Comments from CASAC NO_X & SO_X Secondary NAAQS Review Panel on EPA's *Draft Integrated Science Assessment for Oxides of Nitrogen and Sulfur – Environmental Criteria*
(December 2007)

Comments received:

Dr. Praveen Amar

This write up addresses the first three charge questions from NCEA. The Charge Questions are reproduced below:

1. To what extent is the evidence on atmospheric chemistry and physics, air quality, and deposition and exposure sufficiently and correctly described, clearly communicated, and relevant to the review of the secondary NAAQS for NO_2 and SO_2?

2. How well characterized are the relevant properties of the ambient air concentrations and deposition of NOx and SOx, including policy-relevant background concentrations, spatial and temporal patterns, and the relationships between ambient air concentrations and ecological exposure?

3. How sufficient is the information on atmospheric sciences and exposures for the purposes of evaluating and interpreting the ecological effects presented in Chapter Four of the draft ISA?

Response:

Chapter 2 (The Atmospheric Chemistry and Physics of Nitrogen and Sulfur Oxides, as well as Annex AX1 with the same Title), and Chapter 3 (Ecological Exposure to Oxides of Nitrogen and Sulfur, and to Ammonia and ammonium, as well as Annex AX2 with the same Title) provide a reasonably detailed description of the atmospheric science, air quality, deposition, and exposure. However, the Chapters can and should be improved for more clear communication. It is understandable that various sections have different authorships. These Chapters and other chapters in the ISA would therefore benefit from the services of an expert technical/scientific editor resulting in a more readable ISA that more clearly communicates the important findings of these Chapters (as well as other chapters).

Specific Comments to improve the ISA are provided below:

Page 2-2: Line 8: It is important to state the more important point first, followed by a minor point. Ammonia is included in this ISA, first because of its role in NOx and SO2 chemistry, and its role in nitrification, and, *second* (and a distant second!), because its oxidation can be a minor source of NOx. There are other parts of this ISA that do suffer from the same issue. That is, first order issues should be mentioned first.

A General comment about time scales of various chemicals/reactions: The ISA does a very good job of providing time scales of various reactions and species. However, it would be very useful if many of these important reactions' time scales are presented in a single Table, where readers can compare them in one place and draw meaningful conclusions.

Page 2-4: Line 17: 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 NOx over a certain time period and over a spatial extent, etc.). I suggest it should be explicitly defined first time it appears.

Page 2-7 (Lines 22-23): Awkward and an out-of-context reference to the fact that NO_3 deposition is a “complex function of wind speed.” What does this mean? Needs an explanation.

General Comment about Section 2.2.2: Halogen Chemistry in the Marine Layer: This section is written rather poorly and seems to be out of context with the main theme of SO2 and NOx chemistry. I found it hard to follow. If it has important implications for the deposition of nitrogen and sulfur compounds on coastal and non-coastal/regional scales, they should be stated.

Page 2-9, General Sulfur Chemistry: Besides SO_2, SO_3 though small in amount compared to SO_2 (about 1 to 3 percent of total emitted SOx in stacks) has been known to cause visibility degradation (“Blue plume” downwind of large power plants burning high sulfur coal, and equipped with pollution controls of SCR and FGDs). It needs to be addressed here or in the PM document.

Page 2-10: Line 1: It is stated that aqueous-phase oxidation of SO_2 is responsible for about 80% of the total oxidation (implying that the remaining 20 percent is by homogeneous gas phase oxidation or by metal-catalyzed reactions). However, the ISA should note that the situation is lot more complex than that. For example, which of the various oxidation pathways dominates depends on the details of the local accumulation of the co-pollutants such as ozone, hydrogen peroxide, hydrocarbons, ammonia, and catalytic metals (Fe, Mn, and others). This will have an impact on final deposition levels of sulfur.

Page 2-14: A clear explanation of S (IV) and S (VI) would be helpful.

Page 2-21: Section on Satellites: A comment similar to the comment on Halogen Chemistry above. This section appears to have been written out-of-context and needs to be integrated with the larger context of estimating ecological exposures to S and N deposition and how satellite data may be helpful in providing total loadings of S and N on larger scales that only satellites can provide. Same comment on Table 2.6-1. May be, the Table needs to be removed.

Page 3.2: SOx Emissions: Lines 14-18: The statement that sources other than electric utilities “make only a very minor contribution” to overall SO_2 emissions is quite inaccurate and needs to be corrected. In 2003, the non-EGU sources in the US contributed 31% of the total SO_2 emissions (at 5 mm tpy compared to about 11 mm tpy for EGUs). For example, industrial, commercial, and institutional (ICI) boilers burning coal and oil produce about one mm tpy of SO_2 in the US. Same text appears in the Annex and needs to be corrected. Also, the Summary (page 3-59) needs to be corrected.

Page 3.9 NH_3 Emissions, Lines 23-28: Very awkward description of ammonia emissions. Three-Way catalysts and ammonia emission from them are NOT the primary source of ammonia, and therefore, a description of ammonia emissions must start with known large sources of ammonia (livestock and agricultural operations). Please rewrite for more effective communication and drop the words “for these reasons...”

A potentially important point about ammonia emissions is the geographic shift in ammonia emissions that seems to have taken place in the US between 1980s and late 1990s and may still be accelerating. The attached slide, courtesy of Dr. Bruce Hicks, NOAA, shows that the "center of ammonia emissions" may be shifting from Midwest to the Southeast and the Carolinas. That is, ammonia emissions (in N kg/ha) have increased by about 2 to 3 Kg/ha in the Southeast and gone down by 1 to 2 kg/ha in the Midwest. This shift in density of ammonia emissions has obvious implications on the regional atmospheric chemistry of SOx, NOx, and ammonia and the resulting regional wet and dry deposition patterns for both sulfate and nitrates. ISA should address the impact of this potential trend in geographic change in ammonia emissions.

Page 3-10: Section 3.4: Evaluating Emission Inventories: The ISA should note that the FIRST step to evaluate EIs is not by looking at the ambient concentrations, but by taking into account the methods that are used to produce emission inventories themselves (use of emission factors, use of CEMs, QA/QC methods, uncertainty in determining spatial and temporal profiles, speciation factors for VOCs and primary PM emissions, etc.).

Page 3-11, Section 3.5.2 NO2: Say "NO_2 interaction with vegetation is MORE DIFFICULT TO UNDERSTAND than…."

Page 3-16 Line 10: Not clear about the distinction between "aerosol-phase" and "solid-phase". Are they not the same in the context of atmospheric chemistry of aerosols?

Page 3-16, Line 7: "Title IV Reductions in NOX and SO_2" and not N and S.

Page 3-17, Figure 3.6-3: The Title needs to be modified to indicate that the Figure also shows trends, if any (2002 to 2006).

Page 3-19, Lines 8-10: Please rewrite for clarity.

Page 3-21: Satellites: same comment as above. Please note the larger context of S and N deposition.

Page 3-34: Section 3-9: Harvard Forest: I have a comment similar to the comment on Halogen Chemistry above. It reads as an independent piece without being integrated into the ISA. It is too long and not clear. Please shorten it and rewrite.

Page 3.12 PRB Concentrations of NOx and SOx: This is well-written section and does a very good job of responding to the Charge Question 2 on the subject of PRBs of NO_2, SO_2, and nitrate and sulfate deposition over various regions in the US and at different time scales.

A General Comment on Dry Deposition: The ISA needs to be more clear and explicit that we only ESTIMATE dry deposition and therefore comments about total deposition (wet and dry) and about the relative contribution of each pathway have a level of uncertainty that is hard to determine.

In summary, Chapters 2 and 3 and annexes address the first three charge questions on atmospheric science and ecological exposure in a satisfactory manner. However, the whole document needs a thorough technical and scientific editing job as well as a better integration of some of the sections (Halogen Chemistry, Harvard Forest, satellites use) into the overall ISA.

Chapter 5: Findings and Conclusions

General Comment: This Chapter does a good job of summarizing the ISA with major "take home" messages. As noted above for Chapter 2 and 3, this Chapter does need a thorough scientific editing job for it to communicate complex concepts in a clear manner.

Specific Comments follow:

Page 5-2 Section 5.2.2: The conclusion drawn here that current routine monitoring is "adequate" or 'fully adequate" after listing major problems with measurement of gaseous and particulate species does not seem to be justified. I think it is a matter of tone and the revised language should indicate WHY the current network is adequate.

Page 5-3 Line 30: Please see the comments for Chapter 2 about SO_2 emissions from sources other than power plants. They are not "very little," since they are about 1/3 of the total SO_2 emissions.

Page 5-11: Lines 20-31: Not clear why there is no relationship between recent trend in N deposition and trends in nitrate concentrations in surface waters. Have the recent reductions in NOx emissions in the eastern US because of the "NOx SIP Call" taken into account?

Page 5-36: Line 20: Please see my comment above on "adequate monitoring." Here, it says that the monitoring networks are "inadequate." Need to be consistent.

Dr. Andrzej Bytnerowicz

Chapter 4. Effects of Acidification and Nitrogen Enrichment on Ecosystems and Other Welfare Effects

General Comments:

This is a well written and comprehensive chapter presenting state of the scientific knowledge on ecological effects of acidification, nitrogen nutrient additions and other welfare effects of N and S. The chapter is very informative and is based on the relevant and current peer-reviewed literature from North America and Europe.

What seem to be missing are research and monitoring needs and recommendations that could help in establishing a sound national program leading to a better understanding of biological effects of N and S deposition which would possibly lead to establishment of a national, biologically-based NOx and SOx standards.

Specific comments:

Page 4-4, Figure 4.1.-1. should be changed to Table 4.1.-1.
Why eutrophication is not shown as a possible disturbance if forests?
In row 7 (atmospheric pollutant), the end products of deposition are shown, but not the pollutants causing biological effects (e.g., NO_2, SO_2, HNO_3, NH_3, particulate NO_3, particulate NH_4).

Page 4-5, point 7 – ammonia (NH_3) should be listed as well.

Page 4-9, Figure 4.2-1 mixed up with Fig. 4.2-2.

Page 4-13, lines 12-27. Elevated levels of tropospheric ozone and land disturbances such as catastrophic fires should be mentioned as factors affecting water resources of ecosystems and their leaching potential.

Page 4-22, lines 25-27. This could be a good recommendation for future research needs.

Page 4-29, lines 27-28. Reduced cold tolerance is also caused by euthrophication.

Page 4-35, line 14. These effects on epiphytes, if I recall, were also caused by NO_2 and SO_2.

Page 4-35, section 4.2.2.2.3. The described effects are to a large extent not caused by acidity but direct toxic effects of SO_2 on plants.

Pages 4-38 through 4-44. Change SO_4^+ to SO_4^{2-}.

Page 4-66, lines 26-28. Reference is needed.

Page 4-73, lines 28-32. It is a very important statement – clearly no single "definitive" critical load for US ecosystems is possible. The eco-regional approach to the CL issue seems to make most sense.

Page 4-98, lines 15-17. Is it contribution of gaseous HNO_3 or of total dissolved NO_3^-?

Page 4-121, lines 18-20. In regard to changes in lichen species composition, there differences in responses to reduced vs. oxidized N. It has been proposed that elevated levels of HNO_3 have negative effects on sensitive lichens such as *Ramalina menziesii* in the San Bernardino Mountains of southern California (Riddell et al., 2008). Such effects are attributed more to the direct HNO_3 toxicity than NO_3^- deposition. There is also a high probability that the reduced N resulting from high NH_3 and particulate NH_4^+ could affect lichens downwind of the Los Angeles pollution sources area (Prof. Eva Barreno, personal communication). However, it has to be remembered that the disappearance of lichens in southern California could also be caused by high levels of ambient ozone in the area (Nash and Sigal, 1998; Sigal and Nash, 1983).

Page 4-122, lines 20-26. It should be added that increased mortality of the high elevation trees in areas of elevated N deposition could be partially caused by their increased sensitivity to frost.

Page 4-129, section 4.3.3.1.4. This section should be incorporated into the forests section (4.3.3.1.1) (see my remarks below).

Page 4-131, section 4.3.3.1.6. This section should be divided and moved into "forests" and "arid & semi-arid" ecosystems (see my remarks below).

Page 4-147, lines 28-30. Transitional ecosystems (as mentioned in the previous sentences) should also be added.

Page 4-152, lines 15-18. I do not see a logical link here. If estuaries and coastal water are inherently sensitive to increased N loading, that should not be because of the high releases of N inputs back to the atmosphere (high microbial activity). Increased release of N into the atmosphere would as an avoidance mechanism in presence of excessive N loads.

Page 4-154, lines 21-24. Ranges of deposition that may be affecting sensitive species seem to be mixed up – levels in alpine ecosystems should be lower than in other terrestrial ecosystems (see Baron et al. 2000; Bowman et al., 2006) cited in this ISA document.

Page 4-162, line 8. S deficiency level at <80 µg/g seems to be very low. In Scots pine foliage in the pristine area of Europe the lowest recorded level of S was ~400 µg/g (Molski et al., 1981).

Page 4-176. Section on the direct effects of HNO_3 on plants should be considered and possibly added.

Page 4-180, Table 4.2-2. Add "of" after "Example".

Page 4-186, Table 4.2-9. Change "eith" to "with" in the second line.

Page 4-189. Table 4.3-2. in the column “Factors that govern vulnerability”, add a sentence “Interactions with other contributing stressors such as elevated levels of ozone or drought”.

