland ecosystems,”
- 7 n) “alteration of species richness, species composition and biodiversity in wetland
- 8 ecosystems,”
- 9 o) “alteration of biogeochemical cycling of C in freshwater aquatic ecosystems,”
- 10 p) “alteration of species richness, species composition and biodiversity in freshwater
- 11 aquatic ecosystems,”
- 12 q) “alteration of the biogeochemical cycling of N in estuarine aquatic ecosystems,”
- 13 r) “alteration of the biogeochemical cycling of C in estuarine aquatic ecosystems,”
- 14 s) “alteration of species richness, species composition and biodiversity in estuarine
- 15 aquatic ecosystems,”

16  
17 “The evidence is sufficient to infer a causal relationship between:

- 18 t) “exposure to NO, NO<sub>2</sub>, and PAN and injury to vegetation” and
- 19 s) “exposure to HNO<sub>3</sub> and changes to vegetation.”

20  
21 On the basis of this substantial body of accumulated evidence, I recommend that a schematic  
22 diagram similar to Figure 1.3-1 be included in Chapter 1 to illustrate the “cycle of reactive,  
23 chemically **reduced** nitrogen species. I also recommend that:

- 24 a) Chemically reduced (NH<sub>x</sub>) and also organic forms (NC<sub>x</sub>) be included among the nitrogen
- 25 pollutants of concern in many of the 20 policy-relevant questions listed in Section 1.4 on
- 26 pages 1-17 through I-20 in Chapter 1, and \
- 27 b) Appropriated answers about chemically reduced (NH<sub>x</sub>) forms and if possible also organic
- 28 forms (NC<sub>x</sub>) of reactive Nitrogen (Nr) be presented in REA Chapters 2, 3, and 4.

#### 29 30 Air Quality Analyses

- 31 **4. To what extent are air quality characterizations and analyses presented in Chapter 3**
- 32 **technically sound, clearly communicated, appropriately characterized, and relevant to the**
- 33 **review of the secondary NAAQS for NO<sub>x</sub> and SO<sub>x</sub>?**

34  
35 With the exception of the reservations stated in answer to the Charge Questions about the  
36 Scope of the Review, I believe that the analyses presented in Chapter 3 are technically sound,  
37 clearly communicated, and appropriately characterized.

- 38  
39 **5. Section 3.2.1 describes an approach for evaluating the spatial and temporal patterns for**
- 40 **nitrogen and sulfur deposition and associated ambient concentrations in the case study**
- 41 **locations. This draft document includes the analysis for the Adirondacks case study. Does**
- 42 **the Panel agree with this approach and should it be applied to the other Case Study Areas?**

43  
44 The approach used for evaluating the spatial and temporal patters for of N and S deposition and  
45 associated ambient concentration seems very reasonable to me. This approach proved to be useful in  
46 the Adirondacks Case study and I expect it to be reasonable for other case studies as well.

1 **6. Section 3.2.2 describes the relative contributions of ambient emissions of nitrogen and**  
2 **ammonia to nitrogen deposition for the case study areas. To what extent is the approach**  
3 **taken technically sound, clearly communicated, and appropriately characterized?**  
4

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

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

10  
11 On the assumption that my presumption is correct, I consider this combination of modeling and  
12 measurement approaches to be reasonable. But I must confess that it took me a very long time to  
13 finally understand the rationale behind the statement on lines 10-12 on page 3-13 that "In order to  
14 calculate total nitrogen (by which I suppose the author meant deposition of total reactive nitrogen) the  
15 two chemical species from the NADP (i.e., NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>) were added together and then added to  
16 the total dry (deposition?) nitrogen-estimated values from CMAQ.  
17

18 It also took me a very long time to understand what was meant by the term "zero-out of NO<sub>x</sub>  
19 emissions" as used in most of the figure captions on pages 3-63 through 3-112) and periodically in the  
20 associated text.  
21

22 With regard to the questions of "clearly communicated and appropriately characterized" I offer the  
23 following comments:  
24

25 1) What a delight it was to find the following firm statement on lines 15-20 on page 3-70:  
26

27 "Figures 3.2-42 examines the relative impact of emissions on NH<sub>3</sub> of the deposition of total  
28 reactive nitrogen. Figure 3.2-42 shows that NH<sub>3</sub> emissions represent a significant contribution to  
29 total reactive nitrogen in most case study areas, although the impact varies by season and by area.  
30 The smallest impact of NH<sub>3</sub>, 10% occurs in the Potomac case study area in February. The  
31 largest impact of NH<sub>3</sub>, 73% occurs in the Neuse Case study in July. The Neuse case study has  
32 the largest overall impact of from NH<sub>3</sub> of any of the case study areas, across all four seasons."  
33

34 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  
35 three very confusing sentences that reveal clearly why EPA's constant use of the terms "reduce,"  
36 "reducing" and "reduction" is so often confusing and ambiguous:  
37

38 "One possibility is that reducing NO<sub>x</sub> reduces HNO<sub>3</sub>, which limits ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>)  
39 formation (and for existing aerosol, a reduction in HNO<sub>3</sub> shifts the equilibrium towards the gas  
40 phase), thereby increasing the lifetime of NH<sub>3</sub>. A net increase in NH<sub>3</sub>/NH<sub>4</sub> results. Because the  
41 deposit velocity of NH<sub>3</sub> is much higher than the deposition of NH<sub>4</sub><sup>+</sup> aerosol, dry deposition of  
42 NH<sub>x</sub> increases.  
43

44 The terms "reduce," "reducing" and "reduction" have both chemical and numerical meanings.  
45 Fortunately we have the unambiguous terms "decrease" and "decreasing" which have only a  
46 single (always numerical) meaning. So why not use the unambiguous term "decrease" instead of  
47 the word "reduce" when our intended meaning is numerical and thus reserve the term "reduce"  
48 for its chemical meaning?  
49

50 **Is this what was meant by the sentence quoted above?:**  
51

1 “One possibility is that **decreasing** emissions of NO<sub>x</sub> **decreases** air concentrations of HNO<sub>3</sub>,  
2 which limits ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) formation (and for existing aerosol, a **decrease** in  
3 HNO<sub>3</sub> emissions shifts the equilibrium towards the gas phase), thereby increasing the  
4 atmospheric lifetime of gaseous NH<sub>3</sub>. A net increase in the ratio of gaseous NH<sub>3</sub> to NH<sub>4</sub><sup>+</sup> aerosol  
5 in the atmosphere results. Because the deposit velocity of gaseous NH<sub>3</sub> is much larger than the  
6 deposition velocity of NH<sub>4</sub><sup>+</sup> aerosol, dry deposition of NH<sub>x</sub> increases.  
7

## 8 Case Study Analyses

- 9 **1. Attachment 2 presents a GIS analysis to define geographical areas that are sensitive to**  
10 **acidification and nutrient enrichment. Are the national geospatial data sets chosen**  
11 **adequate to identify sensitive areas? Are there other data sets that have not identified by**  
12 **this analysis that we should consider? Does the Panel agree with approach or can they**  
13 **suggest alternatives?**  
14

15 I have only limited experience with the several data bases that were used in the GIS analysis used in  
16 an attempt to define geographic areas that are sensitive to acidification. Thus I have only limited  
17 professional experience on which to base a detailed judgment in response to this question.  
18

19 Nevertheless, my general impression derived from study of the summary map on page 18 of  
20 Attachment 2, and my general awareness of soil, vegetation, surface and ground waters, and the  
21 topographical, meteorological, and climatic factors that are relevant to acidification and nutrient  
22 enrichment, lead me to conclude that the GIS approach used was generally sound. I know of no  
23 additional data sets that should be included in this analysis.  
24

- 25 **2. Attachment 3 presents our current progress on evaluating the effect of aquatic acidification**  
26 **in the Adirondacks. It describes the use of the MAGIC model to evaluate ANC levels in**  
27 **selected lakes and streams in the Adirondacks and Shenandoah. To what extent is the**  
28 **approach taken technically sound, clearly communicated, and appropriately characterized?**  
29

30 I have no direct experience on which to base an informed judgment in response to this question.  
31 However, several of my colleagues tell me that the MAGIC model is very appropriate for these kinds  
32 of analyses.  
33

- 34 **3. Attachment 4 presents our current progress on evaluating the effect of terrestrial**  
35 **acidification. It outlines a plan to use the Simple Mass Balance Model to evaluate current**  
36 **deposition levels on forest soil ANC for sugar maple in the Kane Experimental Forest and**  
37 **red spruce in the Hubbard Brook Experimental Forest. To what extent is the approach**  
38 **taken technically sound, clearly communicated, and appropriately characterized?**  
39

40 I have studied Attachment 4 with considerable care and consider that the approach taken so far (since  
41 this is still a work in progress) is technically sound, clearly communicated, and appropriately  
42 characterized.  
43

- 44 **4. Attachment 5 presents our current progress on evaluating the effect of aquatic nutrient**  
45 **enrichment. It outlines a plan to evaluate how changes in nitrogen deposition affect the**  
46 **eutrophication index in two estuaries: the Chesapeake Bay and Pamlico Sound. The**  
47 **analysis will model one stream reach (Potomac River and Neuse River) to determine the**  
48 **impact on the eutrophication index for the estuary. To what extent is the approach taken**  
49 **technically sound, clearly communicated, and appropriately characterized?**  
50

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

3  
4 **5. Attachment 6 presents our current progress on evaluating the effects of terrestrial nutrient**  
5 **enrichment. It describes an approach to evaluate the effects of nitrogen deposition on the**  
6 **Coast Sage Scrub community in California and in mixed conifer forests in the San**  
7 **Bernardino and Sierra Nevada Mountains. To what extent is the approach taken**  
8 **technically sound, clearly communicated, and appropriately characterized?**  
9

10 I have no experience with any of the western state ecosystems that are discussed in Attachment 6.  
11 Thus I have no professional experience on which to base an informed response to this question.  
12

### 13 Additional Effects

14 **1. In this chapter, we have presented results from some initial qualitative analyses for**  
15 **additional effects including the impact of sulfur deposition on mercury methylation, the**  
16 **impact of nitrous oxide on climate change, and the impact of nitrogen deposition on carbon**  
17 **sequestration. Are these effects sufficiently addressed in light of the focus of this review on**  
18 **the other targeted effects in terms of available data to analyze them?**  
19

20 Chapter 6 provides a useful overview of the impact of sulfur deposition on methylation of mercury  
21 which seems to me to be very worthy of consideration with regard to setting appropriate limits on the  
22 amount of air emission of sulfur oxides that should be permitted in various regions of the US. I see  
23 little reason for worry about nutrient enrichment or acidification effects of carbon sequestration. I do  
24 believe, however, that nitrous oxide emissions should be incorporated in EPA's review of the  
25 NAAQS for nitrogen pollution and its effects on terrestrial and aquatic ecosystems.  
26

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

28  
29 **1. The purpose of Chapter 7 is to summarize the Case Study results and characterize the**  
30 **relationship between levels of an ecological indicator and the associated degree of**  
31 **ecologically adverse effects. To what extent is this approach technically sound, clearly**  
32 **communicated and appropriately characterized at this point of the review? Does the Panel**  
33 **have any further suggested refinements at this time?**  
34

35 I believe that the attempt being made in Chapter 7 to building a scientifically sound linkage between  
36 carefully selected ecological indicators and the extent and magnitude of ecologically adverse effects  
37 is a very complicated but very desirable goal.  
38

39 In the development of Chapter 7, and even more in Chapter 8, it appears that EPA is deliberately  
40 trying to build a case for making some modest decrease in emissions of nitrogen oxides (NO<sub>x</sub> --  
41 which is already recognized as a Criteria Pollutant ) --and of course would help decrease the adverse  
42 acidification and nutrient enrichment effects of total acidifying deposition and of total reactive  
43 nitrogen -- without also having to decrease the amounts of chemically reduced and organic forms of  
44 nitrogen that can be emitted into the air.  
45

46 I believe that the extent of decrease in reactive nitrogen pollution loads that are needed to protect  
47 sensitive terrestrial and aquatic ecosystems of this country cannot be achieved without taking steps to  
48 also include significant decreases in the amounts of chemically reduced and perhaps also organic  
49 forms of total reactive nitrogen.  
50

1 **Considerations in the structure of the NO<sub>x</sub>/SO<sub>x</sub> Secondary Standard (Chapter 8)**  
2

- 3 **2. Chapter 8 begins to explore how a secondary NAAQS might be structured to address the**  
4 **targeted ecological effects discussed in the assessment. The next draft of this document will**  
5 **include one or more examples of how this structure might be used to relate specific levels of**  
6 **air quality indicators with a corresponding ecological indicator for a given location and/or**  
7 **scenario. To What extent is the described approach technically sound, clearly**  
8 **communicated and appropriately characterized at this point of the review? Does the Panel**  
9 **have any further suggested refinements at this time?**  
10

11 In Section 8.1 – *Possible Structure of a Secondary Standard* – the diagram in Figure 8.1-1 was  
12 especially informative of the approach that is currently being considered. The example given  
13 was based on the ecological indicator ANC (acid neutralizing capacity) and assumed that the  
14 pollutants of concern were only the chemically oxides form of reactive nitrogen (NO<sub>x</sub>) and sulfur  
15 (SO<sub>x</sub>) , and not also the chemically reduced forms of reactive nitrogen (NH<sub>x</sub>).  
16

17 Even though I was disappointed that only oxidized form of reactive nitrogen were considered in  
18 this illustration, I believe this diagram provides a very rational basis for considering various  
19 aspects of a secondary standard for total reactive nitrogen and sulfur.  
20

21 The opening sentences of the first two paragraphs of Chapter 8 illustrate why it appears that EPA  
22 is deliberately trying to build a case for dealing exclusively with oxides of nitrogen and oxides of  
23 sulfur (which are already identified as Criteria Pollutants) rather than having also to deal with the  
24 chemically reduced and organic forms of reactive nitrogen) which also contribute to the many  
25 adverse acidification and nutrient enrichment effects of nitrogen and sulfur pollution (but are not  
26 yet recognized as Criteria Pollutants).  
27

28 The two lead sentences read as follows:

29 Paragraph 1: “

30 “The previous chapters have provided an understanding of the risks associated with current  
31 deposition of nitrogen and sulfur associated with ambient atmospheric concentrations of NO<sub>x</sub>  
32 and SO<sub>x</sub>.”  
33

34 In this sentence, please note especially the words “current (not anticipated future) deposition”  
35 and “ambient (not anticipated future) concentrations” and “NO<sub>x</sub> and SO<sub>x</sub>” rather than “total  
36 total reactive nitrogen (Nr), or” total acidifying deposition” or “NO<sub>x</sub>, NH<sub>x</sub>, and SO<sub>x</sub>.”  
37

38 Paragraph 2:

39 “In this chapter, we discuss constructing a standard based on achieving a uniform level of  
40 ecosystem protection. We explore a framework by which ambient atmospheric  
41 concentrations of NO<sub>x</sub> and SO<sub>x</sub> can be translated into a measure of ecosystem effects, using  
42 then transformation functions described below.”  
43

44 In this sentence, please note once again the words “ambient (not anticipated future)  
45 concentrations” and “NO<sub>x</sub> and SO<sub>x</sub>” rather than “total total reactive nitrogen (Nr), or” total  
46 acidifying deposition” or “NO<sub>x</sub>, NH<sub>x</sub>, and SO<sub>x</sub>,” and the words “uniform (not regional, local,  
47 or ecosystem-specific) level of ecosystem protection.”  
48

49 A glimmer of hope with regard to consideration of both chemically reduced and oxidized form of  
50 reactive nitrogen is contained in the sentence on lines 20-23 on page 8.5:  
51

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

**Dr. Douglas Crawford-Brown**

I am charged primarily with Scope of the Review, and so my comments are primarily on that issue. The specific Charge Question addressed is:

“Scope of the Review: Chapters 1 and 2 provide the background, history and framework for this review, including a discussion of our focus on the four 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 sulphur? Does the panel have any further suggested refinements at this time?”

This review also considers Chapters 7 and 8, as these are the core of the document in regards to an eventual regulatory decision.

As with my review of the ISA, my conclusion here is that the REA does in fact satisfy the goal in the Charge Question, subject to the comments below. The correct effects are considered (there may be more effects one could note, but the ones considered here are the most significant and are likely to bound the areas of concern adequately), and the correct relationships to atmospheric and ecologic variables are considered (again to the extent these are needed to draw the primary conclusions). The document is well written, being easy to follow and nicely organized, although the wheels fall off a bit – or are not even present - in Chapters 7 and 8). The authors have culled the most important conclusions from an immense literature, focusing the reader properly onto the key findings. A theme that will emerge below, however, is my feeling that the available data and analyses may support the need for considering a reduced NAAQS for NO<sub>x</sub> and SO<sub>x</sub>, but is insufficient to suggest the actual ambient levels needed to avoid demonstrably adverse effects (which I contrast with effects alone, which may or may not be sufficient to deem adverse).

This document would benefit greatly from an Executive Summary similar to the one in the ISA. There is a large amount of information here, but it can be boiled down to a few key conclusions. My fear is that failing to do that, the authors may find specific parts of the document picked in the policy process because they support a desired conclusion and policy solution. There needs to be a concise and unambiguous statement of the key scientific conclusions, and an Executive Summary is exactly the place to put these.

I found Chapter 1 very well written. The document lays out the relevant policy questions and even relates these (in contrast to past documents) clearly to the task of deciding whether the NAAQS needs to be revised and, if so, how the information would be used to do that.

Figure 1.4-1 is quite interesting, but it also lays clear the one glaring problem with a secondary NAAQS, since the key element is the Ecological Effect Function. I don't see where such a function is sufficiently well established to allow use in setting a secondary standard, other than perhaps as an analogue to an effects threshold in non-cancer human health risk assessment,

1 probably with some margin of safety inherent in it due to the inability to draw a proper line  
2 between effect and adverse effect.

3  
4 Chapter 2 begins by listing the appropriate effects, and I agree with the selection of these based  
5 on the information in the ISA. Table 2.1-1 is particularly useful in providing a road map to the  
6 material in the entire document. In the previous draft, I was unclear as to the purpose of the case  
7 studies. In the present draft, this point is clearer, and I agree with the idea that given the very  
8 large inhomogeneity in both exposure conditions and species across different geographic areas,  
9 the best that can be done is to select a few representative but sensitive regions and determine  
10 where the ambient levels would need to be to protect these. The one thing missing is a clear  
11 statement as to how unique these case study areas are. One can't set national standards based on  
12 a few outliers in the national distribution, and I believe a better case can be made in the  
13 document as to why these particular areas studied are not in the extremes of the tail of inter-site  
14 distributions of sensitivity.

15  
16 I particularly like the structure of the assessment outlined in the seven steps. While the  
17 committee may have disagreements over specific methodological issues, these seem to me the  
18 appropriate steps and an innovative way to get at the issue of a secondary NAAQS that relies  
19 maximally on available data. I fully support the EPA staff in this choice of framework, even if in  
20 the end they must execute it somewhat more qualitatively than might be desired. The point is that  
21 it is the right way to be thinking about the NAAQS.

