



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON D.C. 20460

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SCIENCE ADVISORY BOARD

November 18, 2008

EPA-CASAC-09-002

The Honorable Stephen L. Johnson  
Administrator  
U.S. Environmental Protection Agency  
1200 Pennsylvania Avenue, N.W.  
Washington, D.C. 20460

Subject: Peer Review of EPA's *Integrated Science Assessment (ISA) for Oxides of Nitrogen and Sulfur – Environmental Criteria (Second External Review 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 EPA's *Integrated Science Assessment for Oxides of Nitrogen and Sulfur – Environmental Criteria (Second External Review Draft)* (EPA/600/R-08/083, August 2008) (see Enclosure 1 for the Panel roster). This letter has been reviewed and approved by the chartered CASAC at the public conference call on October 30, 2008 (see Enclosure 2 for the CASAC Roster). Overall, the Panel found the second draft ISA to be much improved and very comprehensive. In this letter, the CASAC Panel offers general comments and recommendations to further strengthen the ISA followed by responses to the Agency's charge questions. Comments from the individual Panel members are provided in Enclosure 3.

1. EPA has done a good job in response to the Panel's concern regarding imbalance in the discussion of NO<sub>x</sub> deposition vis-à-vis reactive nitrogen (Nr) deposition and how the various components of Nr contribute to acidification and nutrient enrichment. (Reactive nitrogen refers to the sum of NO<sub>x</sub>, reduced NH<sub>x</sub>, and organic nitrogen.) However, there remain instances in the second draft where appropriate adjustments have not been made. In finalizing the ISA, EPA should carefully consider if references to concentrations of particular species and/or deposition effect are made correctly, and in particular whether and when the term "NO<sub>x</sub> deposition" should be replaced with "Nr deposition" for clarity and accuracy.
2. The exclusion of the non-ecological welfare effects of NO<sub>x</sub> and SO<sub>x</sub> (e.g., effects of particulate matter on visibility degradation and climate, and materials damage) in this

NAAQS review process continues to be an area of concern for the Panel. For a document entitled “*Integrated Assessment for Oxides of Nitrogen and Sulfur – Environmental Criteria*” a focus entirely on ecological effects makes its title a misnomer. The Agency maintains that these effects are discussed in the assessment documents of other criteria pollutants and consequently a full treatment in the current review is unnecessary. To ensure that the ISA represents a meaningful assessment of environmental criteria, EPA should either rename the document “*Ecological Criteria*” (which is probably not feasible) or keep “*Environmental Criteria*,” but state clearly in which Agency documents the omitted NO<sub>x</sub>/SO<sub>x</sub> welfare effects are treated and, at a minimum, provide a short synopsis of the key non-ecological effects in the appendix.

3. Nitrogen is an essential and often limiting plant nutrient. In certain locations, the effects of increased Nr deposition may be viewed as ecologically and economically beneficial. The Agency should make certain that the treatment and discussion of the impacts of Nr deposition in the ISA are balanced.
4. Given the importance of this document as a foundation for further analyses, there remains a general need to carefully review the draft for editorial integrity, with particular focus on clarity and accuracy.

#### **Responses to EPA’s Charge Questions:**

1. **We have added an executive summary of the major findings and conclusions to the second draft ISA. We have also created a "key findings" section that is intended to provide highlights of these conclusions. We are seeking CASAC panel advice and comments on these additions to the ISA. To what extent do they provide an appropriate level of detail and convey the important scientific conclusions of the assessment?**

The Panel is pleased with the inclusion of an Executive Summary in the ISA report and found the general tone and scope to be appropriate. However, the Panel does recommend that the current draft of the key findings be merged into the executive summary to create a single summary document.

The Executive Summary should incorporate additional conclusions from the ISA regarding the geographical distribution and magnitude of effects of current acidification and nitrogen deposition in various parts of the United States. An explanation of the implications of the extent of current acidification and nitrogen enrichment on ecosystems in terms of lost or degraded ecosystem services (e.g., changes in biodiversity, local species extinction, and lost habitat) should be considered. The authors should also include further explanatory text on emissions sources and atmospheric transport and transformation processes that lead to deposition. Brief statements summarizing recent and long-term trends in both ambient air concentrations and deposition loads should be clarified because they currently appear contradictory.

The Panel cautions the Agency about the overly generalized statements in the current draft ISA that need to be qualified because they are not applicable to all ecosystems and

locations. Acidification, nitrogen enrichment, and mercury methylation effects are indeed important for specific sensitive ecosystems within the United States, but generalizations need to be made more cautiously.

The summary text (and both ISA and REA documents in general) should be carefully reviewed to determine where total reactive nitrogen is the appropriate term to use rather than oxides of nitrogen. EPA should also consult the specific wording suggestions provided within the individual Panel members' written comments.

- 2. Chapter 1 has been revised to clarify the scope or focus of this assessment on effects related to the deposition of nitrogen and sulfur compounds. In addition, we have added a discussion of the framework for evaluation of causality for assessing ecological effects. Do these revisions adequately characterize the scope of the assessment? Does the CASAC panel have recommendations for revisions to the causality framework? Is it appropriately applied in the draft ISA?**

The CASAC Panel generally agreed that Chapter 1 provides a clear, concise introduction to the ISA. The chapter includes an outline of the intended scope of the current assessment, a brief history of past SO<sub>x</sub> and NO<sub>x</sub> NAAQS reviews, and a proposed framework for the determination of causality in relationships between the pollutants of concern and the resulting environmental responses.

There have been substantial advances to the scientific evidence since the publication of the most recent Air Quality Criteria Documents for NO<sub>x</sub> and SO<sub>x</sub> in 1993 and 1982, respectively. Several Panel members recommended expanding the historical summary of secondary SO<sub>x</sub> and NO<sub>x</sub> reviews and associated technical documents to include references to major EPA or inter-agency publications. A few examples include the 1985 *EPA Acidic Deposition Phenomenon and Its Effects: Critical Assessment Document*, the 1990 *NAPAP State of Science and Technology and Integrated Assessment Reports*, and the 1995 *EPA Acid Deposition Feasibility Study report to Congress*.

The proposed framework for evaluation of causality is logical and clearly presented. This framework appears to be followed in subsequent chapters (3 and 4), which contain a number of concise, declarative statements that “the evidence is sufficient to infer a causal relationship between X causal agent and Y effect.” In most cases, the identified causal agents are usually “acidifying deposition” or “reactive nitrogen deposition,” and thus appear to be non-specific to the traditional NO<sub>x</sub> and SO<sub>x</sub> criteria pollutant definitions. It would be helpful to include some similar statements of causality that relate emissions to air quality to deposition in Chapter 2. Additionally, expanding this causality framework to include a concept such as a “significantly contributing factor” as a subset of a “causal factor” (i.e. “the evidence is sufficient to infer a causal relationship between Nr deposition, for which oxidized N is a significantly contributing factor, and Y and Z effects”) is advised. This concept of a “significantly contributing factor” could be important in considering effects resulting from pollutant mixtures, as well as for considering effects which result from or are modified by the cumulative influences of both current and historical pollutant deposition.

- 3. Chapters 2 and 3 from the first draft have been combined. Substantially more information has been included on NH<sub>3</sub> emissions, NH<sub>3</sub> measurement techniques, NH<sub>3</sub> and NH<sub>4</sub> concentrations. Additionally, information on NO<sub>x</sub> and SO<sub>x</sub> including ambient concentrations, deposition levels and their spatial and temporal relationships has been added. Have these revisions to Chapter 2 improved its assessment of the currently available scientific knowledge on atmospheric sciences and its relevance to the evaluation of environmental effects presented in later chapters?**

The revisions and additions to Chapter 2 have substantially improved the document. EPA has been very responsive to the Panel's comments on the previous draft. As a result, this version is much improved and constitutes a solid scientific basis for the *Risk and Exposure Assessment (REA)*. However, there are a few areas where additional information could provide useful context for evaluating the risk and exposure assessment work. In particular, because the REA relies so heavily on the Community Multiscale Air Quality (CMAQ) model predictions of deposition, the section on chemical transport model (CTM) models should be augmented with specific CMAQ model performance statistics on wet- and dry-deposition. Also, comparisons should be made between measurements and model parameterizations for wet- and dry-deposition. Some discussion of sensitivity to critical parameters, such as dry deposition velocity, precipitation intensity, and depositional resistances, is needed as well.

The additional maps were helpful for forming visual links between modeled emissions, concentration, and deposition. Nevertheless the varying spatial scales and color schemes make that comparison difficult. These linkages should be made more explicit either with maps in which the scales or colors are consistent, or with scatter plot comparisons in matched grid cells (e.g. concentration vs. deposition).

The current title, 'Source to Dose' should be reworded as 'Source to Deposition' or something similar to reflect the environmental endpoint. Terms that might be unfamiliar to a more general audience (e.g., compensation point, ozone production efficiency, and nitrogen cascade) should be defined. Wherever possible, units should be consistent and clearly stated: it is not always clear if mass S really means mass of sulfur or whether it is really mass of sulfate, SO<sub>4</sub><sup>2-</sup>. We recommend the consistent use of mass of sulfur throughout the document, unless clearly stated otherwise. Also, it is important to note that all deposition flux units should be presented in kg/ha-yr rather than kg/ha. Similarly, the ISA should express all nitrate deposition data in units of kg/ha-yr of nitrogen. The summary section of Chapter 2 (Table 2-25) should be expanded to include information on the regional changes in wet- and dry-deposition in the western United States.

Finally, the measurement section should include a discussion of passive samplers and additional discussion on historical emissions and deposition. The Panel recognizes that high quality historic data on emissions and atmospheric deposition of NO<sub>x</sub>, NH<sub>x</sub>, and total reactive nitrogen are limited, so more discussion as to how these values are currently estimated, both from field measurements as well as in atmospheric models (e.g., CMAQ), and their relevance to MAGIC and other water-quality models would be useful. In the interest of trimming some of the length of the chapter, some material could be put in the appendices: in particular, the

tropospheric chemistry discussion and the high-time-resolution data (important but less relevant for ecological time-frames).

- 4. We removed or eliminated redundancy, added summary sections, added additional references and reorganized Chapter 3. Revisions to the ecological effects sections are given below. Have the revisions improved the characterization of the ecological effects?**
  - a. Consistent with CASAC comments, we expanded our characterization of the quantification of chemical effects of acidification in aquatic ecosystems, added new conceptual diagrams, and further discussed interactions between acidification and plant disease.**

The revised Chapter 3 is logically organized and generally well written. It provides comprehensive information on the ecological effects of NO<sub>x</sub>, NH<sub>x</sub>, and SO<sub>x</sub> deposition in aquatic and terrestrial ecosystems – including acidification, nutrient enrichment, and sulfur-deposition induced methylation of mercury. The conceptual diagrams are useful and the discussion of interactions between acidification and plant disease is well written and up to date.

Important items missing from Chapter 3 include:

- Observation that despite recent decreases in acidifying deposition and some improvement in surface water acid-base status there are widespread observations of ongoing soil acidification (i.e., decreases in soil exchangeable base cations);
  - Comparison of MAGIC with other watershed models (see Sullivan et al., 2006);
  - Recognition that mercury contamination occurs in terrestrial food webs (see Rimmer et al., 2005); and
  - Probable linkage between atmospheric N deposition and biogenic emissions of NO and VOCs.
- b. We expanded the discussion of quantitative relationships between nitrogen deposition and ecological effects, including published critical loads in the U.S. and Europe. In addition, the nitrogen enrichment section was expanded to include new discussions on carbon budgeting, biogenic nitrous oxide and methane. Information on the linkages between effects and both reduced and oxidized forms of nitrogen was emphasized, to the extent data were available.**

Information on the published critical loads data from Europe is mostly contained in Table 3-24, as adapted from Acherman and Bobbink (2003). This table summarizes biological indicators and related critical loads for major ecosystem types in Europe and is probably sufficient for this document. However, the Panel recommends that the recent reports of the International Cooperative Program (ICP) Forests and ICP Modeling and Maps also be considered for updated information on critical load modeling efforts in European forests. The summary of the dose-response curves for N deposition and ecological indicators presented in Table 3-25 is valuable and should greatly help in developing a large-scale evaluation of critical loads in the US and their spatial adaptation.

The section of Chapter 3 dealing with the carbon cycle of the Earth as related to N deposition is comprehensive and based on recently published studies. EPA staff should make sure that the presentation recognizes that nitrogen and sulfur are essential to plant growth, and thus can influence carbon sequestration, with nitrogen often being the limiting nutrient in terrestrial ecosystems. The evidence presented shows that ambient N deposition can result in increased atmospheric emission of N<sub>2</sub>O and CH<sub>4</sub>.

**c. The section on “other” welfare effects was updated to include information on the direct phytotoxic effects of nitric acid.**

Although a good discussion of direct effects of nitric acid is provided, it should be emphasized that most of the damaging effects of HNO<sub>3</sub> have been observed in relatively short-term exposures at above-ambient concentrations of the pollutant. Long-term effects of lower air concentrations that more closely approximate ambient levels of HNO<sub>3</sub> should be investigated. Similarly, visible injury to plant foliage due to exposure to NO, NO<sub>2</sub> or NH<sub>3</sub> have been demonstrated primarily at concentrations that rarely occur in ambient air.

**5. In revising the ISA, we have incorporated additional information on the indicators of exposure and ecological effects, including increased emphasis on quantified relationships in the presentation of information of results in tables and summary discussions in Chapter 4. What are the views of the CASAC panel on our revisions to focus on quantitative relationships between airborne nitrogen and sulfur compounds and ecological indicators?**

The effort made to perform an analysis of existing literature on ecological indicators relevant to deposition and acidification is commendable. The meta-analysis appears to be extensive and appropriate for the ISA. Much literature has been compiled, including a smattering of studies involving high application of N (up to typical fertilizer levels). A summary of traditional forest and grassland fertilizer studies could strengthen this study, as well. Much of this literature is old, but still very relevant – especially the early fertilizer studies by C.O. Tamm et al. in Sweden. The tradeoffs associated with the use of nitrogen fertilizer in enhancing the productivity of forests, crops and grasslands versus the deleterious environmental impacts associated with excess nitrogen being released into the environment, especially surface waters, should be articulated more clearly.

The analysis of indicators is particularly important since a secondary standard (if proposed and promulgated) needs to be expressed in terms of SO<sub>x</sub>, NO<sub>x</sub>, or NO<sub>x</sub> + NH<sub>x</sub> (Nr) and then properly linked to the effects through the relevant ecological indicators and causality frameworks. In the summary, it would be desirable to continue fortifying the linkages in the chain of causation between emission – atmospheric concentration – deposition – dosage – effect – ecosystem services. An example of such an end-to-end causality illustration would help. A synchronized array of trend charts for each parameter/indicator in the causality chain could be an effective way to illustrate the overall framework and key aspects of systems behavior. While it may not be necessary to have quantitative trend values for each of the parameters in the causality chain ensemble in the ISA, graphically indicating (e.g., dashed trend lines) the poorly understood parameters would be a more realistic representation of the current state of the causality

framework. It is also appropriate to recognize how the causality framework may be used in both prospective and retrospective analyses.

In summary, with incorporation of the Panel's recommendations to strengthen the document, this second draft ISA will provide appropriate scientific support for the risk and exposure assessments. The CASAC was pleased to review this second draft of the ISA and looks forward to the Agency's response.

Sincerely,

*/Signed/*

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

*/Signed/*

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

Enclosures

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

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

**CHAIR**

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

**PANEL MEMBERS**

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

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

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

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

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

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

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

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

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

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

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



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

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

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Enclosure 2: Roster of the chartered CASAC

**U.S. Environmental Protection Agency  
Clean Air Scientific Advisory Committee**

**CHAIR**

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

**MEMBERS**

**Dr. Joseph Brain**, Philip Drinker Professor of Environmental Physiology, Department of Environmental Health, Harvard School of Public Health, Harvard University, Boston, MA

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

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

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

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

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

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Enclosure 3: Compilation of Individual Panel Member Comments on EPA’s *Integrated Science Assessment (ISA) for Oxides of Nitrogen and Sulfur – Environmental Criteria (Second External Review Draft)*

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## Dr. Praveen Amar

Question # 3: Chapters 2 and 3 from the first draft have been combined. Substantially more information has been included on NH<sub>3</sub> emissions, NH<sub>3</sub> measurement techniques, NH<sub>3</sub> and NH<sub>4</sub> concentrations. Additionally, information on NO<sub>x</sub> and SO<sub>x</sub> including ambient concentrations, deposition levels, and their spatial and temporal relationships has been added. Have these revisions to Chapter 2 improved its assessment of the currently available scientific knowledge of atmospheric sciences and its relevance to the evaluation of environmental effects presented in the later chapters?