Replies to the assigned questions:

1. How well are the major effects of NOx as it contributes to nitrogen enrichment of the ecosystems appropriately identified and characterized?

Generally the effects of NOx contribution to the N enrichment of various ecosystems are well described. These effects are divided into the terrestrial, transitional, aquatic (fresh water and estuarine and coastal water) ecosystems. Two case studies (alpine and sub-alpine communities in Colorado and in Chesapeake Bay) are described. Some other case studies could be possibly added – such as the mixed conifer forest of the San Bernardino Mountains (Fenn and Poth, 1999; 2001; Fenn et al., 2003) and grassland ecosystems in the San Francisco Bay area (Weiss, 1999).

2. To what extent do the discussions and integration of evidence across scales (e.g.. various species, communities, ecosystems, and regions) correctly represent and clearly communicate the state of science?

Generally the effects (biogeochemical processes and biological effects) have been described (as in point 1) for the terrestrial, transitional and aquatic ecosystems from a perspective of the effects indicators. Some confusion is caused by separating herbaceous and plants and shrubs (4.3.3.1.4) and mycorrhizal and microbial activity (4.3.3.1.6) into separate sections. Information contained in those sections should be incorporated in to the forests (4.3.3.1.1) and arid and semi-arid ecosystems (4.3.3.1.3). Lichens could stay alone since their evaluation surveys have been done mostly for larger geographic areas encompassing various ecosystems (often including agricultural or the urban-wildland interface). What is missing are the desert ecosystems – effects of N deposition in these N-limited systems, especially in the vicinity of strong N sources areas, should be mentioned. A good example is the Mojave Desert in California which is strongly affected by N deposition from the Los Angeles area. There are only a few references referring to those problems, however, research is ongoing at the University of California in Riverside (Allen et al., 2008).

3. How well characterized are the relationships between ambient atmospheric nitrogen concentrations, nitrogen deposition and total nitrogen loads, and environmental effects?

These relationships are not well described. This is mainly caused by a lack of sufficient understanding of these relationships. Understanding responses of ecosystems to N addition are often based on fertilization experiments, using mainly NH_4NO_3 or $(NH_4)_2SO_4$ additions and assuming that these additions would simulate wide spectra of atmospheric N deposition scenarios. More experiments on natural N deposition gradients, with the adequately identified N components (gases, aerosols and soluble ions), should be conducted. Deposition of N to forest ecosystems is calculated mostly from throughfall data with an assumption that wet and dry deposition components are included. This approach has been used at large scales in Europe and helped in calculating critical loads for N and S deposition and acidity (ICP Forests and ICP Maps and Modeling products). However, the N dry deposition component, especially when there is not sufficient precipitation to remove N deposited on foliage and other surfaces to throughfall solution, may be grossly miscalculated. The inferential method (using information on ambient concentrations of major N deposition drivers, their deposition velocity as well as canopy characteristics, such as leaf area index, LAI) may be helpful in such cases. This method could also be applied in such ecosystems (grasslands, deserts, alpine and sub-alpine ecosystems) where throughfall cannot be used at all or is very difficult to be applied. The inferential method has numerous limitations and uncertainties, however, it can be used for large geographic areas. This method is the basis for the CASTNet estimates of N dry deposition at the national scale. It has to be remembered, however, that there is not enough data for ambient NH_3, which is one of the main drivers of N dry deposition. In addition, understanding of N deposition in complex (mountain) terrains is still poor.

4. To what extent has the draft ISA adequately characterized the contribution of oxidized and reduced forms of nitrogen to ecological effects related to nutrient enrichment?

Contribution of reduced vs. oxidized forms of atmospheric nitrogen to nutrient enrichment effects are not well understood and subsequently not well described in the ISA. The main reason for that is an inadequate understanding of the chemical environment of ecosystems for which the effects of N deposition are being described. As I mentioned above, most of knowledge on the ecosystem responses comes from the fertilizer studies. Such experiments are well suited for understanding biological effects of N in the wet deposition dominated ecosystems, such forests in the eastern United States. However, in the arid and semi-arid ecosystems, where large portion of N deposition may result from gaseous HNO_3, NH_3 or particulate NO_3^- or NH_4^+, fertilization experiments may quite poorly mimic the real-world interactions between the atmosphere and ecosystems (vegetation, soils and surface water components).

Recommendations:

1. While SO_2 and NOx concentrations should be monitored for health reason (primary standards), they have very limited application for evaluation of environmental (ecological) effects. Therefore there is a need for monitoring concentrations of major drivers of N & S deposition. For S, this is mostly SO_4 in wet precipitation measured nationally (e.g. NADP network). However, for N, not only wet NO_3 and NH_4 deposition (also measured nationally), but also dry deposition of gaseous HNO_3, NH_3 and particulate NO_3 and NH_4 as well as the organic compounds should be included. Activities of the national monitoring networks, especially CASTNet should be continued and expanded, especially in the underrepresented Western US.
2. For preliminary determination of HNO_3 and NH_3 “hot spots”, use of passive samplers should be considered. Passive samplers have already been successfully used in monitoring networks in California: Sequoia National Park (Bytnerowicz et al., 2003), Lake Tahoe (Gertler et al., 2006), or Joshua Tree National Park (Allen et al., 2008). Presently these samplers are used in various monitoring campaigns in the US (Sierra

Nevada, Southern California, Columbia River Basin), Canada (Athabasca Region), and Europe (Bucegi National Park in Romania).

3. National efforts in ecological monitoring of N & S deposition effects are needed. Such efforts could be similar to those in Europe under the auspices of the UN Economical Commission for Europe, namely the ICP Forests Level and ICP Modelling and Mapping efforts. Monitoring results from the ICP Forests Level II plots have allowed for determination of CL and their exceedances. The newly developed US Forest Service Experimental Forests network for CL estimates consists of 21 sites across the US. Research collaboration within the US as well collaboration with the Canadian and European partners is planned. This new effort will help to determine if the CL approach could be applied and be practical in the US.
4. If successful, the monitoring efforts in the USFS Experimental Forest Network could be expanded into a denser national network. It is envisioned that USFS Forest Inventory and Analysis (FIA) Phase 3 (Forest Health Monitoring) sites could be utilized for such efforts. The Intensive Site Monitoring (ISM) site that would integrate the FIA Phase 3 and the ICP Forests Level II-type plots will be established in the San Bernardino Mountains of southern California this summer.
5. Effective collaboration between EPA, various national monitoring networks, and land management agencies such as US Forest Service or National Park Service, in developing a national program for monitoring and evaluation of N & S effects on ecosystems, including CL calculations, should be encouraged.

References:

Allen, E.B., L. E. Rao, R.J. Steers, A. Bytnerowicz, and M.E. Fenn. 2008. Impacts of atmospheric nitrogen deposition on vegetation and soils in Joshua Tree National Park. In R.H. Webb, L.F. Fenstermaker, J.S. Heaton, D.L. Hughson, E.V. McDonald, and D.M. Miller, eds. The Mojave Desert: Ecosystem Processes and Sustainability. University of Nevada Press, Las Vegas. In press.

Báez, S., Fargione, J., Moore, D.I., Collins, S.L., and Gosz, J.R. 2007. Atmospheric nitrogen deposition in the northern Chihuahuan desert: Temporal trends and potential consequences. J. Arid Environ. 68, 640-651.

Bytnerowicz, A., Tausz, M., Alonso, R., Jones, D., Johnson, R., and Grulke, N. 2002. Summer-time distribution of air pollutants in Sequoia National Park, California. Environmental Pollution, 118, 187-203

Fenn, M.E., Haeuber, R., Tonnesen, G.S., Baron, J.S., Grossman-Clarke, S., Hope, D., Jaffe, D.A., Copeland, S., Geiser, L., Rueth, H.M., and Sickman, J.O. 2003. Nitrogen emissions, deposition, and monitoring in the western United States. BioScience 53, 391-403.

Fenn, M. E., and Poth, M. A. 1999. Temporal and spatial trends in stream water nitrate concentrations in the san Bernardino Mountains, southern California. J. Environ. Qual., 28, 822-836.

Fenn, M. E., and Poth, M. A. 2001. A case study of nitrogen saturation in westen U.S. forests. Sci. World J., 1, 433-439.

Gertler, A., Bytnerowicz, A., Cahill, T. A., Arbaugh, M., Cliff, S., Kahyaoğlu-Koračin, J., Tarnay, L., Alonso, R., and Fraczek, W. 2006. Local air quality threatens Lake Tahoe’s clarity. California Agriculture, 60, 53-58.

Molski, B., Bytnerowicz, A., and Dmuchowski, W. 1981. Content of sulphur and fluorine compounds in Scots pine needles as an indicator of air pollution in Poland. Silva Fennica, 15, 4, 419-421.

Nash, III, T. H., and Sigal, L. L. 1998. Epiphytic lichens in the san Bernardiono Mountains in relation to oxidant gradients. In: Miller, P. R., McBride, J. R. (eds.) Oxidant Air Pollution in the Montane Forest of Southern California. A Case Study of the San Bernardino Mountains. Ecol. Stud., vol. 134, Springer, New York, 223-234.

Riddell, J., Nash III, T. H., and Padgett, P. 2008. The effect of HNO3 gas on the lichen *Ramalina menziesii*. Flora, 203, 47-54.

Sigal, L. L., and Nash, III, T. H. 1983. Lichen communities on conifers in southern California: an ecological survey relative to oxidant air pollution. Ecology, 64, 1343-1354.

Weiss SB. 1999. Cars, cows, and checkerspot butterflies: Nitrogen deposition and management of nutrient-poor grasslands for a threatened species. Conservation Biology 13, 1476-1486.

Ms. Lauraine Chestnut

Charge question 11 (appropriateness and comprehensiveness of conclusions?)

The review of relevant economic valuation studies is included only as an appendix and is not incorporated into the conclusions. Table 5.5-2 lists some results of water quality valuation studies in the Chesapeake Bay, but I don't see discussion of this table in the text. As a result of both of these factors the treatment of the economic valuation literature seems disconnected from the review of the science. It is not clear how the review of the economics literature contributes and fits into this ISA. There was mention in the introduction that economic valuation may be helpful in assessing what effects are adverse, but I don't see any discussion of how the current literature may be useful in this regard in the appendix or in the findings and conclusions. There seems to me something circular in this idea that the economics studies can help assess when an affect is adverse. When it comes to direct use values, then it may be so. However, for total value (including nonuse, bequest, and even some indirect use values) this is not so clear. The public can only assess these values when they are fully informed about what the changes to the ecosystem resources are, including an understanding of the implications of these changes on the quality of the many ecosystem services that these resources provide. This information and understanding has to have its foundations in the science.

Charge question 12 (adequate information and guidance for the exposure, risk and policy assessments?)

In reviewing the ISA I kept looking for two types of information that seem to be key to this process of considering secondary standards:

1. What information is there that tells us when a change in an ecosystem might be considered adverse?

2. What levels of deposition/exposure can a system tolerate without incurring adverse changes?

Perhaps these questions are to be addressed more explicitly in the risk assessment phase. I didn't see them explicitly addressed in the ISA. A few observations related to the question of what exposures can be tolerated include:

1. Exposures that can be tolerated vary for different resources and different locations according to several known characteristics.

2. It will be very hard to say what levels of N deposition can be tolerated when there are significant other sources in aquatic systems (esp estuaries).

3. The answer may be different for recovery of currently injured sources than for prevention of future degradation.

4. The question is complicated by episodic events (e.g. spring runoff) that cause temporary but damaging increases in exposures.

The ISA notes that the current secondary standards for SO2 and NO2 were not set to address the effects of deposition, but has the case been made that these standards are not sufficiently protective? Perhaps this is obvious, but if current standards are being met and adverse affects are still occurring, then the standards are not adequate. Related to this issue is the question of whether adverse effects of deposition will continue once the primary NAAQS for PM are met. These standards are going to require further reductions in SO2 and NOx emissions. At what point in this process does it need to be assessed whether the reductions in deposition that will result will be sufficient to protect ecosystem resources, or is this not relevant?

Dr. Douglas Crawford-Brown

This review focuses primarily on Chapter 5: Findings and Conclusions, although it draws on information in the earlier chapters from which the Findings were drawn. My first very general comment is that the Findings did, I believe, comport with the major conclusions one might draw from the earlier chapters. At least, they summarized what I took to be most of the main points in these earlier chapters, although I caution that I am not an ecologist and so there may have been significant points made earlier that did not make their way into Chapter 5.

It was a bit hard (perhaps too hard) to get the subsections of Chapter 5 to match the way the earlier chapters were organized. This is due largely to the fact that Chapter 5 itself does not have any systematic approach to presenting the findings and conclusions concerning effects (which is really the focus of the NAAQS process). The effects are divided between Acidification; Nitrogen Nutrient Enrichment; and Other Welfare Effects. Then these three major classes of effects are subdivided in various ways (such as Aquatic; Terrestrial; etc). However, the subdivisions are not consistent across the classes of effect. I suppose this might be because some of the subdivisions are relevant for one class of effects and not others, but I can't see any reason why this should be the case. It would have been much more helpful to have the three major classes subdivided into the same set of subsections so the reader can quickly go through and find, for example, the Biochemical Effects for all three classes. The needed information is all there, I just wanted a more consistent structure to the presentation of it.