22  
23 The ecosystem services discussion in Chapter 2 was interesting to read. It presented the subject  
24 well, and it is evident to me that ecosystem services is one lens through which to view a  
25 secondary NAAQS (although it doesn't capture issues such as inherent rights of other species).  
26 My problem lies in a disconnect between the detailed discussion of ecosystem services and the  
27 specific Ecological Effect Functions in Figure 1.4-1. I don't believe the document, or even the  
28 current state of the science, allows for development of such a Function needed to determine how  
29 much a specific ecosystem service is impacted by a given N or S loading, or how adverse is a  
30 given decline in ecosystem service. I wouldn't be inclined to support a position that says any  
31 decline is automatically adverse; the same applies to my position on human health impacts. Due  
32 to this methodological and computational gap, the Ecosystem Services discussion in Chapter 2  
33 comes off as more interesting than truly informative – a good idea that can't quite be pulled off  
34 when the data are analyzed.

35  
36 The uncertainty discussion, as in almost all of the REAs we have reviewed, is quite generic and  
37 qualitative. But given the nature of this exercise, I am not sure a more quantitative approach to  
38 uncertainty would inform the final decision. This is because, while there are quantitative  
39 uncertainties having to do with the data and modelling, an equally important uncertainty is the  
40 conceptual relationship between the case studies and any sort of statement about the impact of a  
41 national standard.

42  
43 As Chapters 3, 4 and 5 are outside my area of expertise, especially with respect to specifying  
44 where the staff should look for representative but sensitive case study areas, I don't provide  
45 comments here, other than to note that Chapters 4 and 5 are of little use given their sketchy  
46 nature.

1  
2 The heart of the REA is found in Chapters 7 and 8. Table 7.1-1 agrees with the information  
3 provided in Chapter 1, so at least the methodology is consistent on this point. The framework of  
4 thinking laid out in this Chapter is appropriate, although provided here in much too sketchy a  
5 form for me to agree or disagree with how it is being executed. There remain two areas in which  
6 substantial disagreement can arise between individuals reviewing the document: (1) the  
7 methodological steps in calculating impacts on a given case study site and (2) drawing summary  
8 conclusions across sites. At the moment, the document does not fully clarify the first, and the  
9 second issue is dealt with more through aspirations than any clear approach. But I must withhold  
10 judgment until the final report is prepared. The staff is at least headed in the right direction, have  
11 a proper roadmap in front of them and have the expertise on hand to carry out these tasks.  
12

13 In Chapter 8, the phrase “uniform level of ecosystem protection” occurs, and seems to become a  
14 key idea in how a NAAQS might be considered. This idea really needs more of an explanation.  
15 Given the high levels of inhomogeneity, and the fact that the conclusions rest ultimately on case  
16 studies of sensitive areas, and the quite diverse kinds of effects being considered, I don’t  
17 understand what is meant by a “uniform level of ecosystem protection”. It surely doesn’t mean  
18 that the level of effect will be the same across all ecosystems in the country, or even that the  
19 same ambient level will produce the same level of effect everywhere, or that the effects will be  
20 equally adverse in some deeper sense. And there is no common metric to which all these diverse  
21 effects can be reduced. So, just what does it mean?  
22

23 Again, Figure 8.1-1 is the right kind of structure, but I don’t see how the Ecological Effect  
24 Function will be developed as anything other than a threshold model. And I don’t see where a  
25 margin of safety is recognized or introduced. But it is still the right conceptual approach if it can  
26 be pulled off methodologically.  
27

28 Much of the discussion in Section 8.2 seems to me of a policy nature, belonging in a much  
29 earlier chapter. It almost comes across as being filler here while the staff tries to figure out  
30 exactly how they will execute the ambitious steps in Figure 8.1-1. I recommend moving it to the  
31 front of the REA in either Chapter 1 or 2.  
32

33 The rest of the Chapter 8 strikes me as a lot of scientific detail with little to connect it all to the  
34 final calculations. I can’t comment on many of the equations proposed, because they relate more  
35 to environmental transport and fate than to effects. But it is evident to me that there is still a large  
36 gap between methodologies to estimate deposition and methodologies to relate these loadings to  
37 any specific effect that will drive a NAAQS.

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**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<sub>x</sub>) and sulfur dioxide (SO<sub>2</sub>). 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

1 important component of the critical load, there will undoubtedly be some errors. I find it  
2 disconcerting that for the terrestrial acidification assessment a steady-state model is being  
3 used. First, is it a good idea to use a dynamic model for the aquatic assessment and a  
4 steady-state model for the terrestrial assessment? While I agree with the authors that  
5 critical loads are a steady-state phenomenon, ecosystems are not. Forest ecosystems are  
6 losing exchangeable cations and presumably accumulating sulfur and nitrogen. This  
7 makes these systems by definition not a steady-state and increasingly sensitive to inputs  
8 of acidic deposition. While the application of a steady-state model is easy, it would  
9 seem to be problematic as an assessment tool. There are clear limitations in using a  
10 steady-state model for critical loads assessments. Finally, I don't understand how the  
11 critical loads will be determined for the coastal and terrestrial nutrient case studies.  
12 SPARROW is a statistical model and it is not clear how this can be used to evaluate  
13 greater and lower N loads.  
14

15 2. *Nitrogen saturation.* Throughout the text, N saturation is referred to. However, I could  
16 not find any discussion of this phenomenon in the introductory sections. It is discussed  
17 in the ISA but not (that I could find) in the REA. A brief summary of N saturation might  
18 be helpful.  
19

20 3. *Time scale disconnect.* There appears to be a disconnect between the time scales used  
21 for the atmospheric modeling and the effects assessments. Ecosystem effects of air  
22 pollutants are largely manifested over decades to multiple decades. Certainly the  
23 simulations conducted by MAGIC are conducted with what I believe to be the  
24 appropriate temporal perspective. I believe the time-scale for nutrient effects on  
25 ecosystems similarly have a long-term perspective. In contrast, the deposition/CMAQ  
26 analysis seems to be largely focused on a short-term or seasonal perspective. Why?  
27 There seems to be a complete disconnect in the atmospheric and effects modeling  
28 concerning time-scale of analysis. Isn't the primary concern here ecological effects?  
29 Do seasonal or monthly patterns in air concentration or deposition have any relevance for  
30 this long-term analysis of ecosystem effects?  
31

32 4. *Climate.* I am a bit surprised that no discussion is given to changing climate. The  
33 framework to be developed is examining effects that will play out over the next decades.  
34 It is projected that climate will also change substantially over the same period. Climate  
35 change will affect hydrology and ecosystem response to air pollution. Climate change  
36 should be mentioned and needs to be addressed in future assessments.  
37

38 5. *Establishing standards around ambient air concentrations.* In Chapter 8, limited  
39 discussion was advanced in establishing ecosystem effects around ambient air  
40 concentrations. While I can see that this might be a desirable objective, as we currently  
41 have primary standards and some quasi secondary standards based on ambient air  
42 concentrations. However, for ecosystem effects, I do not see this approach as workable.  
43 I think the standard needs to be based ultimately on total sulfur and total nitrogen  
44 deposition. There are many species of sulfur and nitrogen all which contribute to  
45 ecological effects but having different residence times in the atmosphere. These  
46 residence times vary in time and space. The key driver of ecological effects is long-term

1 total deposition. Establishing standards around ambient air concentrations would seem  
2 to be intractable.

- 3  
4 6. *Spatial variability in sensitivity.* I'm not sure if this consideration is relevant for the  
5 nutrient case studies, however, the acidification case studies will exhibit considerable  
6 spatial variability in sensitivity to acidic deposition. There is a range of ecosystem  
7 sensitivity to acidification from highly sensitive to highly insensitive. How will this  
8 range of ecosystem response to acidic deposition be addressed when establishing the  
9 critical load? Will all ecosystems be protected? 90%, 50%. Some discussion of this  
10 consideration would be helpful.

11  
12 **Written Document Considerations:**

- 13  
14 1. *Written perspective.* The document is written from the "we" perspective (i.e., we did  
15 this..., we analyzed that...). I find this approach somewhat disconcerting. The reason  
16 being it is not clear who owns the document. Is this EPA's document or the contractor's  
17 document? Who are we? I would like to see the document altered.
- 18  
19 2. *Typos, errors, writing mistakes.* As with the last draft of the ISA, the REA (and the 2<sup>nd</sup>  
20 draft of the ISA) is filled with mistakes and typos. I point out many of these in my  
21 specific comments (see below). However, these are by no means all the mistakes. This  
22 document needs to be carefully read, proofread and edited for consistency and to  
23 eliminate the mistakes.
- 24  
25 3. *Redundancy.* There are many redundant sections in the document. This makes a very  
26 long document, longer than it needs to be. The document should be edited to eliminate  
27 the redundant text.
- 28  
29 4. *Tense.* The REA switches back and forth from the past to present tenses. I can see  
30 writing in either tense. However, the document should be edited so it is written in a  
31 consistent tense.

32  
33 **Specific comments:**

- 34  
35 Page 1-2, line 16 Units of ANC  $\mu\text{eq/L}$ ?  
36  
37 Page 1-11, line 24 I don't agree with the statement. Most published studies  
38 document inputs of oxidized and reduced N. A few don't, but  
39 most do.  
40  
41 Page 1-12, line 10 Space missing.  
42  
43 Page 1-12, line 13 I would change the wording. Acidification is an environmental  
44 effect due primarily to sulfur and secondarily nitrogen in most  
45 environments.  
46

1	Page 1-13, line 12	As above, need to define N saturation.
2		
3	Page 1-13, line 19	Change air to atmosphere.
4		
5	Page 1-15, line 22	alpine
6		
7	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.
8		
9		
10		
11	Page 2-2, table 2.1-2	Under aquatic acidification also include hydrologic flow paths under sensitivity variable.
12		
13		
14	Page 2-4, line 15	Eliminate comma
15		
16	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.
17		
18		
19		
20	Page 3-8	I would like to see a brief description of organic N deposition, including sources.
21		
22		
23	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 <sub>3</sub> /ha-yr).
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31		
32	Page 3-12, line 10	data are ...
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34	Page 3-13, line 1	data were...
35		
36	Page 3-13, line 6	Change to... kg/ha-yr.
37		
38	Page 3-13, line 7	data were...
39		
40	Page 3-16, line 5	Need to clarify the time interval kg/ha-yr?
41		
42	Page 3-16, table 3.2-2	It is not clear what this table is. Some additional text is necessary.
43		
44	Page 3-19	It would be helpful to put the Adirondack Park and the Shenandoah National Park boundaries and the Chesapeake and
45		

1 Pamlico watershed areas on the map so the reader can understand  
2 the scope of the analysis relative to the total resource.  
3  
4 Page 3-25, line 7,8 Change to... kg N-ha/yr.  
5  
6 Page 3-35, line 12 Change to... fairly uniform.  
7  
8 Page 3-36, figure 3.2-14 Why show figures of both monthly and seasonal deposition? Isn't  
9 this redundant?  
10  
11 Page 3-38, figure 3.2-16, 17, 18, 19  
12 These figures are difficult to read and are they really helpful?  
13  
14 Page 3-40, line 4 Change to... generally uniform...  
15  
16 Page 3-50, lines 3, 17 and Page 3-51, line 6  
17 Change...drop to decrease  
18  
19 Page 3-50, figure 3.2-28 and elsewhere  
20 Aren't the monthly patterns in wet deposition strongly driven by  
21 the quantity of precipitation? Wouldn't patterns for a different  
22 year with different precipitation patterns be different? As a result,  
23 this temporal section is misleading because it is strongly affected  
24 by the meteorology for that year. If true, why include all this  
25 analysis? As a minimum, this fact should be clarified and some  
26 data provided on 2002 as a reference year.  
27  
28 Page 6-1, line 3-4 Rephrase. Every wetland has sulfate. The production of methyl  
29 mercury is largely mediated by sulfate reducing bacteria.  
30  
31 Page 6-1, line 22 Also phosphorus (or N) can be important as it regulates aquatic  
32 productivity and therefore mercury concentrations in aquatic  
33 organisms (Driscoll et al. 2007).  
34  
35 Page 6-2, line 4 Change to...Industrial Revolution.  
36  
37 Page 6-2, line 28 This sentence needs to be clarified. Ionic mercury can be reduced  
38 and evaded and separately methylated. Methyl mercury is not  
39 reduced. Where does this 1-2% come from? The extent of  
40 methylation is highly variable from ecosystem to ecosystem.  
41  
42 Page 6-4, line 14-16 Why is methane needed? Why do you need HgS in the equation?  
43 Define MeHg<sup>+</sup>.  
44  
45 Page 6-4, line 20 Also anoxic conditions.  
46

1	Page 6-4, last paragraph	There are other studies that probably should be cited (Branfireun et al. 1999), (Jeremiason et al. 2006).
2		
3		
4	Page 6-5, line 12	Change to...methylation can occur within.
5		
6	Page 6-5, figure 6.1-2	Hg can also be supplied from sediments.
7		
8	Page 6-6, line 3	Change to... anoxia, sulfate).
9		
10	Page 6-6, line 5	Change to... response, hydrology, nutrient loading, limnology).
11		
12	Page 6-10, line 4	Is this really true? I do not believe it. % methyl mercury is highly variable. Need to correct.
13		
14		
15	Page 6-12, line 5	Change to... oxidizing $\text{NH}_4^+$ .
16		
17		
18	Page A3-1, line 15	Subscript 2.
19		
20	Page A3-1, line 20	hydrogen ion, and $\text{Al}^{n+}$ .
21		
22	Page A3-1, line 20 and throughout the document	
23		I don't think the writers of this document understand the concept
24		of buffering capacity. Buffering capacity is the resistance of a
25		system to changes in pH. I would recommend eliminate using the
26		term here and elsewhere or change the phrasing to use it correctly.
27		An alternative could be acid neutralizing capacity or acid-base
28		status.
29		
30	Page A3-2, 1 <sup>st</sup> paragraph	I suggest adding a sentence or two about
31		immobilization/mobilization of $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ by plants/soil
32		organic matter.
33		
34	Page A3-2, line 10	There are numerous chemical indicators.
35		
36	Page A3-2, line 12	$\text{NO}_3^-$ , $\text{Al}^{n+}$
37		
38	Page A3-2, line12	Change to... of base cations; and ANC.
39		
40	Page A3-2, line 27	Change to... precipitation enters the soil and soil water to
41		emerge...
42		
43	Page A3-2, line30	$\text{K}^+ + \text{Na}^+ + \text{NH}_4^+ - (\text{SO}_4^{2-} + \text{NO}_3^- + \dots)$ in ( $\mu\text{eq/L}$ )
44		
45	Page A3-3, line 5	Change to... low pH.
46		

1	Page A3-3, line 6	Change to... This is the acid neutralizing capacity (ANC), or the
2		...
3		
4	Page A3-5, line 4	acidic surface waters (14%; ANC<0 µeq/L).
5		
6	Page A3-5, line 26	United States
7		
8	Page A3-6, line 24	Need to define the time and mass basis of deposition (e.g., kg
9		SO <sub>4</sub> /ha-yr or kg S/ha-yr).
10		
11	Page A3-7, line 12	Change to... weathering rates and limited neutralizing of acid
12		inputs.
13		
14	Page A3-8, line 5	Again need to define the time and mass basis of deposition.
15		
16	Page A3-9, line 19	Al <sup>n+</sup>
17		
18	Page A3-9, line 21	with limited leaching
19		
20	Page A3-9, line 23	EPA-administered Long-Term Monitoring (LTM) program.
21		
22	Page A3-15, line 12	SO <sub>4</sub> <sup>2-</sup>
23		
24	Page A3-16, line 9	comma
25		
26	Page A3-16, line 19	it's the acid neutralizing capacity of a ...
27		
28	Page A3-16, line 21	The acid neutralizing capacity of a ...
29		
30	Page A3-17, line 3	20 µeq/L (limited protection)
31		
32	Page A3-16, line 12	This sentence makes no sense. At ANC = 0 µeq/L a water is
33		chronically acidic.
34		
35	Page A3-17, line 8	Sub and super script
36		
37	Page A3-20, line 5	Units should be eq/ha-yr.
38		
39	Page A3-20, line 7,8	I would eliminate the term occult deposition simply call it cloud
40		and fog deposition.
41		
42	Page A3-20, line 10	Units meq/m <sup>2</sup> -yr
43		
44	Page A3-22, line 24	This description needs to be expanded or clarified. There are
45		more than 200 NADP sites.
46		

1	Page A3-28, line 25	in the catchment
2		
3	Page A3-29, line 19	400 meq/m <sup>3</sup>
4		
5	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.
6		
7		
8	Page A3-33	There needs to be some discussion on the time and nitrogen retention assumptions used to obtain critical loads.
9		
10		
11	Page A4-1	I would change the title to Forest Acidification Case Study.
12		
13	Page A4-1, line 17	hydrogen ions
14		
15	Page A4-1, line 19	where strong acids
16		
17	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.
18		
19		
20		
21	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.
22		
23		
24		
25	Page A4-9, line 18	Should be (Driscoll et al. 2001).
26		
27	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 <sup>2+</sup> in Pennsylvania.
28		
29		
30		
31	Page A4-19, line 1	Again need to specify the mass and time basis of deposition.
32		
33	Page A4-28, line 10	acidity input neutralized by
34		
35	Page A4-28, line 18	parties
36		
37	Page A4-49	Need to indicate the units of the figure.
38		
39	Page A4 References	Should be BioScience.
40		
41	Page A5-18, 1 <sup>st</sup> paragraph	Need to use metric units.
42		
43	Page A5-26, line 6	Need to define Nr.
44		
45	Page A5-30	SPARROW is a steady-state model. Will need to demonstrate how you can use it.
46		

1		
2	Page A5-55, line 7	were from
3		
4	Page A5-58, line 6, 8	Does the SAV coverage really have this level of significant
5		figures?
6		
7	Page A6-10, line 1	Change to... Mediterranean climate. This climate is... \
8		
9	Page A6-25, line 16	result of long-term elevated N deposition rather than pulses
10		
11	Page A6-42, line 7	data are
12		
13	Page 7-3, line 12	Change to... where strong acids are
14		
15	Page 7-11, line 2	catchment to neutralized acid anion deposition is known as acid
16		neutralizing capacity.
17		
18	Page 8-1, line 14	There cannot possibly be a uniform level of ecosystem protection
19		due to the inherent variability in ecosystem sensitivity.
20		
21	Page 8-4, figure 8.1-1	Add climate as a variable/fixed factor.
22		
23	Page 8-5, line 2	What is meant by the point of deposition?
24		
25	Page 8-8, line 14	What about forest acidification?
26		
27	Page 8-8, line 14	How can you say whether precipitation occurs or not. Is there a
28		location where precipitation does not occur? Rewrite sentence.
29		
30	Page 8-10, line 24.	Do you mean deposition is expressed on an equivalence basis?
31		Please clarify.
32		
33	Page 8-11, line 4	This sentence makes no sense and should be rewritten.
34		
35	Page 8-14, line 1	data are
36		
37	Page 8-14, line 20	Do you mean equivalence ratio?
38		
39		

40 **References:**

- 41
- 42 Branfireun, B. A., N. T. Roulet, C. A. Kelly, and J. W. M. Rudd. 1999. In situ sulphate
- 43 stimulation of mercury methylation in a boreal peatland: Toward a link between acid rain
- 44 and methylmercury contamination in remote environments. *Global Biogeochemical*
- 45 *Cycles* **13**:743-750.