### Response:

I would like to note that the previous Chapters 2 and 3, now combined in current Chapter 2, is a great improvement over the first ISA Draft. It is quite clear that very useful and relevant information has been included on reduced form of nitrogen (ammonia emissions, measurement techniques to estimate ambient levels of ammonia and inter comparison of these techniques, as well as concentrations of nitrate in particulate form). Equally useful is the more clear presentation on NO<sub>x</sub> and SO<sub>x</sub> (concentrations, deposition levels, trends in these levels, as well as spatial and temporal character of these two pollutants). EPA staff needs to be commended for this.

I have several specific comments that are outlined below:

1. I think the Title of the Chapter needs to change from “Source to Dose” to “Source and Exposure,” or something similar. This is because this Chapter is NOT about dose. In fact, a quick “search” shows that the word “dose” appears only once in this Chapter of more than 200 pages (page 2-116 to be exact). This is not surprising because this Chapter talks about emissions, concentrations, measurement techniques, trends, etc. but does not talk about dose. In fact, Chapter 3 is about “dose-response” and the word ‘dose’ appears in that Chapter frequently and correctly.
2. On page 2-2, please describe N cascade of Galloway in a little more detail since this is an important concept and not widely understood.
3. Page 2-19: I do not understand “compensation point” of ammonia. Needs some clarification. What is being compensated? Ammonia?
4. Page 2-20: Line 10: I do not think “biogenic production” of ammonia from agriculture (chiefly from livestock) is the right word. It is as anthropogenic as it can get!
5. P (O3): Ozone *Production* Efficiency: It is an important concept. However, I do not think it is clearly defined in the document (as number of molecules of ozone produced per molecule of NO<sub>x</sub> over a certain time period and over a spatial extent, etc.). I suggest it should be explicitly

defined first time it appears. Just like N cascade, it is important concept and needs to be explained clearly.

6. Page 2-20: Para under the Figure: I had made this comment on the first ISA Draft. Ammonia emission totals are dominated by livestock/fertilizer operations because they simply are. They are dominant source of ammonia in their own right and not because mobile sources are not. Please drop the words “for these reasons...” on line 9.

7. I have not thoroughly read the section on Halogen Chemistry (page 2-41). Please make sure it is improvement on the version included in first draft and that it is integrated with the general theme of its relationship with, and effect on, SO<sub>x</sub>/NO<sub>x</sub>/NH<sub>3</sub> chemistry.

8. A general comment: please be consistent and clear that you mean to give quantitative values of nitrogen and sulfur deposition in the units of “N” and “S” for kg of N/ha/yr, and kg of S/ha/yr., etc. If they are given in terms of sulfate (SO<sub>4</sub>) or nitrate (NO<sub>3</sub>), they should be clearly labeled as such. I recommend “N” and “S”. To be inserted

## **Dr. Andrzej Bytnerowicz**

### Question 4. Have the revisions improved the characterization of the ecological effects?

In general, Chapter 3 presents comprehensive information on ecological effects of SO<sub>x</sub> and NO<sub>x</sub>. The chapter is logically organized, contains current knowledge supported by large number of informative tables and figures. Good examples of very informative tables are Table 3-12 presenting summary of knowledge on the effects of fire on nutrient concentrations in forests in California and Nevada and Table 3-15 summarizing N effects on forest carbon cycling. In summary – the revisions improved characterization of the ecological effects in the document.

Summaries in the end of each sub-sections are very useful. Remark - summaries from Section 3.2 are not listed in the Table of Contents.

References in the text and list of citations are not always matching. Some of them are not cited properly. Examples of this deficiency are the references of Bytnerowicz et al., or Temple and Taylor (1983), incorrectly cited in the text as Temple (1983).

Remark - careful technical editing of a final version of this document is recommended.

### Question 4a. Chemical effects of acidification in aquatic ecosystems

Information on acidifying effects of NO<sub>x</sub> and SO<sub>x</sub> aquatic ecosystems is comprehensive. Conceptual diagrams for this section have been correctly chosen. Examples of such diagrams are Figure 3.1 presenting fluxes of major ions associated with S depositions or Figure 3-5 showing the effects of acidic deposition on Ca supply in trees, their physiology, growth and resistance to environmental stresses.

Discussion of interactions between acidification and plant disease is well written and up to date. Interaction of acidity with foliar, membrane-associated calcium, which influences responses of trees to changing environmental conditions, such as cold temperatures and winter injury, is very well described. Remark - a reference to Figure 3-5 should be made in the text.

### Question 4b. Quantitative relationships between nitrogen deposition and ecological effects

Information on the published critical loads data from Europe is mostly contained in Table 3-24 adapted from Acherman and Bobbink (2003). The table summarizes biological indicators and related critical loads for major ecosystem types in Europe and is probably sufficient for this document. However, I would like to recommend that the recent reports of the ICP Forests and ICP Modeling and Maps are also considered for updated information on CL modeling efforts in the European forests. Summary of the dose-response curves for N deposition and ecological indicators presented in Table 3-25 is valuable and should greatly help in developing a large-scale evaluation of critical loads in the U.S and its spatial extrapolation.

The nitrogen enrichment section has been expanded and contains discussion on carbon budgeting, and fluxes of biogenic nitrous oxide and methane. Section on the carbon budget as related to N deposition is comprehensive and based on the recent scientific literature. Figure 3-35 shows interactions between the N and C cycles while Table 3-15 summarizes N effects on forest carbon cycling in Europe and North America. The section is well organized and written and is supported by informative graphs and summary tables. Specific remark – page 3-136, citation of Sutton et al (2008) does not seem to be correct. Section on methane and nitrous oxide flux is based on the meta-analysis of the recently published studies. The presented evidence shows that N deposition results in higher concentrations of these greenhouse gases in the atmosphere.

#### Question 4c. Other welfare effects

Good discussion of direct effects of nitric acid is provided. However, it should be emphasized that the described damaging effects of HNO<sub>3</sub> have been demonstrated in controlled experiments for relatively short-term exposures at highly elevated concentrations of the pollutant. Long-term effects of lower, closer to ambient, levels of HNO<sub>3</sub>, should be investigated. Similarly, visible injury to plant foliage due to NO, NO<sub>2</sub> or NH<sub>3</sub> exposures have been demonstrated only at very high concentrations (controlled studies, industrial spills), at the levels that normally do not occur in ambient air.

Table 3-28 on direct effects of SO<sub>2</sub> should be moved closer to the text describing these effects.

Remark - please see my above comments regarding a need for correct citation of references in this sub-section.

#### Executive Summary

Although it generally adequately summarizes the ISA document, there are several deficiencies that should be resolved:

1. In the Introduction, or in a footnote to it, it should be noted that 1 ppm = 1000 ppb. Readers less familiar with science may not know this fact, and both units are used throughout the text.
2. In the section “Current concentrations and deposition in the US”, there are some statements that are not correct. For instance, on page 2, last paragraph of the first column, a statement is made that the highest mean N deposition of about 9 kg/ha/yr totals is in the Ohio River valley. This value seems to be too low – I suspect that this is only the wet portion of N deposition. On the same page, the second paragraph of the second column, states that the model-predicted values in some regions of the Adirondacks are >20 kg N/ha/yr. In southern California the model-predicted total N deposition can be as high as 32 kg N/ha/yr. Actually, according to Fenn (2008), the highest values can be as high as >100 kg N/ha/yr on the western slopes of the San Bernardino Mountains. However, that high deposition mostly results from deposition of HNO<sub>3</sub>, NH<sub>3</sub> and particulate NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>, not NO and NO<sub>2</sub> as the Executive Summary states.
3. In the section “Ecological effects of N deposition” a clear statement is needed that ecological effects of NO<sub>x</sub> and SO<sub>x</sub> should be considered in a context of often unpredictable climate changes.

Ecological effects of  $\text{NO}_x$  and  $\text{SO}_x$  will also depend on other stressors, such as elevated background levels of ambient ozone, drought, insect and pathogens outbreaks, etc.

4. On Page 6, 3rd paragraph of the first column – a statement “Exposures of  $\text{NO}_2$ , nitric oxide (NO), peroxyacetyl nitrate (PAN) and nitric acid ( $\text{HNO}_3$ ) cause similar forms of plant injury and decreased growth” is not true. Characteristics of foliar injury caused by these various compounds are actually quite different (please see Bytnerowicz et al., 1998 for discussion of this issue).



## Ms. Lauraine Chestnut

### *Charge Question 1: Executive summary and key findings*

The Executive Summary (ES) is a useful addition to the document, but it needs a little more detail to communicate more effectively the nature and magnitude of current harmful effects on ecosystems from N and S deposition in the US. As currently written, it describes the effects that can happen but says too little about the extent to which these are currently happening. The “key findings” document is largely redundant with the ES, but uses some nice formatting and boxes to highlight key points. I suggest merging these into one summary document and making use of text boxes to highlight some of the key conclusions.

The “Scope” section needs a paragraph or two explaining the transport of emissions and their interaction in the atmosphere that result in N and S deposition. The first paragraph in Section 4-1 on page 4-1 in the conclusions section provides a description of this at a level of detail that would be useful in the ES.

A paragraph or two on the major sources of emissions that lead to N and S deposition would be helpful in this section. This information is well described in Chapter 2.

The “Current concentrations” section needs to reconcile the information about declines in ambient concentrations from 1990 to 2005 versus the “10-fold increase” in deposition in the past 100 years. It would be appropriate here and in the Introduction chapter to mention the Acid Rain Program (Title IV) as one of the main reasons for the decrease in emissions (especially SO<sub>2</sub>) from 1990 to 2005 and to note that the reductions from this program are now close to fully implemented and are leveling off. This program is not part of the NAAQS process, but it seems odd not to mention such a major program that was motivated by concern about the effects of acid deposition.

In the section on “Ecological effects of acidification” there needs to be more descriptive information about the effects and their current extent and significance in the US. I’m not sure it comes through clearly that certain species of fish, particularly ones that people like to catch, have died off and cannot live in these acidified lakes and streams. I’m not sure the words “decline in fish species richness” quite gets the significance across. The discussions of the Adirondacks and Shenandoah and expectations of future acidification conditions at current deposition levels are good and are examples of the kinds of descriptive implications appropriate for the ES.

In the section on “Ecological effects of N deposition” there needs to be more descriptive information about the extent and significance of eutrophication of estuarine ecosystems in the US. How many of the major estuaries in the US show significant eutrophication? What is the extent of losses to fisheries and habitat?

The “key findings” section will go away if merged into the ES, but material that is not duplicative should be brought into the ES. In that light here are some specific comments on the key findings:

- The first box would be better labeled “main effects” than key findings. It describes the types of effects, but does not say how widespread or significant these effects are in the US at current deposition levels.
- In the first paragraph after the first box, the parenthetical phrase after “secondary” is confusing. Ecological effects are public welfare effects, as I understand the language of the Clean Air Act. It would be more straightforward to just explain here that this ISA is focusing on ecological effects of deposition, and other welfare effects of PM, SO<sub>2</sub> and NO<sub>x</sub> are dealt with elsewhere.
- In the first set of bullets under effects of acidification, it would be helpful to distinguish between ecosystems that are sensitive and those that are experiencing significant effects on ecosystem functions at current deposition levels.
- The second bullet on deposition levels is good, but seems out of place in this list. A little more location dimension to these numbers would be useful—perhaps a map.
- It might be easier to for the reader if the sections on effects of acidification and N deposition were both subdivided into aquatic and terrestrial subsections.
- The acidification section needs more description of where and how significant are current effects on ecosystems. The last paragraph in this section is good, but the heading needs to be qualified—some ecosystems that are currently experiencing harmful effects....
- Bullets under effects of nitrogen deposition: Separate the points about effects, deposition levels, and monitoring. The monitoring points need some explanation of why these monitoring limitations are problematic. Add some location information on the deposition rates.
- In the section on effects of N deposition add information on where there are significant observed effects in the US now, and describe the extent of the effects.
- The figure on interactions between carbon and nitrogen cycles needs some discussion. It is not clear what the implications are.

*Charge Question 2: Chapter 1*

Some discussion of how Title IV (Acid Rain Program) fits into this history would be appropriate. Also some mention of the 1995 “Acid deposition standard feasibility study” report to Congress would be appropriate as part of the background.

*Charge Question 4: Chapter 3*

Chapter 3 does a much better job now in describing the significance of the effects on ecosystems and of using the “case studies” as examples of these effects. Section 3.3.9 on ecosystem services affected by N deposition is good and helps set the stage for what comes in the REA. It would be useful if something similar were done for acidification in section 3.2.

## Dr. Ellis Cowling

### General Comments on the New NAAQS Review Processes

Before dealing with the details of my specific assignments during the October 1-2, 2008 meeting of CASAC I would like to offer a few general comments about the **current efforts to streamline the NAAQS review processes and how these changes in process are playing out in the case of the CASAC Review of the Secondary (public-welfare based) NAAQS for NO<sub>x</sub> and SO<sub>x</sub>.**

Many of us in CASAC have been very pleased that EPA has recently shown increased willingness to think more holistically – and in more fully integrated ways – about both the policy-relevant science and the practical arts of air quality management aimed at protection of both public welfare and public health. These shifts in both emphasis and approach have included:

- 1) Increased emphasis on scientific questions that are as directly relevant as possible to well-defined policy questions of concern to EPA. This shift to greater policy relevancy in our scientific discussions within CASAC will increase efficiency in the preparation and CASAC review of NAAQS documents, and also help streamline the NAAQS review Process. For example, the following policy-defining statement was recommended as a guide during NAAQS review processes:

*“What scientific evidence and/or scientific insights have been developed since the last review to indicate if the current public-health based and/or the current public-welfare based NAAQS need to be revised or if alternative levels, indicators, statistical forms, or averaging times of these standards are needed to protect public health with an adequate margin of safety and to protect public welfare?”*

- 2) More frequent discussion about both public-welfare and public-health impacts of mixtures of air pollutants;
- 3) Separation of the preparation and review of documentation for a Secondary (public-welfare-based) NAAQS from the (previously always dominating) Primary (public-health-based) NAAQS review processes,
- 4) The decision by the Science Advisory Board (SAB) of EPA in January 2007 to establish a special Integrated Nitrogen Committee (INC) with the following set of objectives:
  - a) Identify and analyze, from a scientific perspective, the problems nitrogen presents in the environment and the links among them,
  - b) Evaluate the contribution an integrated nitrogen management strategy could make to environmental protection,
  - c) Identify additional risk management options for EPA’s consideration, and
  - d) Make recommendations to EPA concerning improvements in nitrogen research to support risk reduction,

- 5) The unprecedented decisions by EPA to undertake an integrated [simultaneous] review of the Secondary NAAQS for two Criteria Pollutants at the same time [Oxides of Nitrogen (NO<sub>x</sub>) and Oxides of Sulfur (SO<sub>x</sub>)], and to facilitate the required CASAC and public reviews of:
- i) an Integrated Science Assessment (ISA) for NO<sub>x</sub> and SO<sub>x</sub> -- to be issued in December 2008,
  - ii) a Risk/Exposure Assessment (R/EA) -- to be completed by July 2009,
  - iii) a Policy Assessment/Rulemaking document prepared in the form of an Advanced Notice of Proposed Rule Making (ANPR) -- by August 2009, and thus to achieve
  - iv) Final Rule Making -- prior to a court-ordered deadline of October 19, 2010.

In view of this demanding series of deadlines following our October 1-2 CASAC meeting, it is obvious that EPA and CASAC now have only about:

- i) **3 months to complete the Final ISA for NO<sub>x</sub> and SO<sub>x</sub>**, and
- ii) **11 months in which to complete reviews of both the First and Second External Review Drafts and then to prepare a Final Draft R/EA for NO<sub>x</sub> and SO<sub>x</sub>**.

But we now have the considerable advantage that the new NAAQS review process envisions preparation of **much more concise and much more policy-focused ISA and R/EA documents** for the present Integrated Secondary NAAQS for NO<sub>x</sub> and SO<sub>x</sub> than has historically been achieved in the **encyclopedic Criteria Documents** that have been prepared during the years since 1970.