I also didn't understand the case studies. I could find no consistency in the way they were approached, or any conclusions that could be drawn from them. There was no explanation of what they are doing within the document (i.e. what the reader is to take from them). They struck me as an arbitrary set of rather poorly detailed cases – I'm sure the authors had some reasons for selecting them, but this was not evident.

My final general quibble is with the highly qualitative nature of many of the conclusions on ecological effects, and the general presumption that an effect is the same as an adverse effect. The chapter is littered with phrases such as "could cause", "are thought to", etc. There is an implicit assumption throughout that ecosystems are in their optimal states before NAAQS-relevant sources are added to the world, and that all these sources can do is weaken ecosystem health. Perhaps the authors don't intend this implicit assumption, or the impression that the phrases I mention count as strong evidence for any sort of belief, but I was left uneasy with many of the conclusions for the reasons above.

I now have some specific comments on parts of Chapter 5:

1. On Page 5-2 at the bottom, the authors conclude that measurements below the detection limit cause "irresolvable uncertainty in these data". I agree with the sentiment here, but there are policy and regulatory decisions that can be made that don't have this "irresolvable uncertainty". For example, if the regulatory limit is well above the detection limit, and all the positive results are below the regulatory limit, then a large number of results below the detection limit does not prevent a decision as to whether a site is in compliance to be made with high levels of certainty.

Whether the “irresolvable uncertainty” has any implications for decisions depends entirely on the kind of decision being taken.

2. On Page 5-4, first bullet, the authors state that “annual NOx has decreased < 35% over the years”. It was not clear whether this is to mean it has decreased by less than 35% of the baseline year (1990) or has decreased TO LESS THAN 35% of the value in the baseline year.

3. On Page 5-6, the authors correctly state that it is possible that small amounts of SO2 may be beneficial. It would be useful to indicate how this amount compares to the levels considered under a NAAQS and the levels currently found in the environment. If the amounts that are beneficial overlap the amounts found in the environment, this has significant implications for the NAAQS. And it also would be useful to characterize the evidence for beneficial effects, since it indicates that the exposure-response curve may be U-shaped. Focusing only on the “bad” effects leaves the document open to charges of bias and presumes there is some sort of monotonic increase of bad effects with exposure, or a threshold below which effects don’t occur (but also are not beneficial).

4. In that same paragraph, the authors state that lack of observation of a change doesn’t mean that no change is taking place (it may have been below the ability to detect such a change). I just want to be sure it is also understood that this statement cannot be used to therefore justify regulatory action; the evidence simply becomes neutral with respect to decisions being taken.

5. On Page 5-11, the second bullet, the authors conclude that a lack of relationship may indicate that the trends are on a time scale longer than is being measured. Well, yes, this could be the case. Or it could just be that there IS no relationship. I find this pattern throughout the document: a tendency to explain away a lack of relationship as being due to some limitation in the data, rather than the simpler, and more truthful, claim that there has been no trend observed to date.

6. On Page 5-12, first bullet, line 16, the term “likelihood” is used. I couldn’t figure out the sense in which it is being used here. I assume it is not in the statistical sense.

7. On Page 5-15, last full paragraph, the final sentence doesn’t seem to me to follow from the evidence presented, unless one assumes that ANC values are the sole determinant of acidic episodes. I won’t comment further on this, because it is not my area of expertise, but this implicit assumption must be made and so I was left wondering where the evidence was given to support it.

8. Throughout the discussion on NOx and SOx deposition, I could not find any recognition, or at least explicit consideration, of deposition onto land that then enters a waterbody through run-off. I am assuming it is being considered even if not called out directly in the text.(?)

9. On Page 5-17, last bullet, the issue of Hg increasing in fish is brought up. I realize that the authors are suggesting here that this increase above “safe” levels is due in part to the effects of acidic deposition, but this section is focused on effects and no specific effect is mentioned (unless one takes the increased Hg itself as an effect, which is what I presume the authors

intend). But there should at least be some mention of the extent to which this increase in Hg is due to the effects of acidic deposition and not just to loading of the original Hg into the waters.

10. On Page 5-18, first paragraph under 5.5, we find another instance in which a change is automatically considered adverse. The argument is that excess N creates "unnatural rates in some species and change in the competitive interactions…". This is then followed by the claim that this will decrease ecosystem health and biodiversity. Again, I am not an ecologist, but my reading of the literature suggests it is far from evident that all such changes weaken ecosystem health (unless one assumes *a priori* that ecosystems are in their optimal state of health absent increased N). Or the key may be in the term "excess". Perhaps the authors have some idea as to what level of N constitutes an "excess" and are referring only to this condition, in which case we have a tautology (the level of N that is "excess" being by definition the level of N that causes weakened ecosystem health). Without addressing this issue, the reader is likely to assume that "excess" is the same as "increased", which would not be true.

11. On Page 5-19 at the top, it seems to me that there is an assumption being made here that all N in the system is bioavailable. I may be wrong in this, but it does seem to me that assumption is inherent in the paragraph. At the bottom of that same page, the authors refer to the "availability of NO3-. I wonder if they mean "bioavailability" or if the two terms are interchangeable.

12. On Page 5-21, line 13, it is noted that a change in shoot-to-root ratio can be adverse. I would guess it is adverse primarily if the ratio increases, not decreases.

13. On Page 5-26, line 12, it is mentioned that the function is not linear, but no indication is given of the kind of non-linearity it represents. Some clarity here would be good (threshold, positive second derivative, negative second derivative, U-shaped, etc).

14. The Regional Trends sections struck me as unsatisfactory throughout the chapter. I was never clear, in any of them, what important conclusions, related to a NAAQS decision, I was to take away. It wasn't even made clear why a regional trend is of interest.

15. On Page 5-31, a list of biological measurements to assess eutrophic condition is provided. But I don't see why this list is here. I can find no way in which it informs the later discussion or conclusions.

16. The discussion of Greenhouse Gases beginning on Page 5-35 is confusing, or at least given in too much of a sketch. I haven't any idea what the reader is take away from this.

17. On Page 5-36, the first sentence states that in the chapter data were "integrated and collectively considered in formulating conclusions". I don't think the chapter accomplished this, or made it evident. I am not saying the conclusions are wrong, or that the authors didn't have good reasons for giving them. I am simply saying that the chapter doesn't lay out all clearly how the data were "integrated and collectively considered". I would be more inclined to say that the data were collected together, the authors considered them, and conclusions were formulated (in ways that are not transparent to the reader).

18. On Page 5-37, line 11, there is an instance of something that appears in other places in the chapter. Some N and S deposition rates are mentioned, but there is no indication given as to whether these are large or small compared to deposition rates one would expect under NAAQS levels. The reader is left, therefore, wondering whether these deposition rates are significant with respect to any decisions that must be taken under NAAQS.

19. The final sentence of the chapter is that "The Chesapeake Bay is an example of a large well-studied estuary that receives 21 – 30% of its total N load from the atmosphere". This seems a very odd way to end the chapter, as this sentence is essentially a *non sequitur* and certainly doesn't summarize any of the important conclusions.

Dr. Paul Hanson

My comments include general thoughts on the organization and content of the ISA, comments on specific chapters and items within the text, and written summaries for the Charge Questions to which I was assigned.

General Comments:

The Integrated Science Assessment (ISA) provides a concise, but occasionally cursory overview of the key scientific issues for nitrogen and sulfur oxides (and related chemical compounds) related to atmospheric chemistry and physics (Section 2), ecological exposures (Section 3), and effects (Section 4). The section on effects is missing a brief discussion of the importance of NOx as an ozone precursor. While the welfare effects of tropospheric ozone need not be fully covered in this ISA in detail since they have recently been reviewed as a part of the recently completed review of photochemical oxidants, the key role that NOx plays as a precursor to ozone formation in the troposphere does need to be included in the ISA.

The ISA would benefit from the addition of a specific section on the complexity of N and S biogeochemical cycles and the need to understand all natural and anthropogenic inputs and outputs to these cycles.

The most readable and best prepared section of the ISA was Section 5 on Findings and Conclusions. In fact, I recommend that Section 5 be brought forward and be presented as the introductory summary of the document. The Findings and Summary text (Section 5) strikes the right balance between the beneficial and adverse effects of N deposition that was largely missing within Section 4. In a lead-off position within the ISA, the Findings and Summary section would provide the key conclusions from which an interested reader might then search for additional details and support within the document and its Annexes. All key conclusions within the Findings and Summary section should include parenthetical references to the pages within the ISA or appropriate Annex that the reader could look to find the justification for the conclusions.

For continuity with the previous Air Quality Criteria Documents (AQCD) for nitrogen and sulfur oxides, summary materials from those documents that have not been changes through the publication of new research might be brought forward and used within the ISA. For example, little new information has become available on the direct effects of NOx and SOx on plant response, but the quantitative understanding of the generally high ambient concentrations needed to illicit adverse responses to direct NOx or SOx exposures should be reiterated within the ISA. Section 5 provides the general statements of limited direct effects at current ambient concentrations, but Section 4 could include a summary of key data from the previous AQCD in support of those statements.

When adverse effects are discussed within Section 4 of the ISA they should (where possible) be referenced to the state of current exposures presented within Section 3. Tell the reader how to interpret a multi-year exposure to 20 to >100 kg N ha^{-1} y^{-1} deposition in an experimental setting relates to measured ambient levels typically maxed out near 10 kg N ha^{-1} y^{-1}.

The authors have not taken full advantage of the Annexes. By my count Annexes 1 and 2 were cited 7 and 11 times, respectively, but Annexes 3 through 10 were cited only 2,1,1,0, 1,0,0, and 1 times, respectively, throughout the entire document. The Annex material should serve as a source of expanded information for the reader to highlight key points made within the ISA. In their current form and level-of-use the Annexes are not very useful to the reader.

References to primary research articles and cross-references to key discussions within the ISA and Annexes are often left out or ignored. This deficiency must be corrected. I offer some suggestions in the specific comments listed below.

I limited literature search for nitrogen deposition and impacts research conducted from 1991 through 2008 produced a number of research articles that are not mentioned or evaluated within the ISA. To the extent that this oversight needs to be corrected I will attach the full listing of references for EPA's use.

Comments on uncertainty – the use of maybe, if, probably, possibly….etc.

Specific Comments:

Chapter 1

Page 1-2 lines 5 to 22: Add a bullet asking if the form of the current secondary standard is appropriate for the evaluation of and protection against adverse effects.

Page 1-5 lines 12 to 15: Even though no substantive research has been generated on the topic of gas phase responses to NOx and SOx since the publication of their respective most recent AQCDs. The ISA should include a brief overview and quantification of the air concentrations of gaseous forms of N and S necessary to generate adverse responses.

Chapter 2

Page 2-16 line 10: The term sensitive ecosystem is used here prior to it being defined in the context of the ISA.

Chapter 3

Page 3-11: Section 3.5.1 is inadequately referenced. The authors should either add references or point to a more detailed discussion within an Annex or to pages within a previous AQCD where such a discussion can be found. The following reference might be quoted as a demonstration of how HNO_3 is incorporated into foliage:

Hanson PJ, Garten CT (1992) Deposition of $H_{15}NO_3$ vapor to white oak, red maple and loblolly-pine foliage - experimental-observations and a generalized-model. New Phytologist 122:329-337.

Garten CT, Schwab AB, Shirshac TL (1998) Foliar retention of N-15 tracers: implications for net canopy exchange in low- and high-elevation forest ecosystems. FOREST ECOLOGY AND MANAGEMENT 103: 211-216.

Vose JM, Swank WT (1990) Preliminary estimates of foliar absorption of N-15 labeled nitric-acid vapor (HNO3) by mature eastern white-pine (Pinus-strobus) CANADIAN JOURNAL OF FOREST RESEARCH 20:857-860.

Page 3-11: A number of useful references could have been added/cited within this section. For example:

Ammann M, Siegwolf R, Pichlmayer F, et al. (1999) Estimating the uptake of trafficderived NO2 from N-15 abundance in Norway spruce needles. Oecologia 118: 124-131.

Boyce RL, Friedland AJ, Chamberlain CP, et al. (1996) Direct canopy nitrogen uptake from N-15-labeled wet deposition by mature red spruce. CANADIAN JOURNAL OF FOREST RESEARCH 26: 1539-1547.

Nussbaum S, Vonballmoos P, Gfeller H, et al. (1993) Incorporation of atmospheric (NO_2)-N-15-nitrogen into free amino-acids by Norway spruce picea-abies (l) karst. Oecologia 94:408-414.

Qiao Z, Murray F (1998) Improvement of the N-15 dilution method for estimation of absorption of NOx by plants supplied with N-15-labelled fertilizer. New Phytologist 138:13-18.

Segschneider HJ, Hutzen H, Forstel H, et al. (1993) Uptake of (NO2)-N-15 and metabolic transfer of the (NO2)-N-15 nitrogen to various nitrogen fractions of sunflowers. ISOTOPENPRAXIS 29:51-57.

Vallano DM, Sparks JP (2008) Quantifying foliar uptake of gaseous nitrogen dioxide using enriched foliar delta N-15 values. New Phytologist 177: 946-???

Vonballmoos P, Nussbaum S, Brunold C (1993) The relationship of nitrate reductaseactivity to uptake and assimilation of atmospheric (NO2)-N-15-nitrogen in needles of norway spruce (Picea-abies [l] Karst). Isotopenpraxis 29: 59-70.

Page 3-11 lines 24 to 25: A reference is needed for this statement. Perhaps the following:

Hanson PJ, Rott K, Taylor GE, et al. (1989) NO_2 deposition to elements representative of a forest landscape. Atmospheric Environment 23:1783-1794.