- 1 Driscoll, C. T., Y.-J. Han, C. Y. Chen, D. C. Evers, K. F. Lambert, T. M. Holsen, N. C.  
2 Kamman, and R. K. Munson. 2007. Mercury contamination in forest and freshwater  
3 ecosystems in the Northeastern United States. *BioScience* **57**:17-28.
- 4 Driscoll, C. T., G. B. Lawrence, A. J. Bulger, T. J. Butler, C. S. Cronan, C. Eagar, K. F. Lambert,  
5 G. E. Likens, J. L. Stoddard, and K. C. Weathers. 2001. Acidic deposition in the  
6 northeastern United States: Sources and inputs, ecosystem effects, and management  
7 strategies. *BioScience* **51**:180-198.
- 8 Jeremiason, J. D., D. R. Engstrom, E. B. Swain, E. A. Nater, B. M. Johnson, J. E. Almendinger,  
9 B. A. Monson, and R. K. Kolka. 2006. Sulfate addition increases methylmercury  
10 production in an experimental wetland. *Environmental Science and Technology*  
11 **40**:3800-3806.
- 12 St. Clair, S. B., J. E. Carlson, and J. P. Lynch. 2005. Evidence for oxidative stress in sugar maple  
13 stands growing on acidic, nutrient imbalanced forest soils. *Oecologia* **145**:258-269.
- 14 Warby, R. A. F., C. E. Johnson, and C. T. Driscoll. (in press). Continuing acidification of organic  
15 soils across the northeastern USA: 1984 - 2001. *Soil Science Society of America Journal*.  
16  
17  
18

**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 NOx and SOx...

Page 1-10 line 23: N<sub>2</sub>O 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

1 “there is currently no published national assessment of empirical critical loads for N in the U.S.....”  
2 Table 3-25 is a nice summary of what is known. The REA needs to reflect the limited amount of data  
3 available for developing quantifiable thresholds, and appropriately characterize those ecosystems for  
4 which it might appropriately be applied. Avoid inappropriate extrapolations. Lines 14 to 19 on page  
5 4-16 of the ISA include good statements that should be used within the REA to qualify the nature of  
6 ecosystem sensitivity.

7  
8 Page 1-15 lines 21 and 22: Similarly, the wording may need to be changed here to suggest if these levels  
9 represent an appropriate threshold for all or just some sensitive grasslands.

10  
11 Page 1-15 line 30: Add a reference for the sentence ending on this line.

12  
13 Figure 1.3-3 still doesn't show the productivity enhancement effect of N, which is clearly a dominant  
14 process in the N cycle.

15  
16 Bottom of page 1-17: Should some mention be made at this point to N standards for water pollution? It  
17 isn't necessary, but might be a useful connection. Section 3.3.6 of the ISA and the associated annex might  
18 be cited.

19  
20 Figure 1.4-1 doesn't adequately capture the integrated nature of NO<sub>x</sub> and SO<sub>x</sub> pollution that is being  
21 attempted in this document. Are they truly intertwined all along this process or do they only come  
22 together after deposition takes place?

## 23 24 **Chapter 2**

25  
26 In Table 2.1-1 ANC should be defined, productivity should be added as an ecosystem service where  
27 appropriate, and N leaching might be added as an indicator of terrestrial nutrient enrichment. The  
28 characteristics of sensitivity for terrestrial nutrient enrichment might be updated.

29  
30 Sections of Table 2.3-1 still need to be filled in.

## 31 32 **Chapter 3**

33  
34 Page 3-4 lines 6 and 7: Check the wording. 30 to 70% of the animal wastes can't be emitted as NH<sub>3</sub>.  
35 Should it read 30 to 70% of the N losses from animal wastes?

36  
37 Page 3-5 lines 10 to 15: Are there not any natural sulfur emissions in and around Yellowstone or in other  
38 hot springs areas of the country? I realize they may be inconsequential....

39  
40 Pages 3-10 to 3-11: Question: Have all of the emissions reductions resulting from past clean air  
41 legislation been realized? Will new standards for ozone impact the likely deposition rates for N in the  
42 future? Should such a discussion be included someplace in this document?

43  
44 Chapter 3 doesn't include much on temporal changes in deference to the maps of recent conditions.  
45 Those are fine, but I think some discussion of where we have been and where we are going should be  
46 included in the REA. Figures 2-59 or 2-103 from the ISA might be considered.

47  
48 Page 3-12: Super and subscripts for charge are missing for SO<sub>4</sub><sup>-2</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup>.

49  
50 Question: Do the QMAC estimates of deposition to terrestrial systems include foliar uptake of NO or NO<sub>2</sub>  
51 near urban areas or along major roadways where air concentrations are high enough to drive this

1 pathway?  
2  
3 Table 3.2-2 is not well defined. It needs references.  
4  
5 I was disappointed by how much information was still not added to the document (especially in this  
6 Chapter). We are being asked to provide comment on a document that has a lot missing from it.  
7  
8 Captions to Figure 3.2-12, -13, and -14 need to be reworded to "...nitrogen deposition by source and  
9 quarter.... The most interesting data in many cases has to do with the source of N forms rather than the  
10 season of the year.  
11  
12 Figures 3.2-22, -23, -24, and -25 lack units (presumably kg/ha as for N).  
13  
14 Captions to Figure 3.2-27 and -28 need to be reworded to "...sulfur deposition by source and quarter....  
15  
16 Page 3-54: Again...we don't have much to review yet.  
17  
18 Page 3-54 line 14: Reword as..."Public welfare effects associated with direct exposure to NOx and SOx  
19 do not occur for current ambient concentrations."  
20  
21 Page 3-54 line 23: The discussion on pages 1-10 and 1-11 seems to disagree with this statement. The  
22 REA has already been defined to deal with total reactive N.  
23  
24 The discussion of Data and Tools (Section 3.2.2.2) should probably be presented earlier within Chapter 3  
25 (perhaps around page 3-17).  
26  
27 Figures 3.2-35 and -36: Adding pixels for actual forest cover within these maps would be useful to better  
28 reflect the actual extent of the forest types. The coastal sage map (Figure 3.2-37) appears to be drawn  
29 this way.  
30  
31 The text for Figures 3.2-39, -40, -41, -42, -43, and -44 is way too small and the figure captions are  
32 inadequate. Please revise.  
33  
34 Page 3-70: At this point of the discussion it occurred to me that a case study for an area dominated by  
35 NH3 deposition (i.e., Iowa, Minnesota, Illinois) should probably be added to the REA. It wouldn't  
36 necessarily show adverse effects, but it would complete the picture of total reactive N deposition across  
37 the US. Page 3-103 of the ISA provides some rationale for not including such a case study since  
38 agricultural areas are overwhelmed by fertilizer additions. However, limited natural areas (forests,  
39 prairies) are embedded within areas dominated by agriculture.  
40  
41 **Chapter 4**: Incomplete and not reviewed.  
42  
43 **Chapter 5**: Incomplete and not reviewed.  
44  
45 **Chapter 6**  
46  
47 Figure 6.1-4: SRB should be defined in the figure caption.  
48  
49 Page 6-16 line 13: Remove the word "often". Fungi should probably also be recognized as an important  
50 contributor to decomposition.  
51

1 Increased nitrogen does affect the N content of green leaves. Is this pattern well established for litterfall  
2 as well? Does the pattern differ by vegetation type (i.e., trees, grasses, crops...)?

3  
4 Page 6-17: Some of this material might be better left to the ISA document. Lines 24 to 28 are not  
5 needed here.

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

10  
11 Chapter 6 seems to lack summary conclusions:

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

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

## 14 15 **Chapter 7**

16  
17 Page 7-5 line 4: Replace "ecosystem health" with another term. It isn't and perhaps can't be defined.

18  
19 Page 7-5. Line 7: Change to "this is hypothesized to change...." Or provide the references that show  
20 proof.

21  
22 Page 7-5 line 21: Spell out CSS.

23  
24 Page 7-7 Table 7.1-1: Replace "tree health" with a more meaningful term or terms such as rate of  
25 growth, survival....

26  
27 Page 7-8: The deposition levels proposed are appropriate for 'sensitive' ecosystem, but not all  
28 ecosystems. A concept of one size does not fit all will need to be worked into the conclusions of the REA.  
29 While protection of sensitive systems may be a justification for a new standard and level, it shouldn't be  
30 interpreted as having the same effect on all areas of the US. That is, lowering inputs to areas currently  
31 unaffected will not help them. Pages 3-78 and 3-79 of the ISA include text that might be useful in  
32 clarifying this point.

33  
34 Chapter 7 ends abruptly and seems incomplete.

## 35 36 **Chapter 8**

37  
38 Page 8-1 lines 14 and 15: The concept of achieving a standard based on a "uniform level of ecosystem  
39 protection" seems at odds with the REA document. The REA clearly states that the impacts of N and S  
40 deposition are localized throughout the US and subject to the correct combinations of deposition and  
41 susceptibility of the target terrestrial and aquatic ecosystems.

42  
43 Page 8-4 Figure 8.1-1: An air quality based estimate of total N and S form deposition may not be  
44 sufficient information to judge impacts on acid neutralizing capacity. A data layer on extant edaphic  
45 conditions is needed. The deposition metric should probably also be enhanced to allow for the  
46 estimation of biological immobilization (i.e., plant and microbial uptake of some fraction of the total  
47 deposition).

48  
49 Page 8-5 lines 1 to 3: Plant uptake needs to be included in this list.

50  
51 Page 8-28 lines 2 to 9: I don't agree with the assumption that annual accumulation of N inputs into wood

1 increment can be ignored in this analysis. Except for low or no productivity ecosystems this is a  
2 significant sink for atmospheric N deposition that must be included in the calculation of N available for  
3 other soil interactions.

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

6  
7 **Attachment 3**

8  
9 Page 1 line 16: The phrase “a host of biogeochemical processes” is too vague. Please expand this  
10 concept.

11  
12 **Attachment 4**

13  
14 Pages 2 and 3: Table 1.1-1 is not filled in. The term forest health should be replaced.

15  
16 Pages 12 and 13: Table 1.2-2 is not complete.

17  
18 Page 31: The authors conclude that the simple mass balance method would be used in the REA. What  
19 caused the authors to exclude the dynamic model method? Lack of input data? Lack of validation?

20  
21 Page 32: All evapotranspiration does not occur at the surface of the soil profile. Did the authors mean to  
22 imply evaporation alone?

23  
24 Page 42 line 17: Is the nitrogen immobilization mentioned here microbe and plant or just microbe?

25  
26 Figure 3.1-2 is missing units.

27  
28 Page 53: The conclusions need work. The imbalances for Ca, Mg, and Al suggested for forest soils are  
29 for localized sensitive systems. As worded, the conclusions would be taken as a broad generalization for  
30 all US ecosystems.

31  
32 **Attachment 5:** No comment

33  
34 Attachment 6

35  
36 Page 6: Table 1.2-2 is missing too much information to be fully evaluated.

37  
38 The studies cited and discussed for the CSS system should be closely evaluated to determine which were  
39 based on manipulative studies capable of determining cause-and-effect relationships versus those that  
40 represent correlation studies for which relationships between known variables and measured responses  
41 were assumed to be viable explanations for adverse responses.

42  
43 Studies highlighted in the ISA within Tables 3-15, 3-17, 3-18, and 3-19 might have a larger presence  
44 within the REA.

45  
46 Figure 5.1-1 and -2: In my opinion the change in CSS seen in Figure -1 doesn't correlate very well with  
47 the dominant deposition patterns in -2. How well does N deposition really correlate with change? How  
48 much does land use change through time get in the way of the interpretation of N deposition cause and  
49 effects in this case study?

50  
51 Page 46 lines 4 versus line 15: The conclusion of “compelling evidence” on line 4 does not seem to

- 1 agree with the authors conclusion about the research still underway on line 15. A word change seems in
- 2 order.
- 3
- 4 Page 47 line 5: Is a modification of a valued ecosystem an ad

1 **Dr. Rudolf Husar**

2  
3 These comments are addressing primarily the 1st draft REA section: Additional Effects. It also  
4 includes both general comments on the approach to the REA as well as comments on sections of the the  
5 first REA draft document.  
6

7 **Comments on REA Chapter 6: Additional Effect**

- 8  
9 *1. Charge: In this chapter, we have presented results from some initial qualitative analyses for*  
10 *additional effects including the impact of sulfur deposition on mercury methylation, the impact of*  
11 *nitrous oxide on climate change, and the impact of nitrogen deposition on carbon sequestration.*  
12 *Are these effects sufficiently addressed in light of the focus of this review on the other targeted*  
13 *effects in terms of available data to analyze them?*  
14

15 Overall, this chapter is a good effort to illustrate additional, non-ecological risks associated with  
16 anthropogenic N and S. Indirect sulfur impacts are well captured by the problem of sulfur-induced  
17 methylation of mercury, which then causes the effects in biota. The interaction of nitrogen and carbon  
18 cycles is also properly illustrated in the section on nitrogen-induced changes in the carbon sequestration.  
19 The utility of the section on N<sub>2</sub>O impact on climate is less obvious.  
20

21 This chapter is clearly a first draft. In the introduction it would be helpful to provide more extensive  
22 rationale and criteria on the general approach for selecting these Additional Effects. The rationale should  
23 also include why some obvious additional effects on materials, visibility and soil are not being  
24 considered. See further discussion regarding these effects in the general comments on REA below.  
25

26 **6.1 Sulfur and Mercury Methylation**

27 Page 6-2 Line 10: Currently, i.e. since 1995, coal combustion was, indeed, the main cause of  
28 anthropogenic mercury deposition. However, prior to the regulatory action, around 1990, the  
29 anthropogenic mercury emissions were dominated by other sources. Since deposited mercury has  
30 a long residence time in soil and biota, much of the mercury methylation occurs on the  
31 accumulated mercury from solid waste and other agricultural, medical, residential usages.  
32

33 Page 6-2 Line 13: Atmospheric mercury particles cannot possibly remain in the atmosphere for  
34 more than two years. Even stratospheric particles, have atmospheric residence time of less than  
35 two years. As with the rest of ambient aerosols their atmospheric residence time is less than a  
36 week in the planetary boundary layer and less than 3-4 weeks in the mid-troposphere.  
37

38 Page 6-3: Figure 6.1-1 represents the mercury cycle in the ecosystem. It has many compartments  
39 and arrows representing the mercury flow and transport/transformation processes. It is  
40 recognized that full quantification of the mercury cycle through air, water, land and biota is not  
41 possible at this time. However, it would be helpful, at least in the text, to highlight the main  
42 flows and processes that dominate the mercury cycle.

1 **6.2 Nitrous Oxide**

2 Page 6-10: I find little justification for this section on the climate impact due to anthropogenic  
3 N<sub>2</sub>O. As stated in the REA, N<sub>2</sub>O contributes only about 6% of GHGs and the man-induced  
4 sources of atmospheric N<sub>2</sub>O are only 10% of that, i.e. .6% of the GHGs.  
5

6 Page 6-12 Line 31: The statement “that nitrogen addition increased N<sub>2</sub>O emission by 215%”  
7 could benefit from a reference, compared to what?

8 **6.3 Carbon Sequestration**

9 Page 6-13: This section is an appropriate illustration of the interdependence of nitrogen (sulfur?)  
10 and carbon cycles through air, land, water and biota. The meta-analysis of existing literature is an  
11 appropriate method for illustrating the interdependencies of the earth system components and  
12 how changes in one set of environmental chemicals may have intended and unintended  
13 consequences throughout the earth system.

14 ***General comments on the first draft REA***

15

16 This REA focuses on ecosystem welfare effects that result from the deposition of total reactive  
17 nitrogen and sulfur.” I concur with D. Johnson that exclusive focus on “negative” effects of N  
18 and S deposition is a flawed approach. It ignores the broader context and the full dynamics of  
19 eco system responses to anthropogenic N and S deposition. The beneficial effects of  
20 atmospheric S and N fertilization should also be considered. This would also require definitions  
21 and/or conventions on what’s harmful and what’s beneficial.  
22

23 The man-induced nitrogen and sulfur deposition should be compared quantitatively to the  
24 naturally occurring N, S flows. This will allow estimating the significance of the man-induced  
25 stress, compared to the naturally occurring values. By avoiding such broader context, the risk  
26 assessment will be susceptible to criticisms of incompleteness and possibly irrelevance to actual  
27 ecological risk estimation.  
28

29 Page 1-2 Line 9: “In the Act (Section 109 B 2) the purpose of the secondary NAAQS is to  
30 protect the public welfare from *any* known or anticipated adverse effects...” Clearly, a  
31 secondary NAAQS includes all welfare effects, not only the effects on the ecosystem. This fact  
32 is not followed through in the REA and ISA.  
33

34 Page 1-2 Line 19: “Adverse public welfare effects are based on an assessment of how  
35 ecologically adverse impacts translate into adverse impacts on public welfare” In this sentence  
36 as well as throughout the REA welfare effects only include effects on ecosystem . As stated  
37 above welfare effects include damage to materials, visibility, soils, climate.  
38

39 ***Specific comments on sections of the first draft REA***

40

41

1 Page 1-13: Figure 1.3-2 representing the sulfur cycle should be made more quantitative. The  
2 schematic Figure on the biogeochemical cycles of sulfur is good. However, such a general  
3 Figure should be fortified by adding magnitudes to the flows represented by the arrows. The  
4 transfer rates, say over the US, can be estimated from the model runs, or based on the empirical  
5 evidence. There is ample literature on biogeochemical cycles that estimates the magnitude and  
6 importance of the various flow rates.

7  
8 Page 3-5 Line 4: “ ...combustion of fossil fuels by electric utilities (~66%) “ This percentage is  
9 inconsistent with 71% EGU contribution shown in the pie diagram, Figure 3.1-5.

10  
11 Page 3-8: The section layout for 3.1.4 on Deposition starts with the total deposition maps that  
12 are obtained by combining the model and measured values. The description of the data and  
13 tools is given after that. The customary approach is first to present the input data, tools and  
14 methods and then the resulting computed values. Also, as discussed at the October CASAC  
15 meeting, a separate section on CMAQ model comparison with the observations for the key N, S  
16 species would be most desirable.

17  
18 Page 3-8: Section 3.1.4.1 on Nitrogen Deposition has many useful quantitative numbers.  
19 However, the source and estimation methods for these estimates are not well documented.

20  
21 Page 3-10: The useful Figure 3.1-7 on oxidized N deposition should be augmented with  
22 separate Figures for dry and wet deposition of N. The wet deposition Figure should also  
23 compare the model and measured oxidized N deposition.

24  
25 Page 3-11: Ditto for reduced N deposition.

26  
27 Page 3-12: Ditto for reduced S deposition.

28  
29 Page 3-12: Section 3.2. could be subdivided such that the procedures for model-observation  
30 data fusion has a more extended separate sub-section.

31  
32  
33

**Dr. Dale W. Johnson**

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As has been noted in previous reviews, I feel that this document is unbalanced with respect to the effects of nitrogen deposition. Some very simple facts need to be acknowledged and considered: 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 CO<sub>2</sub> / 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. As scientific reviewers, we have the responsibility to treat this and all other subjects 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<sup>-1</sup> yr<sup>-1</sup>? 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<sub>x</sub> 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.