### **Specific Comments on the ISA for the Secondary Nitrogen and Sulfur Pollution NAAQS Standards**

The present Second Draft ISA is a very huge volume which consists of:

Chapter 1 – an appropriately short (10 page) “**Introduction**,”

Chapter 2 – an exhaustive (202 page) analysis of “**Source to Dose**” relationships for both NO<sub>x</sub> and SO<sub>x</sub>,

Chapter 3 – a similarly exhaustive (237 page) analysis of **Ecological and Other Welfare Effects**. This chapter is appropriately focused on five critically important impacts of atmospherically deposited reactive nitrogen and sulfur compounds – acidification and nutrient enrichment of aquatic and terrestrial ecosystems and sulfur induced increase in methylation of mercury,

Chapter 4 – a reasonably short (33 page) **Summary and Conclusions** chapter that includes many statements of conclusion from the science that is reviewed Chapters 2 and 3,

Glossary – a very neat set of definitions for many of the specialized terms used in Chapters 1-4,

References – an exhaustive (124 page) list of (nearly 3000 scientific literature citations!) most of which are relevant to the possible revision of the current NAAQS standards for nitrogen and sulfur pollution. It would be very valuable to identify a limited number of

these documents that are especially significant in terms of the policy purpose for which this ISA was written.

Having carefully reviewed all of these several parts of this Second Draft ISA, I was:

- 1) **Generally satisfied with the parts of Chapters 1-3 that deal with oxides of nitrogen and sulfur, but was disappointed that much less attention continues to be given in Chapters 2 and 3 to the quantitative importance and significant biological impacts of chemically reduced forms of total reactive nitrogen. This is true with regard to both acidification and nutrient enrichment of aquatic and terrestrial ecosystems.**
- 2) **In spite of the ‘relatively less attention’ comment mentioned in comment 1 (above), I was very pleased to read in Chapter 4 the 23 bold-face-type statements regarding the “sufficiency of evidence to infer a causal relationship between ‘acidifying deposition’ and/or ‘Nr deposition’” and each of the many adverse acidification and nutrient enrichment effects of atmospheric deposition reactive nitrogen and sulfur pollution on aquatic and terrestrial ecosystems that are discussed in Chapters 2 and 3.**
- 3) **At the same time, however, I was disappointed that almost all of the non-bold-faced-type conclusions among the Summary and Conclusions statements in Chapter 4 were notably lacking in specific articulation of the quantitative importance and significant biological impacts of chemically reduced and organic forms of reactive nitrogen in both terrestrial and aquatic ecosystems.**
- 4) **This lack of specific articulation of the quantitative importance and significant biological impacts of chemically reduced and organic forms of reactive nitrogen was especially worrisome in the final “Conclusion” statement in the Executive Summary of this ISA.**

#### **Specific Comments on the Executive Summary of the ISA**

This final Conclusion in the Executive Summary includes the following two statements both of which are incorrect and misleading in terms of their relevance to the policy purpose for which this ISA is being written:

“Acidification is driven by the deposition resulting from NO<sub>x</sub> and SO<sub>x</sub> pollution.”

“In addition to acidification, deposition resulting from NO<sub>x</sub>, along with other sources of reactive nitrogen (e.g., fertilizers, waste water, and atmospheric ammonia deposition), causes a suite of ecological problems including biodiversity losses, disease, eutrophication, and harmful algal blooms.”

Permit me to offer the following improved and more accurate wording of the final Conclusion of the Executive Summary (please note especially the explicit recognition of both reduced and oxidized forms of reactive nitrogen -- both of these chemical forms of nitrogen are significant “Pollutants of Concern” as well as causal factors in both acidification and nutrient enrichment:

## Conclusion

The three main effects of nitrogen and sulfur pollution presented in this ISA are acidification, nitrogen enrichment, and methylation of mercury. Acidification of ecosystems is driven primarily by atmospheric deposition of NO<sub>x</sub>, NH<sub>x</sub>, and SO<sub>x</sub>. These three pollutants cause a cascade of effects that harm both aquatic and terrestrial ecosystems including localized extinction of fish populations and other aquatic species, and slower growth and injury to forests. In addition to acidification, atmospheric deposition resulting from NO<sub>x</sub> and NH<sub>x</sub> emissions, along with other sources of reactive nitrogen (e.g., fertilizers and waste waters) cause a suite of ecological problems including biodiversity losses, disease in aquatic and terrestrial organisms, as well as eutrophication and harmful algal blooms in both fresh water, estuarine, and ocean ecosystems. Both gaseous sulfur compounds and particulate sulfate can interact with methanogenic bacteria to produce methyl mercury, a powerful toxin that can bioaccumulate to toxic amounts in food webs at higher trophic levels (e.g., otters, king fishers.)

**Specific Comments on the Value of the Recently-Posted Document Titled  
“Selected Recommendations and Findings from the Integrated Nitrogen  
Committee” and  
an earlier Resolution by the Integrated Nitrogen Committee of EPA’s Science  
Advisory Board**

As many of us on the CASAC NO<sub>x</sub>/SO<sub>x</sub> Secondary NAAQS Panel will recall, during our October 30, 2007 CASAC meeting, the following *Resolution* was received from the SAB’s Integrated Nitrogen Committee.

**Resolution from the Integrated Nitrogen Committee of the Science Advisory Board --  
for Consideration by the CASAC Secondary NAAQS NO<sub>x</sub> and SO<sub>x</sub> Review Panel**

During the ongoing meeting of the EPA Science Advisory Board’s Integrated Nitrogen Committee (INC) -- meeting at SAB Headquarters in Washington DC on October 29-31, 2007 -- the several members and Chair of the INC, Dr. James Galloway of the University of Virginia, asked me (as the CASAC-designated liaison person to the Science Advisory Board’s Integrated Nitrogen Committee) to present the following Resolution (which was developed and approved by the INC) for consideration during the CASAC review of the NAAQS for NO<sub>x</sub> and SO<sub>x</sub> during our CASAC Conference Call Consultation on October 30, 2007.

### Resolution

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

This Resolution is an important part of the scientific foundation and rationale behind my concern that the “Second External Review Draft of the ISA for Oxides of Nitrogen and Sulfur – Environmental Criteria” and the First Draft of the “Risk and Exposure Assessment for Review of the Secondary National Ambient Air Quality Standards for Oxides of Nitrogen and Oxides of

Sulfur” are not consistent with the central idea of this Resolution – that both chemically reduced and chemically oxidized forms of reactive nitrogen must be considered in the current round of reviews of the NOx/SOx Secondary NAAQS Standards.

Further justification for these ideas -- and policy recommendations that derive from the extended deliberations of the SAB’s Integrated Nitrogen Committee -- are contained in a recently completed Summary Document titled: “*Selected Recommendations and Findings from the Integrated Nitrogen Committee.*” This document was recently posted on the SAB website and thus is available for public review at the following URL:

<http://yosemite.epa.gov/sab/sabproduct.nsf/MeetingCal/EFB3E4663E2143F885257465006C5B32?OpenDocument>

## **Dr. Douglas Crawford-Brown**

I am charged primarily with Question 1, and so my comments are primarily on that question. However, since this Charge Question covers the Executive Summary and a “key findings” section, the review makes reference to other chapters where these materials are found. The specific Charge Question addressed is:

1. We have added an executive summary of the major findings and conclusions to the second draft ISA. We have also created a "key findings" section that is intended to provide highlights of these conclusions. We are seeking CASAC panel advice and comments on these additions to the ISA. To what extent do they provide an appropriate level of detail and convey the important scientific conclusions of the assessment?

The short answer is yes and yes. They provide the appropriate level of detail (with a few caveats noted below) and convey the most important conclusions from other chapters. As I will note below, however, it is less clear where this “key findings” section is located. Given the Charge Question, I had expected to find it in the Executive Summary or listed in the Table of Contents. It is in neither.

In the Executive Summary on Page 1, there is a segue-way needed between gas and deposition effects. The first section ends by saying that the existing NAAQS were set on the basis of direct exposure to gases. Then the next paragraph begins by stating that this document focuses on deposition of NO<sub>x</sub> and SO<sub>x</sub>, which will be dominated by the particulate phase. A reader will wonder whether the current document is therefore a supplement to the previous NAAQS, or has changed the focus of concern – and if so, why.

Then in the same area of the document, the authors state that understanding the ecological effects requires considering many reduced forms of N. While I agree with this, the statement does not say “in addition to the oxidized forms”, and so the reader will again be confused, wondering if the NAAQS has changed completely to deposition rather than gas phase, and to reduced rather than oxidized forms. It is simply a problem with the way this sentence is structured, not with the list of forms shown or the intent of the sentence.

In the next paragraph, there is a discussion of the extent of decrease in NO<sub>x</sub> and SO<sub>x</sub>. The numbers are correct given data in later chapters, but there needs to be clarity as to what the 35% and 50% figures refer to. Are these mean annual levels measured at monitors; mean levels of exposure (perhaps population-weighted)? Something else? A few words of explanation would resolve this problem.

And then later, the comment is made (correctly) that N deposition has been increased 10 fold over the past century. The problem with this statement is that it seems to contradict the finding that ambient levels have been in fact going down over the past decade. The problem lies, of course, in specifying the different periods of time over which the trends are being discussed. Surely N deposition has been going down as ambient levels have gone down, even if they went up quite a bit more prior to the recent decline. Or, is the difference between the two sections that



the first refers specifically to NO<sub>x</sub> and the latter to all forms of N deposition, with perhaps the reduced forms continuing to go up (I doubt this is the case, but just want to be sure)? If I am confused, the average reader probably will be as well.

I fully support the conclusion on the inadequacy of the current monitoring network for deposition. Some more comment is needed on how that system might be better structured to resolve the specific areas of uncertainty found in the ISA.

I believe the later chapters support the conclusion that “available evidence is sufficient to infer a causal relationship between acidifying deposition at current levels and effects on the following aspects of ecosystem structure and function:

- (1) biogeochemistry related to terrestrial and aquatic ecosystems;
- (2) biota in terrestrial and aquatic ecosystems.”

As with the previous ISA, however, I remain less convinced that we can quantify this causal relationship sufficiently to determine an ambient concentration that would be judged to produce an acceptable level of impact, and nothing in the subsequent chapters makes me more comfortable with this task. Surely the ecosystem effects must be treated somewhat like the human health effects, where a change in some measure of health is not in itself evidence of unacceptably high adversity of effect. At some point, the changes noted in ecosystem measures of health do become high enough to consider not just present but adverse, but the ISA is not yet able to establish where that might be in most cases. I suspect this will drive the regulatory process to rely on the primary standards, with the secondary effects providing supporting evidence for the need to further lower ambient levels – even if it cannot specify how far they should be lowered.

With respect to climate change, I disagree with the way the following statement is introduced and phrased: “N deposition often increases primary productivity. This does not necessarily increase C sequestration. C budgets are complicated by numerous factors that influence carbon exchange (e.g. climate).” The problem with the phrase is that in later chapters, the argument is made that nitrogen oxides can contribute to climate change both by being greenhouse gases and by reducing carbon storage in flora. The phrase “This does not necessarily increase C sequestration” is correct, but I would suggest that on average the increase in primary productivity will offset the adverse effects on plant growth. Perhaps I am wrong in this, but the later chapters don’t provide any data to suggest the correct answer one way or the other, and so the statement in the Executive Summary strikes me as an off-hand way to disarm a possibility that runs counter to the story being told (that NO<sub>x</sub> is bad for climate change). A much better scientific analysis is needed in the document to provide any firm conclusions one way or the other, or the impression will be left that the EPA staff have deliberately chosen only some aspects of the N-climate change connection to bolster their case.

I agree completely with the focus on acidification and nitrogen enrichment as the two primary set of effects. There is sufficient evidence in later chapters to infer a causal relationship between current ambient levels in some geographic areas and adverse ecological effects. But I am less convinced by the methyl mercury argument. I don’t mean I don’t believe the case is made for sulfate leading to methyl mercury, but rather that I don’t see sufficient evidence to suggest that

current levels of sulfate are causing methyl mercury concentrations that are of concern. I suppose the argument could be made that any methyl mercury increase is too much given current levels of methyl mercury in the food chain, but this argument isn't made or supported in later chapters.

On the issue of causal relationships, found in Chapter 1, the authors have done a good job of both classifying the causal categories and explaining the criteria for judging causality. As with previous ISAs, however, it is much less clear that any formal framework has been used to determine whether a given body of evidence does or does not satisfy these criteria, or how the criteria are to be balanced when one is satisfied but not another. The result is a purely subjective judgment of the strength of causality. I would agree that all judgments are in the end subjective, but there are judgments where the basis for that subjectivity is reached in a systematic fashion clearly elucidated, and judgments that result from reflection in a way that can't be – or isn't - described. I believe the current ISA falls into the latter group. I suspect, therefore, that different stakeholders would come to different judgments even when faced with the same information. Having said that, I still support the particular judgments of causality made in the ISA even if the document doesn't let me see clearly the thinking that led to them.

A significant problem I continue to have is that the causal judgments are too generic. The question that seems to be asked is whether there is a causal connection between deposition and effect at some level of deposition, rather than at the levels of deposition that currently exist or might exist under alternative NAAQS. I always take it for granted that any substance will produce adverse effects at some level of exposure, and so I was looking for a bit more policy-relevant judgments of causal connections in the current document. The levels of deposition at which the causal connection has been established needs to be specified for each effect.

With respect to the Key Findings section, I am generally comfortable that this reflects the major findings as described in other parts of the document. However, this section shares a problem I already noted above: that the claims of effects make little or no reference to the loadings and ambient concentrations at which the effects may be considered both causal and adverse. As a result, the reader is left with the impression that all of these effects may be taking place under the current NAAQS and would be alleviated with a lower NAAQS, neither of which is actually established elsewhere in the ISA. I think this problem is especially acute in the discussion of methyl mercury production, where I would disagree that evidence presented elsewhere in the ISA does not support a claim that sulfates currently are causing any of the fish advisories mentioned.

As to the quantified relationships on page 4, I am not sure I would call these relationships. They are instead levels at which effects have been noted. But it also is the case that the effects are not shown to be of levels considered adverse in any sense of that word defined in the ISA.

Finally, there is a policy issue I would like to raise. I believe the ISA lays the appropriate groundwork for assessing whether current levels of N and S deposition are protective, and draws the right scientific conclusions on this issue. However, it is necessary to ask whether any continuing effects are due to the need for a lower NAAQS, or from a failure to fully enforce the current NAAQS. I see no discussion of that point, and would expect at least a sentence or two on this important issue. The policy solution is quite different depending on the answer.

## Dr. Charles T. Driscoll

The second draft of the ISA is an improvement over the first draft. There are still many mistakes and errors that need to be fixed. Although the authors indicate they have eliminated redundancy, I find the document continues to be highly repetitive.

I would like to see the units of deposition expressed as kg/ha-yr.

I do not like the term acidifying deposition. Why introduce a new term? I understand where the authors are coming from, but we have three decades of acid or acidic deposition; why create unnecessary confusion?

Many references cited do not include the et al.

I had difficulty with units and many of the figures. It would be very helpful to clarify the mass basis of concentrations, emissions, deposition (e.g., mass as S vs. mass as SO<sub>4</sub>). I had difficulty in the atmosphere section with English units. It is difficult to relate these to the metric units in the effects section. If it is necessary to present English units please also present their metric equivalent.

I found several of the figure and tables very difficult to read due to small fonts. I understand that space is an issue but anything that could be done to help this situation would be helpful.

Sometimes there is a difference in the balance of the summary comments. Some comments are emphasized in the summary sections but are barely mentioned in the body of the text. I have tried to point these out in my specific comments.

### **Specific comments:**

#### **Executive Summary**

I liked the Executive Summary. I think it could be improved by adding some context to the beginning of the executive summary.

Page 1, para 1, line 2            Concise? Please give me a break.

Page 1, para 2, line 6            nitrogen

Page 1, para 2, line 10           Define Nr

Page 2, para 4, line 3 and 8    Change to... limited data exist

Page 3, para 4, line 18	Change to... S deposition is generally the primary cause of chronic acidification with secondary contributions from nitrate due to N deposition.
Page 3, para 4, line 18	Change to... 1980s and 1990s
Page 3, para 4, line 20	Change to... were no longer acidic during baseflow in the...
Page 3, para 5, line 3	Change to... Northeast, Southeast and Mountain West
Page 4, para 4, line 6	between 5.5 and 10 kg N/ha-yr
Page 5, para 2, line 1	Lichens are among the ...
Page 6, para 1, line 8	This statement is misleading. Watersheds with high production of methyl mercury have been widely observed, not only the Northeast.
Page 6, para 4, line 16	Rewrite sentence. Particulate sulfate interact with methanogenic bacteria. This sentence is not correct and doesn't make sense. How about the activity of sulfate reducing bacteria generates methyl mercury?