Page 3-12 line 21: A reference is needed for the 1 ppb compensation point quoted here.

Figure 3.6-1: Why is this figure used? Shouldn’t it be a summary of NOx and SOx issues?

Figure 3.6-2. The caption should read ‘Aggregate map **of** the majority of routine U.S. monitoring stations.’

The Figure and brief paragraphs on page 3-17 seem unnecessary.

Section 3.7.1 would be improved with the inclusion of the graph demonstrating the nature of NOx concentrations through time (i.e., over decades). Is this data not available? The graphics provided for SOX and nitrogen and sulfur deposition in subsequent sections nicely demonstrate the declining nature of N and S inputs to most regions from the late 1980s early 1990s in when compared to 2004 to 2006 data.

For places where a complete continuous record exists it would be appropriate to include a graphic showing the full trajectory of N and S deposition through measured time.

Captions for the Figure 3.8-x series need to include a description of the source of the data within the figures.

Statements made at the top of page 3-41 need to be referenced to their source literature. In general, Section 3 suffers from inadequate attribution of the primary source data.

The total and background axes with the figures on pages 3-52, 3-53, 3-55, and 3-56 should be made the same. As drawn, the figures make it difficult to judge the level of background N or S levels against current totals. I would also recommend that the bottom graph in each of these figures be changed from a percentage of background to a quantitative amount of the indicated exposure measure above background. Low background levels near zero make the calculation of percent changes of little value. That is, a large percentage of a really small value is often still a really small value.

Page 3-58 lines 28: This is a key point. Where are the data or references to back it up? A citation to a publication, or another EPA report needs to be included here. Additional references are also needed on page 3-59.

Please consider bringing the following Annex figures forward to this section of the ISA: AX4.1-1, AX4.1-2, AX4.1-3,

Chapter 4

I would prefer to see this section organized along the lines of direct versus indirect effects of NOx and SOx. That approach has served the community well in the preceding AQCDs, and it better reflects that nature of the current N and S standards (gaseous exposures). Specifically Section 4.4.2 should be moved ahead of the discussion of acidification and nitrogen nutrient additions. This recommendation is not offered to perpetuate the use of a gaseous form of the welfare standard, but rather to recognize the history of NOx and SOx regulations. Delegating the primary effects of NOx and SOx exposures to a hidden corner at the back of the report seems inappropriate.

Page 4-2 line 1: The term biosynthesis may need further definition.

Section 4.1.3: The discussion of critical loads might be better located following the discussion of all direct and indirect effects. Redundant could all be combined together into one section on the critical loads relevant to the combined and interacting effects of the full range of adverse effects of N and S inputs. Such a section should describe the need for a comprehensive biogeochemical cyclingbased assessment of the N and S cycles in support of the concept of critical loads.

Page 4-6 lines 10 and 11: Where are the dose-response relationships?

Page 4-7 line 28: A reference is needed for this statement.

Page 4-8 line 1: A reference is needed for this statement.

Figure 4.2-1 contains the wrong image. It has been inadvertently swapped with the figure for the image in Figure 4.2-2.

Top of page 4-12: References to these statements are needed.

Page 4-12 lines 20 and 21: A reference is needed for the C:N statement.

Page 4-12 line 28: N may also be retained for long periods within plant biomass.

Page 4-12 line 29: A reference is needed for this statement.

At some point within Section 4 it would be useful to summarize the percent of US land area (perhaps within regions) anticipated to be impacted by direct effects of N and S forms, acidification, N deposition, etc. A table would suit this purpose nicely.

References are needed in Section 4.2.1.4 on base cation leaching.

Page 4-26 line 22: OC needs to be defined.

Section 4.2.2.2 is a good discussion (needing references) that might serve the reader better if it occurred earlier in the document.

Page 4-28 line 25: Would it be appropriate to change the word “gradual” to ‘accelerated’?

Page 4-29 lines 14 to 22: References for these statements are needed.

Page 4-31 line 10 and 11: The authors should be careful when using as phrase like “contributed to”. In many cases the data probably showed only a correlation with an observed effect rather than proof of a specific mechanism responsible for the effect. Similarly, on Page 4-31 line 26, should “indicated” be ‘hypothesized’?

Page 4-33 lines 19 and 20: Can this statement be made more quantitative?

Section 4.2.4.1 is an excellent section that is well referenced. Use it as an example when modifying other portions of Section 4.

Page 4-64 line 23: An “in review” paper is not an acceptable inclusion in the ISA.

Page 4-65 line 8: Were these regions acidic naturally or as a result of anthropogenic N and S additions? Can such a distinction be made?

Page 4-66 lines 26 to 28: Add the literature citation for this statement.

Page 4-70 line 21: I think this heading should be numbered. Perhaps 4.2.4.2.2.

Bottom of page 4-70 and top of page 4-71. The text should be expanded to show the components of the analysis of McNulty et al. (2007). The reader doesn’t have sufficient information. Is such information present in an Annex? If so, please direct the reader to the text. How are variable rates of plant productivity used in this analysis?

Page 4-71 line 30: A reference for this statement is needed.

Page 4-104 lines 14 to 24: This material is unnecessarily redundant with material in Sections 2 and 3.

Page 4-121 line13: Is a change in productivity or biodiversity necessarily an adverse effect? This question should be discussed in the context of N and S deposition or loading.

Within section 4.4 the discussion on direct phytotoxic effects should be moved to the front of Section 4. The discussion of direct phytotoxic effects should also include a description of the key exposure response relationships know to drive adverse direct effects. Such information could easily be lifted and reused from prior AQCDs since little new information is available on this topic. The following references may have been published since the last N and S AQCDs and should be considered for inclusion in the ISA discussion:

Ammann M, vonBallmoos P, Stalder M, et al. (1995) Uptake and assimilation of atmospheric NO2-N by spruce needles (Picea abies): A field study. WATER AIR AND SOIL POLLUTION 85:1497-1502.

Desantis F, Allegrini I (1992) Heterogeneous reactions of SO2 and NO2 on carbonaceous surfaces. ATMOSPHERIC ENVIRONMENT PART A-GENERAL 26:3061-3064.

GunthardtGoerg MS, Schmutz P, Matyssek R, et al. (1996) Leaf and stem structure of poplar (Populus x euramericana) as influenced by O-3, NO2, their combination, and different soil N supplies. CANADIAN JOURNAL OF FOREST RESEARCH 26:649-657.

Kainulainen P, Holopainen JK, Oksanen J (1995) Effects of so2 on the concentrations of carbohydrates and secondary compounds in scots pine (pinus-sylvestris l) and norway spruce (picea-abies (l) karst) seedlings. New Phytologist 130: 231-238.

Manninen S, Huttunen S (2000) Response of needle sulphur and nitrogen concentrations of Scots pine versus Norway spruce to SO2 and NO2. ENVIRONMENTAL POLLUTION 107:421-436.

MENG FR, COX RM, ARP PA (1994) Fumigating mature spruce branches with so2 - effects on net photosynthesis and stomatal conductance. CANADIAN JOURNAL OF FOREST RESEARCH 24:1464-1471.

Qiao Z, Murray F (1997) The effects of root nitrogen supplies on the absorption of atmospheric NO2 by soybean leaves. NEW PHYTOLOGIST 136: 239-243.

Qiao Z, Murray F (1998) The effects of NO2 on the uptake and assimilation of nitrate by soybean plants. ENVIRONMENTAL AND EXPERIMENTAL BOTANY 39:33-40.

Thoene B, Schroder P, Papen H, et al. (1991) Absorption of atmospheric no2 by spruce (picea-abies l karst) trees .1. no2 influx and its correlation with nitrate reduction. New Phytologist 117:575-585.

Vassilakos C, Katsanos NA, Niotis A (1992) Physicochemical damage parameters for the action of so2 and no2 on single pieces of marble. Atmospheric Environment 26: 219-223.

Wolfenden J, Pearson M, Francis BJ (1991) effects of over-winter fumigation with sulfur and nitrogen dioxides on biochemical parameters and spring growth in red spruce (Picea-rubens Sarg) Plant Cell and Environment 14:35-45.

Wulff A, Karenlampi L (1996) Effects of long-term open-air exposure to fluoride, nitrogen compounds and SO2 on visible symptoms, pollutant accumulation and ultrastructure of Scots pine and Norway spruce seedlings. Trees 10:157-171.

A brief section on the role of NOx as an ozone precursor should be added to Section 4.4. This need not be very long, but it should provide sufficient information to inform the reader that NOx pollution is often indirectly responsible for known adverse effects of photochemical oxidants on vegetation (and materials too for that matter). The reader can simply be pointed to the recent AQCD for ozone and other photochemical oxidants.

Some mention should be made of the potential for anthropogenic N additions to fertilize natural ecosystems leading to the sequestration of CO_2 from the atmosphere. This could be added as a counter point to the discussion of N2O emissions to be expected from N saturated systems. If the authors don't provide this discussion and show that the issue was considered others might demand that it be added later.

The Tables should be embedded with the text to which they apply or moved to their corresponding Annex.

Chapter 5

I really enjoyed reading Section 5. I found it to be concise informative and easy to follow. As I've already stated I believe it should be presented at the front of the document. I does, however, need to be populated with references to direct the reader to the appropriate portions of the ISA, ISA Annexes or other published work that support each statement.

Page 5-2 line 13: Should “nitrification” be ‘eutrophication’?

Page 5-4 lines 16 to 18: Although this statement may be true, I don’t believe it is supported within the ISA as written.

Section 5 might be rearranged to include:

- 5.4 Direct Phototoxic Effects of NOx and SOx
- 5.5 Indirect effects of acidification and nitrogen nutrient enrichment
- 5.6 Other effects

Page 5-7 line 29: Should this read ‘Inorganic aluminum….’?

Page 5-18 lines 19 and 20: Reword as “…ecosystems causes fertilization of trees and grasslands accelerating growth in some species….
The words “inadvertent” and “unnatural” seemed inappropriate to me.

Page 5-19 line 9: Change to “When N increases to….”

Page 5-20 lines 24 and 25: N is also retained in biomass.

Page 5-37 lines 27 and 28: I would change “many forest ecosystems” to ‘sensitive forest ecosystems’. There are many forest ecosystems that probably will show little if any adverse effects from this level of N deposition for a long time.

Most of the Tables should be used in their respective Sections and associated with some descriptive text. Table 5.7-1 did seem appropriate to the Summary and Findings section.

Draft Text for an Answer to ISA Charge Question #10:

Several additional effects are discussed, including mercury methylation, direct gasphase effects on foliage, and N_2O as a greenhouse gas. How well does the draft ISA characterize the evidence on these topics?

Designating the direct effects of gas phase NO_x and SO_x as an ‘additional effect’ is inconsistent with prior AQCDs that appropriately delineated direct versus indirect effects of the defined criteria pollutants. I would argue that the ISA should return to this format and characterize gas phase effects of nitrogen and sulfur oxides as direct effects that are seldom expressed under current atmospheric conditions. That discussion could then be logically followed by a discussion of the indirect effects of acidification, nitrogen nutrient additions, sulfur-induced mercury methylation, the production of the greenhouse gas N_2O, the production of tropospheric ozone, and the interactive influence of global anthropogenic N additions on carbon sequestration within natural ecosystems. The last item on the stimulation of ecosystem carbon sequestration is not currently discussed within the ISA, but should be considered as an addition.

Some references related to N deposition and carbon sequestration:

Grace J (2004) Understanding and managing the global carbon cycle. Journal of Ecology 92:189-202.

Hyvonen R, Agren GI, Linder S, et al. (2007) The likely impact of elevated [CO2], nitrogen deposition, increased temperature and management on carbon sequestration in temperate and boreal forest ecosystems: a literature review. New Phytologist 173:463-480.

Korner C (2000) Biosphere responses to CO2 enrichment. Ecological Applications 10:1590-1619.

Makipaa R, Karjalainen T, Pussinen A, et al. (1999) Effects of climate change and nitrogen deposition on the carbon sequestration of a forest ecosystem in the boreal zone. CANADIAN JOURNAL OF FOREST RESEARCH 29:1490-1501.

Nadelhoffer KJ, Emmett BA, Gundersen P, et al. (1999) Nitrogen deposition makes a minor contribution to carbon sequestration in temperate forests. Nature 398:145-148.

Norby RJ (1988) Nitrogen deposition: a component of global change analyses. New Phytologist 139:189-200.

Oren R, Ellsworth DS, Johnsen KH, et al. (2001) Soil fertility limits carbon sequestration by forest ecosystems in a CO2-enriched atmosphere. Nature 411:469-472.

Schindler DW, Bayley SE (1993) The biosphere as an increasing sink for atmospheric carbon - estimates from increased nitrogen deposition. Global Biogeochemical Cycles 7:717-733.

Dr. Dale Johnson

The quality of the review is very mixed, especially in Section 4. The first part is fraught with inaccuracies, misconceptions, and bias, the last part is even handed and complete. Indeed, there seems to be a real dichotomy between two different authors who seem to have written this section, and the second one has a much more complete and balanced view of the situation. Again, I stress the need for looking at all points of view – which in total this document does, but only in certain parts and these parts do not adequately make their way into the summary sections. The focus is on the negative effects, which leaves this document open for severe criticism once it is released.