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

1 Johnson, 1985), both of which are cited later in the Terrestrial Case Study, that  $Al^{3+}$  increases to  
2 the  $3/2$  power of  $Ca^{2+}$ , for example, as total mineral acid anion (e.g., nitrate and sulfate)  
3 concentrations increase, and this happens even if there is NO CHANGE IN THE SOIL AT ALL.  
4 Thus, if the soil is already acid, the introduction of mineral acid anions will cause the immediate  
5 mobilization of Al and acidification of soil solutions and probably surface waters long before any  
6 change in the soil takes place. Conversely, if the mineral acid anion concentrations are reduced,  
7 one should see a very rapid recovery. In short, the soil solution can change very quickly and  
8 almost independently of the soil, and this has major implications for the effects of N and S  
9 deposition on aquatic ecosystems.

10  
11 Attachment 4, p. 1. lines 16-29: Same exact comment above applies here and in this case, our  
12 small book is cited as a source but only part of the story (the soil part, not the soil solution part)  
13 is reviewed. This is an important point – please include it in the next draft.

14  
15 Attachment 4, p. 5, lines 10-17: Same comment as above here. It is not necessarily true that  
16 “inorganic Al does not become mobilized until after soil Ca is depleted” if the soil is already  
17 acidic, as many unpolluted soils indeed are.

18  
19  
20 Question 4 Response: The revisions have improved the characterization of adverse ecological  
21 effects, but I see no real consideration of the potential positive effects of N deposition as yet.  
22 Timber production is mentioned, but only in a negative context and I see little or nothing on C  
23 sequestration. The one pager for section 5 refers to case studies and gives no indication that this  
24 approach will be changed.

25  
26 Question 4b: I see no discussion on effects on carbon budgeting as yet – have I missed  
27 something? I do see Carbon Sequestration is listed as a potential section 6.3 – this is a good  
28 thing. Looking forward to seeing it.

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

3  
4  
5 Chapters 7 and 8 (Sent 19 Sept 2008)

6  
7 Chapter 7: We are asked if the approach is technically sound to consider “ecologically adverse  
8 effects”. For the most part, yes, it is. However, once again, I note that this section focuses  
9 entirely on negative effects of N. This document should also consider cases where increased  
10 production could be a positive effect – such as on timber production and C sequestration.

11  
12 p. 7-1, lines 21-27: This is a real mouthful. Can it be simplified and broken into at least two  
13 sentences?

14  
15 p. 7-3, line 12: Why “inorganic and mineral acids”? They are basically the same thing.

16  
17 Section 7.1.4:

18  
19 Chapter 8: Many questions are posed to the panel here and I will not repeat them. I had problems  
20 with the conceptual framework for the calculations, as noted below.

21  
22  
23 Section 8.3.3: I had a very difficult time following this section and do feel like I ought to be able  
24 to. It would help a great deal if units could be specified in the various equations and the  
25 assumptions were clearly spelled out in the beginning. For example, is it assumed that base  
26 cation concentrations will remain at pre-industrial levels? The equations would suggest so, as  
27 would the statement on p. 8-29, lines 13-15. I cannot really agree with the assumption state here  
28 that “pre-industrial base cation concentrations effectively set the long-term capacity of the  
29 catchment to neutralize acidic deposition because it represents the only source of base cation  
30 input that is sustainable over the long-term”. For one thing, soils in humid regions always  
31 naturally acidify and therefore there is no long-term steady state base cation flux until soils  
32 become extremely acidic– it is always slowly decreasing. I also think that the implicit  
33 assumption here that base cation concentrations in streams will not increase over the long-term  
34 in response to acidic inputs is flawed – some soils have a very large exchangeable base cation  
35 pool and could buffer such inputs for a much longer term than the typical attention span of  
36 scientists and policy makers, let alone the public.

37  
38 p. 8-29, lines 18-19: This statement makes no sense. At steady state, the leaching rate of base  
39 cations is, by definition, equal to weathering inputs, not “at lesser or greater rates”.

## Dr. Donna Kenski

1  
2  
3  
4 Overarching concerns: EPA staff have clearly made a great effort in pulling this document (and  
5 its companion ISA) together, and should be commended for the high-quality (and quantity)  
6 produced thus far. Nevertheless its current incomplete status and the pressing schedule make it  
7 hard to see how all the remaining tasks can be completed, and reviewed, in sufficient time to  
8 meet the predetermined deadlines. Staff and contractors to EPA need to be realistic in judging  
9 how much can really be done in the remaining months. If it is time to set priorities, perhaps that  
10 is something that can be discussed at this meeting.

11  
12 The CAA requirement that the secondary standard be in the form of a concentration standard is  
13 going to require us to tolerate a much higher level of uncertainty than usual in the standard  
14 setting process, because of the need to employ multiple models to characterize the  
15 concentration-deposition-ecological effect-ecological indicator linkage. Consequently, the REA  
16 in general needs to be much more comprehensive and transparent in describing the levels of  
17 uncertainty encountered at each of these steps and their impacts on overall uncertainty. For  
18 example, so much hinges on the CMAQ estimates of deposition, and yet there is little  
19 information given in the REA or the ISA on CMAQ performance. It seems from the ISA that  
20 CMAQ has really only been evaluated in terms of its annual estimates of aerosol deposition, and  
21 those are accurate to within a factor of 2. No CMAQ performance evaluation is given for  
22 deposition to specific locations, particularly locations that share characteristics of the sensitive  
23 areas focused on in this analysis. Likewise, none is given for measurements with a shorter time  
24 frame than annually. A clear-eyed discussion of these uncertainties for CMAQ and for the other  
25 models used to support the REA (MAGIC, ASTRAP, Sparrow) is a critical component that  
26 needs to be incorporated.

27  
28 Charge Questions: Scope of the Review

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

33  
34 Generally, the review seemed to focus on appropriate variables, although as noted above, the  
35 complete scope may be too broad to accomplish before the court's deadline. The  
36 policy-relevant questions posed in Sec. 1.4 weren't actually addressed directly (perhaps it's still  
37 too soon, given the incomplete case studies) but I did note that questions 3 and 4 of that list (i.e.,  
38 to what extent do receptor surfaces influence dry deposition, and can effects of NO<sub>x</sub> be  
39 distinguished from effects due to total reactive nitrogen) did not seem to be discussed or  
40 addressed by any of the case studies in Attachments 3-6, although Chap. 3 did present a nice  
41 graphical characterization of the areas and their relative proportions of NO<sub>x</sub> vs total and other  
42 forms of N nitrogen. However, most of that was modeled data and little comparison to  
43 measured values was presented for comparison. Perhaps more of that is coming in the second  
44 draft, since there were lots of missing sections to Chap. 3.

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

5  
6 Air Quality Analyses (Chapter 3)

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

10  
11 The analyses in Chap. 3 could more accurately be described as modeled estimates of air quality,  
12 rather than air quality characterizations, which I think of as based on measured data. While the  
13 graphs were useful and logically presented, there was very little measured data given for  
14 comparison, so it is not possible to judge their 'soundness'. Combined with the lack of CMAQ  
15 validation discussion (mentioned above), it becomes more important to see these in the context  
16 of measured data as well. But this may be premature if the next draft is meant to include such  
17 comparisons.

18  
19 I would have liked more discussion of the monthly patterns of deposition shown, for example, in  
20 Figs 3.2-14 through 3.2-19. Clearly wet deposition is driven largely by precipitation, but what  
21 drives the other components of deposition? Are these emission patterns or meteorological  
22 patterns or biological activity patterns? Some discussion of the importance of these various  
23 temporal scales for the ecological effects modeled is probably appropriate as well. A minor  
24 complaint on the communication of the results: the color scheme for Figures like 3.2-6 etc. is  
25 not intuitive. The scheme used was almost a rainbow-like scale, which is easy to interpret and  
26 would have been fine, but instead green was sandwiched between yellow and orange, breaking  
27 the natural progression of colors (red -> orange -> yellow) that most of us have internalized and  
28 making it harder to visually establish a continuous gradient of concentration changes.

- 29  
30 2. *Section 3.2.1 describes an approach for evaluating the spatial and temporal patterns for*  
31 *N and S deposition and associated ambient concentrations in the case study locations.*  
32 *This document includes the analysis for the Adirondacks case study. Does the Panel*  
33 *agree with this approach and should it be applied to the other case study areas?*

34  
35 It was a sound approach and a useful exercise that may give as clear a picture of deposition as  
36 we're likely to get. With the additions/changes noted above, I would welcome this analysis for  
37 the other areas.

- 38  
39 3. *Section 3.2.2 describes the relative contributions of ambient emissions of nitrogen and*  
40 *ammonia to nitrogen deposition for the case study areas. To what extent is the approach*  
41 *taken technically sound, clearly communicated, and appropriately characterized?*

42  
43 This was an interesting exercise that was very useful in establishing the relative importance of  
44 NO<sub>x</sub> and NH<sub>3</sub> emissions to overall N deposition and the relative responsiveness of deposition to  
45 changes in emissions. It was very helpful to establish this kind of personal internal calibration  
46 in a strong visual way. It is also a critical comparison to establish in making a strong case for the

1 ability of a NO<sub>x</sub>-concentration based standard to be sufficiently protective, despite our  
2 understanding that impacts are really driven by total nitrogen. Given the lack of spatial and  
3 temporal variability in the contributions of NO<sub>x</sub> to oxidized N and NH<sub>3</sub> to reduced N, those  
4 maps probably don't need to be shown, just described instead. The results look perfectly logical  
5 and convincing, although I resist accepting these results completely until seeing further  
6 documentation of CMAQ's performance. The REA notes that the RSM has been validated for  
7 PM and O<sub>3</sub>, but it's not clear whether that validation translates to deposition parameters as well.  
8 Presumably the missing section 3.2.2.5 on uncertainty will address some of these issues. Again,  
9 as above, the color scale on all these plots is counterintuitive. Using the color red to depict no  
10 impact and green for 100% impact is contrary to general mapping conventions and at least in my  
11 case, caused me to continually misinterpret the plots.

### 12 Case Study Analyses (Attachments 2-6)

- 13  
14 6. *Att. 2: Are the national geospatial datasets chosen adequate to identify sensitive areas?*  
15 *Are there other data sets that have not been identified by this analysis that we should*  
16 *consider? Does the panel agree with this approach or can they suggest alternatives?*  
17

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

- 26  
27 7. *Att. 3: re MAGIC model to evaluate ANC levels in selected streams and lakes in*  
28 *Adirondacks and Shenandoahs. To what extent is the approach taken technically sound,*  
29 *clearly communicated, and appropriately characterized?*  
30

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

- 42  
43 8. *Att. 4: use of SMB model to evaluate current deposition on forest soil ANC for sugar*  
44 *maple in Kane Experimental Forest and red spruce in Hubbard Brook Experimental*  
45 *Forest. To what extent is the approach taken technically sound, clearly communicated,*  
46 *and appropriately characterized?*

1  
2 The selection of the study area was reasonable and the description of the method was clear.  
3 Without results it's not possible to say too much more. The Table 3.1-2 had some numbers that  
4 need to be explained further, however. The range of critical N loads vary by a factor of 10 over  
5 the 3 study periods shown, and each of the methods gives very different results. Why the big  
6 difference? The text mentions biomass changes; is this the sole reason? Is this magnitude of  
7 change in biomass typical? How comparable are the methods? The text in Section 1.1.1 was  
8 unnecessarily repetitive and could be tightened up; no need to quote the ISA at such length.

- 9  
10 9. *Att. 5: Aquatic nutrient enrichment—evaluate how changes in N deposition affect the*  
11 *eutrophication index in two estuaries: Chesapeake Bay and Pamlico Sound. To what*  
12 *extent is the approach taken technically sound, clearly communicated, and appropriately*  
13 *characterized?*  
14 10. *Att. 6: Terrestrial nutrient enrichment—evaluate effects of N deposition on CSS*  
15 *community in California and mixed conifer forests in San Bernardino and Sierra Nevada*  
16 *Mountains. To what extent is the approach taken technically sound, clearly*  
17 *communicated, and appropriately characterized?*

18  
19 Additional Effects (Chap. 6)

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

24  
25 This was an adequate review of these effects. The focus appropriately belongs on acidification  
26 and enrichment effects.

27  
28 Synthesis and Integration of Case Study Results into the Standard Setting Process (Chap 7)

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

33  
34 I'm still uncertain about exactly how the case studies ultimately are used. Are they merely for  
35 scientific support and justification, or do the model results from them get incorporated eventually  
36 into a quantitative relationship that can be plugged into the framework presented in Chapter 8?  
37 I think the confusion stems from the incomplete nature of this chapter. When it is fleshed out in  
38 the next version with real data, the application of the case study results should be obvious.

39  
40  
41 Considerations in the Structure of the NO<sub>x</sub>/SO<sub>x</sub> Secondary Standard (Chap 8)

- 42  
43 1. *Is the suggested overall structural framework for a secondary standard technically sound*  
44 *and logically presented?*  
45

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

- 4
- 5 2. *Is the description and development of the deposition transformation function (Fig 8.1.1)*  
6 *between air quality indicators and the deposition metric clear and technically sound?*  
7
  - 8 3. *Is the description and development of the ecological effect function (Fig. 8.1.1) between*  
9 *the deposition metric and the ecological indicator clear and technically sound?*  
10
  - 11 4. *Does the discussion adequately capture the potential use of categorical variables versus*  
12 *continuous variables when accounting for the variability of atmospheric, landscape, and*  
13 *ecological factors?*  
14

15 These were all fine.

- 16
- 17 5. *Are there any key elements missing from the framework?*  
18

19 There needs to be a more complete discussion of how a standard can accommodate geographic  
20 variation; i.e., how to equitably control NO<sub>x</sub> and SO<sub>x</sub> to adequately protect sensitive areas  
21 without overcontrolling in areas that are far less sensitive to acid deposition. Section 8.3.1 made  
22 reference to varying factors within the transformation function by location, and the fact that  
23 deposition loads will vary by location, but it was not clear from the text how this translates to  
24 variation in the standard. It seems that the standard must account for different concentrations in  
25 different regions, but how that is specified is still pretty fuzzy.

26

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

33

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

- 37
- 38 6. *Does the framework need to be expanded or revised to accommodate the appropriate*  
39 *consideration of ecological indicators besides ANC when developing a secondary*  
40 *NAAQS for NO<sub>x</sub> and SO<sub>x</sub>*  
41

42 Isn't that the point of the case studies? It seems premature to answer this question until those  
43 results are complete. ANC seems adequate for acidification effects, but the other case studies  
44 weren't really far enough along to evaluate. The chapter should include some discussion of how  
45 the standard might account for multiple indicators.

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

2  
3 Section 8.3.2.4 needs additional attention. It mentions possible work on MCIP and CMAQ to  
4 incorporate measurements, which would be great and I highly encourage. But is it really  
5 possible to produce results and incorporate them into the next draft?  
6

7 Section 8.3.3 on the deposition-indicator links could benefit from a discussion of how influential  
8 the various parameters are on the outcome, at least in a qualitative sense. It would help the  
9 reader (and presumably the Administrator) evaluate which are the critical parameters controlling  
10 the relationship. There also needs to be some discussion or graphical analysis of the  
11 geographic sphere of influence of NO<sub>x</sub>/SO<sub>x</sub> concentrations on each sensitive area. For  
12 example, if the indicator were set at an ANC of 50 ueq/L in the Adirondacks, how much would  
13 NO<sub>x</sub> and Sox need to be reduced to reach that ANC, and over what geographic area?  
14 Somewhere the document needs to lay out that visual frame of reference for the geography of  
15 influence on the sensitive areas. We know that deposition is some function of distance, and that  
16 high concentrations close to a sensitive receptor will be more influential than the same  
17 concentrations far way; how far away is far enough to have negligible impact?  
18

19 Specific comments, typos, etc.:

20  
21 p. 3-3, Fig 3.1.2 (also Fig 3.1-5) Avoid use of pie charts, as they make it difficult to make  
22 quantitative comparisons. Bar charts are almost always preferable. The use of 3-D  
23 unnecessarily complicates these figures and also makes it more difficult to visually compare  
24 the slices of the pies.

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

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

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

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

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

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

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

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

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

39 p. 8-14: Equation numbers don't follow the text  
40

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

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

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

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

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

- 1 Attachment 2, p. 11, line 8: remove 'Nitrogen Containing Chemical Species'
- 2 Attachment 2, p. 11, line 18: Containing -> Including
- 3 Attachment 2, p. 16, line 4: remove meter
- 4
- 5 Attachment 3: fix the subscripts and superscripts throughout. Too many grammar errors
- 6 and typos to enumerate here – this whole section needs careful editing.
- 7 Attachment 3, p. 6, line 24: deposition is more like 17 and 13 kg/ha according to the Figure
- 8 3.1-1, not 15 and 10.
- 9 Attachment 3, p. 8, line 4: deposition is more like 18 and 11 kg/ha according to Fig. 3.2-1.
- 10 This makes me distrust the % declines in these species, here and on p. 6, but I didn't
- 11 recalculate them.
- 12 Attachment 3, p. 12, Fig. caption: 12 streams are shown, not 13. Lots of other typos in this
- 13 caption.
- 14 Attachment 3, p. 16, line 26: >50 should be <50
- 15 Attachment 3, p. 17, lines 6-8: Fig. 4.1-2 doesn't imply that biota are not often harmed
- 16 below and ANC of 100, only that the harm is less severe than for lower ANC
- 17 Attachment 3, p. 17, line 12: It doesn't make sense to say that an ANC of 0 protects surface
- 18 waters from becoming acidic. waterbody
- 19 Attachment 3, p. 17, line 17: change 'deposition – critical load' to 'deposition less than
- 20 critical load'
- 21
- 22 Attachment 4, p. 1, line 6: should be 'sulfur loads *to* and effects *on* a chosen...'
- 23 Attachment 4, p. 10, line 4: on -> at
- 24 Attachment 4, p. 11, line 16: not clear, reword
- 25 Attachment 4, p. 11, lines 21-22: not clear, reword
- 26 Attachment 4, p. 23, line 22: HBEF
- 27 Attachment 4, p. 25, line 8: litterfall
- 28 Attachment 4, p. 33, line 17: put weathering on its own line
- 29 Attachment 4, p. 38, line 13: Arrhenius
- 30 Attachment 4, p. 48 and 49: It would be helpful for these figures to include the HBEF as
- 31 well; its very hard to place it accurately given the map on p. 21
- 32
- 33
- 34
- 35
- 36
- 37

1 **Dr. Naresh Kumar**

2  
3 COMMENTS ON SECTION 6.1. SULFUR AND MERCURY METHYLATION

4 GENERAL COMMENTS

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

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

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

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

23 SPECIFIC COMMENTS

- 24
- 25 • To date, there has been *no* unequivocal demonstration of sulfate limitation in US or  
26 global waterways such that natural sulfate addition or subtraction alone has produced a  
27 change in methylation rates or mercury in fish. Such demonstrations have occurred only  
28 in experimental manipulations of microcosm ecosystems. Since fish take up only a  
29 fraction of the methylmercury in the water column and biota of lower trophic levels, there  
30 is always an excess of MeHg in studied water bodies. And downtrends in sulfate addition  
31 have always been matched by downtrends in divalent mercury deposition, so that it is not  
possible to separate sulfate availability from divalent mercury burden.
  - 32 • It is mentioned that “*Mercury concentrations have increased approximately 2 to 5 times*  
33 *since the onset of the industrial revolution and appear in even the most remote locations*  
34 *on the Earth (Munthe et al., 2007; U.S. EPA, 2006).”* The accepted global average ratio  
35 of atmospheric mercury mass now compared to the period prior to the Industrial