### **Chapter 1. Introduction:**

Page 1-1, line 1	Eliminate concise
Page 1-4, line 19	Define PM

### **Chapter 2:**

Unfortunately I did not have an opportunity to review this section in detail and so therefore I do not have any detailed comments.

I would like to see some discussion on values of deposition prior to the Industrial Revolution (background deposition). This would include sulfate, nitrate, ammonium, chloride, calcium, magnesium, sodium and potassium. This information is critical to ecosystem effects models.

It would also be good to see some discussion of historical emissions from about 1850 forward. This is critical to ecosystem effects models.

Finally, in the spirit of making suggestions to simplify the document I would ask the EPA to consider that this atmospheric chapter is to support the effects section. Ecological effects largely occur via deposition and over the time scale of decades. As a result the focus of chapter 3 could be largely on long-term deposition patterns. Seasonal deposition is really not important in ecosystem effects. If it was desired a considerable portion of this material could be shifted to the annex.

### **Chapter 3:**

This section covers most of the major issues concerning ecological effects of air pollutants. It is comprehensive and generally well done. There are a few sections that are emphasized in the summary section but really were not discussed in the body of the chapter. For example there is now some literature suggesting that there is a compensatory response of dissolved organic carbon to changes in acidic deposition. I think the science is still developing here but this is an important point and it should be mentioned in the body of the chapter, possibly as a short section in 3.2.3.1.

There is an analysis of the extent of N limitation in remote lakes that is presented in Chapter 4. This is an analysis of the stoichiometry of water chemistry from the National Surface Water Survey. This analysis helps quantify the extent of N limitation. I would urge that this analysis be presented in 3.3.3.3 or another section of chapter 3.

MAGIC is an important tool used in the REA. I would like to see some text discussing how the structure of MAGIC affects prediction. This could include a comparison of MAGIC with other watershed models. For example see Sullivan et al. (2006).

The science is emerging on mercury contamination in terrestrial food chains (e.g., Rimmer et al. 2005). There should probably be some mention of mercury contamination in the terrestrial food chain.

Finally a question. Is it worthwhile to mention the linkage of atmospheric N deposition and biogenic emissions of NO and VOCs? I don't think the literature is compelling here but there may be some linkages between N deposition and soil emissions of NO and between foliar N and VOC emissions. Is this a welfare effect? It is a linkage with atmospheric chemistry.

Page 3-4, line 25	I don't understand the line at the end about wetlands. Aren't wetlands included in other ecosystem services described above?
Page 3-6, line 2	hydrogen ion
Page 3-6, line 7	eastern U.S.
Page 3-8, line 20	H <sup>+</sup>
Page 3-8, line 30	southeastern
Page 3-10, line 1	northeastern
Page 3-10, line 8	You should mean oxidizing NH <sub>4</sub> <sup>+</sup>
Page 3-11, line 9	section ?

Page 3-12, line 14	This statement is not correct. Under conditions of low soil base saturation (<20%) and elevated concentrations of strong acid anions, Al is mobilized from soil to drainage water (Cronan and Schofield 1990).
Page 3-14	You discuss episodic acidification but fail to discuss chronic acidification. This seems a bit out of place without a discussion of chronic acidification.
Page 3-16, figure title	Italics <i>in-situ</i>
Page 3-17, line 12	above 0 $\mu\text{eq/L}$
Page 3-17, line 13	Italics <i>in-situ</i>
Page 3-24, line 8	Do you mean N deposition?
Page 3-24, line 17	than forests
Page 3-24, line 25	by oxidizing $\text{NH}_4^+$
Page 3-25, line 16	pool of exchangeable base cations
Page 3-26, line 13	northeastern U.S.
Page 3-26, line 18	cite DeHayes et al. 1999
Page 3-29, line 1	northeastern U.S.
Page 3-30, 1 <sup>st</sup> paragraph	You should probably reference the study of St. Clair et al. (2005) who document a relationship between enzyme antioxidant levels in sugar maple foliage and soil and foliar calcium.
Page 3-31, line 4	eastern U.S.
Page 3-33, line 13	eastern North America
Page 3-36, line 26	Acid neutralizing capacity is the most readily...
Page 3-40, line 2	northeastern U.S.
Page 3-42, line 3 and 32	eastern U.S.
Page 3-45, line 17	is typically decreased by acidic deposition
Page 3-46, line 16	I could not find Sullivan et al. in press in the references

Page 3-48, line 34	northeastern U.S.
Page 3-49, line 6	I question the statement that recent soil acidification appears to be modest. I refer the authors to (Likens et al. 1996, Bailey et al. 1996, Bailey et al. 2005). I am also attaching a recently accepted paper Warby et al. (in press). The rates of soil nutrient cation lost are high.
Page 3-49, line 12	northeastern U.S.
Page 3-51, line 1	What is meant by “pre-disturbance”?
Page 3-51, line 2	This sentence seems to be inconsistent with the text in 3-90.
Page 3-51, line 6	The authors should look at Gbondo-Tugbawa and Driscoll (2003) who evaluate historical forest cutting and soil and water acidification.
Page 3-52, lines 26-28	The first two bullet points are at odds with the text in 3-90 and Zhai et al. (2008).
Page 3-54, table 3.7	This table does not include Zhai et al. 2008, Chen et al. 2005b, c, Driscoll et al. 2001 among others.
Page 3-55, line 19	eastern U.S.
Page 3-55, line 22	an indication of acid base status
Page 3-56, line 17	eastern U.S.
Page 3-57, line 8	eastern U.S.
Page 3-57, line 15	northeastern U.S.
Page 3-57, line 28	Italics <i>in-situ</i>
Page 3-66, line 25, Page 3-67, line 3-4	Up to this point in the text, I have not seen any literature on effects on birds and now it is mentioned in the summary. This does not seem appropriate. If it is not important enough to be discussed in the body of the text, it probably should not be in the summary. There was a paper by Hames et al. 2002 on acid rain effects on songbirds in the Northeast.



Page 3-74, line 5	What is mildly acidic? Give an ANC value?
Page 3-83, line 2	that further reductions in acidic deposition
Page 3-83, line 25	Do you mean suitable?
Page 3-87, line 11	As shown in Figure 3-22, N retention actually has been increasing in the Adirondacks. Correct statement.
Page 3-103, line 24	Define GHG
Page 3-117, line 27	Space after wetlands
Page 3-118, line 7	Missing reference
Page 3-127, line 26	Section?
Page 3-138, line 7	Should this be °C?
Page 3-139, line 8	northern U.S.
Page 3-139, line 10	table
Page 3-143, line 1	Missing space
Page 3-144, line 20	italics <i>in-situ</i>
Page 3-144, line 22	Usually this is referred to as the Experimental Lakes Area (ELA).
Page 3-145, line 2	period
Page 3-149, line 4	Change to... algal detritus
Somewhere in 3.3.4	I believe studies have shown increased biogenic NO <sub>x</sub> emissions in response to N additions. Isn't this a relevant consideration and shouldn't it be included in the review? Also, I believe that foliar VOCs emissions are a function of foliar N which is influenced by atmospheric N deposition. Should this effect be addressed in this section?
Page 3-153, line 19	methanotrophic
Page 3-158, line 7	denitrifying
Page 3-161, line 19	Is positive relationship correct? This seems inconsistent with the remainder of the section.

Page 3-169, line 2	Who is they?
Page 3-176, line 1	eastern U.S.
Page 3-176, line 11	northern U.S.
Page 3-176, line 13	table
Page 3-176, lines 2 and 26	These sentences are identical. Do you really want the same sentences on the same page?
Page 3-177, line 16	bioindicator
Page 3-180, lines 4, 5	italics <i>in-situ</i>
Page 3-182, line 17	italics <i>in-situ</i>
Page 3-184, line 4	Change to... Among the most sensitive...
Page 3-185, line 12	eastern U.S.
Page 3-185, line 25	In the West,
Page 3-186, line 12	NH <sub>4</sub> <sup>+</sup> twice
Page 3-192, lines 14, 15	Northeastern
Page 3-196, line 6	italics <i>in-situ</i>
Page 3-200, line 4 and elsewhere	Control should be changed to reference
Page 3-206, line 26	Aren't changes in biodiversity changes in structure?
Page 3-209, line 7	period
Page 3-216, line 15	table
Page 3-218, line 19	Change to... all fish consumption advisories
Page 3-225, line 5	Methylation is prevalent in ecosystem in other regions besides the Northeast. This sentence should be changed.

Page 3-227, somewhere in here

Studies have also shown elevated concentrations of Hg in songbirds and bats via the terrestrial food chain. This should be mentioned (e.g., Rimmer et al. 2005).

Page 3-228, 2<sup>nd</sup> paragraph

You change the symbol for methyl mercury here. The text should be changed to be consistent.

Page 3-232, lines 10, 11

The first letter of several of the names are in lower case.

Page 3-236, line 1

H<sup>+</sup>

#### **Chapter 4**

Page 4-1, line 12

role in transporting N

Page 4-4, line 19

Define p NO<sub>3</sub><sup>-</sup>

Page 4-4, line 23

Define FRM

Page 4-5, line 4

is very sparse over

Page 4-6, line 7 and throughout the document

I do not like the term acidifying deposition. Change to acidic or acid deposition.

Page 4-6, line 13

energy by oxidizing NH<sub>4</sub><sup>+</sup> to NO<sub>3</sub><sup>-</sup>

Page 4-6, line 17

(see Table 4-1), including soil base saturation, aluminum concentration and C:N ratio.

Page 4-6, line 21

are increasingly neutralized by

Page 4-7, line 8

toxicity, decreased ability of plant roots to take up nutrient cations, and elevated leaching of Ca<sup>2+</sup> from needles

Page 4-9, line 15

eastern U.S.

Page 4-9, line 17

western U.S.

Page 4-10, line 6

eastern U.S.

Page 4-10, line 9

indicator of acid-base status

Page 4-10, line 11

pH, Ca, SO<sub>4</sub><sup>2-</sup> and

Page 4-10, line 20	Southern Appalachian Mountains
Page 4-11, line 1, 17	eastern U.S.
Page 4-11, line 19	the Central and Southern Appalachian Mountains
Page 4-11, line 24	northeastern U.S.
Page 4-13, bullet 1	Were effects on birds really discussed in Section 3? If not it probably should not be emphasized here.
Page 4-14, line 30	Change to... were on average 30 µeq/L.
Page 4-15, line 1	Change to: would need on average to recover
Page 4-15, line 16	northeastern U.S.
Page 4-15, line 23	Was DOC change discussed in Section 3? This is an important issue and probably deserves a paragraph in Section 3.
Page 4-16, line 26	Change to... to a state more removed from a condition of N saturation.
Page 4-18, line 8	West
Page 4-18, line 27	western U.S.
Page 4-20, line 27	western U.S.
Page 4-23, line 3	southwestern U.S.
Page 4-23, line 4	Sonoran Desert
Page 4-23, line 20	Isn't reducing biodiversity altering ecosystem structure?
Page 4-26, lines 10, 15	eastern U.S.
Page 4-27, line 3	dissolved inorganic N?
Page 4-27, line 4	phosphorus
Page 4-27, 1 <sup>st</sup> paragraph	Was this analysis of lake stoichiometry in the ELS discussed in Section 3? If not it should be as it is an important conclusion.
Page 4-27, line 13	eastern and western U.S.

Page 4-29, line 6	western U.S.
Page 4-31, line 12	eastern U.S.
Page 4-32, paragraph 2	Should these units be metric?
Page 4-34, line 10	This statement is incorrect. Methylation is a widespread phenomenon. It occurs in many areas besides the Northeast and southeastern Canada.

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## KEY FINDINGS

The main effects evaluated in the ISA are acidification, nitrogen enrichment and mercury methylation.

Acidification is driven by deposition of nitrogen oxides and sulfur oxides, and results in a cascade of effects that harm terrestrial and aquatic ecosystems, including slower growth and injury to forests, and localized extinction of fishes and other aquatic species.

Nutrient enrichment results from deposition of nitrogen oxides, along with other sources of reactive nitrogen (e.g., fertilizers, wastewater, and atmospheric ammonia deposition), and it causes a suite of ecological problems including biodiversity losses, disease, eutrophication, and harmful algal blooms.

Particulate sulfate can interact with methanogenic bacteria to produce methylmercury, a powerful toxin that can bioaccumulate to toxic amounts in higher trophic levels (e.g. otters, and kingfishers).

This draft Integrated Science Assessment is a concise synthesis and evaluation of the most policy-relevant science to help form the scientific foundation for the review of the secondary (ecological or welfare-based) national ambient air quality standards for nitrogen oxides and sulfur oxides.

## Ecological effects of acidification

Deposition of some nitrogen and sulfur species can cause acidification, altering biogeochemistry and affecting biota in terrestrial and aquatic ecosystems across the U.S. Major effects on biota include a decline in some forest tree species, such as red spruce and sugar maple; and a loss of biodiversity of fishes, zooplankton, and macroinvertebrates.

- The sensitivity of terrestrial and aquatic ecosystems to acidification from sulfur and nitrogen deposition is predominantly governed by surficial geology.

- Deposition of inorganic nitrogen and sulfur species routinely measured was as high as 9.6 kg N/ha/yr and 21.3 kg S/ha/yr, respectively, in the U.S. in 2004–2006.
- Areas most sensitive to terrestrial effects from acidifying deposition include forests in the Adirondack Mountains of New York, the Green Mountains of Vermont, the White Mountains of New Hampshire, the Allegheny Plateau of Pennsylvania, and high-elevation forest ecosystems in the southern Appalachians.
- Many of the most acid sensitive surface waters in the U.S. are in the Northeast (see figure below) and mountainous West.



Regions of the eastern U.S. that contain appreciable numbers of lakes and streams sensitive to deleterious effects from acidifying deposition. (Source: Stoddard et al., 2003)

## Biogeochemical effects

Acidifying deposition alters biogeochemistry in terrestrial and aquatic ecosystems.

- In terrestrial ecosystems, ecological effects are linked to changes in soil chemistry, including soil base saturation, inorganic aluminum concentration in soil water, and soil carbon-to-nitrogen ratio.
- In aquatic ecosystems, ecological effects are linked to changes in surface water chemistry, including sulfate concentration, nitrate concentration, sum of base cations, acid neutralizing capacity, surface water

inorganic aluminum concentration, and surface water pH.

Examples of biogeochemical indicators of effects from acidifying deposition on ecosystems	
Ecosystem	Biogeochemical Indicator
Terrestrial	<ul style="list-style-type: none"> <li>• Soil base saturation</li> <li>• Inorganic Aluminum concentration in soil water</li> <li>• Soil carbon-to-nitrogen ratio</li> </ul>
Aquatic	<ul style="list-style-type: none"> <li>• Sulfate</li> <li>• Nitrate</li> <li>• Base cations</li> <li>• Acid neutralizing capacity</li> <li>• Surface water inorganic Aluminum</li> <li>• pH</li> </ul>

## Biological effects

Acidifying deposition alters ecosystem structure.

- Biological effects of acidification in terrestrial ecosystems are generally linked to aluminum toxicity and decreased ability of plant roots to take up base cations.
- Decreases in acid neutralizing capacity and pH and increases in inorganic aluminum concentration contribute to declines in zooplankton, macroinvertebrates, and fish species richness in aquatic ecosystems.

Examples of biological indicators of effects from acidifying deposition on ecosystems.	
Indicator	Measure
<b>Terrestrial ecosystems</b>	
• Red spruce	• Percent dieback of canopy trees
• Sugar maple	• Dead basal area, crown vigor index, fine twig dieback
<b>Aquatic ecosystems</b>	
• Fishes, zooplankton, crustaceans, rotifers	• Presence/absence • Fish condition factor • Biodiversity

Ecosystems will continue to be acidified by current emissions. For example, in the Adirondacks, the current rates of nitrogen and sulfur deposition exceed the amount that would allow recovery of the most acid

sensitive lakes. In the Shenandoah Mountains, historically deposited sulfate has accumulated in the soil and is slowly released from the soil into stream water where it causes acidification and makes parts of this region sensitive to current loading. Numeric models suggest that the number of acidic streams will increase under the current deposition rates.

## Ecological effects of nitrogen deposition

Nitrogen deposition causes ecosystem enrichment and eutrophication that alters biogeochemical cycles and harms biota, such as native lichens, and alters biodiversity of ecosystems, such as grasslands and meadows. Nitrogen deposition contributes to eutrophication of estuaries and the associated effects including toxic algal blooms and fish mortality.