Specific comments:

p. 1-2, lines 5-22: Here I ask my recurring question: why the complete focus on adverse effects? Nitrogen is the limiting nutrient for most terrestrial ecosystems and therefore there is the distinct possibility of beneficial effects as well. Again, I do not advocate excusing air polluters on this basis, but I think a fair and complete assessment requires that this side be discussed. To fail to do so risks losing credibility for the entire effort.

p. 4-2, Title: The very title of this section clearly shows an bias toward adverse effects and such a bias is completely unacceptable in a document that purports to be scientifically objective.

p. 4-3, lines 7-8: It is very hard to imagine that increasing N deposition will fail to cause “change” in any ecosystem, whether it be beneficial or harmful change. I think there is a need to be more specific here.

p. 4-7, line 24: Acid cations that build up during soil acidification include, importantly, Al^{3+} as well as H^+.

p. 4-7 line 25: Soil acidification IS a natural process. There is no doubt of this. Extremely acidic soils can be found in pristine parts of the world. You should elaborate on such processes here – carbonic acid, organic acids, plant cation uptake.

p. 4-7, line 28: Where have decreases in pH attributable to acidic deposition been found in the US? You should cite references here.

p. 4-8, line 6: The B horizon lies below the Oa horizon? Since when? This can happen in some cases, but is the exception rather than the rule. What happened to the A and E horizons? Does this author know anything about soils and soil genesis?

p. 4-8, lines 15-17: Actually, the situation with hardwoods is much more complicated than that and this statement is misleading. Hardwoods, by taking up larger amounts of Ca, actually acidify sub surface soil horizons more than conifers to even though they may enrich surface horizons with Ca by litterfall recycling. There is a classic paper by Alban (1982) that clearly show this and should be cited here. Also, an excellent source of information is the review paper by Stone (1975).

p. 4-8, line 28 and throughout: “SO_4^+”?? Since when is sulfate a cation? This is an embarrassing mistake. Sulfate is an anion: SO_4^{2-}

p. 4-10, lines 5-6: Some oil crops have S demands that are in line with S deposition.

p. 4-10, lines 25-31: There are MANY other references besides Sullivan et al 2004 that show this.

p. 4-11, line 30: Add this to the list: “3) greater growth causing more cation uptake and therefore more soil acidification”

p. 4-12, lines 2-9: Ammonium is also acidifying: it is either taken up by plants or microbes, thereby releasing H^+, or is nitrified, creating nitric acid.

p. 4-14, lines 17-31: This is a good description of the leaching and acidification processes.

p. 4-15, lines 1-13: There are some significant problems with this section. First of all, it is stoichiometrically impossible for the soil changes described by Bailey et al to have been caused by any known level of acidic deposition – I wrote a letter to the editor about this and felt that their reply was inadequate (Johnson, 2006). I insist that this be included in the discussion. Secondly, there are several examples in the literature – even an entire book – written about studies where plant cation uptake as well as atmospheric deposition has caused substantial soil acidification (Johnson and Todd, 1990; Richter and Markewitz, 2001; Trettin et al., 1999). This review of the soil acidification literature for the US is totally inadequate and misleading.

p. 4-16, lines 17-26: In nature, the rate of soil weathering seldom exceeds the rate of acidification – that is why soil naturally acidify. So it is not realistic to assume that soil weathering will aid in the recovery of acidified soils.

p. 4-18, Figure 4.2-2: It appears that you have the wrong figure here. I see a soil profile, not an in situ bioassay.

p. 4-23, line 16: “lowered or INCREASED plant productivity”

p. 4-24, lines 2-3: why spell out potassium and sodium but not Ca and Mg?

p. 4-24, line 30: Al is not toxic to all tree roots. Some plants tolerate it and like acidic soils.

p. 4-26, line 12: Do you mean Nitrogen to Carbon ratio? If so, the usual expression is carbon to nitrogen ratio.

p. 4-31, lines 10-13: I thought that the red spruce decline was largely attributed to climatic factors. What about Art Johnson’s work?

p. 4-37, lines 5-10: How about some of the N-loving invasive grasses in the southwestern US like Bromus species? Edie Allen has shown that N deposition clearly facilitates this in southern California.

p. 4-43, line 22: Do you mean cation here?

p. 4-43, lines 25-26: In the study of Lawrence et al, did H^+ and Al^{3+} decrease to make up the difference between base cation decreases and mineral acid anion decreases? Something surely had to, otherwise charge balance was not maintained.

p. 4-44, lines 4-5: How were strongly acidic organic anions estimated?

p. 4-63: A discussion of capacity/intensity and anion mobility concepts for water acidification is needed here. Namely, that a strong acid anion such as sulfate or nitrate passing through an acid soil can mobilized H^+ and Al^{3+} with no delay because these acid cations are most available on exchange sites to balance the anions. This reaction does not require soil change and is instantly reversible if strong acid anion inputs cease. This is quite a different matter from the case where soils acidify. An already acidic soil, whether by natural acid production or by acid rain, is a necessary but not sufficient condition for the acidification of soil water – strong acid anions are also needed.

p. 4-84, lines 13-23: This is very interesting – we did not expect that soils of the northeast would have such buffering with respect to sulfate. Very important point.

p. 4-91, Figure 4.2-17: The y-axis legends on this figure are messed up.

p. 4-104, line 30: “unnatural growth rates?” Again, this reflects the negative bias that seriously detracts from this entire document. Just say increased growth rates and let the reader decide if it is good or bad.

p. 4-105, lines 16-17: Once again, this statement reflects the negative bias that seriously detracts from this entire document. I suspect that you would also be looking for negative effects if N limitations were increased rather than decreased in the endless search for negative consequences. Please let us simply state what we think will happen and leave out these value judgements.

p. 4-106, lines 9-10: At LAST! We see the mention of potential beneficial effects.

p. 4-111, lines 3-17: Once again, there is too much negative bias here. I raise once again the issue of global C and the potential for N pollution to make the terrestrial C balance better (Kauppi et al., 1992; Magnini et al., 2007).

p. 4-121, lines 12-32: This is as close to a balanced presentation as I have yet seen in this document. It needs to be up front along with all the potential negative effects.

p. 4-122, lines 15-16: Of course adding the limiting nutrient causes the next most limiting nutrient to become limiting – everyone who has ever worked with fertilization knows this. Why is this a bad thing? Is it healthier for a forest to be N limited than Ca, K, or Mg limited? Once again, an unnecessary value judgement here.

p. 4-123-124: At last we see the new article by Magnini and a balanced discussion about it. I think this kind of alternative view needs to be more up front as well.

p. 4-126: Good discussion of potential effects on grasslands and invasive species problems in relation to N.

p. 4-127-128: Again, a very good discussion of potential N effects on arid and semi-arid lands. N inputs in these areas could be a real problem and there is not much to be seen in the way of benefits.

p. 4-161-162: Good discussion of the non-acidifying effects and biological role of sulfur.

p. 5-6, lines 19-31: Some of that good discussion and balanced treatment seen on the last pages of section 4 need to make their way into this summary.

p. 5-7, line 29: Aluminum is toxic to SOME tree roots.

p. 5-8: Again, Some of that good discussion and balanced treatment seen on the last pages of section 4 need to make their way into this summary.

p. 5-12, lines 2-4: This is a very important yet seldom recognized point about surface water vs soil acidification.

p. 5-18, lines 19-20: Once again, why must we say unnatural? Why not just INCREASED growth rates? And then go on to elaborate about how you do not want this to happen in certain places (if indeed you do want to maintain N deficiencies).

p. 5-21: Good summary about N effects on growth, both positive and negative.

References:

Bailey, S. W., S. B. Horsley, and R. P. Long. 2005. Thirty years of change in forest soils of the Allegheny Plateau, Pennsylvania. Soil Sci. Soc. Am. J. 69:681-690.

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.

Johnson, D.W., and D.E. Todd. 1990. Nutrient cycling in forests of Walker Branch Watershed: Roles of uptake and leaching in causing soil change. *J. Environ. Qual.* 19: 97-104.

Kauppi, P.E., Mielikäinen, K. and Kuusela, K., 1992. Biomass and carbon budget of European Forests, 1971 to 1990. *Science,* 256: 70-74.

Magnini, F., Mencuccini, M., Borghetti, M., Berbigier, P, Beringer, P., Delzon, S., Grelle, A., Hari, P., Jarvis, P.G., Kolari, P., Kowalski, A.S., Lankreijer, H. Law. B.E., Lindroth, A., Loustau, D., Giovanni, M., Moncreiff, J.B., Rayment, M., Tedeschi, V., Valentini, R. and Grace, J. 2007. The human footprint in the carbon cycle of temperate and boreal forests. Nature 447: 848-850.

Richter, D.D., and D. Markewitz. 2001. Understanding soil change. Soil sustainability over millennia, centuries, and decades. Cambridge University Press.

Stone, E.L. 1975. Effects of species on nutrient cycles and soil change. Philos. Trans. R. Soc. Lond. Ser. B Biol. Sci., 721: 149-162.
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.

Dr. Donna Kenski

Overall, this was a fine job summarizing a lot of data. The quality varied from section to section, but most of the relevant information was here. Nevertheless there were some significant shortcomings that should be addressed in future drafts. Most of my comments address the presentation of air quality and emissions data, per Charge Questions 1-3.

The chemistry discussion is adequate. Most of the air quality issues were covered in Chapter 3, and I found them lacking in several ways, especially with respect to the nitrogen species. Most of the gaps were in data on nitrogen species. Section 3.1 needs a map of NOx emissions density (all sources) and a comparison, at least nationally but preferably regionally, of the relative importance of each of the anthropogenic and biogenic sources to total NOx emissions. We're told that soil contributes 10% of NOx emissions globally, and 26% of NO in Illinois, but no estimates are given for soil NOx contribution to US emissions either nationally or regionally. Similarly for biomass burning. The statement that increased wildfires will make emissions from this sector increasingly important should be substantiated with quantitative data. This information is too important to relegate to the Annex, and Table 3.11-2 puts sources in priority order but is not quantitative. The section also needs a description of NOx emission trends, parallel to the discussion of SOx emission trends in Sec. 3.2. While changes in NOx have not been as dramatic as those for SOx, they are documented and the data are readily available. In addition, some information about future-year emissions projections would be nice, along with a brief summary of recent and expected controls on NOx and SOx sources. These analyses have been done by EPA already. Another significant hole in the emissions discussion was NH3. Although we're told that the NEI underestimated NH3 emissions by a factor of 2 or 3, we're never given an estimate of what those emissions are (underestimate or not).

Section 3.6.1, and especially p. 3-15, lines 9-15 is somewhat misleading in its description of the monitoring networks. Sure we have lots of ozone monitors, but ozone monitors don't tell us much about NOx or SOx or NH3. I don't understand why the authors of this section decided to show us plots of ozone and PM2.5 air quality but not plots of SO2, NOx or NH3 concentrations . While it is true as stated in lines 11-13 that NOx and SOx are often monitored at the same sites, the number of NOx and SOx monitors is far less than for ozone or PM25. More relevant would be a plot of just NO2 and SO2 monitors, which would make immediately apparent the significant gaps in spatial coverage of measurements for these gases. Figures 3.6-1 and 3.6-2 leave the reader with the impression that the network of NOx/Sox monitors is much more dense than it really is. Including NATTS, HAPS, CO, and lead sites in Fig. 3.6-2 only obscures the matter further. It may also be worth noting that monitors for both NOx and Sox have been cut from the networks in recent years because their main purpose is perceived to be for comparing to the primary NAAQS. As ambient concentrations for both NOx and SOx have fallen well below the standard throughout the US, the monitors are seen as a lower priority and unnecessary expense. At the same time, monitoring budgets have been cut, leading to monitor shut downs.

Another shortcoming of this section is that it does not address urban-rural differences. Figure 3.6-3, for example, is of limited usefulness in assessing the composition of aerosol that impacts the sensitive, mostly rural regions identified later; differences in urban and rural aerosols have been noted by many. A similar plot, but based on IMPROVE data, would be an improvement, or a plot that shows both urban and rural composition. The majority of monitors, both gas and particle, are in urban areas; rural NOx and Sox monitors are rare. How does the lack of rural NOx and Sox monitors affect estimates of N deposition?

Figures 3.7-2 and 3.7-3, which compares ambient SO2 and SO4 concentrations in the early 1990s with more recent data, are very effective, but the text or caption should note whether Fig. 3.7-3 is showing SO4 concentrations in particulates or in rainfall – its not clear which. A similar set of plots should be shown for NOx and NH3.

I didn't like Fig. 3.7-4 when it showed up in the Sox primary ISA (as I recall from discussions, none of the panel did) and I still don't like it. It is not effectively communicating information about SO2 concentrations; replotting on a log scale would make it much more informative. Especially in this context, the extreme values are less informative than the rest of the distribution.

Figures 3.8-1 thru 3.8-4 are also ineffective. It is difficult to distinguish meaningful differences by comparing the size of the pies in the upper and lower plots, and also to tell if there have been changes in the geographic distribution of the various forms of S and N deposition. NADP produces a much more effective set of plots, at least for wet deposition, similar to Fig. 3.7-2; perhaps those could be substituted here (see http://nadp.sws.uiuc.edu/isopleths/annualmaps.asp) or these could be reworked to show the data in a similar fashion. At least change the pies to bar charts as in Fig. 3.2-1.

Section 3.6.4 on satellite observations was too brief to be useful. It seems clear that the technology holds great promise; it would be helpful to see some support of that notion, rather than just have a laundry list of satellites without any indication of their strengths and weaknesses. Is there useful data for our purposes (N and S deposition) being produced by the satellites now? If so report it here.