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

- 4 • It is stated in the text that “*In the United States, the primary source of mercury to*  
5 *ecosystems is atmospheric deposition due to coal combustion (e.g., coal-fired electric*  
6 *utilities). Other sources include municipal waste combustion, medical waste incineration,*  
7 *chlor-alkali plants, and industrial boilers.*” This sentence appears to propagate the  
8 common misconception that mercury emissions (anywhere) are proportioned exactly the  
9 same as mercury deposition (anywhere else). This is obviously incorrect, since both total  
10 and wet deposition of mercury at any location on earth (or in the United States) is made  
11 up of contributions from hundreds of sources at widely varying distances upwind, and is  
12 not linearly proportional to the fraction of total emissions each source, or source type,  
13 makes up. Therefore, it should be noted that a significant amount of mercury depositing  
14 within the United States originates in other countries, primarily mainland Asia. The  
15 sources of mercury depositing to U.S. ecosystems varies widely, both geographically and  
16 by source, depending on the proximity of U.S. sources and the precipitation climatology  
17 of the setting.
- 18  
19 • It is mentioned that, “*Depending on the particulate association and oxidation state,*  
20 *atmospheric mercury particles can remain suspended in the atmosphere for more than 2*  
21 *years (Evers et al., 2007; U.S. EPA, 2006).*” This sentence should be rewritten or *deleted*.  
22 There is no relation between “particulate association” (an unexplained term) and  
23 oxidation state for mercury; most of the mercury bound to particles is divalent mercury  
24 (or “Hg<sup>+2</sup>,” as used in the report). But the statement that such particle-bound mercury has  
25 an atmospheric lifetime of more than 2 years is not true; due to gravitational settling,  
26 coagulation, etc., Hg<sub>p</sub> has an average lifetime in the atmosphere of several days to about  
27 two weeks, no more. And no source of mercury emissions to the atmosphere issues more  
28 than about 3% of mercury mass in the form of particle-bound mercury, in any case. It is  
29 suggested inserting something like this: “*There are three primary forms of mercury in*  
30 *atmospheric sources of the substance: elemental mercury, reactive gaseous mercury, and*  
31 *particle-bound mercury. Once emitted, the three forms behave very differently in the*  
32 *atmosphere and deposit over very different geographic patterns. It generally takes*  
33 *hundreds or thousands of miles for half of the emitted gaseous elemental mercury to*  
34 *deposit to ground level, while half of the reactive gaseous mercury will deposit within*  
35 *about 150 miles of the source. Particulate-bound mercury, generally 3 percent or less of*  
36 *the emitted mercury mass, deposits in intermediate patterns (M. Cohen, 2004).*”
- 37  
38 • The text states that, “*When deposited into terrestrial and aquatic ecosystems, elemental*  
39 *mercury is oxidized to reactive mercury (Hg<sup>+2</sup>) (Ambrose et al., 2005; U.S. EPA, 2006).*”  
40 A number of statements need to be corrected or nuanced in this passage. Any “deposition”

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

- 9
- 10 • The entire sentence where methylmercury is stated to be “lipophilic” needs to be  
11 corrected. First, mercury cannot be “reduced and methylated to methylmercury”; the  
12 reduced form of mercury is the insoluble elemental mercury,  $Hg^0$ ; because of its  
13 insolubility in water, it is unavailable to sulfate-reducing bacteria for the methylation  
14 process. Of the “deposited mercury pool,” typically half or more is (wet-deposited)  
15 divalent mercury, most of the remainder dry-deposited elemental mercury; of the amount  
16 of divalent mercury dissolving in water bodies, between 1% and 10% may be methylated  
17 and dissolved in the water column. Of this 1% to 10% (depending on the particular water  
18 chemistry; higher fractions for more anoxic waterways), perhaps 10% of that (or 0.1% to  
19 1% of the dissolved divalent mercury) may be taken up into the food web. Second,  
20 mercury is most certainly *NOT* lipophilic, but rather *lipophobic*: it attaches to  
21 protein-based sulfhydryl groups and resides primarily in muscle and nerve tissue (“fish  
22 flesh”). This distinction is important because it is the root of the finding that cooking fish  
23 which may be mercury-laden will in fact not decrease, but increase, the concentration of  
24 the mercury in the cooked product. Any fat that is cooked off is mercury-free, and the  
25 lower weight cooked fish remaining has the same mass of mercury as prior to cooking,  
26 but in a lower-weight portion of fish (with some fat and water mass cooked off), hence  
27 higher net mercury concentration.
  - 28
  - 29 • There seems to be a faulty reference in the sentence “*The majority of U.S. waters are*  
30 *sulfate-limited (Harmon et al., 2007); therefore, decreases in sulfate are likely to*  
31 *promote decreases in methylmercury.*” Harmon et al., 2007, “Using Sulfate-Amended  
32 Sediment Slurry Batch Reactors to Evaluate Mercury Methylation,” *Arch. Environ.*  
33 *Contam. Toxicol.* 52, 326–331 (2007); [DOI: 10.1007/s00244-006-0071-x] does not have  
34 a single word to say about sulfate-limited waterways. The term “-limited,” in fact, occurs  
35 only once in the document, in the introduction, with no reference to the state of U.S.  
36 waters.

1 **Dr. Myron J. Mitchell**  
2  
3

4 **General Comments** (For these general comments my responses are in *italics*.)  
5

6 *The document and associated attachments are extensive and it is a major challenge to provide a*  
7 *cohesive approach to presenting this information. I recognize the difficulty and complexity of*  
8 *pulling all of this together. The potential for providing clearer linkages in this document to the*  
9 *“Integrated Science Assessment for Oxides of Nitrogen and Sulfur – Environmental Criteria”*  
10 *may help maintain focus and reduce the size of the document. More consistency is needed in the*  
11 *use of terms such as oxides of sulfur, oxides of nitrogen, sulfur oxides, nitrogen oxides, SO<sub>x</sub>, NO<sub>x</sub>,*  
12 *etc. Also, in the document there are differences in criteria for sensitivity of various parameters*  
13 *such as ANC. Careful editing would help focus the document and reduce redundant information.*  
14 *The draft document has many noun trains such as “draft revised criteria document”.*  
15

16 **Responses to Charge to the CASAC NO<sub>x</sub>/SO<sub>x</sub> Secondary Review Panel**  
17

18 Scope of the review (Chapters 1 and 2):  
19

20 1. Chapters 1 and 2 provide the background, history, and the framework for this review,  
21 including a discussion of our focus on the four key ecological effect areas (aquatic acidification,  
22 terrestrial acidification, aquatic nutrient enrichment, terrestrial nutrient enrichment). Is this  
23 review appropriately focused in terms of the targeted effect areas and in terms of characterizing  
24 the important atmospheric and ecological variables the influence the deposition and, ultimately,  
25 the ecological impacts of nitrogen and sulfur? Does the Panel have any further suggested  
26 refinements at this time?  
27

28 *Chapter 1 needs a more balanced introduction with respect to the impacts of S and N gaseous*  
29 *constituents and deposition with greater attention earlier in each chapter on the effects of N on*  
30 *ecosystem structure and function including the alteration of species composition. In Chapter 2*  
31 *(Section 2.4) the description of errors in the analyses needs a more rigorous approach that more*  
32 *clearly identifies specific issues related to sources and amount of errors. In its current form*  
33 *Chapter 2 provides very broad descriptions that do not clearly identify the major sources of*  
34 *error that are important to the current assessment. Possibly reference to subsequent chapters*  
35 *that more clearly delineate these errors would be helpful.*  
36  
37

38 Air quality analyses (Chapter 3):  
39

40 1. To what extent are the air quality characterizations and analyses presented in Chapter 3  
41 technically sound, clearly communicated, appropriately characterized, and relevant to the review  
42 of the secondary NAAQS for NO<sub>x</sub> and SO<sub>x</sub>?  
43

44 *The terminology and analyses associated with “policy-relevant background concentrations” is*  
45 *confusing. Some consideration is needed of the adequacy of the current monitoring network in*

1 *evaluating air quality especially in relationship to measurements in urban settings.*

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

7  
8 *This can be a helpful approach. However, within each of these regions there have been other*  
9 *measurements made of associated parameters including precipitation amount, atmospheric*  
10 *deposition, etc. It does not appear that any substantial attempts are being made in this document*  
11 *to compare these current results with previously published results? There is a major emphasis*  
12 *on providing both spatial and temporal patterns using the CMAQ modeling results. Shouldn't*  
13 *these modeling results be compared with other results of deposition measurements for this*  
14 *region? Having some comparisons with these other measurements would be helpful in evaluating*  
15 *the CMAQ deposition estimates. The issues and problems associated with making measurements*  
16 *of air pollution concentrations and converting them to deposition by various inferential*  
17 *procedures needs to be clearly articulated.*

18  
19 3. Section 3.2.2 describes the relative contributions of ambient emissions of nitrogen and  
20 ammonia to nitrogen deposition for the case study areas. To what extent is the approach taken  
21 technically sound, clearly communicated, and appropriately characterized?

22  
23 *Clarification is needed on the relative importance of the emission sources including the accuracy*  
24 *of these emission estimates, atmospheric chemical conversions and the estimates of deposition*  
25 *velocities in evaluating the results of these model outputs. Too much of this section describes*  
26 *model output with little supporting evidence of the relationships noted.*

27  
28 Case Study Analyses (Attachments 2-6):

29  
30 *These attachments are extensive and it would be most helpful if they were more targeted to the*  
31 *issues and needs of the "Risk and Exposure Assessment to Support the joint Review of the NO<sub>2</sub>*  
32 *and SO<sub>2</sub> Secondary National Ambient Air Quality Standards".*

33  
34 1. Attachment 2 presents a GIS analysis to define geographical areas that are sensitive to  
35 acidification and nutrient enrichment. Are the national geospatial datasets chosen adequate to  
36 identify sensitive areas? Are there other data sets that have not been identified by this analysis  
37 that we should consider? Does the Panel agree with this approach or can they suggest  
38 alternatives?

39  
40 *In general, the selected regions and associated data sets appear to be appropriate for this*  
41 *analysis.*

42  
43 2. Attachment 3 presents our current progress on evaluating the effect of aquatic  
44 acidification in the Adirondacks. It describes the use of the MAGIC model to evaluation ANC  
45 levels in selected lakes and streams in the Adirondacks and Shenandoahs. To what extent is the  
46 approach taken technically sound, clearly communicated, and appropriately characterized?

1 *There is some differences in the deposition estimates being used for estimates using the MAGIC*  
2 *versus other approaches in the document (e.g., ASTRAP versus CMAQ). Will this result in some*  
3 *issues relating to congruity of analyses in the document? These analyses have a specific focus*  
4 *on the Grimm and MAGIC models. There have been other efforts to evaluate acid*  
5 *rain/biogeochemical responses in each of these sites (especially the Adirondacks) and hence it*  
6 *would be useful to include some of these other results to indicate either differences or support of*  
7 *these current modeling efforts. In these discussions different levels of ANC are suggested that*  
8 *differ than for other sections in the document. A more consistent approach is needed on setting*  
9 *the ANC limits of concern with respect to sensitivity to acidification and recovery from*  
10 *acidification. Possibly a separate section is needed with respect to ANC and its application to*  
11 *evaluating acidity and the various levels that are used. This would need to be included before*  
12 *the case studies section.*

13  
14 3. Attachment 4 presents our current progress on evaluating the effect of terrestrial  
15 acidification. It outlines a plan to use the Simple Mass Balance Model to evaluate current  
16 deposition levels on forest soil ANC for sugar maple in the Kane Experimental Forest and red  
17 spruce in the Hubbard Brook Experimental Forest. To what extent is the approach taken  
18 technically sound, clearly communicated, and appropriately characterized?

19  
20 *This portion of the document is highly uneven with in some cases substantial detail provided and*  
21 *in other places there are broad generalizations. This makes it difficult for the reader to*  
22 *ascertain the salient points.*

23  
24 4. Attachment 5 presents our current progress on evaluating the effect of aquatic nutrient  
25 enrichment. It outlines a plan to evaluate how changes in nitrogen deposition affect the  
26 eutrophication index in two estuaries: the Chesapeake Bay and Pamlico Sound. The analysis will  
27 model one stream reach (Potomac River and Neuse River) to determine the impact on the  
28 eutrophication index for the estuary. To what extend is the approach taken technically sound,  
29 clearly communicated, and appropriately characterized?

30  
31 *The Chesapeake Bay has been the focus of considerable efforts relating to the effects of nitrogen*  
32 *loading on eutrophication. There have been extensive investigations on this site and there are*  
33 *extensive data sets that can be used in the analyses. A major drawback of this site, however, is*  
34 *that it is not likely that atmospheric nitrogen loading is a major component of the total nitrogen*  
35 *loading. Hence, the Chesapeake Bay will not be very sensitive to changes in atmospheric*  
36 *nitrogen inputs. Although the information on the Neuse River is less extensive, there are similar*  
37 *problems with the overall importance of atmospheric N loading. In attachment 5, page 20 it is*  
38 *indicated that “Previous studies have estimated that wet atmospheric deposition of nitrogen*  
39 *(WAD-N), as deposition of dissolved inorganic nitrogen (DIN:  $\text{NO}_3^-$ ,  $\text{NH}_3/\text{NH}_4^+$ ) and dissolved*  
40 *organic nitrogen, may contribute at least 15% of the total externally supplied or “new” nitrogen*  
41 *flux to the coastal waters of North Carolina”.*

42  
43 5. Attachment 6 presents our current progress on evaluating the effect of terrestrial nutrient  
44 enrichment. It describes an approach to evaluate the effects of nitrogen deposition on the Coastal  
45 Sage Scrub community in California and in mixed conifer forests in the San Bernardino and  
46 Sierra Nevada Mountains. To what extent is the approach taken technically sound, clearly

1 communicated, and appropriately characterized?  
2

3 *The selection of the Coastal Sage Scrub community in California and in mixed conifer forests in*  
4 *the San Bernardino and Sierra Nevada Mountains needs some further justification versus other*  
5 *regions including the alpine and subalpine communities of the eastern slope of the Rocky*  
6 *Mountains in Colorado. These sites in California are certainly important and interesting sites,*  
7 *but it may be difficult to separate the effects of nitrogen deposition versus other air pollution*  
8 *components, especially ozone.*  
9

10 Additional Effects (Chapter 6):  
11

12 1. In this chapter, we have presented results from some initial qualitative analyses for  
13 additional effects including the impact of sulfur deposition on mercury methylation, the impact  
14 of nitrous oxide on climate change, and the impact of nitrogen deposition on carbon  
15 sequestration. Are these effects sufficiently addressed in light of the focus of this review on the  
16 other targeted effects and in terms of the available data to analyze them?  
17

18 *These descriptions seem adequate, but certainly the issues go beyond those associated with*  
19 *carbon sequestration. Some additional discussion of the importance of mercury being found in*  
20 *other components of the ecosystems including song birds should be included.*  
21

22 The purpose of Chapter 7 is to summarize the Case Study results and characterize the  
23 relationships between levels of an ecological indicator and the associated degree of ecologically  
24 adverse effects. To what extent is this approach technically sound, clearly communicated and  
25 appropriately characterized at this point of the review? Does the Panel have any further  
26 suggested refinements at this time.  
27

28 *In its current form this Chapter is highly descriptive. Future revisions will need to include more*  
29 *specific quantitative results that show a clear relationships to the assessment.*  
30

31 Chapter 8 begins to explore how a secondary NAAQS might be structured to address the targeted  
32 ecological effects discussed in the risk assessment. The next draft of this document will include  
33 one or more examples of how this structure might be used to related specific levels of air quality  
34 indicators with a corresponding ecological indicator for a given location and/or scenario. To  
35 what extent is the described approach technically sound, clearly communicated and appropriately  
36 characterized at this point of the review? Specifically, we are asking:  
37

- 38 • Is the suggested overall structural framework for a secondary standard technically sound  
39 and logically presented?
- 40 • Is the description and development of the deposition transformation function (Figure  
41 8.11) between air quality indicators and deposition metric clear and technically sound?
- 42 • Is the description and development of the ecological effect function (Figure 8.1-1)  
43 between the deposition metric and ecological indicator clear and technically sound?
- 44 • Does the discussion adequately capture the use of categorical variables versus continuous  
45 variables when accounting for the variability of atmospheric, landscape and ecological  
46 factors?

- Are any key elements missing from the framework?
- 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<sub>x</sub> and SO<sub>x</sub>?
- Does the panel have any further suggested refinements at this time?

*Providing a clear scientific linkage that is policy relevant between concentrations of SO<sub>x</sub> and NO<sub>x</sub> and resultant S and N deposition and subsequent translation to ecosystem level effects is a major challenge. There are good linkages between concentrations of SO<sub>x</sub> and NO<sub>x</sub> and deposition, but the linkage to ecosystem level effects is more complicated due to inherent variability across the United States of the sensitivity of these systems. There are major problems with respect to both having confidence in calculated deposition velocities and how to ascertain “functional forms”. A clear delineation of which ecosystem types are most important with respect to specific ecological effects (e.g., acidification in the northeast, N deposition affecting biological community structure in the mountain west, etc.) is required. Such categorization will be very important in setting secondary standard(s) that will be relevant to those effects which are of greatest importance to various regions that have different relative representations of various ecosystem types.*

**Specific Comments in which *italics* indicate specific changes.**

Page(s)	Lines(s)	Comment
xv	3-5	Why should this definition only include terrestrial ecosystems?
1-1	8	Change to “The NAAQS <i>have been</i> established for pollutants”.
1-2	8	Change to “complex interactions among relevant <i>chemical</i> species of”.
1-3	10	Clarify more specifically who is “we”. Do you mean EPA?
1-3	19	“Chapter 2” should be in bold font.
1-4	1-5	This does not agree with provided definition on nitrogen enrichment (page xv, lines3-5)
1-5	13	Change to “ <i>This draft</i> ”.
1-5	15	Delete “held”.
1-5	24	Change to “identified the critical <i>components</i> to be”.
1-5	25	Specify the title of the “Administrator” here and elsewhere in the document.