- Multiple forms of reactive nitrogen (e.g., ammonia, ammonium ion, nitrogen oxides, nitric acid, nitrous oxide, nitrate, urea, amines, proteins, and nucleic acids) contribute to the ecological effects of nitrogen enrichment. However, most ecological experiments have deposition data for only a subset of the total of reactive nitrogen chemical species.
- Deposition of inorganic nitrogen species was as high as 9.6 kg N/ha/yr in 2004-2006.
- At least one important component of N, ammonia, is not measured routinely in any national network, but may account for greater than 80% of total reduced nitrogen deposition.
- Existing monitoring networks are inadequate to characterize the full extent of regional heterogeneity in nitrogen and sulfur deposition, and very likely underestimate the total nitrogen deposition across wide areas of the U.S.
- Ecological effects can occur at nitrogen deposition rates as low as 2 kg/ha/yr.



## Biogeochemical effects

### Reactive nitrogen deposition alters the biogeochemical cycling of nitrogen.

- Atmospheric nitrogen deposition is the main source of new nitrogen to terrestrial ecosystems. The onset of nitrate leaching from soils is an indicator of excess nitrogen in these systems and is calculated to begin at values ranging from ~5 to 10 kg N/ha/yr for forests in the eastern U.S. Importantly, nitrogen deposition can profoundly affect ecosystems prior to the onset of nitrate leaching.
- The contribution of atmospheric nitrogen deposition to total nitrogen loads varies by wetland-type; freshwater bogs are the most sensitive, and salt marshes are the least sensitive. Nitrogen mineralization increases with nitrogen addition, which can increase nitrogen export from wetland to adjacent surface waters.
- Atmospheric nitrogen deposition is the main source of nitrogen to headwater streams, lower order streams, and high elevation lakes. Elevated surface water  $\text{NO}_3^-$  concentrations due to nitrogen deposition occur in both the eastern and western U.S.

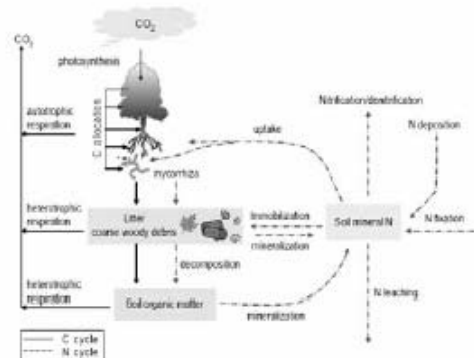
Examples of biogeochemical indicators of effects from reactive nitrogen deposition on ecosystems	
Ecosystem	Biogeochemical Indicator
Terrestrial and Wetland	<ul style="list-style-type: none"> <li>• <math>\text{NO}_3^-</math> leaching</li> <li>• Nitrification/denitrification</li> <li>• <math>\text{N}_2\text{O}</math> emission</li> <li>• <math>\text{CH}_4</math> emission</li> <li>• Soil C: nitrogen ratio</li> <li>• Foliar/plant tissue [N], C:N, N:Mg, N:P</li> <li>• Soil water [<math>\text{NO}_3^-</math>]</li> <li>• Soil pore water [<math>\text{NH}_4^+</math>]</li> </ul>
Freshwater and Estuarine Aquatic	<ul style="list-style-type: none"> <li>• Chlorophyll a</li> <li>• Water [<math>\text{NO}_3^-</math>]</li> <li>• Dissolved inorganic nitrogen</li> <li>• Dissolved oxygen</li> <li>• N:P ratio</li> </ul>

- The contribution from atmospheric nitrogen deposition can be greater than 30% of total nitrogen loadings in some of

the most highly eutrophic estuaries in the U.S., including the Chesapeake Bay.

### N deposition affects primary productivity, thereby altering biogeochemical cycling of carbon.

- Nitrogen deposition can accelerate plant growth and change carbon allocation patterns (see figure below), which can increase their susceptibility to severe fires, drought, and wind.
- Nitrogen deposition causes changes in ecosystem carbon budgets. However, whether nitrogen deposition increases or decreases ecosystem carbon-sequestration remains unclear. For example, a limited number of studies suggest that nitrogen deposition may increase carbon-sequestration in forests, but has no apparent effect on carbon-sequestration in non-forest ecosystems.
- Productivity of many freshwater ecosystems and most estuaries and coastal water ecosystems is nitrogen limited. Nitrogen deposition can cause eutrophication of aquatic ecosystems.



### Interactions between the carbon and nitrogen cycles.

Methane and nitrous oxide are green house gases that have biogenic sources and sinks. Nitrogen deposition alters methane and nitrous oxide fluxes in terrestrial and transitional ecosystems.

- Nitrogen addition increases the flux of nitrous oxide from soils to the atmosphere in coniferous forests, deciduous forests, grasslands, and wetlands.
- Nitrogen addition can reduce methane uptake in coniferous and deciduous forest. In wetlands, nitrogen addition can increase methane production, but has no apparent effect on methane uptake.

## Biological effects

Multiple biological indicators have shown that nitrogen deposition alters ecosystem structure.

- Addition of nitrogen to most ecosystems causes changes in primary productivity and growth of plants and algae, which can alter competitive interactions among species. Some species grow more than others, leading to shifts in population dynamics, species composition, and community structure. The most extreme effects include a shift of ecosystem type in terrestrial ecosystems, and hypoxic zones that are devoid of life in aquatic ecosystems, which typically results from nitrogen loading from multiple sources.

Examples of biological indicators of effects from nitrogen deposition on ecosystems	
Ecosystem	Biological Indicators
Terrestrial and Wetlands	<ul style="list-style-type: none"> <li>• Altered community composition, biodiversity and /or population decline. Taxa affected include: diatoms, lichen, mycorrhiza, moss, grasses and other herbaceous plants.</li> <li>• Plant root: shoot ratio</li> <li>• Terrestrial plant biomass/production</li> </ul>
Aquatic	<ul style="list-style-type: none"> <li>• Phytoplankton biomass/production</li> <li>• Toxic or nuisance algae blooms</li> <li>• Submerged aquatic vegetation</li> <li>• Fauna from higher trophic levels</li> </ul>

### Quantified relationships between deposition levels and ecological effects

- Lichens are the most sensitive terrestrial taxa to nitrogen with clear adverse effects

occurring at 3 kg N/ha/yr in the Pacific Northwest and Southern California.

- The onset of declining biodiversity was found to occur at levels of 5 kg N/ha/yr and above within grasslands in Minnesota and in Europe.
- Altered species composition of Alpine ecosystems and forest encroachment into temperate grasslands was found at 10 kg N/ha/yr and above in both the U.S. and Canada. A brief list of deposition levels and associated effects is shown below.

Examples of quantified relationships between deposition levels and ecological effects	
Kg N/ha/yr	Ecological effect
~1.5	Altered diatom communities in high elevation freshwater lakes and elevated nitrogen in tree leaf tissue high elevation forests in the U.S.
3.1	Decline of some lichen species in the Western U.S. (critical load)
4	Altered growth and coverage of alpine plant species in U.S.
5	Onset of decline of species richness in grasslands of the U.S. and U.K.
5.6 - 10	Onset of nitrate leaching in Eastern forests of the U.S.
5-10	Multiple effects in tundra, bogs and freshwater lakes in Europe (critical loads)
5-15	Multiple effects in arctic, alpine, subalpine and scrub habitats in Europe (critical loads)

## Sulfate effects on mercury methylation

Mercury is highly neurotoxic and enters the food web in its methylated form. Because sulfate can stimulate bacterial production of methyl mercury, sediments and biota in wetlands and other aquatic ecosystems can have elevated concentrations of methyl mercury. In 2006, 3,080 fish advisories were issued in the U.S. due to the presence of methyl mercury in fish.

## Dr. Paul J. Hanson

I found the second draft of the Integrated Science Assessment (ISA) to be greatly improved. Panel suggestions on the first draft appear to have been incorporated for the most part. The requested Executive Summary is well crafted and a nice introduction to the ISA, but some wording changes may still be in order. My specific comments and editorial suggestions are listed below.

### Specific comments and suggested edits:

#### **Executive Summary**

Page two, second column: Change to “Numerical modeling experiments can help fill in these data gaps and suggest that local and even regional areas of high concentration and deposition may exist where measured data are unavailable. Subscript the 2 in NO<sub>2</sub>.

Page 4 last paragraph: The last statement is not correct. The onset of leaching is not a fixed constant that applies to all eastern forests. This text should be changed to indicate that such a threshold applies to a defined set of sensitive eastern forests.

Page 5: Change the first two sentences to: “N deposition often increases primary productivity, but may not lead to enhanced carbon sequestration.” In the first paragraph change “However, alteration...” to ‘Alteration...’ I would add the word possible to the following: “The increase in growth is greater for some species than others, leading to possible shifts in population dynamics, species composition, community structure and, in extreme instances, ecosystem type.” Growth changes are not a guarantee of cascading effects. The paragraph on lichens seemed too general. Are the limits for lichen response true for all ecosystems, or only sensitive ones?

Page 5 last paragraph: Should organisms be animals? Elemental mercury is taken up by plants.

Page 6 third paragraph: Change to “Acute exposures to NO<sub>2</sub>,...” Delete the word “Overall”.

Page 6 last paragraph: Consider the following changes:

“...deposition resulting from NO<sub>x</sub> and SO<sub>x</sub> pollution. It causes a cascade of effects that harm susceptible terrestrial and aquatic ecosystems, including slower growth and injury to forests, and localized extinction of fishes and other aquatic species. In addition to acidification, deposition resulting from NO<sub>x</sub>, along with other sources of reactive nitrogen (e.g., fertilizers, wastewater, and atmospheric ammonia deposition), causes a suite of ecological changes within sensitive ecosystems including biodiversity losses, disease, eutrophication, and harmful algal blooms. Particulate sulfate can interact with methanogenic bacteria to produce methylmercury, a powerful toxin that can bioaccumulate to toxic amounts in higher trophic levels (e.g. otters and kingfishers).

**Chapter 1:** No comments.

## **Chapter 2**

The font size for the text within figures on pages 2-96 through 2-100 is too small. These figures need to be adjusted.

Figures 2-41 , 2,42, 2-43, and 2-44: Using the same color scheme for an alternate range of concentrations in the comparison of Total vs. background concentrations masks what should be the main message of these figures. Background levels are very, very low. The need to visualize where background levels are highest over a range from very-low to low seems unnecessary. If the authors really want this specificity they should choose an alternate color scheme for the background map.

## **Chapter 3**

Tables 3-11 to 3-26 within Section 3.3 provide an appropriate and site-specific level of detail to allow the readers to understand the indicators and levels of deposition of importance for specific ecosystems and the responses being highlighted.

## **Chapter 4**

For the bolded conclusion statements on pages 4-17 through 4-31 determine if you can change “alteration” to a statement of directional change if the data warrant (e.g., change alteration to increase in the statement of N deposition effects on N<sub>2</sub>O emissions).

### **Comments on the Key Findings draft (1 October 2008):**

Page 1 first yellow box:

In the third paragraph I recommend changing the word “problems” to ‘changes’ to avoid the judgmental nature of the first term. As with many other locations in the document it is important that this statement not be interpreted as applying equally to all ecosystems throughout the United States.

Second yellow box:

While the statement may be factually correct it tends to imply that acidification leading to adverse effects is taking place in all ecosystems. I don’t believe this is true. One size doesn’t fit all and levels of deposition, acidification, and adverse effects are not consistent across the US.

The bullets at the top right portion of page 1 are just right in my opinion. They contain the detail needed for the reader to draw the appropriate conclusion.

Right hand column of Page 2 – yellow box:

I would change the first lines to “Nitrogen deposition causes ecosystem element enrichment and eutrophication....”

Page 2, second column, first bullet:

Modify the text to read “...nitrogen enrichment. However, most ecological experiments and observations have ....”

Page 2, second column, third bullet:

Is Ammonia always 80% of total reduced N or only in locations with high N deposition totals?

Page 2, second column, last bullet:

Add the words 'insensitive ecosystems' to the end of the bullet.

Page 3, column 1, first bullet:

I don't believe that this statement is true in natural ecosystems dominated by nitrogen fixing species (alder thickets/forests; and perhaps early successional oldfields). The last statement of this bullet needs further expansion. I'm not clear on the intent.

Page 4, first column, first bullet under the Biological Effects heading:

Near the end of the statement the terms 'terrestrial ecosystems' is too general. This is not true for all terrestrial ecosystems.

Page 4:

Bullets ending column 1 and beginning column 2 are well worded.

Page 4, second column, yellow box:

The statement suggesting that 5.6 to 10 kgN/ha/y drives the onset of nitrate leaching in eastern forests is wrong. It only applies to specific systems and locations within eastern US forests.

I agree with the suggestion of one panel member (can't remember who) that spatially explicit information on the areal extent of acidification, nitrogen enrichment, and sulfate effects on mercury methylation might all be made clear in the executive summary.

## Dr. Rudolf Husar

These comments pertain primarily to Charge Question 5 with brief comments on other sections.

*ISA Charge Question 5. In revising the ISA, we have incorporated additional information on the indicators of exposure and ecological effects, including increased emphasis on quantified relationships in the presentation of information of results in tables and summary discussions in Chapter 4. What are the views of the CASAC panel on our revisions to focus on quantitative relationships between airborne nitrogen and sulfur compounds and ecological indicators?*

- It is commendable that effort was made to perform an analysis of existing literature on indicators relevant to deposition and acidification. The meta-analysis appears to be extensive and appropriate for the ISA
- The analysis of indicators is particularly important since the a secondary standard (if proposed and promulgated) needs to be expressed in terms of Sox / Nox and then properly linked to the effects through the indicators and a causality framework.
- It would be desirable to continue fortifying the linkages in the causality chain between emission - atmospheric concentration – deposition – dosage – effect – ecosystem services.
- An example of such an end-to-end causality illustration would help. A synchronized array of trend charts for each parameter/indicator in the causality chain could be an effective way to illustrate the overall framework and key aspects of systems behavior.
- In the ISA it may not be necessary the have quantitative trend values for each of the parameters in the causality chain ensemble. In fact, graphically indicating (say dashed trend lines) the poorly understood parameters would be a more realistic representation of the current state of the causality framework.

A recurring general concern regarding the ISA, voiced by several panel members over multiple meetings, is the near-complete avoidance of the non-ecological welfare effects of NOX and SOX, such as particle effects on visibility and climate, materials damage etc. It is understood that some of these effects are discussed in other assessment documents and full treatment of these in this ISA is not necessary.

This document is titled “Integrated Assessment for Oxides of Nitrogen and Sulfur – **Environmental** Criteria” but by design, it focuses on the ecological effects. Fine, no problem here. However, since Environment includes air, land, water, biota I see two possibilities:

- Either rename the document to ‘**Ecological** Criteria’ – probably not feasible
- Or keep “**Environmental** Criteria” but state it clearly
  - in which docs other NOx/Sox welfare effects of are being treated
  - provide a short synopsis of the key non-ecological effects in the appendix, so this ISA document can meaningfully represent an assessment of Environmental Criteria.

## Detailed Comments on Specific Sections of ISA Document

Page 1-3: The schematic Figure on the biogeochemical cycles of NO<sub>x</sub> and SO<sub>x</sub> is good. However, during the June 2008 CASAC it was suggested that such a general Figure should be fortified by adding magnitudes to the flows represented by the arrows. The transfer rates, say over the US, can be estimated from the model runs, or based on the empirical evidence. There is ample literature on biogeochemical cycles that estimates the magnitude and importance of the various flow rates.

Page 2-47: Figure 2-20 is again a qualitative schematic of the sulfur flows in the and out of the atmosphere. At the minimum, estimating the magnitude of dry and wet deposition would be most helpful.

Page 2-47: Multi-phase SO<sub>x</sub> chemistry is reviewed in considerable detail including the relative humidity effects on deliquescence. It is puzzling why this detailed behavior of particles is relevant for ISI which is to support ecological effects and not the atmospheric effects of particles.

Page 2-54: Same comment as above. Why discuss deliquescence of nitrate particles when atmospheric effects of particles are not considered.

Page 2-56: Section 2.6.5 “Transport-Related Effects” is a rather haphazard collection of references that neither explain the general features of S and N transfer in the atmosphere nor is a comprehensive list of literature. Calling it Transport Effects is misleading, since the section covers transport processes and phenomena, not effects.

In addition to Transport Phenomena a statement on the general role of meteorological processes shaping pollutant transport, governing thermodynamics (e.g. gas-particle equilibrium and reaction kinetics) and removal processes. Showing the precipitation pattern would provide considerable explanatory support to the pattern of S and N deposition and the resulting effects. An explicit discussion of the atmospheric life time of various sulfur and nitrogen species would be most helpful.