Section 3.6.5 could be removed to Annex 2.

This chapter should have left us with an understanding of the relative importance of NOx, NH3, and organic nitrate deposition nationally and regionally, but at the end I still felt unable to assess those except in a qualitative way.

Ultimately, the question we want to answer is, what kind of secondary standard would be adequately protective of our sensitive ecosystems. Here I think the ISA was not very helpful. I was searching for information that explicitly linked ambient concentrations or emissions with deposition and more importantly with acidification effects. How are ambient concentrations related to deposition? Are these essentially equivalent? Can we compare (using GIS tools or other quantitative techniques) the distribution of concentrations (or deposition) to the distribution of sensitive ecosystems?

Some other general comments:

The various chapters and subsections make occasional mention of shortcomings in the data and areas that are poorly understood, but these shortcomings aren't collectively addressed anywhere. These data gaps and research needs should be explicitly discussed and summarized in the conclusions. Doing so would help us better understand some of the limits to our knowledge and also hopefully help EPA target research efforts and support future reviews.

Another concern I have is that NHx isn't addressed comprehensively here because the focus is NOx and SOx, and it may not be comprehensively discussed in the PM ISA, because the focus there is PM. When or where does NHx get its due? If we always consider it as a smaller part of something else, it may never get dealt with adequately. I appreciate that NHx's contributions to deposition and acidification were discussed here at some length, but we seem in danger of marginalizing its very important role in nitrogen and sulfur deposition be cause it is a lesser player, without doing the research to adequately characterize its role.

More specific comments:

p. 2-29 line 6-7 The concluding sentence, that coverage of monitoring networks is thin over large expanses of the US, is true, but not a conclusion that follows from the previous discussion, which is only about the adequacy of the monitoring techniques. It is a statement more appropriate for Sec. 3.6.1.

p.3-7 line 7-9 overrepresentation is a poor word choice. Perhaps higher density would be better.

p. 3-13, eqn 3.5-4 Isn't the second = sign supposed to be a + ?

p. 3-16, caption to Fig. 3.6-2 should be ..majority *of* routine…

p. 3-35, caption to Fig. 3.9-1 should read …25th and 75th quartiles…

p. 4-7 Throughout this Section (4.2) the concept of base saturation is discussed and a few benchmark figures (base saturation less than 20%, for example) are mentioned, but it does not explain how base saturation is quantified until p. 4-24. A brief definition at the beginning of this section would be a useful addition since it may not be familiar to the many in the atmospheric community.

pp. 4-7 - 4-191 Somehow in this entire chapter, $SO4^{2-}$ morphed into $SO4^{+}$. Search and replace gone awry? Very disconcerting.

pp. 4-9, 4-18 Figures 4.2-1 and 4.2-2 have been switched. The captions are correct but the figures themselves are reversed.

p. 4-24 Later in the document there are maps of sensitive areas (although not enough—much more of the data could/should have been summarized graphically). Any available to show soil base saturation, or Ca:Al ratios, which might be helpful here?

p. 4-24 Change in terms soil water -> soil solution is confusing. Are these the synonyms or is there some subtle difference?

p. 4-26 line 12 Calcium should be Carbon

p. 4-64, section 4.2.4.2 This section suffers from a lack of integration. It's difficult to assess the extent and distribution of these sensitive areas without some graphical help. Figure 4.2-12 is a start, but only tells part of the story; Figure AX4.3-2 does a much better job showing the location and extent of acidification. Also, acidified streams and lakes are sometimes mentioned separately and sometimes together; it is not clear whether regions with acidified streams necessarily also have acidified lakes, and vice versa.

p. 5-16, lines 5-14 Although this section is supposed to be about recent trends in acidification recovery, this last bullet doesn't say anything about recovery and seems out of place. The parent section 4.2.4.2.1 emphasizes that this WSA survey is summer data and therefore biased low, but that caveat is not repeated here, as it should be. These results also don't jive with later data (i.e., on p. 5-17, 66% of Adirondack streams currently have high Al). It would be useful to have a graphical assessment of the geographic extent of acidification either here or as suggested earlier, in section 4.2.4.2. Figure AX4.3-2 is very helpful in this regard.

p. 5-36 lines 19-23 Absolutely true that regulatory networks cannot adequately characterize regional heterogeneity (on a scale that matches that of the sensitive ecosystems) and hotspots. But the statement about hotspots identified at research sites was not discussed in the text, except in reference to Hg. If this is documented it should be discussed in the body of the ISA, not mentioned first in the summary.

p. 5-36, line 25 lead should be led

p. 5-38 This section comes to an abrupt end; is something missing?

Dr. Naresh Kumar

Information provided in the Integrated Science Assessment document on atmospheric chemistry and physics, air quality, and deposition and exposure is concise, but sufficiently comprehensive. Specific comments are:

Page 2-2, Lines 6 & 7: Nitric acid doesn't contribute to the acidity of particles, so there is a need to reword the sentence.

Page 2-2, Lines 23 & 24: It would be meaningful to mention the contribution to NOx emissions from mobile sources and electric utilities (e.g., According to NEI 2003, 55% of NOx emissions were from mobile sources and 22% were from electric utilities).

Page 2-5, Line 7: The following reactions should be added before Equation 2.2-2

$$O_3 + NO_2 \rightarrow NO_3 + O_2$$
$$NO_3 + NO_2 \rightarrow N_2O_5$$

Page 2-5, Line 15: The nitrate radical, NO_3 should be included as part of the photolysis.

Page 2-6, Lines 7 thru' 16: The paragraph should also mention the negative radiative forcing caused by nitrate particles.

Page 2-6, Line 28: Add "from the free troposphere" at the end of the sentence.

Page 2-7, Line 9: Add "except at lower temperatures" at the end of the sentence.

Page 2-8, Line 13: There is no SO_4^{2-} in Equation 2.2-15.

Page 2-8, Line 22: "diatonic" should be "diatomic".

Page 2-9, Line 31: Change "high" to "moderate"

Page 2-9, Line 32: After "in the aqueous phase in cloud droplets", add "by reaction with H_2O_2, O_3 or O_2 through catalysis by Fe and Mn.

Page 2-10, Line 7: After "highly soluble", add "as well as hygroscopic".

Page 2-11, Line 3: "Methane sulfuric acid" should be "methanesulfonic acid".

Page 2-12, Figure 2.3-1: Include Fe, Mn and O_2 where reaction from S(IV) to S(VI) is shown.

Page 2-13, Line 18: Add manganese (Mn) to the list of metals that can catalyze oxidation by O_2.

Page 2-17, Line 17: Include Edgerton et al., 2006 and Edgerton et al., 2007 in the list of references on newer methods for measuring nitrate, ammonia and ammonium. SEARCH network has been in place since 1999 and has been widely used by the community, but there is no mention of this network anywhere in the ISA document.

Page 2-21, Line 12: H_2SO_4 should be changed to SO_2.

Page 2-24, Line 22: Add "for IMPROVE and thermal-optical transmittance (TOT) for STN" at the end of the sentence.

Page 2-25, Line 2: Change "well correlated" to "moderately well correlated".

Page 2-26, Line 1: Remove NH_4NO_3 from the list.

Page 2-26, Line 6: After "PM_{10}", add ", partly because NO_3^- contributes smaller fraction to PM_{10} and partly because NO_3- is present in a non-volatile form, such as $NaNO_3$, in the coarse mode.".

Page 3-1, Lines 23 & 24: Electrical utilities and various industries account for about one-third of anthropogenic NOx emissions (not roughly half).

Page 3-20, Line 13: Add description of the SEARCH network. Here is the suggested description to choose from:

Southern Company and EPRI funded SEARCH program has provided a highly instrumented eight-station network since 1998 (and continuing till at least 2010) in the states of AL, FL, GA and MS (Hansen et al., 2003). At present, the suite of measurements made at all sites includes:

1. *24-hr $PM_{2.5}$ filter samples, analyzed for mass, ions (sulfate, nitrate, ammonium), organic carbon(OC), elemental (black) carbon (EC or BC), and elements as measured by X-ray fluorescence (XRF);*

2. *24-hr PM_{Coarse} mass, ions, and XRF elements;*

3. *24-hr gaseous ammonia as collected with an annular denuder;*

4. *continuous (minute to hourly) $PM_{2.5}$ mass, OC, EC, ammonium, nitrate, and sulfate; light scattering and light absorption;*

5. *continuous gaseous ozone, nitric oxide, nitrogen dioxide, total oxidized nitrogen (NO_y), nitric acid, carbon monoxide, and sulfur dioxide; and*

6. *continuous 10-m meteorological parameters: wind speed, wind direction, temperature, relative humidity, solar radiation, barometric pressure and precipitation.*

Page 3-23, Line 22: SEARCH sites have also measured nitric acid (Zhang et al., 2006; Blanchard and Hidy, 2003) since 1998 and the measured hourly concentrations range from less than 1 ppb to more than 10 ppb.

Page 3-42, Line 14: Add “international transport” as one of the issues addressed by global CTMs.

Page 3-43, Line 17: I suggest adding Arnold and Dennis (2006) reference, as they went beyond just testing the operational model performance.

Page 3-47, Line 27: I suggest adding appropriate references to the SEARCH sites here.

References:

- Arnold, J.R. and Dennis, Robin L. (2006). Testing CMAQ chemistry sensitivities in base case and emissions control runs at SEARCH and SOS99 surface sites in the southeastern US. *Atmos. Environ*. **40** (26) 5027-5040.
- Blanchard, C.L. and Hidy, GM. (2003). Effects of changes in sulfate, ammonia, and nitric acid on particulate nitrate concentrations in the southeastern United States. *J. Air Waste Mange. Assoc.* **53** 283-290.
- Edgerton, E.S., Hartsell, B.E., Saylor, R.D., Jansen, J.J., Hansen, D.A., and Hidy, G.M. (2006). The Southeastern Aerosol Research and Characterization Study: Part III. Continuous Measurements of $PM_{2.5}$ Mass and Composition. *J. Air Waste Mange. Assoc.* **56**, 1325-1341.
- Edgerton, Saylor, Hartsell, Jansen, Hansen (2007) Ammonia and Ammonium Measurements from the Southeastern U. S., *Atmos. Environ.***, 41,** 3339-3351.
- Hansen, D.A., Edgerton, E.S., Hartsell, B.E., Jansen, J.J., Kandasamy, N., Hidy, G.M., and Blanchard, C.L. (2003). The Southeastern Aerosol Research and Characterization Study: Part 1 – Overview. *J. Air Waste Mange. Assoc.* **53** 1460-1471.
- Zhang, Y., Liu, P., Queen, A., Misenis, C., Pun, B., Seigneur, C., and Wu, S.-Y. (2006). A comprehensive performance evaluation of MM5-CMAQ for the Summer 1999 Southern Oxidants Study episode—Part II: Gas and aerosol predictions. *Atmos. Environ.* **40** (26) 4839-4855.

Dr. Myron J. Mitchell

General Comments

The December 2007 version of the "Integrated Science Assessment for Oxides of Nitrogen and Sulfur – Environmental Criteria" has done a very good job in summarizing a substantial amount of information. Included within this analysis is discussion on the relevance of this information to policy decisions. There is some reference and discussion to results from European analyses. It would be interesting to make some further explicit comparisons of the success or lack of success of the European analyses including the relevance of these analyses to both interpretations and policy implications in the United States.

In the various sections, however, there is sometimes substantial repetition and overlap. Some of this is likely inevitable, but having additional cross referencing among chapters would also be helpful. Removing some of this overlap will make the document more readable and reduce the overall length. In Chapter 3 (ECOLOGICAL EXPOSURES TO OXIDES OF NITROGEN AND SULFUR, AND TO AMMONIA AND AMMONIUM) some further discussion of the issues related to model parameterization, assumptions and differences in the predictions of concentrations and deposition would be helpful in placing results in the context of the overall confidence levels of predicted values both across temporal and spatial scales.

In Chapter 4 (EFFECTS OF ACIDIFICATION AND NITROGEN ENRICHMENT ON ECOSYSTEMS AND OTHER WELFARE EFFECTS) more attention should be given to the potential importance in at least some watersheds of other sources of sulfate that will affect the recovery from acidification. These sources can include organic sulfur mineralization and the weathering of sulfur bearing minerals.