1	1-6	5	Change “NAAQS for NO <sub>2</sub> <i>was set at 0.053 ppm</i> ”.
2			
3	1-6	10	Change to “secondary NAAQS values for SO <sub>2</sub> under”.
4			
5	1-6	13	Change to “of evidence from vegetation effects ”.
6			
7	1-6	19	Change to “EPA was aware that SO <sub>x</sub> has other”.
8			
9	1-6	25	Here and elsewhere be consistent in the use of terms SO <sub>x</sub> and sulfur dioxides.
10			
11			
12	1-7	17	Change “completed by EPA at <i>this time</i> ”.
13			
14	1-7	20-23	Change to “Administrator’s conclusions that (1) based upon the then-current scientific understanding of acid deposition, it would be premature and unwise to prescribe any regulatory control program, and (2) when the scientific uncertainties had been <i>substantially</i> reduced through ongoing research efforts, EPA would draft and support an appropriate set of control measures”.
15			
16			
17			
18			
19			
20			
21	1-8	3	Change to “ <i>Due to</i> the complexities and <i>substantial</i> remaining”.
22			
23	1-8	20-21	Change to “long-term”.
24			
25	1-9	28	Be more explicit with respect to this “Federal Register notice”.
26			
27	1-10	7	Why “beyond full implementation of Title IV....”?
28			
29	1-10	7	Change “to presented in the <i>2005 NAPAP</i> Report”.
30			
31	1-10	10	Be more specific with respect to which “recent reports”.
32			
33	1-10-11		It would preferable to start with a clearer definition of the different forms of nitrogen oxides and then discuss some of the confusing terminology.
34			
35			
36			
37	1-11	6	Are another group of individuals using different terminology for nitrogen oxides?
38			
39			
40	1-11	12	Change to “deposition of <i>reactive</i> nitrogen”
41			
42	1-11	19	Change to “In many <i>regions</i> ”.
43			
44	1-11	22	Change to “assessing <i>the impacts of nitrogen deposition</i> ”.
45			
46	1-11	24-26	This is not true most research does consider separately the oxidized

1			and reduced forms of nitrogen inputs especially for natural
2			ecosystems. In many cases the total input of reduced nitrogen is
3			less well known than that of oxidized nitrogen.
4			
5	1-12	13-14	With reduction in S deposition the relative importance of N
6			deposition in contributing to acidification has increased. This
7			should be noted in this introductory information.
8			
9	1-13	5	The statement “sometimes limiting” with respect to N is
10			misleading. Nitrogen is often a limiting nutrient with respect to
11			primary production in terrestrial ecosystems. Even though N may
12			be a limiting nutrient does not necessarily imply, however, that
13			there may not be substantial ecosystem damage. Changing N
14			inputs can alter ecosystem structure including altering the system
15			from a more desirable state. Such factors are especially important
16			with respect to the evaluation of N deposition in the western U.S.
17			Such secondary effects need to be considered in setting standards.
18			
19	1-13	6	Change to “acidification, nutrient enrichment, eutrophication, and
20			changes in species composition”.
21			
22	1-14	7-9	Other effects including changes in species composition and
23			community structure need to be included for both terrestrial and
24			aquatic systems especially associated with N inputs.
25			
26	1-14	10-24	Clearly there have been substantial studies of acidic deposition
27			effects in the eastern U.S., but some consideration is needed of
28			effects in the western U.S. where the effects appear to be
29			substantially different especially with respect to N deposition
30			influences.
31			
32	1-14	26	Does the reference to “high elevation lakes” refer to the western
33			U.S.?
34			
35	1-14	31	In this section the issue of changes in “community composition” is
36			mentioned and this needs to be included earlier in the document.
37			
38	1-15	1-4	This statement on alteration of aquatic communities needs to be
39			made congruous with earlier statements on overall effects of S and
40			N deposition.
41			
42	1-15	22	Change to “alpine”.
43			
44	1-16	5	Provide some information on what are these “other factors”. Do
45			you mean periods of relatively high microbial activity?
46			

1	1-16	8	Be more explicit on the relationship (e.g., positive or negative) between “oxygen content, temperature, pH, and supply of labile organic carbon”.
2			
3			
4			
5	1-16	11	Be more explicit on what are these conditions. Do you mean for conditions the amount of wetlands and linkages to drainage waters?
6			
7			
8			
9	1-16	Figure	1.3-3 should explicitly have a category for changes in species composition that may differ from altered biodiversity.
10			
11			
12	2-1	9-12	This listing needs to explicitly include effects on community structure and species composition.
13			
14			
15	2-1	16-18	This statement begins to raise the issue associated with different effects depending on region in the U.S.
16			
17			
18	2-1-2		The absence of case studies in the Rocky Mountain west is problematic.
19			
20			
21	2-4		This introduction can be improved with a more focused approach. There is considerable repetition in this part of the document.
22			
23			
24	2-5	4-5	Change to “data <i>were not sufficiently available</i> to perform”.
25			
26	2-5	18	Clarify in scaling-up clarify how this will be done with respect to sensitive areas (e.g., will this be done for all sensitive areas or will the scaling be a function of other sensitive areas with similar characteristics?
27			
28			
29			
30			
31	2-6	27	Change to “ <i>need</i> for them”.
32			
33	2-6	28	A citation is needed for the “MEA” here. Later it is indicated that MEA (2005).
34			
35			
36	2-7	3	Care should be made in the use of the term “regulating” since this term has a different meaning in the context of environmental regulations such as those associated with laws formulated by the EPA. Maybe a clarifying phrase is needed to avoid any confusing recognizing that the term regulation has a different meaning in an ecological context.
37			
38			
39			
40			
41			
42			
43	2-6	14	Are there different references for the MEA? Here it is indicated: MEA, 2005b. Also see Line 17 (MEA, 2005b).
44			
45			
46	2-7		This section needs some further articulation with respect to the

1			description of ecosystem services. Is this description based solely
2			on what is provided in (U.S. EPA, 2006)? It would be helpful to
3			provide some further references that link these statements to other
4			informational sources.
5			
6	2-7	16	Change to “interest in the risk assessment <i>described in the current</i>
7			<i>document</i> ”.
8			
9	2-7	20-22	A better description is needed that clarifies the association of NO <sub>x</sub>
10			deposition and eutrophication.
11			
12	2-7	23-25	This statement is poorly worded.
13			
14	2-7	26-31	The wording of this section needs much better clarification. It is
15			confusing whether a linkage or several linkages are being
16			evaluated.
17			
18	2-8	Figure 2.2-2	Ecosystem Services: the ecological processes or functions having
19			monetary or non-monetary value to <i>individuals or society</i> .
20			
21	2-9	1-2	Change to “We have begun identifying the primary ecosystem
22			service(s) affected by <i>either acidification and/or enrichment</i> and
23			for major ecosystem types and components (i.e., terrestrial
24			ecosystems, soils”.
25			
26	2-9	4	Change to “The impacts <i>affecting various</i> ”.
27			
28	2-9	6-7	Change to “ <i>These impacts on ecosystem services</i> will be”.
29			
30	2-9	10	Change to “tourism. <i>Effects on fisheries</i> (decreased”.
31			
32	2-9	21	Change to “tourism. <i>Effects on fisheries</i> ”.
33			
34	2-9	27-28	Change to “hazard mitigation. <i>Methods for evaluating linkages to</i>
35			<i>measurements and ecosystem services</i> may include”.
36			
37	2-10	5	Clarification is needed on what is meant by “community”.
38			
39	2-10	7	Change to “changes in stand density, shifts in”. <i>Densification</i> is
40			jargon. Change to “shifts in lichen community species
41			composition”.
42			
43	2-10	14	Delete “intake”.
44			
45	2-10	15-16	Why distinguish between “Native Americans and Alaska native
46			Villagers”?

1	2-13	2-4	Change to “ <i>Our approach in evaluating risk assessment relies upon various analytical tools and techniques, data sources, and other forms of analyses each of which has inherent uncertainties</i> ”.
2			
3			
4			
5	2-13	6	Change to “affect the <i>level</i> of its response”.
6			
7	2-13	10-11	This is not a very succinct or complete description of the errors associated with modeling approaches.
8			
9			
10	2-13	12	Change to “involved <i>with the transformation and fluxes of nitrogen and sulfur constituents</i> ”.
11			
12			
13	2-13	14-15	It would be more helpful to be more explicit in describing the sources of uncertainty. For example with respect to deposition, wet deposition of S and N can be relatively well characterized compared to dry deposition. The major issue associated with the errors related to dry deposition are associated mostly with the modeling of deposition velocities. Also, be more specific in what is being implied with the use of the term “ecological modeling”.
14			
15			
16			
17			
18			
19			
20			
21	2-13	14-21	This section needs to include more specific information. It would be most helpful to explicitly state the major sources of error in risk estimates.
22			
23			
24			
25	2-13	22-30	These statements are very general. At a minimum specific examples need to be supplied that show actual examples of these errors and importance to the assessment.
26			
27			
28			
29	2-14	2-3	It is anticipated that these discussions will provide sufficient detail on these sources of error in risk assessment.
30			
31			
32	2-14-15		References should also include citations to the actual literature and not rely solely on EPA documents.
33			
34			
35	3-1	10	Change to “The deposition <i>results</i> ”.
36			
37	3-1	26	Change to “The total amount of NO <sub>x</sub> emitted in the USA in 2002”.
38			
39	3-2	3-4	Change to “primary emitters of NO <sub>x</sub> , mainly as NO and NO <sub>2</sub> ”.
40			
41	3-2	5	Change to “utilities, with <i>additional</i> contributions”.
42			
43	3-2	9	Change to “remainder of anthropogenic emissions”.
44			
45	3-2	10	Delete “component”.
46			

1	3-2	15-16	Delete “in the pie charts in”.
2			
3	3-2	16-17	Change to “ <i>Results are shown on both a national basis (contiguous states only) as well as for the eastern</i> ”.
4			
5			
6	3-2	18	Delete “For this display”.
7			
8	3-3	1-2	Delete “Note that emissions from Alaska and Hawaii are not included in any of these charts”.
9			
10			
11	3-3	5-6	(not shown) with the on-road sector <i>being</i> the largest contributor, followed by emissions”.
12			
13			
14	3-3	8	Change “overall” to “ <i>national</i> ”.
15			
16	3-3	12	The figure caption needs more information (e.g. that Hawaii and Alaska are excluded in these results).
17			
18			
19	3-3	15	Change to “ <i>contiguous states</i> ”.
20			
21	3-4	3	Change to “emissions <i>from</i> fertilized”.
22			
23	3-4	5	Clarify what is meant by “30%–70%”. Does up to 70% of the waste mass be converted to emitted NH <sub>3</sub> ?
24			
25			
26	3-4	9	Change to “impact from <i>the input of</i> total reactive”.
27			
28	3-4	10	Explicitly state what is meant by “This”.
29			
30	3-4	12	Change to “Total <i>USA</i> emissions of”.
31			
32	3-5	9	Change to “utilities using <i>coal</i> ”.
33			
34	3-5	12	Change to “up to 10 <i>ppm</i> ”.
35			
36	3-5	13	This becomes a little confusing since the figure does not provide emission data from Hawaii and Alaska. Why not include values for these states in these figures.
37			
38			
39			
40	3-5	13-14	Sulfur is found in other forms besides amino acids in vegetation so change to “Sulfur is a macronutrient (typically being 1 to 2%) and is released as SO <sub>2</sub> if vegetation is combusted (Levine and Pinto, 1998)”. Also, there can be other forms of gaseous releases of sulfur components from vegetation (as well as soil) including H <sub>2</sub> S, COS, methyl mercaptan, etc. I am not sure where in the document these biogenic sulfur sources should be included.
41			
42			
43			
44			
45			
46			

1			
2	3-6	1-2	Delete since information has been included in my suggested modification.
3			
4			
5	3-6	3-6	Change to “The <i>proportion</i> of SO <sub>2</sub> emissions from major sources are shown in Figure 3.1-5 both on a national total basis well as for the eastern and western United States”.
6			
7			
8			
9	3-6	6	Why not include Alaska and Hawaii for completeness?
10			
11	3-6	14-16	The relative importance of this error needs to be stated explicitly.
12			
13	3-7	2-5	Not sure the term "policy-relevant" is a useful term with respect to defining background concentrations. What is the basis of the actual value being used? Is it based on a specific time period or some calculation that attempts to separate out natural versus anthropogenic emissions? How can the general effects of N fertilizers and N atmospheric deposition in affecting NO <sub>2</sub> flux be evaluated? Is this 100 ppt based on some type of area weighted basis or some other form of calculation?
14			
15			
16			
17			
18			
19			
20			
21			
22	3-7	4	Delete “policy-relevant”?
23			
24	3-7	25	Change to “This source distinction and quantification will”.
25			
26	3-8	13-14	Further information should be provided on the source and methods for estimating these deposition values. This information is provided later on page 3-13. This information should be provided earlier in the document.
27			
28			
29			
30			
31	3-8	19	Not sure what “Great Waters” means.
32			
33	3-8	19-23	References are needed here.
34			
35	3-9	Figure 3.1-6.	Reduce the significant digits in the figure legend to nearest 1/10th.
36			
37	3-10	Figure 3.1-7.	Reduce the significant digits in the figure legend to nearest 1/10th.
38			
39	3-11	Figure 3.1-8.	Reduce the significant digits in the figure legend to nearest 1/10th.
40			
41	3-11	9-10	Further details on how these deposition estimates were derived should be provided. This information is provided later on page 313. This information should be provided earlier in the document.
42			
43			
44			
45	3-12	Figure 3.1-9.	Reduce the significant digits in the figure legend to nearest 1/10th.
46			

1 3-12-13 See previous comments on the placement of this information  
2 within the document.  
3  
4 3-12-16 Isn't much of this information relevant to the overall predictions of  
5 N and S deposition. It was not clear why this more extended  
6 discussion was focused on the case studies. Was there a different  
7 type of analyses done for deposition for the case study regions than  
8 for the overall U.S.?  
9  
10 3-16 Aren't all these abbreviations already provided and hence Table  
11 3.2-1 can be deleted.  
12  
13 3-16 Are these formulas included to show the conversions from formula  
14 compound mass to nitrogen or sulfur mass? If this is there only  
15 use then Table 3.2-2 should be deleted.  
16  
17 3-17 11 Has the western case study been identified?  
18  
19 3-20 Within each of these regions there have been other measurements  
20 made of associated parameters including precipitation amount,  
21 atmospheric deposition. Is there any attempt being made in this  
22 document to compare these current results with previously  
23 published results?  
24  
25 3-23 There are well established geographic patterns in N and S  
26 deposition across the Adirondacks. Shouldn't these be  
27 acknowledged? There has also been substantial work on deposition  
28 estimates in the Adirondacks using other approaches. For wet only  
29 deposition for example see: Ito, M., M.J. Mitchell and C.T.  
30 Driscoll. 2002. Spatial patterns of precipitation quantity and  
31 chemistry and air temperature in the Adirondack Region of New  
32 York. Atmospheric Environment 36:1051-1062. Also other  
33 studies have evaluated the relative contribution of wet and dry  
34 deposition. See for example: Mitchell, M.J., C.T. Driscoll, J.  
35 Owen, D. Schaefer, R. Michener, and D.J. Raynal. 2001 Nitrogen  
36 biogeochemistry of three hardwood forest ecosystems in the  
37 Adirondack Mountains. Biogeochemistry 56: 93-133. Would  
38 some comparisons with other investigations be warranted?  
39  
40 3-25 This repeats a previous comment with respect to the inclusion of  
41 previous analyses of these regions in these cases studies.  
42  
43 3-26-53 There is considerable detailed treatment of the results provided by  
44 the CMAQ modeling including temporal and spatial results. With  
45 so much emphasis on these model results it would be useful to  
46 provide some other confirmation of these deposition values.

1	3-54	14-15	This is not entirely true. There can be instances where ambient concentrations of NO <sub>x</sub> and SO <sub>x</sub> are directly deleterious. These conditions, however, have not been generally found in the USA during the period of concern associated with acidic deposition effects. For Europe conditions in the “black-triangle” and other centers of high pollutant concentration there were direct impacts especially associated with SO <sub>x</sub> .
2			
3			
4			
5			
6			
7			
8			
9	3-55-70		The format and output of the CMAQ modeling runs are provided in some detail. Some further comparison of the CMAQ results, especially, in the areas of test cases, would be helpful in providing some objective measurements of the model results.
10			
11			
12			
13			
14	3-70-72		The model results need to be verified with actual data that show these relationships. Clearly the model functional relationships and parameterization will effect overall model output. It is important that it be clearly identified when model outputs are producing results that have been verified elsewhere or whether there are currently no empirical and experimental results that provide data to verify these results. Such arguments can also be made for the other N gaseous constituents.
15			
16			
17			
18			
19			
20			
21			
22			
23	3-70	16	It is suggested that there is “statistical imprecision in the modeling”. There are other important sources of model error that need to be considered including uncertainty in model formulations.
24			
25			
26			
27	3-82	7-9	Statements such as “Figure 3.2-55 shows that NO <sub>x</sub> emissions account for almost all oxidized nitrogen deposition in the Adirondacks Case Study Area, while Figure 3.2-56 shows that NH <sub>3</sub> emissions account for almost all reduced nitrogen deposition” have important implications with respect to making recommendations associated with NO <sub>x</sub> emission controls. Are these results verifiable and can the emissions also be linked to specific geographical areas?
28			
29			
30			
31			
32			
33			
34			
35			
36	3-87		How are these high emission locations ascertained? Is this a function of the location of specific monitoring locations (e.g., CASTNET sites).
37			
38			
39			
40	3-112		This section on uncertainty (3.2.2.5) that has yet to be completed needs to include not only statistical issues, but also uncertainties in the model formulations and associated parameters.
41			
42			
43			
44	3-113-114		This is a relatively limited reference list with considerable reliance on EPA documents. This section would be strengthened by inclusion of results from the peer reviewed scientific literature that
45			
46			

1 support the suggested findings.  
2  
3 4-1  
4 5-1 The sections on “ACIDIFICATION” and “NUTRIENT  
5 ENRICHMENT” include only outlines, but the suggestion of the  
6 importance of providing uniform terminology is encouraging.  
7  
8 6-1-10 This section gives a useful review of recent findings linking the  
9 cycling of S and Hg. This section also includes more references to  
10 the referred literature related to this topic  
11  
12 6-10-13 The section on NITROUS OXIDE provides additional information  
13 on this N gas and provides a clear indication of the importance of  
14 this gas including its linkage with N deposition and its important  
15 role as a “greenhouse” gas.  
16  
17 6-13-18 The synopsis on CARBON SEQUESTRATION provides a useful  
18 overview of important interactions between N deposition, warming  
19 and the carbon cycling in terrestrial ecosystems. This is a very  
20 large and important subject area. As suggested a detailed analyses  
21 is beyond the scope of this review. The term carbon sequestration  
22 does not really capture the total content of this section.  
23  
24 6-19-22 More emphasis in the description of aquatic effects should be  
25 placed on changes in the phytoplankton community structure that  
26 has been most noted in the western U.S.  
27  
28 7-1  
29 7-15 In its current version this “Synthesis and Integration of Case Study  
30 Results” is highly descriptive. This will need to be improved with  
31 specific quantitative results that show a clear relationships to the  
32 assessment.  
33  
34 8-1  
35 8-30 Clearly providing a clear scientific linkage that is policy relevant  
36 between concentrations of SO<sub>x</sub> and NO<sub>x</sub> and resultant S and N  
37 deposition and subsequent translation to ecosystem level effects is  
38 a major challenge. Clearly there are good linkages between  
39 concentrations of SO<sub>x</sub> and NO<sub>x</sub> and deposition, but the linkage to  
40 ecosystem level effects is more complicated due to inherent  
41 variability across the United States of the sensitivity of these  
42 systems to acidification, eutrophication and changes in biotic  
43 composition. It will be important to formulate an approach that  
44 takes into account these geographical patterns of sensitivity.  
45  
46 8-4-5 Figure 8.1-1 needs to indicate in some format that these ecological