Page 4-1: Chapter 4, “Summary and Conclusions” supposed to summarize the content of Chapter 2 (Emissions, Atmospherics) and Chapter 3 (Ecological Effects) of NO<sub>x</sub> and SO<sub>x</sub>. The way in which Chapter 4 has been written, only about 10% of the 40 page summary deals with the emissions, ambient concentrations, transport and deposition. 90% is about the effects and associated summary tables. Table 4-4 for N is useful and similar compilation for S would be useful as well. Given the sizable effort invested in the compilations this Chapter appears to be an integration Chapter rather than just a Summary Chapter.

Page 4-1 Line 11: Section 4.1.1 “ Relevant Chemical Families and Constituent Species” is a single paragraph, loaded with inaccuracies and dubious rationale. Examples: “particulate nitrate is .... not a member of the oxidized N family of species”. So, particulate nitrate is not an oxidized N? Line 17: “Only SO<sub>2</sub> is present in concentrations

relevant for atmospheric chemistry and environmental exposures. “ So, the 10,000 excess death per year, mostly from sulfate are not relevant?”

Page 4-2 Line 1: Stating that the 2001 US NO<sub>x</sub> emissions were approximately “~23.19 Tg” is misleading since it implies that the accuracy of US NO<sub>x</sub> emissions is known with better than 1% accuracy. For most of us the NO<sub>x</sub> emission accuracy is not better than 20% , i.e. 23+/- 2 Tg.

Page 4-2 Line 5: “Biogenic NO<sub>x</sub> sources .....include biomass burning, *lightning*, and soils”. I wonder which biota in the sky are responsible for lightning??

Page 4-2 Line 5: “Biogenic NO<sub>x</sub> sources are substantially smaller than anthropogenic .....”. On global scale anthropogenic and natural nitrogen emissions to the atmosphere are comparable ([http://www.visionlearning.com/library/module\\_viewer.php?mid=98](http://www.visionlearning.com/library/module_viewer.php?mid=98)).

Page 4-5 Line 1: It is true that the measurements of particulate NO<sub>3</sub> and NH<sub>4</sub> are subject to positive and negative errors. However, the measurement of particulate sulfate is among the most accurate and reliable among the sampling methods.

Page 4-5 Line 5: “This assessment concludes that...”. This complicated sentence is incomprehensive.

Page 4-10 Line 26: “However, there is no apparent relationship between recent trends in N deposition and trends in NO<sub>3</sub> concentrations in these surface waters.” This statement has significant consequences regarding the conclusions as stated below.

Page 4-27 Line 8: “The evidence is sufficient to infer a causal relationship between N deposition and the alteration of biogeochemical cycling of N in fresh water aquatic ecosystems”. Is this consistent with the statement that N deposition trends are not matched by corresponding N concentration trends?



## Dr. Dale Johnson

This draft is an improvement in some ways but I believe that it needs to include assessments of the possibility of beneficial effects of N deposition. It now contains detailed descriptions of N and S cycles and recognized the fact that nitrogen (but not sulfur) is often a limiting nutrient. It now considers the potential for N deposition to enhance production and C sequestration specifically within the body of the text – and then summarily dismisses such a possibility and mentions nothing of it in summary statements. It appears that the treatment of the potential benefits of sulfur are discussed much more extensively than those for nitrogen (although I fully recognize that N deposition is probably not important for crop systems, given how much they are fertilized).

Specific comments:

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

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

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

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

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

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

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

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

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

p. 3-133, lines 1-8: Of course it is true that when you add a limiting nutrient you will run up against the next limiting nutrient – this is very well known. Is this then a wholly bad thing or was the addition of the limiting nutrient “good” to start with?

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

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

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

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

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

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

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

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

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

### General References

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

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

Richter, D.D., D. Markewitz, H.L. Allen, R. April, P.R. Heine, and R. Urrego. 1994. Soil chemical change during three decades in an old-field loblolly pine (*Pinus taeda* L.) ecosystem. *Ecology* 75:1463-1473.

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

### References on the effects of fire:

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

Baird, M., Zabowski, D., and R.L. Everett. 1999. Wildfire effects on carbon and nitrogen in inland coniferous forests. *Plant Soil* 209:233-243.

Bayley, S.E., Schindler, D.W., Parker, B.R., Stainton, M.P., and K.G. Beaty. 1992. Effects of forest fire and drought on acidity of a base-poor boreal forest stream: similarities between climatic warming and acidic precipitation. *Biogeochem.* 17:191-204.

Certini, G. 2005. Effects of fire on properties of forest soils: a review. *Oecologia* 143: 1-10.  
Chorover, J., Vitousek, P.M., Everson, D.A., Esperanza, A.M., and D. Turner. 1994. Solution chemistry profiles of mixed-conifer forests before and after fire. *Biogeochem.* 26:115-144.

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- ecosystem. *Ecology*. 59(3):489-497.
- Dyrness, C.T., Van Cleve, K., and J.D. Levison. 1989. The effect of wildfire on soil chemistry in four forest types in interior Alaska. *Can. J. For. Res.* 19:1389-1396.
- Grier, C.C. 1975. Wildfire effects on nutrient distribution and leaching in a coniferous ecosystem. *Can. J. For. Res.* 5:599-607.
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- Khanna, P.K. and R.J. Raison. 1986. Effect of fire intensity on solution chemistry of surface soil under a *Eucalyptus pauciflora* forest. *Aust. J. Soil Res.* 24:423-434.
- Khanna, P.K., Raison, R.J., and Falkiner, R.A. 1994. Chemical properties of ash derived from *Eucalyptus* litter and its effects on forest soils. *For. Ecol. Manage.* 66:107-125.
- Knight, H. 1966. Loss of nitrogen from the forest floor by burning. *For. Chron.* 42(2):149-152.
- Neary, D.G., C.C. Klopatek, L.F DeBano, PF. Ffolliot. 1999. Fire effects on belowground sustainability: a review and synthesis. *For. Ecol. Managem.* 122: 51-71.
- Raison, R.J. and J.W. McGarity. 1980. Some effects of plant ash on the chemical properties of soils and aqueous suspensions. *Plant Soil* 55:339-352.
- Rashid, G.H. 1987. Effects of fire on soil carbon and nitrogen in a Mediterranean oak forest of Algeria. *Plant Soil* 103:89-93.
- Trabaud, L. 1994. The effect of fire on nutrient losses and cycling in a *Quercus coccifera* garrigue (southern France). *Oecologia*, 99: 379-386.
- Williams, M.R. and J.M. Melack. 1997. Effects of prescribed burning and drought on the solute chemistry of mixed-conifer forest streams of the Sierra Nevada, California. *Biogeochem.* 225-253.

## **Dr. Donna Kenski**

### Overarching comments:

There is an impressive amount of new material in this new draft. EPA has been very responsive to the panel's comments on the previous draft. As a result this version is much improved and constitutes a solid scientific basis for the REA. I find only one major shortcoming, and that is in its discussion of CMAQ's performance characteristics. After reviewing the REA and noting its reliance on CMAQ, it seems more important than ever to thoroughly describe CMAQ's performance especially with respect to modeling wet and dry deposition. The ISA includes plenty of useful new information on CMAQ, all of which is a welcome addition, including the Tampa Bay modeling exercise (although the accompanying Figs. 2-29 through 2-37 are so small as to be practically unreadable). The existing text on CTM deposition performance (Sec. 2.8.3.2) compares results for 23 different models (including CMAQ?), but no CMAQ specific data are given. Is the factor-of-2 performance of these models for wet deposition adequate for supporting the REA analyses and the standard-setting process? Dry deposition performance is probably even more variable. Section 2.8.4 has some limited statistics on RADM performance – but the REA doesn't propose any applications of RADM, so do we really need this? A more thorough discussion of these deposition uncertainties, specific to CMAQ as much as possible, is still needed.

### Charge Questions:

Exec. Summary: This was a great addition that was just the right length and tone. I liked the simple summaries of causal evidence and the emphasis on current concentrations.

Chap 1: Addition of the causality framework was helpful. The way the causal judgments were carried through the document was great – i.e., in the summary, throughout Chapt. 3, and in the conclusions in Chap. 4.

Chap 2: Nice review of NH<sub>3</sub> measurement methods. Expanded information on CTM models, especially CMAQ, is well written and very helpful, although still more is needed on CMAQ performance with respect to wet and dry deposition. The additional tables on various monitoring programs are nice (although hard to read – the font size in all tables has shrunk a little too much). I also like the new maps and the source attribution summary. All in all, this is a much stronger section than it was.

Chap 4: Like the executive summary, I thought this summary chapter was just about the right length and struck the right tone.

### Specific comments, typos, etc:

p. 2-2, Table 2-1: Improved formatting and detail in this table makes it much easier to read.

p. 2-4, line 4; remove 'the'

- p. 2-4, lines 5-8: It seems more appropriate to consider all electricity generation together for this analysis, rather than split it into utility and industrial categories. Then it's clear that electricity generation is almost equal to mobile sources in NO<sub>x</sub> emissions.
- p. 2-4 thru 2-6: the added maps, figures 2-1 through 2-4, are very nice.
- p. 2-7, lines 29-30: marine transport is 60% of land-based NO<sub>x</sub> in Europe? Can that be true?
- p. 2-20, lines 3-5: although vehicle NH<sub>3</sub> is only 8% of total NH<sub>3</sub>, it can be locally significant (i.e., in cities). This is evident in Fig. 2.12 but bears noting in the text as well.
- p. 2-27, Figure caption. Good clarification and explanation of this figure!
- p. 2-30, top of page: 2NO<sub>2</sub>O<sub>5</sub> should be N<sub>2</sub>O<sub>5</sub>
- p. 2-30, line 13: what is 'organic coating' referring to? Organic compounds on the particle surface? Not clear.
- p. 2-34, line 30: instantiations?
- p. 2-37, line 4: incomplete sentence.
- p. 2-38, line 35: should snow be soot?
- p. 2-95, Fig. caption 2-27 is garbled.
- p. 2-96, line 2: predations ->predictions
- p. 2-101, line 9: incomplete sentence
- p. 2-122, line 14: change first 'and' to 'by'
- p. 2-122, lines 17-21: Note that SEARCH makes continuous NH<sub>3</sub> measurements at several sites (not all of the network though). Discussion of their denuder difference method might be added to the text.
- p. 2-155, Fig. 2-75: Isn't this a map of particle NO<sub>3</sub> concentration (not gas phase)?
- p. 2-161: Figure 2-80 is the same as Figure 2-74
- p. 2-199, line 15: Section 0?
- p. 4-1, line 14: typical/y

## Dr. Myron J. Mitchell

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

*Be consistent in the order of multiple citations throughout the document. Either cite by date or alphabetically. Within the document the citations are not complete or consistent including the need to use letters for multiple citations by the same author and same year. It would be helpful to have unified and consistent units throughout the document. There is a mixture of English and metric units (i.e., SI) in the current document. The correct SI abbreviations and units should be used throughout the document. If English units are used, the equivalent values using SI units provided in parenthesis would be helpful.*

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

1. We have added an executive summary of the major findings and conclusions to the second draft ISA. We have also created a "key findings" section that is intended to provide highlights of these conclusions. We are seeking CASAC panel advice and comments on these additions to the ISA. To what extent do they provide an appropriate level of detail and convey the important scientific conclusions of the assessment?

*In general the information level in the executive summary is suitable. However, the executive summary and key findings need to be placed in the broader context of other environmental issues including climate change, invasion of exotics, extreme events, changes in CO<sub>2</sub> concentration etc. These other environmental affects can dampen and/or amplify the environmental effects associated with SO<sub>x</sub> and NO<sub>x</sub>. Some changes related to other effects are suggested within my detailed comments. Within the key findings there are a number of issues that need to be addressed and these are provided within my detailed comments.*

2. Chapter 1 has been revised to clarify the scope or focus of this assessment on effects related to the deposition of nitrogen and sulfur compounds. In addition, we have added a discussion of the framework for evaluation of causality for assessing ecological effects. Do these revisions adequately characterize the scope of the assessment? Does the CASAC panel have recommendations for revisions to the causality framework? Is it appropriately applied in the draft ISA?

*The information provided in Chapter 1 seems appropriate with respect to the overall approach.*

3. Chapters 2 and 3 from the first draft have been combined. Substantially more information has been included on NH<sub>3</sub> emissions, NH<sub>3</sub> measurement techniques, NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> concentrations. Additionally, information on NO<sub>x</sub> and SO<sub>x</sub> including ambient concentrations, deposition levels and their spatial and temporal relationships has been added. Have these revisions to Chapter 2 improved its assessment of the currently available scientific knowledge on atmospheric sciences and its relevance to the evaluation of environmental effects presented in later chapters?

*There is certainly more detail on atmospheric chemistry in Chapter 2. I am not certain whether all of this detail including issues related to analytical technique, artifacts, differences in instrumentation, etc. are necessary with respect to having sufficient information to set standards. I would suggest placing some of these details in an appendix. More explicit linkages need to be made on what we know as well as what we do not know and how this information is needed for setting standards for NO<sub>x</sub> and SO<sub>x</sub>. The details provided in this section are somewhat overwhelming including extensive graphics and results from specific sites. A clear summary of what is known related to setting NO and SO standards would help bring all of this information into focus. In particular the issues relating to the estimates of deposition velocities need to have a central place in this document. One example that I am aware of is for the Egbert, Ontario site in Canada where both concentration measurements and deposition values were compared using CASTNET and CAPMoN approaches. The concentration data are almost identical, but the deposition estimates are quite different. The issue related to confidence in modeled deposition velocities needs to be placed in the context of the CMAQ predictions. The flow of information could be improved with better use of headings to direct the reader to the content of major sections. Also, some further discussion is warranted about how other factors such as climate change, extreme events (e.g. fire, hurricanes, ice storms), invasion of exotics, etc. can also have a major impact on ecosystem response and can have a major influence on the expression of acidic deposition impacts on ecosystems. These results need to be placed in an historical framework since for the effects analyses the longer time scales (i.e., decades) are most relevant.*

4. We removed or eliminated redundancy, added summary sections, added additional references and reorganized Chapter 3. Revisions to the ecological effects sections are given below. Have the revisions improved the characterization of the ecological effects?

*This section has many problems in the citations and references. Some of the sections in this chapter are redundant. For example in section 3.2.1.3 there is a review of N accumulation and nitrate leaching and in section 3.3.2 there is a section on N enrichment effects on N cycling. A major challenge is placing the nitrogen atmospheric deposition concerns in the context of other environmental issues including wastewater treatment and fertilizer contributions to the nitrogen loading to surface waters. It is clear that there are often quite different current conditions and responses among regions such as the Rocky Mountain West versus the Northeast especially with respect to nitrogen. The need for different standards or approaches needs to be considered that focus on specific types of ecosystems (e.g., alpine, northern hardwoods, etc.). It would be helpful to have some better comparisons among model predictions (e.g., MAGIC versus PnET-BGC as well as other models). Also, some better use of the PIRLA I and PIRLA II results in showing the historical patterns of acidic deposition.*

- a. Consistent with CASAC comments, we expanded our characterization of the quantification of chemical effects of acidification in aquatic ecosystems, added new conceptual diagrams, and further discussed interactions between acidification and plant disease.

*Certainly more details are provided. However, there is considerable redundancy in the document. A clearer delineation of particular areas of focus is needed.*



b. We expanded the discussion of quantitative relationships between nitrogen deposition and ecological effects, including published critical loads in the U.S. and Europe. In addition, the nitrogen enrichment section was expanded to include new discussions on carbon budgeting, biogenic nitrous oxide and methane. Information on the linkages between effects and both reduced and oxidized forms of nitrogen was emphasized, to the extent data were available.

*The more you can do to pull together information from these divergent informational sources and provide those points that indicate divergence or divergence related to deposition and ecological effects will improve this document.*

c. The section on “other” welfare effects was updated to include information on the direct phytotoxic effects of nitric acid.

*The inclusion of additional information on the direct phytotoxic effects of nitric acid was helpful.*

5. In revising the ISA, we have incorporated additional information on the indicators of exposure and ecological effects, including increased emphasis on quantified relationships in the presentation of information of results in tables and summary discussions in Chapter.