More Detailed Comments

Page	**Comment**
xx	Change to: Dr. Myron Mitchell, Distinguished Professor and Director of Council on Hydrologic Systems Science, College of Environmental and Forestry, State University of New York, Syracuse, NY
xxxv	Change to: The removal of gases and particles from the atmosphere to surfaces by rain or other forms of precipitation
2-2	Change to: contributing to the acidity of cloud, fog, and rain water and ambient particles in the atmosphere.
2-3	Change to: few hours during summer days of high photon flux to roughly 24 h during winter with less

2-4	Change to: 2002). The mechanisms for transporting the NO_X precursors, the factors controlling the
2-6	Change to: on the conventional 100-year time horizon of ~296 – i.e., N_2O is nearly 300 times more effective on a per molecule basis for trapping heat in the atmosphere than carbon dioxide (CO_2)(IPCC,
2-13	Indicate location of “Mace Head” in line 3.
2-18	Be more explicit in what is the interference by NO_Z compounds in line 1.
2-20	Reword to clarify the issue related to: also lead to artifact volatilization and associated positive bias in [HNO_3] measured downstream
2-20	Would this be an appropriate place to discuss issues related to differences between CASTNET and the Canadian (CAPMoN) dry deposition comparisons. I believe most of the differences are associated with the dry deposition modeling versus the actual measurements of gaseous chemical species.
2-22	Figure 2.6-1 needs to provided with better resolution of the contour lines.
2-24	Should Teflon be indicated to be a registered name? ®
3-1	Delete: (The category label for NH_3 and NH_4^+ is NH_X.)
3-1	Substitute “approximately” for “roughly” here and elsewhere in the document.
3-2	Change to: Where N is in excess of biotic demand, gaseous N emissions increase by microbial transformation.
3-2	The issue related to “Although N_2 is not reactive in the troposphere, N_2O is a greenhouse gas (GHG) with a significant global warming potential (GWP) from its direct radiative forcing and from its...” maybe should be linked to the discussion in Chapter 2.
3-3	Change to: Emission rates of NO from cultivated soils depend chiefly on N fertilization levels
3-3	Change to: can have wide variation around this value
3-3	Change to: N in plants is present mostly as amine (NH2) groups in amino acids.
3-3	Change to: will make emissions from this source increasingly important
3-8	This statement needs clarification: Emissions of SO_2 from burning vegetation are generally in the range of 1 to 2% of the biomass burned (e.g., Levine et al., 1999).

This would suggest that 1 to 2% of biomass gets converted to SO_2. This seems to high with respect to the average S concentration in vegetation. Does this study suggest that 1 to 2% of the S in biomass is converted to SO_2?

3-9 Be more explicit about which pattern in the statement: Anthropogenic emissions of NH_3 show a strikingly different pattern from those of NO_X or SO_2.

3-10 Does the statement “Results from some more recent emissions evaluation studies have been mixed, with some studies showing agreement to within ±50%” imply that some of these studies show that agreement is greater than 50%?

3-21 Figure 3.6-7. Routinely operating North American precipitation and surface water networks: Upper left, Canadian Air and Precipitation Monitoring Network (CAPMoN); upper right, Integrated Atmospheric Monitoring Deposition Network (IADN); bottom, National Atmospheric Deposition Monitoring Program (NADP) with TIME/LTM surface chemistry sites.

This figure shows a symbol of N-saturated forests. What is the source of this designation? What is the coverage associated with the symbol? Other Ecological Resources are also noted, but the source of these designations is not included in the figure legend.

3-22
3-23 Some further discussion of differences of these European monitoring efforts compared to those in the U.S. may be helpful. Also, some discussion on differences with the Canadian monitoring efforts should be included.

3-47 Change to: parameterizations of atmospheric chemical and physical processes in models.

3-48 Change to: In a watershed, everything that is deposited in its area

4-1 Change: Structure refers to the species richness, abundance, and community composition that ultimately relate to ecosystem biodiversity.

To something like: Structure may refer to a variety of measurements including the species richness, abundance, community composition as well as landscape attributes. The biotic components comose the biodiversity of an ecosystem.

4-1 Change to: Competition among and within species and tolerance to environmental stresses are key elements of survivorship

4-1 Change to: Function refers to the suite of processes and interactions among the ecosystem components and their environment that such as nutrient and energy flow as well as other attributes including water dynamics and the flux of trace gases.

4-2 Change to: related to functions of energy flow and nutrient cycling

4-2 Change to: Energy moves from one organism to another through food webs, until it is ultimately released as heat. Nutrients and water can be recycled. Air pollution alters the function of ecosystems when elemental cycles or the energy flow is altered. This alteration can also be manifested in changes in the biotic composition of the ecosystem.

4-6 The use of “we” seems awkward in this type of discussion. I would suggest rewording.

4-8 It may also be useful to include the term “forest floor” when discussing the O horizon of forest soils.

4-8 For the documentation of soil acidification the following reference should be included: Sullivan, T.J., I.J. Fernandez, A.T. Herlihy, C.T. Driscoll, T.C. McDonnell, N.A. Nowicki, K.U. Snyder, and J.W. Sutherland. 2006. Acid-base characteristics of soils in the Adirondack Mountains, New York. Soil Science Society of America Journal 70: 141-152.

4-11 Not only is the fate of carbon-bonded sulfur an issue, but also the fate of ester sulfate needs to be considered.

4-11 This might the be place to at least mention that sulfate isotopic have indicated the potential for the net mineralization of organic S contributing to sulfur imbalances for watersheds. This has been found in studies both the United States and Europe. Some relevant references would include:

Novák, M. M. J. Mitchell, I. Jacková, F. Buzek, J. Schweigstillová, L. Erbanová, R. Prikryl and D. Fottová. 2007. Processes affecting oxygen isotope ratios of atmospheric and ecosystem sulfate in two contrasting forest catchments in Central Europe. ES&T 41(3): 703-709. DOI: 10.1021/es0610028

Likens, G.E., C.T. Driscoll, D.C. Buso, M.J. Mitchell, G.M. Lovett, S.W. Bailey, T.G. Siccama, W.A. Reiners, C. Alewell. 2002. The biogeochemistry of sulfur at Hubbard Brook. Biogeochemistry 60:235-316.

Gbondo-Tugbawa, S.S., C.T. Driscoll, M.J. Mitchell, J.D. Aber and G.E. Likens. 2002. A model to simulate the response of a northern hardwood forest ecosystem to changes in S deposition. Ecological Applications 12:8-23.

In addition, some mentioned should be included about the potential role of weathering reactions for contributing to sulfate in some watersheds. A good example is:

Shanley, J.B., B. Mayer, M.J. Mitchell, R.L. Michel, S. Bailey and C. Kendall. 2005. Tracing sources of streamwater sulfate during snowmelt using S and O isotope ratios of sulfate and ^{35}S activity. Biogeochemistry 76:161–185

4-14 The is also strong evidence of the importance of winter time processes and the possible linkage to climate in affecting nitrate losses. See for example:

Eimers, M.C., Buttle, J.M., Watmough, S.A., 2007. The contribution of rain-on-snow events to annual NO_3-N export at a forested catchment in central Ontario, Canada. Applied Geochemistry, 22: 1105-1110.

Campbell, J.L., M. J. Mitchell, P. M. Groffman, L. M. Christenson. 2005. Winter in northeastern North America: An often overlooked but critical period for ecological processes. Frontiers in Ecology 3(6):314-322.

Park, J, M.J. Mitchell, P.J. McHale, S.F. Christopher and T.P. Myers. 2003. Interactive effects of changing climate and atmospheric deposition on N and S biogeochemistry in a forested watershed of the Adirondack Mountains, New York State. Global Change Biology 9:1602–1619.

4-20 to
4-22 There is evidence that episodic acidification associated with droughts and the mobilization of sulfate is also important. This has been shown for studies in Canada and the northeast U.S. See for example:

Eimers, M.C., Watmough, S.A., Buttle, J.M., Dillon, P.J., 2007. Drought-induced sulphate release from a wetland in south-central Ontario. Environmental Monitoring and Assessment, 127: 399-407.

Eimers M.C. and Dillon P.J. 2002. Climate effects on sulphate flux from forested catchments in south-central Ontario. Biogeochem. 61: 337–355.

Mitchell, M.J. K.B. Piatek, S. Christopher, B. Mayer, C. Kendall and P. McHale. 2006. Solute sources in stream water during consecutive fall storms in a northern hardwood forest watershed: a combined hydrological, chemical and isotopic approach. Biogeochemistry 78: 217-246.

4-26 Should this heading be Changed to: 4.2.2.1.3 Soil Nitrogen: Carbon to Nitrogen Ratio

Not sure if the emphasis is on Ca and if the ratio indication is appropriate.

4-33
& Elsewhere Change SO_4^+ to: SO_4^{2-}

4-39 Change to: The increasing trend in Virginia streams is presumably the result of decreased soil solution sulfate concentration and net desorption in the soil in response to decreased S deposition.

4-41 As indicated above (see comments for 4-14) that there is other evidence that changes in winter time conditions can affect nitrate export.

4-42 Other studies in the Adirondacks have also identified the importance of within lake processes in affecting nitrate losses from lake/watersheds. See for example:

Ito, M., M. J. Mitchell, C.T. Driscoll, R. M. Newton, C.E. Johnson, and K.M. Roy. 2007.Controls on surface water chemistry in two lake-watersheds in the Adirondack region of New York: differences in nitrogen solute sources and sinks. Hydrological Processes 21:1249-1264.

Ito, M., M.J. Mitchell, C.T. Driscoll and K.M. Roy. 2005. Nitrogen input-output budgets for lake-watersheds in the Adirondack region of New York. Biogeochemistry. 72:283-314.

4-44 Change to: with the exception of streams in Shenandoah National Park, Virginia, which appear to exhibit decreases in adsorbed sulfate in soils.

4-62 to 4-63 The discussion in this section needs to differentiate between bedrock geology and surficial geology. Surficial geology is a much more important predictor of the sensitivity to acidification than bedrock geology. Differences in surficial geology can be especially important for predicting sensitivity to acidification within a region.

4-73 Some of this discussion on critical loads is repetitious from previous sections although this previous section is referenced.

4-82 I don't believe the following statement is true for the Adirondacks: However, recent research suggests that N has accumulated in soils over time in the Adirondacks and that some forests have exhibited declining retention of N inputs. The result has been increased leaching of NO3 to surface waters.

See for example:
Mitchell, M.J., C.T. Driscoll, S. Inamdar, G. McGee, M. Mbila, and D. Raynal. 2003. Nitrogen biogeochemistry in the Adirondack mountains of New York: hardwood ecosystems and associated surface waters. Environmental Pollution 123:355-364.

Mitchell, M.J., C.T. Driscoll, J. Owen, D. Schaefer, R. Michener, and D.J. Raynal. 2001 Nitrogen biogeochemistry of three hardwood forest ecosystems in the Adirondack Mountains. Biogeochemistry 56: 93-133.

4-112 Wetlands after droughts can also serve as nitrate sources when rewetted. See for example:

Watmough S.A., Eimers M.C., Aherne J. and Dillon P.J. 2004. Climate effects on nitrate export from forested catchments in south-central Ontario. Environ. Sci. Technol. 38(33): 2383–2388.

Also, some mention of the role of N-fixation should be included for wetlands; see:
Hurd, T. M., D. J. Raynal, and C. Schwintzer. 2001. Symbiotic N-fixation of Alnus incana spp. rugosa in shrub wetlands of the Adirondack Mountains, New York. Oecologia 126: 94-103.

4-129 The following paper could be referenced showing the effect on N additions on understory communities in the Adirondacks:

Hurd, T.M., A.R. Brach, and D.J. Raynal. 1998. Responses of understory vegetation of Adirondack forests to nitrogen additions. Can J. For. Res. 28: 799-807.

4-162 There is fairly good evidence that for forest ecosystems with closed canopies that throughfall sulfate is a good estimate of total sulfur deposition. See:
Lovett G.M., Thompson A.W., Anderson J.B. and Bowser J.J. 1999. Elevational patterns of sulfur deposition at a site in the Catskill Mountains, New York. Atmospheric Environment 33: 617–624.

4-179 An evaluation of nitrate sources to waters with respect to atmospheric deposition needs to separate how nitrogen deposition loading leading to more nitrate loss versus atmospherically deposited N being found directly in drinking water. Forest watershed level work using stable isotopes shows predominantly that almost all of the nitrate in surface and ground waters has been biotically derived. See for example:

Burns, D. A. and Kendall, C.: 2002, Analysis of $\delta^{15}N$ and $\delta^{18}O$ to differentiate NO_3 sources in runoff at two watersheds in the Catskill Mountains of New York', Water Res. Res. 38(9), 1–11.
Piatek, K.B., M.J. Mitchell, S.R. Silva and C. Kendall. 2005. Sources of nitrate in Adirondack surface water during dissimilar snowmelt events. Water, Air and Soil Pollution 165:13-35.

Kendall, C.: 1998, 'Tracing nitrogen sources and cycling in catchments', in C. Kendall and J. J. McDonnell (eds), Isotope Tracers in catchment hydrology, Elsevier Science, BV, pp. 519–576.

5-3 Not sure we have good estimates for some pollutants such as ammonia. This statement seems contradictory:

> Despite the aforementioned limitations, for the purposes of identifying and quantifying the atmospheric concentrations and deposition totals causing ecological effects, these measurement techniques and sampling frequencies are fully adequate. Nevertheless, the coverage of the networks is very thin over large expanses of the interior United States.

5-6 As stated previously the importance of superficial geology needs to be emphasized.

Dr. Armistead Russell

While I think the current ISA for Oxides of Nitrogen and Sulfur-Environmental Criteria provides much of the needed information for the process of reviewing the secondary NAAQS for NOx and SOx, at present the document is in need of significant modification to provide such information efficiently and effectively. The document should be read and edited for relevancy of the information being provided, and how it is provided, to the ultimate goal of the review of, and providing the scientific basis for possibly changing, the associated secondary NAAQS.

One step in this process would be to look at Chapter 5 and edit what is presented there to specifically provide a summary of what information is needed to provide a scientific foundation for a review of the standard. Having edited the summary chapter, then go back and write the chapters to bring forth the specific points needed to provide the basis for what is in Chapter 5.