1 indicators may not be constant over the United States (e.g., N  
2 deposition levels with respect to changes biotic community  
3 structure being more sensitive in the Mountain west than the  
4 eastern U.S.). These issues are outline on lines 1-7, page 8-5.  
5  
6 8-5 22 The problem in not including reduced N chemical species in any  
7 formulations associated with N deposition effects is highly  
8 problematic. I am not sure it is feasible to focus solely on NO<sub>x</sub>.  
9  
10 8-9 There are major difficulties in setting national standards for SO<sub>x</sub>  
11 and NO<sub>x</sub> concentrations without taking into account regional  
12 effects.  
13  
14 8-13 As suggested the development of these “functional forms” will be  
15 critical and may have both spatial as well as temporal components.  
16  
17 8-13 Clearly EPA is making heaving reliance on the CMAQ model  
18 suggesting the importance of validating results using other  
19 approaches and the linkages between gaseous concentrations and  
20 specific deposition levels.  
21  
22 8-14-17 The issues of deposition velocities are not trivial. For example  
23 look at the differences in deposition associated with the estimates  
24 at the same site for CAPMoN and CASTNET. Although  
25 CAPMoN and CASTNET provide similar concentrations of gases  
26 the deposition velocities are higher for CAPMoN verus  
27 CASTNET.  
28  
29 8-23 The discussion of uncertainties needs to include the various issues  
30 associated with the calculation of deposition velocities.  
31  
32 Attachments  
33  
34 2, pg 2 5 Change “to reflect *most recent* conditions”.  
35  
36 2, pg 2 14-15 Not sure that there is a relationship between steepness and base  
37 cation leaching rates versus the role of slope in affecting the  
38 contact of drainage waters to soils and the relative contributions of  
39 ground waters to drainage with groundwaters generally being more  
40 rich in base cations than waters derived from shallower soil  
41 sources.  
42  
43 2, pg 3 30 Isn’t a threshold of 400 µeq/L or less considered acid sensitive?  
44 Would a threshold of 100 µeq/L better? Also, note that the correct  
45 symbol for liter is “L” not “l”. Change for entire document.  
46

1 2, pg. 5 Figure 3.2-1. Give a citation for the Acid Sensitive Waters  
2 (USGS).  
3  
4 2, pg. 7 Why was there no selection of a threshold for sulfate deposition?  
5 Is this awaiting the determination of critical load? At a minimum  
6 the European critical load could be used.  
7  
8 2, pg 8 Same comment for total N and S deposition and the assignment of  
9 a value as that provided by sulfate.  
10  
11 2, pg. 9 The inclusion of high elevation could also be justified by other  
12 criteria such as the potential contribution of occult (fog)  
13 deposition. If occult deposition accounted for in the CMAQ  
14 estimates. This also relates to rationale provided with respect  
15 topographic position (Attachment 2, page 17).  
16  
17 2, pg 9 25-28 This is confusing with respect S and N deposition since it was  
18 suggested above that no criteria for S and N deposition were  
19 defined. If these top quartiles are used the actual values need to be  
20 supplied that make up these quartiles. Also, the year or years from  
21 which these deposition data are derived needs to be given  
22 explicitly.  
23  
24 2,pg 10 14 Why “Total nitrogen (Kjeldahl)”. Do you mean total dissolved  
25 nitrogen or total dissolved Kjeldahl nitrogen. Why exclude nitrate  
26 in surface waters?  
27  
28 2,pg 11 Although there are weak linkages between N deposition and N  
29 solute concentrations in surface waters, it would be preferable to  
30 provide the data layer of actual N solute concentrations in surface  
31 waters.  
32  
33 2, pg12 18-19 Provide these nutrient concentrations available from the National  
34 Nutrient Database. Provide a citation for this and the other data  
35 bases.  
36  
37 2, pg 15 These N deposition data layers seem to be redundant from data  
38 layers previously described.  
39  
40 2, pg 16 More clearly delineate the difference between “content” and  
41 concentration”. Content should be reserved for the total amount  
42 (mass, molar value) of a an element on a per unit area while  
43 concentration is the amount (mass, molar value) of an element per  
44 unit of mass (sometimes) expressed as %.  
45  
46 2,pg 18 The delineation of the location of acidophilic lichens appears to

1 have a strong boundary based upon state borders especially notable  
2 in Arizona and an absence in New Mexico.  
3  
4 3, pg 10 Here and elsewhere “ $\mu\text{M}$ ” is not a correct abbreviation. The  
5 abbreviation for mole is “mol”.  
6  
7 3, pg 12 Note that these ANC levels are lower than those suggested to be  
8 considered to be of concern in Attachment 2.  
9  
10 3, pg 15 There have been other models (e.g., PnET-BGC) that have been  
11 applied particularly to the Adirondacks to evaluate especially  
12 temporal patterns of acidification. Wouldn't it be helpful to at  
13 least do some comparisons using other models besides MAGIC.  
14  
15 3, pg 18 8 Change to “ $\text{SO}_4^{2-}$ ”.  
16  
17 3, pg 21 Clarify how the ratios of wet to dry deposition were derived.  
18  
19 3, pg 22 15 Are the total deposition values used in the MAGIC calculations  
20 different from deposition estimates used elsewhere in the entire  
21 document?  
22  
23 3, pg 22 27-29 Some elaboration on how ASTRAP derived deposition would be  
24 helpful and how these estimates confirm or differ with the CMAQ  
25 estimates.  
26  
27 3, pg 23-26 There is considerable discussion of the calibration of MAGIC in  
28 this section. Some of this could be reduced and inclusion of other  
29 ways of comparing model output with other published results  
30 including other models (e.g. PnET-BGC) would provide additional  
31 perspectives of these results.  
32  
33 3, pg 29 Similar to previous comments, although the discussion and  
34 definition of the F-factor provides background information this is  
35 not a novel approach, but rather one that could be cited. More  
36 emphasis of the validation and comparisons with actual  
37 measurements versus description of the model development would  
38 be more helpful.  
39  
40 3, pg 31 Figure 5.1-1. Trends in LTM monitored lakes in the Adirondacks  
41 of New York would be improved if specific lake classes were used.  
42 It is not clear from these figures how a general trend for the LTM  
43 monitored lakes were obtained.  
44  
45 3, pg 32 Figure 5.1-2. The modeled values appear to be substantially  
46 different that those of the measured values. Doesn't this bring into

1 question to validity of the predictions for 2010? I don't believe the  
2 results of this figure are discussed within the document.  
3  
4 3, pg 35 Clearly the document is incomplete at this stage.  
5  
6 4, pg 1-2 This seems repetitious of information provided in the main  
7 document.  
8  
9 4, pg 5 "M" is not the correct SI abbreviation for mole. The correct  
10 abbreviation is "mol".  
11  
12 4, pg 4-9 Not sure that this much restating of what has previously been  
13 found about Al and Ca relationships is needed.  
14  
15 4, pg 11 Would it be more efficient to cross reference the description of  
16 ecosystem services as provided in the main document?  
17  
18 4, pg 18-20 Are the details of the history of the Kane Forest needed in this  
19 document?  
20  
21 4, pg 21-25 Similarly to the previous comment, are all these details about  
22 Hubbard Brook needed for this document?  
23  
24 4, pg 26-47 This is difficult to follow due to the level of detail. Perhaps a more  
25 generalized format in which could be imbedded specific references  
26 to the literature or the inclusion of appendices so that the major  
27 theme of the discussion is not lost.  
28  
29 4, pg 50 Not sure of the importance of the inclusion of the section on  
30 "Implications for other systems" in this document.  
31  
32 4, pg 51-52 The uncertainties issues need to be better integrated into the overall  
33 document.  
34  
35 4, pg 53 The "Conclusions" summarize the important issues and these  
36 issues should be the focal points of this entire section with a need  
37  
38 6, p 43 The figure on this page (Figures 5.1-1 5.1-2) appears to have an  
39 inappropriate numbers. Shouldn't they be 6.1-1 and 6.1-2?  
40

1 **Mr. Richard Poirot**

2  
3 These comments pertain primarily to REA Chapter 3 (Sources, Ambient Concentrations, and  
4 Deposition), for which the following charge questions were provided.

5  
6 **Question 1:** To What Extent are the air quality characterizations and analyses presented  
7 in chapter 3 technically sound, clearly communicated, appropriately characterized, and  
8 relevant to the secondary NAAQS for NO<sub>x</sub> and SO<sub>x</sub>?

9  
10 **Question 2:** Section 3.2.1 describes an approach for evaluating the spatial and temporal  
11 patterns for nitrogen and sulfur deposition and associated ambient concentrations in the  
12 case study locations. This draft document includes the analysis for the Adirondacks Case  
13 Study. Does the Panel agree with this approach and should it be applied to the other  
14 Case- Study Areas?

15  
16 **Question 3:** Section 3.2.2 describes the relative contributions of ambient emissions of  
17 nitrogen and ammonia to nitrogen deposition for the case-study areas. To what extent is  
18 the approach taken technically sound, clearly communicated, and appropriately  
19 characterized?

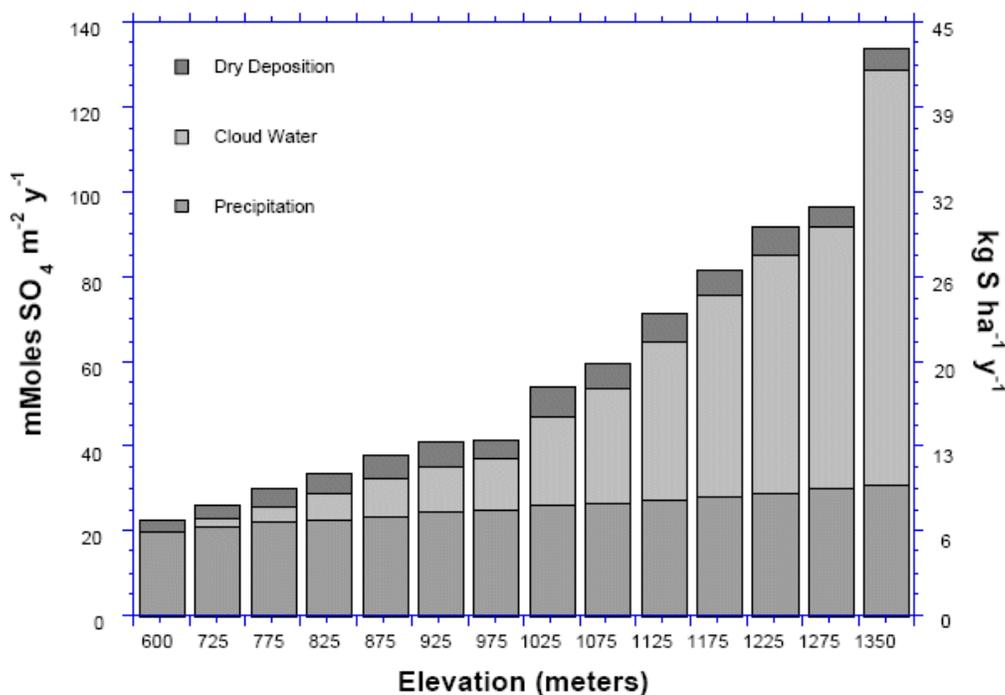
20  
21 Assuming the many and important missing “placeholder” sections are filled in, I think the air  
22 quality characterizations and analyses presented in chapter 3 will provide a technically sound,  
23 clearly communicated, appropriately characterized, and relevant to the secondary NAAQS for  
24 NO<sub>x</sub> and SO<sub>x</sub> (although it still remains unclear to me what kind of 2ndary standards are being  
25 contemplated). Many of these placeholders refer to evaluations of model performance, and  
26 since the majority of the chapter consists of presentation of intensively graphical model results,  
27 filling the placeholders will be key to providing confidence in the model results. The technical  
28 approach appears to be reasonable, but without a better sense of model performance (including  
29 both CMAQ and the RSM meta-model), the technical soundness and relevance to NAAQS can’t  
30 really be evaluated.

31  
32 The presentation of the information is clear (even beautiful), but there is minimal discussion or  
33 interpretation of the graphical results, which makes it difficult to maintain interest in looking so  
34 many pictures. Conversely, it might be informative to poll the model results in ways that might  
35 provide a better understanding of relationships among the various metrics of air quality,  
36 deposition and environmental effects. For example: what would the maps look like that show  
37 the ratios of S deposition to S emissions; N (oxidized) deposition to N (oxidized) emissions; N  
38 (reduced) deposition to N (reduced) emissions. What would maps look like that show ratios of  
39 S (or N) deposition to ambient SO<sub>2</sub> (or NO<sub>2</sub>) concentrations? What if modeled S emissions were  
40 rolled back to show alternate lower maximum levels of SO<sub>2</sub> (and/or NO<sub>2</sub>) – what would be the  
41 subsequent changes in S (and/or N) deposition in sensitive downwind areas? If sections of the  
42 Adirondacks were considered to be experiencing adverse levels of acidifying deposition, how  
43 could the models be used to determine the “significant contributing area” – or perhaps some  
44 combination of emission size, and frequency upwind – such that a non-attainment area might be  
45 defined to better include the contributing emissions? A possible approach for an improved

1 secondary SO<sub>x</sub> or NO<sub>x</sub> NAAQS might consider (much) lower levels but averaged over larger  
2 areas or longer averaging times.

3  
4 With the caveat that the model performance needs to be more clearly examined and documented,  
5 I think the more detailed approach applied here for the Adirondack case study is reasonable, and  
6 could be applied to other case study areas. One possible concern – possibly more relevant to the  
7 Adirondacks than to most of the other case study areas – is whether the 12 km gridding might be  
8 coarse relative to the spatial variability in deposition, terrestrial & aquatic ecosystems and  
9 associated effects. Potentially the larger grid cells may fail to adequately capture orographic  
10 increases in precip volume & deposition and the additional increases from occult deposition at  
11 highest elevations (or in certain coastal areas) – in comparison with variations in sensitive  
12 terrestrial and aquatic biota within these grid cells. See for example: Miller, E.K. et al. 1993.  
13 Atmospheric deposition to forests along an elevational gradient at Whiteface Mountain, NY  
14 USA. Atmos. Environ. 27A:2121-2136.

15



**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).**

16  
17 Possibly this influence of occasionally large terrain, deposition and species variations within the  
18 relatively large grid cells could be evaluated by conducting a higher resolution sensitivity  
19 analyses within selected grid cells in the Adirondacks case study area. Alternatively, it might at  
20 least be possible to disaggregate the coarser modeled dry dep. estimates to combine with the  
21 higher resolution wet dep. estimates from the Grimm & Lynch approach. Arguably the dry dep  
22 totals and variability may be less important than wet dep at more remote receptor locations.  
23 Possibly also a terrain-based cloud deposition model could be added to provide added detail for  
24 higher elevations or in coastal areas.

1  
2 Regarding the soundness of the technical modeling approach to estimate the relative  
3 contributions of ambient emissions of oxidized and reduced nitrogen to nitrogen deposition for  
4 the case-study areas – the approach seems sound but again there is a need to evaluate the  
5 performance of the models (CMAQ + RSM). Trust but verify. This evaluation could/should  
6 extend where possible to subcomponents of the models such as emissions inputs and space/time  
7 patterns of modeled estimates of wet oxidized N and wet reduced N deposition.

8  
9 That being said, I do like the approach of directly linking the estimates of changes in Nr  
10 deposition to changes in specific emission sources. I would think a similar approach could also  
11 be taken to zero out and otherwise reduce SOx emissions from different source categories. Down  
12 the road, this may allow a bundling & comparing of projected “optional” future emission  
13 controls (small, medium, large, etc.) to desired reductions in deposition in sensitive areas, in  
14 comparison to the associated concentrations in atmospheric NOx & SOx concentrations (in the  
15 event the layers say we have to stick with the traditional indicators). What new NAAQS limits of  
16 these indicators (perhaps averaged over larger - or much larger - areas than single monitors)  
17 would be necessary to achieve the desired reductions of Nr and/or S deposition in sensitive  
18 areas?

19  
20 In addition, if you were to add various levels of SOx (and NOx) emission reductions to your  
21 modeled scenarios, it would be a snap to calculate and display the resulting changes in sulfate  
22 and nitrate aerosols (and in their visibility effects) that would result from any changes in S & N  
23 emissions or deposition or SO<sub>2</sub> & NO<sub>2</sub> concentrations. This would allow you to (a) consider a  
24 more complete set of welfare benefits that would result from any revised NAAQS based on  
25 deposition effects and/or (b) might lead to and help justify alternative ambient air indicators – for  
26 example the sum of total atmospheric oxidized S and N compounds (sum in ug/m<sup>3</sup> of S from  
27 SO<sub>2</sub> and pSO<sub>4</sub> and N from NO, NO<sub>2</sub>, HNO<sub>3</sub>, and pNO<sub>3</sub> or somesuch) – that might not be  
28 considered if only deposition-related effects are considered, but which might, set at the right  
29 levels, result in large deposition-related benefits.

30  
31 **Other Minor Comments:**

32  
33 p. 3-1 lines 16-23: This is a good example of what seems like an intentional sense of vagueness  
34 regarding which pollutants and secondary transformation products are or are not the subject of  
35 this review, and/or available as potential indicators for secondary NAAQS. Why are nitric acid  
36 and PNO<sub>3</sub> considered part of “NOx”, while SOx includes only gaseous SO<sub>2</sub>?

37  
38 p. 3-4, Figure 3.1-3: This figure just doesn’t look right – and seems inconsistent with the  
39 reduced nitrogen deposition map in Figure 3.1-8 on p. 3-11.

40  
41 p. 3-4, lines 3-5: Does confined feeding really increase animal wastes, or does it just increase  
42 atmospheric emissions from them?

43  
44 p. 3-4, line 12: Figure 3.1-4 does not show annual 2002 SO<sub>2</sub> emissions “by state”.

45  
46 p. 3-5, line 4: I would change “Industrial” to “Anthropogenic”.

- 1  
2 p. 3-5, lines 10-15: Should marine DMS emissions be mentioned here?  
3  
4 p. 3-6, lines 14-16: Can you provide any quantitative indication of how large these fire SO<sub>2</sub>  
5 emission underestimates are?  
6  
7 p. 3-8, lines 5-7: Does this increased deposition of reduced nitrogen also pertain over the  
8 100-year period of the preceding sentence. Can you say something more precise about trends  
9 over the past several decades?  
10  
11 p. 3-12, lines 10-14: This description relates to how NADP interpolates its wet deposition data.  
12 However, later you indicate using the precip-volume-enhanced estimates from Grimm & Lynch  
13 (2004). So which was it? One general concern is that the 12 km gridding may overly smooth  
14 some of the more extreme orographic increases in precip – and you seem to exclude cloud water  
15 deposition. Possibly this could be handled by conducting some sensitivity analyses for grid  
16 cells containing higher elevation terrain – especially for the Adirondack and Shenandoah case  
17 studies.  
18  
19 p. 3-16, line 11: Why not also describe CASTNet (& AIRMoN dry) data for HNO<sub>3</sub>, NO<sub>3</sub>, NH<sub>4</sub>,  
20 SO<sub>4</sub>?  
21  
22 p. 3-23, lines 4&5 and lines 11&12: say roughly the same thing twice.  
23  
24 p. 3-23, line 7: “(25% wet vs. 6% dry)” and 69% what?  
25  
26 p. 3-23, line 12: Change “does” to “do”.  
27  
28 p. 3-54, line 17: You could add “current and historical” before “atmospheric deposition”.  
29  
30 p. 3-55, lines 20-21: Can you provide any indication of if and how well the RSM technique  
31 (and for that matter the underlying CMAQ model) works for all the SO<sub>x</sub>, NO<sub>x</sub> and reduced N  
32 species you will use it for?  
33  
34 p. 3-57, line 5: Am I missing something or did you only use a couple (zero-outs) of these 210  
35 control runs? So what was the purpose of the other runs?  
36  
37 p. 3-71, line 8: Delete one “deposition” in “greater deposition of oxidized nitrogen deposition”.  
38  
39 p. 3-71, lines 8-15: I would think formation of aerosol NH<sub>4</sub>NO<sub>3</sub> would tend to increase the  
40 transport distance, but would not lead to any net decrease or increase in Nr deposition. It all  
41 gets deposited eventually. An exception might be if aerosols persist long enough to transport  
42 out of the (US or North American) domain.  
43  
44 p. 3-73: I must have blinked somewhere, because I didn’t expect to see this large, international  
45 “sugar maple case study” area discussed npreviously. Its not listed as a “Case Study Location”

1 in Table 2.1-1 on page 2-2&3. It reminds me to ask for a clearer “up-front” description (& map)  
2 of all the intended case study areas.  
3

1 **Mr. David Shaw**

2  
3  
4 **General Comments**

---

5  
6 Thank you for addressing the outcome of this REA. I believe that this makes the document  
7 more focused.