*This revised version certainly is more complete than the previous version. A major challenge is placing the issues related to  $NO_x$  and  $SO_x$  effects in the context of other ecosystem changes including effects due to climate change, invasion of exotics, extreme events. There is also substantial reliance on a variety of models that are used to predict a variety of parameters. These models have different spatial and temporal resolutions. Also, some clearer delineation is needed on the overall model performance and the confidence of predictions. How does this confidence effect the ability to make accurate assessments of the effects of  $NO_x$  and  $SO_x$ ?*

## **Specific Comments**

### **For Key Findings the following issues need to be addressed:**

#### This statement is not true:

Particulate sulfate can interact with methanogenic bacteria to produce methylmercury.

*This relationship is for sulfate in soil and wetlands not “particulate sulfate”.*

#### For the statement:

The sensitivity of terrestrial and aquatic ecosystems to acidification from sulfur and nitrogen deposition is predominantly governed by surficial geology.

*Change to include regional differences.*

#### For the statement:

In aquatic ecosystems, ecological effects are linked to changes in surface water chemistry, including sulfate concentration, nitrate concentration, sum of base cations, acid neutralizing capacity, surface water inorganic aluminum concentration, and surface water pH.

*Also indicate these effects are influenced by historical inputs to these systems.*

For the statement:

At least one important component of N, ammonia, is not measured routinely in any national network, but may account for greater than 80% of total reduced nitrogen deposition.

*This statement gives impression that N deposition is greatly underestimated without the inclusion of NH<sub>3</sub>. Provide clarification on the degree of the relative importance of NH<sub>3</sub> deposition across the U.S.*

For the statement:

Existing monitoring networks are inadequate to characterize the full extent of regional heterogeneity in nitrogen and sulfur deposition, and very likely underestimate the total nitrogen deposition across wide areas of the U.S.

*Indicate where the actual geographical problems occur.*

The following statement is not true:

Atmospheric nitrogen deposition is the main source of new nitrogen to terrestrial ecosystems.

*Across terrestrial ecosystems for the total U.S. N fertilizers are the dominant form of input.*

*Clarify that N atmospheric deposition's relative importance varies among regions.*

For the following statement:

Nitrogen deposition causes changes in ecosystem carbon budgets. However, whether nitrogen deposition increases or decreases ecosystem carbon-sequestration remains unclear. For example, a limited number of studies suggest that nitrogen deposition may increase carbon-sequestration in forests, but has no apparent effect on carbon-sequestration in non-forest ecosystems.

*Clarify that these effects are highly spatially variable including whether there are decreases or increases in C sequestration.*

For the following statement:

Productivity of many freshwater ecosystems and most estuaries and coastal water ecosystems is nitrogen limited.

*This suggests that N is the major limiting nutrient for freshwater systems. This is not generally true. This statement needs to be placed in context of P which often as important than N as a limiting nutrient for freshwater systems.*

For the following statement and related section:

Biological effects, Multiple biological indicators have shown that nitrogen deposition alters ecosystem structure.

*This section needs to be placed in the context of other agents of change including climate, exotic introductions, extreme events, etc.*

Page	Line	Comment
xvii		Change to “ <i>chloride ion.</i> ”
xviii		Change to “ <i>fluoride ion</i> ”
1		Within the body of the text “Nitrogen” should be changed to “nitrogen”.
1		Throughout the text corrections need to be made for subscripts that are lacking in some cases (e.g., NO3 should be NO <sub>3</sub> , NO2 should be NO <sub>2</sub> , SOX should be SO <sub>x</sub> , etc.).
1		Change to “In the years 2004-2006, S deposition in the United States.”
2		Change “inferred” to “modeled.”
2		Change to “Although deposition in most areas of the United States <i>was dominated by</i> wet deposition, there were some exceptions, including parts of California here N deposition was primarily dry.”
2		Change to “The <i>sparse</i> coverage of monitoring sites in many areas, especially in the rural West, <i>results in little or no</i> data on deposition totals in a <i>substantial</i> number of potentially sensitive places.”
2		Change to “Numerical modeling <i>efforts</i> can help fill-in these data gaps and <i>may</i> suggest that local and even regional areas of high concentration and deposition exist where <i>currently</i> no data exist.
4		Some of most severe acidification may also occur during the summer after periods of drought especially in those watersheds with substantial portions of wetlands. These rewetting episodes are associated with acidification due to the oxidation of previously reduced sulfides.
2-1	8-18	Isn’t there some merit in changing the definition of nitrogen oxides to be the same as that used by atmospheric scientists and air quality control experts?
2-4	2	Change “Roughly” to “ <i>Approximately.</i> ”
2-6	6	Change to “The N content in fossil fuels and chemical forms vary strongly.”
2-6	7	Change “running” to “operating conditions”.
2-7	35	I thought that the effect of “stack height” effect was relatively minor with respect to the overall dispersion distance of pollutants from combustion.
2-8	16	Change to “of the various products of <i>N</i> transformations.”

- 2-8 22 Change to “synthetic and organic *N* fertilizers.”
- 2-8 29 Change to “*N* metabolism in soils is strongly dependent on soil substrate concentrations of *both N and labile carbon constituents* as well as physical.”
- 2-8 30 Change to “Where *available N*.”
- 2-9 11-12 Change to “such as the *differences* between shortgrass and tallgrass prairie for example.”
- 2-9 18-19 Change to “Local contributions to soil NO<sub>x</sub> can be greater *per unit area* than the global average.”
- 2-10 28 Delete extra “,” in “(e.g.,.” Note this occurs twice in this line.
- 2-11 14-16 This statement is a little confusing. It suggests there a combination of both atmospheric residency time as well as heat trapping efficiency that produces this value of 300? These two parameters need to be clearly separated. Isn’t the heat trapping capacity on a per molecule 310 times that of carbon dioxide?
- 2-11-12 Reword as follows: However, N<sub>2</sub>O is an intermediate product along with NO from the complex soil metabolism described in Section 2.2.2.1. A brief description of N<sub>2</sub>O emissions and its contribution to the U.S. GHGs is described below.
- 2-12 16-17 Delete: These emissions resulted from the fuel combustion, industrial practices, and stimulation of biogenic sources through agricultural practices enumerated above.
- 2-12 18-19 Change to “*From* 1990 and 1998.”
- 2-12 23 Change to “Biogenic production of N<sub>2</sub>O *from soil* accounted for > 75%.”
- 2-12 27 Change to “may be *affected* by environmental conditions.”
- 2-12 28-29 Change to “*enhancing* denitrification, and potentially increasing N<sub>2</sub>O emissions.”
- 2-13 8 Change to “emissions originated *from*.”
- 2-13 10 Change to “either *as* SO<sub>2</sub> or SO<sub>3</sub>.”
- 2-13 14 Change to “can not accurately be *used to calculate* the contribution of local sources to selected environmental.”
- 2-13 18-19 Delete “with most counties east of the Mississippi River in warmer colors (greater emissions densities) than most counties in the West.”

- 2-15 6 Change to “98 and 160 tons total SO<sub>2</sub> per square mile, respectively.”
- 2-18 4 In addition to carbon-bonded S (amino acid) there is also inorganic sulfate.
- 2-22 1-3 This is a confusing sentence that needs to be reworded.
- 2-22 10 Change to “have been performed *for* a number.”
- 2-22 12 Change to “it can be treated *conservatively* on these scales.”
- 2-23 30 Change to “may have been underestimated or *were* increasing.”
- 2-24 6 Change to “proved useful for *estimating*.”
- 2-25 11 Change to “volatility. This pattern, however, has not appeared in previous emissions factors and inventories.”
- 2-26 10 Change to “available in numerous *references* (Seinfeld.”
- 2-26 11 Change to “recounted here with special *attention* to.”
- 2-26 12-13 Change to “are schematized in Figure 2-15. NO<sub>2</sub>, itself an oxidant, can react to form.”
- 2-26 16-17 Change to “to HNO<sub>3</sub> and can contributing to the acidity of cloud, fog, and rain water.”
- 2-27 Figure Caption 2-15 As stated previously it would be helpful to have the definitions of “NO<sub>x</sub>” and “NO<sub>y</sub>” be consistent with the atmospheric science literature.
- 2-29 2 Delete “highways.”
- 2-29 7 Change to “Reaction 7:.”
- 2-29 14 Delete “schematic.”
- 2-29 17 Change to “this chapter are:.”
- 2-30 2 Change to “NO<sub>3</sub>:.” Note I would suggest that if reactions are provided after a statement this statement should end with a “:” throughout the document.
- 2-32 15-16 Be consistent in the order of multiple citations throughout the document. Either cite by date or alphabetically.
- 2-34 4 Change to “decomposition ranges.”

- 2-34 6 Change to “uptake *by* vegetation.”
- 2-34 7 Change to “Reaction 21 *is* thermally.”
- 2-34 11 Change to “concentrations of their precursors.”
- 2-34 12 Change to “found in most environments, ranging from remote.”
- 2-34 14 Change to “downtown metropolitan areas, especially.”
- 2-35 5 Change to “because many factors important for P(O<sub>3</sub>) are omitted.”
- 2-35 6 Change to “VOCs *that* are mostly absent during early morning hours.”
- 2-35 11-12 Delete “at a monitoring site in Shenandoah National Park, VA.”
- 2-35 18 Change “from commercial aircraft are very similar.”
- 2-35 20 Delete “included in model calculations.”
- 2-35 27 Change to “(1998, 2001).”
- 2-35 32 What is implied by the use of the term “correlation patterns”? See also page 2-36, line 1.
- 2-36 7 Change to “2001 , 2003).”
- 2-37 10 Change to “Brown et al. (2006) found.”
- 2-38 1-2 Change to “available for reaction thus increasing P(O<sub>3</sub>).”
- 2-38 5 Change to “amounts. However, only.”
- 2-38 8-11 Change to: “It is important to recognize that *the studies of* both Schultz et al. (2000) and Singh et al. (1996) involved aircraft sampling at *high altitude that* can significantly under-represent sea salt aerosols. These aerosols are important contributors to total NO<sub>3</sub> (defined to be HNO<sub>3</sub> + pNO<sub>3</sub> ) and large fractions of NOY(Huebert, 1996).”
- 2-38 12 Change to “budgets based *upon their studies.*”
- 2-38 14 Change to “domine, 2002) that.”
- 2-38 19 Change to “*Hence*, HNO<sub>3</sub> recycling.”
- 2-38 33 Delete “observed.”

- 2-38 34 Change “(Reaction 18) *constitutes a.*”
- 2-39 6 Change to “and kerosene soot, *and found that.*”
- 2-39 16 Delete “observed.”.
- 2-39 18 Change to “Longfellow et al. (1999).”
- 2-39 20 Change to “NO<sub>3</sub>/N<sub>2</sub>O<sub>5</sub> and HO<sub>2</sub>/HO<sub>2</sub>NO<sub>2</sub>.”
- 2-40 11-12 Change to “Daytime observations of HNO<sub>2</sub>, when rapid photolysis depletes ambient concentrations to very low levels, implies large sources of photoinduced.”
- 2-48 4 Change to “Jacobson (2002).”
- 2-48 12 Change to “~5 x 10<sup>-3</sup> with.”
- 2-50 6-7 Is there still a quantifiable plum “further downwind”. Why are conditions even “more oxidizing than in background air”?
- 2-55 18 The correct abbreviation for moles is “mol” not “M”.
- 2-56 2 Change to “throughout the Earth’s boundary layer.”
- 2-56 8-9 Does the term “reservoir species” imply chemical species with larger “τ”?
- 2-56 19-20 Change to “Photochemical activity is enhanced by higher temperatures and sunlight.”
- 2-57 1 Change to “distances from their *sources.*”
- 2-59 26-27 The format here is mixed up and needs a “)” at the end.
- 2-60 1 Change to “(2007)”. There are two 2007 references that need to be designated with letters.
- 2-60 1 Delete “parts per billion” and “[]”.
- 2-60 7 See other comment about Dunlea et al. references.
- 2-60 2-34 Change to “The daily average interference for an episode during the summer of 2002 was modeled. Concentration fields for NO<sub>z</sub> species and conversion efficiencies for NO<sub>z</sub> species ranged from ~20% in Baltimore to ~80% in Madison, VA.

- 2-61 1 Change to “activity *was* highest.”
- 2-61 2 Change to “compounds *were* greatest”
- 2-61 7 Delete “On the whole.”
- 2-61 10 What is meant by "can be changing rapidly"? Do you mean changing rapidly in the literature
- 2-65 7 Change to “normal” to “typical.”
- 2-65 12-17 These statements are important in relating the results to actual needs and determination of standards. Similar types of statements are needed throughout the document to focus the results on those issues which are policy relevant.
- 2-66 4-5 This sentence needs to be reworded since “and of the particles against deposition” does not make sense. See also line 9.
- 2-66 11-13 Delete the term “standard” in these statements. There is no actual standard configuration for these devices.
- 2-69 1 Clarify what is meant by “In addition to the elevation by EPA.”
- 2-69 2 Delete “and reported by.”
- 2-69 3-6 Change to “The methods included the use of a tunable diode laser (TDL) absorption spectrometer, a wet scrubbing long-path absorption photometer (LOPAP), a wet effusive diffusion denuder (WEDD), an ion mobility spectrometer (IMS), a Nitrolux laser acousto-optical absorption analyzer, and a modified CL analyzer.”
- 2-69 11-13 Change to: “Hence comparisons of ambient NH<sub>3</sub> instruments have confirmed that no single technique has yet been identified that provides automated, high quality results for continuously determining NH at low concentrations.”
- 2-71 5 Be more explicit in using the term “positive artifact” here and elsewhere. Does this mean to suggest that there are overestimates of concentration measurements? Would a better term be something like artifacts resulting in overestimates.
- 2-71 11 See the comment above and modify to avoid confusion I the term “negative interference.”
- 2-78-81 This section could benefit with more focus on the issues related to evaluating SO<sub>x</sub> and NO<sub>x</sub> at the scales important for this assessment with respect to chemical transport models CTMs.



- 2-81-83 Is this review of global scale issue important for the issues associated with regional/local situations. At a minimum this section could be reduced playing particular attention to those global aspects that can have regional implications.
- 2-87 3 In the Picketering et al. citations remove “;”. These format errors need to be corrected throughout the document.
- 2-88 The previous pages (2-78 to 2-87) need to have a clearer linkage to this deposition section.
- 2-89 9-13 Certainly a major issue that needs focus are the errors and problems with estimating dry deposition and a considerable amount of these concerns related to the calculations of deposition velocities.
- 2-90 13-15 The statement that “Deposition rates are independent of leaf area or stomatal conductance, implying that deposition occurs to branches, soil, and the leaf cuticle as well as leaf surfaces” is misleading since leaf area and stomatal conductance are important, but that other factors also need to be included.
- 2-93-95 The section on “Air Quality Model Evaluation” is a critical part of this document.
- 2-94 3-5 These errors can lead to erroneous predictions especially with respect to those associated with future air quality estimates.
- 2-101-202 Figures 2-38 and 2-39 suggest that the model results are quite different than those for the NADP network sites. Doesn’t this bring into question the model validity for predicting these wet deposition amounts?
- 2-104 12-13 Suggesting that Ext-RADM provides “good” agreement when  $R^2$  values are between 0.4 to 0.7 for most species is misleading since at lower values less than 50% of the variation is being explained.
- 2-105 1-4 These statements suggest a better Ext-RADM result. Is this due to the value representing a larger spatial unit and also an estimate for a longer period?
- 2-108 1-4 I am not sure of the rationale for including in PRB the anthropogenic sources outside of U.S., Canada and New Mexico.
- 2-120 Are the measurement protocols in State and Local Air Monitoring Systems (SLAMS) networks sufficiently similar for these measurements to be comparable to CASTNET.
- 2-131 10 Incomplete sentence.
- 2-198-202 Having this summary is helpful in placing the large amount of information provided in the document in context. Some further inclusion of statements relating

to problems with respect to dry deposition estimates including the issues associated with estimating deposition velocities needs to be included.

- 2-199 18-21 This sentence needs to be reworded and likely separated into a series of sentences.
- 3-4 25-26 Why are wetlands given special attention here?
- 3-7 Figure 3-2 caption. Change to “Diagram illustrates soil horizons *commonly found*”.
- 3-9 8 Change to “(Shanley *et al.*, 2005).”
- 3-9 14-15 References are not cited correctly (these are multiple authors) including a need for a letter designation for Driscoll *et al.* (2001)
- 3-9 20 See comment above regarding citation. It appears that this section has many cases where the references are not cited correctly including the absence of showing that the references are multiple authors.
- 3-11 9 Section “0”?
- 3-12 17 Another line with incorrect referencing being used.
- 3-12 30 Another line with incorrect referencing being used.
- 3-16 Figure 3-3 needs a reference.
- 3-17 Figure 3-4 needs a reference.
- 3-19 3-9 Even in the West the nitrate in surface waters during snowmelt is mostly microbially derived and is not from direct atmospheric input. These statements confuse this issue.
- 3-22 4 There are also large differences in tree species to tolerance of different levels of Al. Note this is indicated later in line 14. A clear statement is needed of the major factors associated with Al toxicity.
- 3-22 14 Figure 3-5 does not clearly depict that Al stress varies with species as suggested with this reference.
- 3-25 2-5 The term buffering is not correctly used here. Reword to : Once base saturation decreases to a critical level (approximately 15–20%), inputs of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> result in exchange of inorganic Al.
- 3-25 9-10 Change to “ If the C:N ratio of soils falls below about 20 to 25, nitrification is stimulated resulting in *net nitrification and increased acidity*.”