8  
9 I still feel that a specific goal of this assessment should be to identify and report sensitive areas  
10 which do not have adequate monitoring. Adopting this longer view in this analysis will enable  
11 the next review process to start from a stronger point. In identifying areas without adequate  
12 monitoring data, we may be able to start the process of getting a stronger data record of results  
13 for future analysis. It is my hope that this will lead to better modeling due to better data.

14  
15 While there are certainly areas that are deficient in monitoring data, there definitely are areas of  
16 strong monitoring data with analysis. I still feel that the areas of certainty do not receive equal  
17 treatment as uncertainty. I feel we must be clear that we do understand causes, effects and  
18 variability in our ecosystem response.

19  
20 On this note, the analyses presented in Chapter 3 of the REA rely heavily on modeling and don't  
21 always reinforce where the measurements are the strongest. It is important to emphasize where  
22 we have the most confidence (e.g. wet deposition, ANC measurements in case study areas) and  
23 the least confidence (e.g. air concentrations and dry deposition of NO<sub>x</sub>/SO<sub>x</sub>, where  
24 measurements are lacking). Much of the information on dry deposition will come from CMAQ,  
25 and the measured data from CASTNet and other special studies could be used to assess the  
26 model at selected locations.

27  
28 **Charge Questions**

---

29  
30 *Scope of the Review*

31 *Question 1*

32  
33 *Chapters 1 and 2 provide the background, history, and the framework for this review,*  
34 *including a discussion of our focus on the four key ecological effect areas (aquatic*  
35 *acidification, terrestrial acidification, aquatic nutrient enrichment, terrestrial nutrient*  
36 *enrichment). Is this review appropriately focused in terms of the targeted areas and in terms*  
37 *of characterizing the important atmospheric and ecologic variables that influence the*  
38 *deposition and, ultimately, the ecologic impacts of nitrogen and sulfur? Does the Panel have*  
39 *any further suggested refinements at this time?*

40  
41 **Pages 1- 1 to 1-10:**

42 I feel that this gives good overall information on the Rational, Background and History. It  
43 might also be a good place to address other pollutants associated with NO<sub>x</sub> and SO<sub>x</sub> analyzing  
44 the whole set of problems associated with these pollutants.

1 **Page 1-8 lines 3-5:**

2 Lines 3-5 state that ‘in spite of the complexities and uncertainties....’ it became clear that a  
3 program to address acid rain was needed. In actuality, it was the evidence of a preponderance of  
4 the scientific data of the NAPAP effort which made it clear that an acid rain program was  
5 needed. This builds on one of my general comments regarding an emphasis on uncertainty  
6 rather than giving equal treatment to those areas where certainty exists.  
7

8 **Page 1-16:**

9 I would recommend adding a discussion on critical loads as the organizing principle of this RAE  
10 assessment. Include the current understanding of ecological indicators and how levels of the  
11 proposed standard will be integrated.  
12

13 **Page 1-20:**

14 It would be helpful to explain how the existing monitoring data will be used to evaluate the  
15 success of the proposed standard? How and when will the existing monitoring networks be  
16 evaluated for adequacy of measuring ecosystem response?  
17

18 **Page 2-10:**

19 I appreciate the effort in adding sulfur and mercury methylation. The fact that it will be  
20 addressed will make this a stronger analysis.  
21

22 **Page 2-11, Table 2.3-1:**

23 I feel that it would be beneficial to add to Cultural Services “chemical and biological degradation  
24 of Constitutionally (federal and states) protected Wilderness areas”. This would apply to  
25 several if not all Targeted Effect Areas. The point being that the ADK case study area, for  
26 example, represents a 6 million acre region, 43% of which is protected by the NYS Constitution  
27 as ‘forever wild’ Forest Preserve. Here, tree cutting is not allowed, yet atmospheric deposition  
28 damages forests and diminishes aquatic ecosystems within these forests. The remaining 57% is  
29 devoted principally to forestry, agriculture, and open-space recreation, a portion of which is  
30 sensitive to negative effects of atmospheric deposition. This landscape holds an additional  
31 cultural value to New Yorkers especially, and to others from the US and around the world.  
32

33 **Pg 2-12:**

34 In the box where “provisioning services” and “cultural services” for Sulfur and Mercury  
35 Methylation are provided, fish kills is listed as an ecological impact. From the literature that I  
36 am familiar with, fish kills or declines in fish populations are not a good indicator of MeHg,  
37 however, declines in the success of species higher in the food web such as loons and humans  
38 occur because of MeHg neuron toxic effects and bio accumulation.  
39

40 *Air Quality Analysis*

41 *Question 1*

42 *To what extent are the air quality characterizations and analyses presented in Chapter 3*  
43 *technically sound, clearly communicated, appropriately characterized, and relevant to the*  
44 *review of the secondary NAAQS for NO<sub>x</sub> and SO<sub>x</sub>?*  
45

46 **Sections 3.1.4 and 3.2:**

1 It seems as if the dataset discussion (Section 3.2) would be more beneficial if it appeared before  
2 the composite deposition maps (Section 3.1.4). These composite maps consist of modeled dry  
3 and measured/interpolated wet deposition. For these maps, are the units actually  $\text{kg ha}^{-1} \text{y}^{-1}$ , or  
4 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  
5 estimates are generally consistent with whatever measurements (e.g. CASTNet) are available,  
6 that one year of modeling is adequate to capture the seasonal/spatial variability in the predictions  
7 (i.e. this is not an atypical year), and that other photochemical models are capable of estimating  
8 dry deposition and could be used to perform such an analysis.

9  
10 **Section 3.2.1.2:**

11 I am interested to know why  $\text{SO}_2$  and  $\text{NO}_2$  from SLAMS/NAMS monitors are not included in the  
12 measured database? While there may not be many  $\text{NO}_2$  monitors in rural areas, there should  
13 still be some measurements of  $\text{SO}_2$  in the case study areas.

14  
15 **Page 3-21 ADK case study area:**

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

18 How were the 44 lakes and ponds selected?

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

20 How representative are these sites of the whole region?

21 Is there an elevational stratification?

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

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

25  
26 Some important facts to point out regarding this region is that 22% of it is above 600 m where the  
27 sensitive spruce fir forest community becomes dominant. Further up above 900 m are key  
28 signature mountain peak ecosystems containing over 100,000 acres.

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

31  
32 **Pages 3-35 through 3-37, and 3-50 through 3-53:**

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

36  
37 **Figures 3.2-29 through 3.2-44:**

38 I would recommend that the metrics for these figures are clearly stated. Also, it would be  
39 helpful to confirm that the “whiskers” are the minimum and maximum and that the boxes are  
40 25<sup>th</sup>/75<sup>th</sup> percentiles.

41  
42 **Figures 3.2-45 onward:**

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

1 **Misc.**

---

2

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

5

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

1 Enclosure 3: *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

4

5

6

*Richard A.F. Warby, Chris E. Johnson\*, and Charles T. Driscoll*

7

8

9

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11 Syracuse, New York, 13244.

12

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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 ( $\text{Ca}_N$ ) and exchangeable aluminum ( $\text{Al}_N$ ). The median  $\text{Ca}_N$  declined by  
24 more than 50%, from 23.5 to 10.6  $\text{cmol}_c \text{ kgC}^{-1}$ , while median  $\text{Al}_N$  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  $\text{pH}_s$  (0.01M  $\text{CaCl}_2$ ) decreased from 3.19 to 2.97. Changes in median  
28 concentrations of other exchangeable cations were either statistically insignificant ( $\text{Mg}_N$ ,  $\text{K}_N$ ) or  
29 very small ( $\text{Na}_N$ ). 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;  $\text{Al}_N$  - 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 H<sub>2</sub>SO<sub>4</sub> and a  
61 combined H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub> mix (2000-4000 mol<sub>c</sub>/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 (SO<sub>4</sub><sup>2-</sup>) and hydrogen ion (H<sup>+</sup>) 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 (28<sup>th</sup> May – 4<sup>th</sup> 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 (25<sup>th</sup> June – 15<sup>th</sup> 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, NH<sub>4</sub>Cl (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 NH<sub>4</sub>Cl 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<sub>e</sub>). Base saturation was determined as the fraction of the CEC<sub>e</sub> occupied by  
214 exchangeable base cations, expressed as a percentage.

215

216 Soil pH was determined in deionized water (pH<sub>w</sub>) and 0.01M CaCl<sub>2</sub> (pH<sub>s</sub>). 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  $\text{pH}_s$  rather than  $\text{pH}_w$  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  $50^\circ\text{C}$ . 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  $60^\circ\text{C}$ .

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  $\text{CEC}_e$  using the soil carbon content ( $\text{Ca}_N$ ,  $\text{Na}_N$ ,  $\text{Mg}_N$ ,  $\text{K}_N$ ,  $\text{Al}_N$ ,  $\text{Acidity}_N$ , Sum  
233  $\text{BC}_N$ , and  $\text{CEC}_{eN}$ , 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  $\text{pH}_s$   
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  $\text{CEC}_e$  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  $\text{Ca}_N$  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  $\text{Ca}_N$  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  $\text{Ca}_N$  decreased from  $34.1 \text{ cmol}_c$   
249  $\text{kgC}^{-1}$  to  $9.0 \text{ cmol}_c \text{ kgC}^{-1}$  (Table 2; Fig. 2). Exchangeable  $\text{Ca}_N$  decreased the most in soils with  
250 higher C content ( $\text{C} > 40\%$ ), which were also the soils with the highest  $\text{Ca}_N$  in 1984 (Table 3;  
251 Fig. 3). In 1984 about 55% of the Oa horizons had  $\text{Ca}_N$  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  $\text{Ca}_N$  in the  
253 Oa horizon.

254

255 Exchangeable  $\text{Mg}_N$  and  $\text{K}_N$  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  $\text{Na}_N$  was statistically significant, but Na  
257 represents a minor fraction of  $\text{CEC}_e$  in these soils.

258

### 259 **Cation Exchange Capacity and Base Saturation**

260 The normalized effective cation exchange capacity ( $\text{CEC}_{eN}$ ) 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  $\text{CEC}_{eN}$  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  $\sim 67.5$   
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  $1.1 \text{ cmol}_c$   
322  $\text{kg}^{-1}$  in 1997. Exchangeable Al increased from 3.3 to  $5.9 \text{ cmol}_c \text{ kg}^{-1}$  in the same period, while  
323 mean  $\text{pH}_s$  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  $\text{CEC}_e$ . 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  $\text{CEC}_e$ .

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<sub>N</sub> and Al<sub>N</sub> 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<sub>N</sub> in CNE/Maine (25.1 cmol<sub>c</sub>  
344 kgC<sup>-1</sup>) 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  $\text{kg ha}^{-1}$  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  $\text{Ca}_N$  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  $\text{CEC}_{\text{eN}}$  and  
484 pH, while in the low ANC class  $\text{CEC}_{\text{eN}}$  decreased by ~8% and pH increased by 0.08 pH units.  
485 Organic horizons in the moderate ANC class showed the largest increase in  $\text{Al}_{\text{N}}$  and  
486 exchangeable acidity, the largest decrease in  $\text{Ca}_{\text{N}}$ , and were the only soils to experience a  
487 decrease in  $\text{pH}_{\text{s}}$ . Changes in the acid-base status of soils in the moderate ANC class were also the  
488 only statistically significant changes, except for  $\text{CEC}_{\text{eN}}$  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
<b>Total N</b>	%	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
<b>Total C</b>	%	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
<b>Na<sup>**</sup></b>	cmol <sub>c</sub> /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
<b>Na<sub>N</sub><sup>**</sup></b>	cmol <sub>c</sub> /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
<b>Mg</b>	cmol <sub>c</sub> /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
<b>Mg<sub>N</sub></b>	cmol <sub>c</sub> /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
<b>K</b>	cmol <sub>c</sub> /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
<b>K<sub>N</sub></b>	cmol <sub>c</sub> /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
<b>Ca<sup>**</sup></b>	cmol <sub>c</sub> /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
<b>Ca<sub>N</sub><sup>**</sup></b>	cmol <sub>c</sub> /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
<b>Sum BC<sup>**</sup></b>	cmol <sub>c</sub> /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
<b>Sum BC<sub>N</sub><sup>**</sup></b>	cmol <sub>c</sub> /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
<b>Acidity<sup>**</sup></b>	cmol <sub>c</sub> /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
<b>Acidity<sub>N</sub><sup>**</sup></b>	cmol <sub>c</sub> /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
<b>Al<sup>**</sup></b>	cmol <sub>c</sub> /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
<b>Al<sub>N</sub><sup>**</sup></b>	cmol <sub>c</sub> /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
<b>CEC<sub>e</sub><sup>*</sup></b>	cmol <sub>c</sub> /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
<b>CEC<sub>eN</sub></b>	cmol <sub>c</sub> /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
<b>Base Saturation<sup>**</sup></b>	%	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
<b>pH<sub>w</sub></b>	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
<b>pH<sub>s</sub><sup>*</sup></b>	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
<b>Number of Samples</b>	19	18	20	21	36	16
<b>Base Saturation</b>	49.7	28.3	48.0*	33.0*	65.0*	42.0*
<b><math>CEC_{eN}</math></b>	68.3	77.2	66.9*	57.0*	55.2	55.7
<b>Acidity<sub>N</sub></b>	31.3*	49.2*	30.7	32.8	20.3	24.2
<b><math>Ca_N</math></b>	20.4	10.1	17.2*	9.4*	28.0*	14.0*
<b><math>Al_N</math></b>	19.7	30.1	18.0	19.3	6.5	6.6
<b><math>pH_s</math></b>	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
<b>Number of Samples</b>	10	13	14	17	51	25
<b>Base Saturation</b>	33.4	25.3	41.4	38.2	65.6**	36.2**
<b><math>CEC_{eN}</math></b>	52.4	60.5	57.3	52.9	69.2	64.4
<b>Acidity<sub>N</sub></b>	35.2	44.6	30.0	32.8	19.9**	38.0**
<b><math>Ca_N</math></b>	13.5	8.2	16.8	8.4	34.8**	17.1**
<b><math>Al_N</math></b>	18.9	27.4	13.7	17.4	6.5**	16.2**
<b>pH<sub>s</sub></b>	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

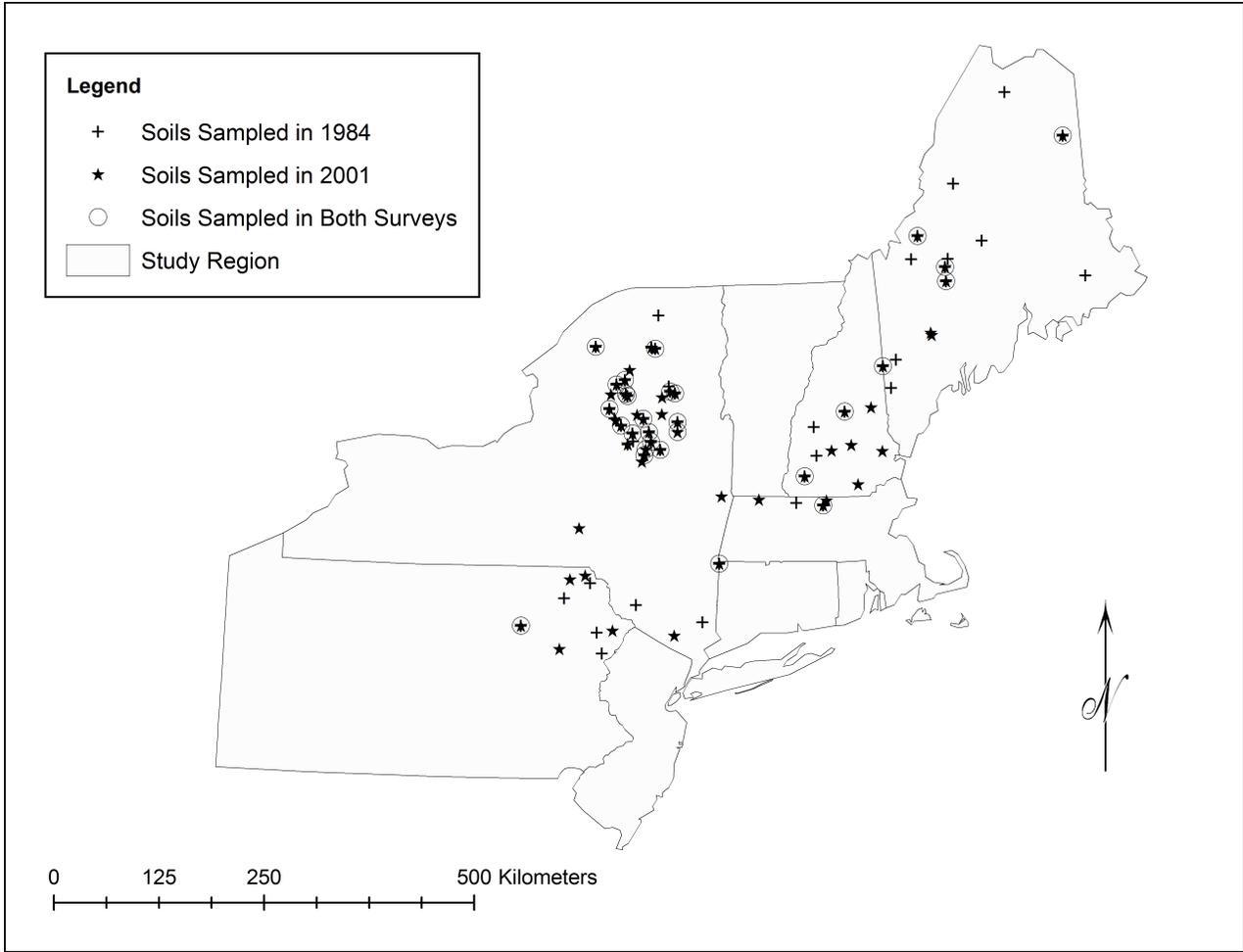
725 **Fig. 2.** Acid-base soil properties of organic horizons for the whole region and the subregions for  
726 1984 and 2001. Boxes indicate the interquartile ranges; whiskers indicate the 10<sup>th</sup> and 90<sup>th</sup>  
727 percentiles; median trends are indicated by the line in the box; dots indicate the 5<sup>th</sup> and 95<sup>th</sup>  
728 percentiles of the outliers. Units for CEC<sub>eN</sub>, Ca<sub>N</sub>, Al<sub>N</sub>, and EA<sub>N</sub> are (cmol<sub>c</sub> kgC<sup>-1</sup>) 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<sub>eN</sub>, Ca<sub>N</sub>, Al<sub>N</sub>, and  
732 EA<sub>N</sub> are (cmol<sub>c</sub> kgC<sup>-1</sup>). 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