- 3-27            Figure 3-6 needs a reference.
- 3-34    18-21    Also grasslands tend to be found on soils with relatively high pH and % base saturation. Aren't grassland associated with acidic soils less common?
- 3-39    16            Change to "in *most* affected."
- 3-39    22            Delete "to a greater extent than  $\text{SO}_4^{2-}$ ."
- 3-39    23-24    Delete "The importance of  $\text{NO}_3$  as an agent of acidification varies by region."
- 3-39    29            Delete "Average."
- 3-40    1            Change to "Surface water  $\text{NO}_3$  concentrations have changed over time and these trends vary by regions".
- 3-40    19            Change "outbreak of gypsy moths, which consumed foliage" to "gypsy moth defoliation."
- 3-40    20-21    Delete " in affected watersheds."
- 3-40    32-33    Change to "annual air temperatures were strongly related to average annual  $\text{NO}_3$  concentrations in stream water".
- 3-41    5-6            Was it really suggested that an increase in pH stimulated primary productivity? If this is the case this should be attributed to the authors of the article.
- 3-41    9            Change to "between recent *temporal* trends."
- 3-42    1-2            Change to "(Aber, 2003). Moreover, spatial patterns of  $\text{NO}_3$  concentrations in surface water across the Northeastern U.S. are consistent with atmospheric N deposition values although there is considerable variation in these concentrations based upon watershed attributes.
- 3-42    15-16    Change to "Within western Virginia and in Shenandoah National Park, concentrations of base cations in streams did not exhibit significant temporal trends from 1988 to 2001."
- 3-42    16-17    If sulfate concentrations did not change indicate this explicitly versus an indirect reference to the role of sulfate adsorption.
- 3-43    1-2            See comment above regarding the results from Virginia.
- 3-43    6-7            Delete "The pH of water quantifies the hydrogen ion concentration, which is toxic to many forms of aquatic life."
- 3-43    12            Explain the derivation of these three pH reference levels.

- 3-43 22 Change to “southwestern Adirondacks acidified more compared to other lakes in the Adirondacks since preindustrial time.”
- 3-44 6 Should this be “(0.18  $\mu\text{eq/L/yr}$ )”?
- 3-45 1 Be explicit in referring to this study. I assume this is Stoddard et al. (2003).
- 3-45 18 Do you mean by more stable that ANC is not affected by ambient  $\text{CO}_2$  concentrations? Make this more explicit.
- 3-45 29 Explain these three cutoff values for ANC.
- 3-45 33 Change to “the oxidation of chemically reduced S-containing minerals.”
- 3-47 11-14 Delete “ANC can be measured in the laboratory by Gran titration or calculated on the basis of the difference between the base cation sum and the mineral acid anion sum. Acidic waters are defined as those having ANC less than or equal to zero  $\mu\text{eq/L}$ ”.
- 3-48 33 Not sure the term “limited” is appropriate.
- 3-50-51 References are needed in this text to support the statements.
- 3-52 The following study provides additional information on ANC patterns within the Adirondacks using a mass balance approach: Ito, M. M.J. Mitchell, C.T. Driscoll and K.M. Roy. 2005. Factors affecting acid neutralizing capacity in the Adirondack region of New York: a solute mass balance approach. *Environmental Science and Technology* 39:4076-4081.
- 3-54 I believe some PnET-BGC simulations by Driscoll’s group have also been done that would provide other estimates of the recovery of ANC.
- 3-56 8 Change to “rain *events*.”
- 3-76 32-33 References needed to support this statement.
- 3-79 1-2 A major problem in making wide scale regional projections is that it is well known that the response even within relatively small areas (e.g. almost adjacent watersheds) that the response to acidic deposition can be quite marked.
- 3-79 3-6 It needs to be emphasized that the water pathways and soil depth can be very important in the capacity to neutralize the effects acidic inputs.
- 3-79 13 It should also be stated that this is a threshold which is generally necessary, but does not always result in enhanced nitrate loss.

- 3-80-81 Some inclusion of issues associated with how biotic response can also be altered by other factors such as climate change, invasion of exotics, extreme events (e.g., drought, ice storms, hurricanes, etc.)
- 3-87 Figure 3-19. Why not cite NADP/NTN as the source versus Sullivan et al. (2006a). Also, the more recent data should be included.
- 3-88 In reviewing the results from the Adirondacks focus on those findings specific to the Adirondacks versus generalities associated with acidification of ecosystems.
- 3-89 The PIRLA I and PIRLA II projects provided some of the most definitive evidence of historical changes in acidification of the Adirondacks. Inclusion of some of the figures produced from this project would strengthen the document.
- 3-89-90 The inclusion of figures showing side by side comparison of MAGIC and PnETBCG hind casting would be instructive especially if placed in the context of the PIRLA reconstructions.
- 3-90 8 Provide figures or tables clearly showing similarities and differences between the MAGIC and PnET-BGC simulations.
- 3-91 Table 3-10. Reference needed
- 3-102-123 The structure of the document results in redundancy with some of the information in this section also being presented in previous sections of Chapter 3.
- 3-127 9 Certainly atmospheric deposition is an important contributor, but it also needs to be stated that other forms of N input generally exceed that from the atmosphere.
- 3-127 23 Even for those watersheds exhibiting substantial nitrate loss the vast majority of the N inputs are either being stored or being denitrified within these watersheds.
- 3-128 1-2 Change to “higher rates of deposition with some of these watersheds showing little nitrate losses.”
- 3-128 12-19 Wetlands can also be sources of nitrogen due to nitrogen fixation such as that associated with alders.
- 3-128 23-24 The case for freshwater eutrophication is not strong. The strongest evidence is associated with changes in the biotic assemblages of lakes especially in the Mountain West.
- 3-129 1-4 A more conservative statement is warranted with respect to the contribution of atmospheric deposition so that it is clear that in general this is not the dominant source of N input that is causing eutrophication.

- 3-129 19-25 It should be emphasized that there is also an issue of transient effects where over the short term the additional N results in additional C fixation (e.g. enhanced primary productivity) but this will not continue as other factors limit production over extended periods.
- 3-130 21 Change to “beech.”
- 3-130 25-31 This affect on frost hardiness needs to be linked to issues of red spruce dieback at high elevations.
- 3-133 6-7 Some further elaboration is needed related to results in Europe that have shown that experimental N additions have resulted in higher forest growth and this high growth resulted in other nutrient deficiencies especially in the form of Mg.
- 3-133-136 This discussion on “N Deposition Effects on Productivity and C Budgets in Terrestrial Ecosystems” is generally well done and provides a good synopsis of existing information.
- 3-142 1-13 The discussion on the historical aspects of N limitation in North American lakes is interesting, but it is important to ascertain which is the type of lake nutritional status are the goals of any regulatory programs. It is not likely that there would be a strong mandate to return to pre-Columbian conditions. This situation may be different with respect to desirable endpoints between the eastern and western U.S.
- 3-146 14-15 This needs to be reworded so as not to give the impression that the N is the major limiting nutrient for most lakes. Clear articulation of differences between more pristine versus more developed regions is likely required.
- 3-147-151 The section on estuaries is generally thorough and provides a good review of the influence of N availability on productivity and other aspects of importance to biogeochemical and biotic responses.
- 3-162 10 Change to “100 y.”
- 3-166 16 Change to “documented.”
- 3-152 33-34 It needs to be explicitly stated that atmospheric N loadings is not the sole contributor to the increased N loading in estuaries.
- R-30 There are two Dunlea et al. (2007) references that need to be designated “a” and “b” respectively.

## Mr. Richard L. Poirot

These comments pertain primarily to Charge Question 2 and Chapter 1 of the 2<sup>nd</sup> draft ISA.

**Question 2. Chapter 1 has been revised to clarify the scope or focus of this assessment on effects related to the deposition of nitrogen and sulfur compounds. In addition, we have added a discussion of the framework for evaluation of causality for assessing ecological effects. Do these revisions adequately characterize the scope of the assessment? Does the CASAC panel have recommendations for revisions to the causality framework? Is it appropriately applied in the draft ISA?**

Chapter 1 provides a clear, concise introduction to the ISA, including a brief history of past NAAQS reviews, an outline of the intended scope of the current assessment, and a proposed framework for the determination of causality in relationships between the pollutants of concern and the resulting ecological responses. Overall I think this chapter looks good, and my comments are mostly minor.

While the scope of the assessment is relatively broadly defined – to include for example consideration of ecological effects resulting from N-nutrient enrichment from deposition of both oxidized and reduced nitrogen – there still seems to be a rather intentional avoidance of questions of how such effects or environmental effects may be related to alternative kinds of NAAQS air-quality-related indicators. This question does get taken up to some extent in Chapter 8 of the Risk and Exposure Assessment. However, it might also be useful to add some discussion and display of the inter-relationships among various air quality, deposition and effects metrics as part of the ISA. It would be useful to know up front if deposition-based or critical load-type NAAQS are a possibility, or are we stuck with SO<sub>2</sub> and NO<sub>2</sub>, again?

As indicated in previous comments, I think its unfortunate that the scope of this assessment was narrowed to exclude consideration of visibility effects from aerosol phase sulfur and nitrogen compounds. I think it would have been possible to copy/paste the same discussion of these effects in both the SO<sub>x</sub>/NO<sub>x</sub> and PM secondary NAAQS ISAs (and then decide which NAAQS - if any - would be most effective for addressing all the welfare effects of S & N emissions). In the current case it might also have led to consideration of useful alternative NAAQS indicators – which consideration of aerosol concentrations & effects would help justify. It can also be noted that the working definitions of NO<sub>x</sub> and SO<sub>x</sub> are somewhat awkward here, as NO<sub>x</sub> is taken to include nitric acid and aerosol nitrate, while SO<sub>x</sub> includes only the gaseous oxidized sulfur compounds.

The historical summary of the secondary SO<sub>x</sub> and NO<sub>x</sub> NAAQS reviews is exceedingly brief, and it seems incomplete for example to mention the 1984 EPA Acid Deposition Critical Assessment Document without also mentioning the 1990 NAPAP State of the Science and Technology and Integrated Assessment Reports, the 1990 CAA Amendments (Title IV), and 1995 EPA Acid Deposition Standard Feasibility Study Report to Congress. Granted, these were not part of the NAAQS review per se, but the 1996 decisions not to revise the secondary SO<sub>x</sub> or NO<sub>x</sub> NAAQS were related to these other activities, and represented a clear decision that

the environmental effects of these pollutants were better addressed by other regulatory mechanisms.

The proposed framework for evaluation of causality is logical and clearly presented. So far as I can tell, it appears to be appropriately (and effectively) applied elsewhere in the document – where chapters 3 and 4 contain a number of clear, persuasive statements that “**the evidence is sufficient to infer a causal relationship between ...X and Y**”. With the exception of a few such statements on direct vegetation effects from exposures to specific gaseous S and N compounds, the identified “causal agents” are almost always either “**acidifying deposition**” or “**reactive nitrogen deposition**”, and thus appear to be intentionally non-specific to the traditional criteria pollutant definitions. I think this is fine – even preferable – if secondary NAAQS are being considered that might be deposition-based, combine S&N or combine oxidized and reduced nitrogen. If such alternative metrics are not being considered, than maybe some of these bullets might be rephrased in more pollutant-specific terms. Also perhaps there could be some causality conclusions in chapter 2, in which causal relationships might be inferred between (current and historical) emissions, ambient air concentrations and deposition of various S and N compounds.

Possibly also, the concept of a “significantly contributing factor” could be introduced here (and used later) as a sort of subset of a “causal factor” (i.e. “the evidence is sufficient to infer a causal relationship between Nr, for which oxidized N is a significantly contributing factor, and Z effects...”). This concept of significant contributing factor could be important in considering effects resulting from pollutant mixtures, as well as for considering effects which result from or are modified by the cumulative influences of both current and historical pollutant deposition.

I think the description of the 2-step process in the causality framework could be more clearly presented. There’s a bit of a logic problem with saying first we will determine the causal relationship and then we will determine what effect has been caused. In reality, the process seems to be more one of starting with identifying rather broad, general causal relationships (for example between total Nr deposition and alteration of terrestrial species richness) and then in step 2 winnowing this down to identify more pollutant-specific and/or species-specific relationships at specific ranges of concentrations/exposures. Additional confusion is introduced by apparent inconsistencies between the 2 steps in the causality framework as described in lines 4 and 5 page 1-7, and the subsequent discussion of 2 steps in sections 1.6.1 and 1.6.2. In the first case, step 2 refers narrowly to the determination of whether levels of exposure can be defined at which effects of concern can be observed (kind of a yes/no threshold answer). In the second case (section 1.6.2), step 2 is more broadly and comprehensively defined to consider effects over a range of exposure conditions with evaluation of the shapes of exposure-response or concentration-response functions. Presumably this would also include consideration of estimated future ecological responses to changes (increases or decreases) in pollutant concentration and deposition. For the most part, this ISA seems much more focused on step 1 type conclusions – although there are some very useful tabular presentations of quantitative relationships between N deposition levels and specific ecological effects such as in Table 4-4. I wonder if the intent is to intentionally focus on step 1-type conclusions in the ISA and then develop more detailed quantitative evaluations of ecological response (i.e. step 2) in the Risk and Exposure Assessment. If this is the intent, why not make it clear?



## Mr. David Shaw

### General Comments

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The executive summary is an excellent contribution to the ISA. This addresses some of my previous concerns regarding a clear message of the document.

#### **Executive Summary, Page 2:**

The paragraph which begins with “Expanding urbanization...” has a last sentence explaining heterogeneous deposition. This last sentence might be benefited by the addition transport.

It seems that it would serve the assessment better to have Section 1.7 (page 1-10) appear at the beginning of Chapter 1.

### Charge Questions

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*Chapter 1 has been revised to clarify the scope or focus of this assessment on effects related to the deposition of nitrogen and sulfur compounds. In addition, we have added a discussion of the framework for evaluation of causality for assessing ecological effects. Do these revisions adequately characterize the scope of the assessment? Does the CASAC panel have recommendations for revisions to the causality framework? Is it appropriately applied in the draft ISA?*

I feel that the scope has been properly modified to include both oxidized and reduced forms of nitrogen. Furthermore, I am pleased at the use of “acidifying deposition” throughout the document. This reflects the actual concern of this type of deposition.

#### **Section 1.1, Page 1-3:**

I still feel that particulate matter should not be omitted from this document. As my previous comments state:

PM plays a significant role in nitrogen and sulfur deposition. I feel that separating out the effects of gas- versus aerosol-phase S/N will be difficult, since wet and dry deposition can include both phases, and atmospheric chemistry and transport affect both phases. The ISA clearly states that “particulate NO<sub>x</sub> and SO<sub>x</sub> will be addressed with the secondary PM NAAQS review,” and it therefore becomes crucial that these two review process tracks are highly consistent with each other. One cannot proceed independently of the other track.

#### **Section 1.6, Table 1-1:**

While the causality framework does seem appropriate, it is unclear as to how much weight is given to each aspect. I do appreciate that it clearly states that that scientific evidence will not have to meet all of the aspects of causality, but it might benefit the group to understand how each will be considered in the weighting process (i.e. if no consistency then not used).

**Section 1.6.1, Table 1-2:**

Again, while the descriptors for weight of evidence seem appropriate, I wonder if these could somehow be associated with the causality aspects. For example, given a “weight” in the form of a number for each aspect, add all the aspect numbers for a total. When this total is calculated, apply to the weight of evidence table. Perhaps “sufficient to infer a causal relationship” is used for aspect numbers of 30 or higher (depending on how the number scheme is set).

**Misc.**

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**Page 1-6, line 16:**

Should read “...analyses used appropriately and...”

**Executive Summary**

There is inconsistency in how NO<sub>x</sub> and SO<sub>x</sub> is typed.