Unlike the ISA's for the two associated primary NAAQS, this document begins in Chapter 2 with the more traditional Criteria Document approach of reviewing the atmospheric physics and chemistry of NOx and SOx, as opposed to a "Source to Dose" presentation, which here would be source to exposure or load. The latter approach led to a much more efficient presentation of the key concepts, data and science. As it currently reads, aspects of Chapter 3 seemed to be somewhat repetitive of information in Chapter 2, and the flow is awkward. Taking a source to exposure/load also leads back to the key idea that the increased environmental exposures can be linked to a source, which is what is controlled. Maybe it is due, in part, to lack of scientific investigation, but it is this type of information that is required for this review. In revising the current Draft ISA, it might be good to have someone read Chapter 5, the Conclusions, first, and then identify what are the major points, and what is needed to support the key findings as to the environmental implications of anthropogenically-influenced increased exposures and loads. Then, the degree to which those key findings are supported in Chapters 1-4 can be assessed, and the discussion of tangential information can be streamlined.

Chapter 2:

As noted above, I think the ISA would benefit from a Chapter 2 that goes from Sources to Environmental Exposure/Load. Chapter 3 should be integrated in. In addition to having atmospheric chemistry and physics, aquatic and soil chemistry and physics should be added. This would save much repetition later on in the report (e.g., about what leads to acidification, its affect, mobilization of aluminum, etc.). Fig. 2.2-1 could have a twin(s) showing what is happening in surface water and the soil-water matrix.

On page 2-3, line 16, one should note they are referring to US emissions. Lines 19-23 are a bit confusing at present. What is important, here, is that virtually all of the fuel-bound sulfur gets oxidized to a volatile component (SO2 or SO3), and that there is very little natural, oxidized sulfur in air over the US, so the sulfur emitted from burning a fuel is quantitatively related to that in the fuel.

The section on Measurement Methods needs to be refocused. The major question to be addressed here is if the current methods employed in the field provide reliable measurements of NOx, NH3, NH_4^+, NO_3^-, SO2 and $SO_4^=$ for levels of interest, and this should be answered quantitatively. At present, there is discussion of the various measurement approaches (some is needed) and lots of discussion on possible interferences, but never does one get the answer to what is the typical uncertainty in the measurements at a typical monitor in the US and how that impacts our ability to accurately quantify environmental exposures. I suspect that the methods employed for most of the species, while subject to some interferences, provides fine data, and that the level of uncertainty is such that we need not concern ourselves with possible interferences and biases. The major exception, of course, is ammonia, which is not even discussed. What really limits our ability to quantify deposition accurately (e.g., do we need more accurate measurements, different kinds?). Quantify the problems, let the reader assess if they are of concern.

More specific comments:

2-1:24-27: What about pSO4?
Rxn 2.2-2: Balance the reaction.
2-5:13: Reactions 2.2-1 and 2.2-2.
Section 2.2.2 It is not apparent the need for so much on Cl chemistry. Also, this section should be preceded by a more comprehensive discussion of N2O5. I would be very tempted to minimize this discussion.

2-9:25: Not sure why you use monomeric. What polymers do you have in mind?
2-10: 28: In both cases, NO3 and H are radicals, not ions.
2-11:2 Ravishankara.
2-13:28: A second reaction for comparison should be added (i.e., the ozone reaction).
2-14:10: What chemistry of NO3- formation is being discussed?
2-15:1: Ammonium nitrate formation as well.
2-17:30 Remove "all".
2-21: Section 2.6.2.2 needs to address accuracy more directly.
2-22…: Section 2.6.3 should be more quantitative.

A section on NH3 measurement is needed.

2-27: Section 2.7.1: It is weird that pNO3 is included here, pSO4 is not.
2-28:28: There is a summary paragraph for NH3 that is about as long as those for the other species, but where is this drawn from?

At present, the summary is a bit sparse.

Chapter 3

The Chapter beings with a discussion of sources, which as noted above, should go in a more integrated Chapter 2. It seems a bit unnatural to not start "the story" with sources. Also, while this chapter starts with sources, one does not get a quantification of such. One should not have to go to the Annexes to get a reasonably quantitative overview. A single table showing the contributions of, say, mobile, non-mobile, utility, biogenic and agricultural sources to oxidized NOx, N2O, reduced N and SOx is required. This might be done on a tons of S and N basis for ready comparison between the oxidized and reduced forms. Some estimate of the transport to North America might also be provided. (A sister Table showing the fate of the above is also suggested.)

A Table of fate of reduced N, oxidized N and SOx is suggested, showing the masses dry and wet deposited by species, as well as the amount transported away from the continent and associated estuaries. Having this table integrated with the table of sources might be of interest from a mass balance perspective.

Figure 3.7-4 As discussed during the SOx-Primary ISA review, this figure is not very effective. First it refers to "… in focus" in focus of what? Further, most of the data is very much at the bottom end, so it is difficult to see what is really happening, and it needs to include more information (what years…). I would have it provide the mean, median, 5 & 95%iles, and the extreme value. Further, it might be given on a log scale as most of the lower level information is now lost.

There is a bit of a contradiction in Chapter 3. On page 3-8, line 11, it says the ratio of N-to-S is 14, close to that in the tissue. The prior line says that approximately half of the S is in the ash. Please explain further.

In considering emissions, it would be good to also provide some information as to future emissions for perspective. CAIR is going to significantly lower emissions in areas where they are currently high. This is important for our further consideration as to how a standard might impact air quality.

Section 3.13 Summary.

This section starts out very roughly. 3.13.1 reads more like a set of bullet points in sentence form. The last paragraph (3-161, l4-6): Is this what you really mean to say, and from what part of the report is it distilled? Table 3.11.1 is rather more concrete at 21%, but does not indicate the reduced N fraction. Also, the first sentence of 3.12.2 is not really taken from something in the text (I might add this to the prior text).

3-60:26 change to "…surface of <u>some</u> coastal…"

What this chapter (or what should become a section of Chapter 2) needs is to focus on what one wants to know, as this section currently has some stuff I like to know, and some of what is not needed to assess a NAAQS. What is really needed? I would say a best estimate (map) of total N and S deposition, a list of estuaries suffering eutrophication with estimates (and uncertainties) of what is contributing. There was too little on ammonia(um) deposition.

Specific comments:

3-2:30: This sentence contains a non-sequiter.
3-3:2: Reactions, not reactivities.
3-4:16: I would remove "small"
3-4:24: "… for example, **<u>is estimated to have</u>** decreased…"
3-9:16: Remove "However"
3-13:13 "is **a** smaller **loss process** than its net thermal decomposition"
3-13:28 Remove "which"
3-14: Section 3.5.5. the source strength given is not a source strength unless one knows the volume. Further, more information on how robust this value might be nationally is needed.
3-23: Section 3.7 is somewhat repetitive of prior sections.
3-23:23-29: What is this paragraph trying to say?
3-23:28: Higher than what?
3-24:1-8: Much more quantitative information is available, e.g., annual average concentrations of the various individual oxidized nitrogen species.
Figure 3.7-2: Put Figure 3.7-3 right below this figure for comparison. Also, can you provide the same figures for oxidized nitrogen species of interest?
3-26:2 "for more complete descriptions"
3-26:7: This is not seen in Fig. 3.7-4.
3-28:6: "correlative"?
3-28:29 "…mean **<u>oxidized</u>** N…"
3-36:6: Units on deposition velocity?
3-36:7-7: Is this a major extrapolation. Please clarify.
Fig. 3.9-3: How significant is "a", and the units for concentration are non-standard.
3-41:3-5: Further explanation as to "why" is needed.
3-43:26-27: Same should be added for regional scale.
3-47:19-17: I would note all of the evaluation work and measurements done by/for the state, RPO's and EPA. It may not get published in the open literature, but these groups probably do most of the model evaluations done.
3-48:12 "This"?
3-50: What is needed here are the best estimates of N deposition using CMAQ.
Figure 3.12-3: How about adding NH3?

Chapter 4:

Chapter 4 reads more like the old Criteria Documents, being rather exhaustive and sometimes appearing to lose the point.

Also, maybe I missed this, but this chapter seems to have ad hoc decided to use SO_4^+ instead of using $SO_4^=$ (or SO_4^{2-}). Why?

There is significant repetition in this chapter. Much of what is in 4.2.1.4 is in pages 4.10-12.

4-1:22: interacti**<u>ng</u>**
4-2:6: "…when **<u>the</u>** nutrient…"
Figure .1-1: For the forest critical chemical limit, what are the units of 1.0? For the Lake, is "0" sensible?

4-7:13 Might you add surface water acidification?
4-8:4: Define Oa
4-8-29: What about NH_x?
Fig. 4.2-1: Wrong figure. (Switch with 4.2-2)
4-11:25: Replace “This” with “The”
4-13:22: “… forested areas**,** it is …”
4-15:27 Define “%” of what.
4-16: “…acidic deposition moblizes…” no comma.
4-16:14-16: Repetitive.
4-19:11-12: Same paragraph.
4-19:16: “…general… generally…”
4-19:28 “or neutralizing”
Fig. 4.2-3 Probably should define ANC in the caption and also add the 0 lines.
4-22:30 All the “in summary” statements get a bit old.
4-24:3: [K]
Section 4.2.22: Repetitive of prior material.
Fig. 4.2-6: “Bad death”? As opposed to “Good death”?
4-39:25-26: Sentence needs a bit more explanation.
4-43::19: “linear**ly**”
4-44:31: Context needed for 5.0, 5.5 and 6.0. Reference to what effects.
4-49: Should not ANC measurement be up front in measurement methods?
4-49:9: Repetitive.
4-49:14: Small is not defined, and why is this viewed as small?
4-49:23-24: Unclear clause at the end.
4-50: Lines 21-22 and 25-26 appear to be contradictory.
4-54:20: Be specific as to at what level.
4-64:23: Lawrence no longer in review, I think.
4-123:L24…: Again, seems repetitive.
4-129:17 Reviewing only the negative effects appears one-sided.
4-130:2: “Results of these studies…”
4-132:30: Confirmed? Support?
4-135:1: What would this equate to in terms of deposition?
4-148:29: define stges.
4-150:26: “probably”? Cite.
4-152.19-27: Largely repetitive.
4-154:5-9 The term significant here must be purely definitional. What is meant by, or determines, significant?
4-156:4…: Repetitive.
4-157:14 “Niwot Ridge where…” remove comma.
Section 4.4.1.2 can be shortened.
4-168:19-21. This need not be stated. It has to be.
4-174:3-14. Be quantitative… at what levels are the impacts found?
4-177:12-31 Use same units as before.
4-177:3-: Provide units on coefficients.
4-178:9-14: Discuss exactly what was measured, provide uncertainties.
4-179:24-25: Is this likely an issue?

4-179: Provide a summary.

Chapter 5:

This chapter is still a bit choppy, but primarily should be revised by asking the question: What information specifically is needed to provide the scientific basis for reviewing the NAAQS secondary NOx and SOx standards.

Specifics:

5-3:8-12: What about ammonia?
5-12:28: "… decreased **<u>in</u>** some…"
5-12:31: be a bit more specific as to how.
5-13:29-30: Could just be my memory, but I don't recall this.
5-16-28: Remove extra "."
5-16:30 Try not to use "many" as opposed to giving a specific fraction.
5-18:5: rearrange sentence" "contributions of CA…acidity) from some …"
5-20:16: "…section discusses…"
5-20:31: "is it "of" or "by"?
5-26:8-28: These are important points, but they did not seem to come out very distinctly in the chapters. (same with 5-27:15-20).
5-28:22: "AQCD**<u>, further studies suggest</u>** productivity…"
5-31:6: awkward sentence.
5-37:16 remove "in"

Overall: Probably the single biggest limitation in this document is acknowledged early on: It does not try to establish critical loads, without which it becomes difficult to know what levels of environmental exposures are acceptable or not. Decision makers and advisors need such information, even if it is fraught with "uncertainties." (I put uncertainties in quotation marks as it seems as though we use that as a reason to not go forward, which is not the case.) The second real need of this ISA is to dig more in to the reduced nitrogen deposition issue.

Mr. David Shaw

Chapter 1 Comments

1) **Message of the document**
   a) This chapter drives the whole document and as such it should say up front that a major part of this assessment is examining.
      i) The strength of a *deposition* approach to both of these contaminants.
      ii) The purpose and consequences of evaluating N and S in tandem.
      iii) This opens with a statement of eliminating particulates in the scope of this scientific analysis, this is not an appropriate message.

2) **Framing Questions**
   a) Some of the framing questions (pg 1-2) need clarification (e.g. bullet 3 line 13) and don't focus the work as well as the more succinct language below (proposed by E.Cowling Individual Comments on the September 2007 Draft Plan for Review of the Secondary National Air Quality Standards for Nitrogen Dioxide and Sulfur Dioxide October 26, 2007. I suggest substituting the framing questions for these:

      i) "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?"

      ii) "What scientific evidence and/or scientific insights have been developed since the last review to indicate whether, and if so, what particular ecosystem components or other air-quality-related public welfare values, are more or less sensitive than the populations of humans for which primary standards are established and for this reason may require a different level, indicator, statistical form, or averaging time of a secondary standard in order to protect public welfare?"

3) **Format**
   a) The format calls for a summary of findings at the end of each major segment of each chapter which is included, but it should also, as much as possible, discuss the relevance of each of those findings with the two questions above. This should be expressed in Section 1.3.
   b) The format should also require that the conclusions in Chapter 5 restate these original questions and summarize all findings within the two reworded framing questions.
   c) The deposition monitoring network maps are too small to show adequacy of the network.
   d) The summaries would serve the document best by ensuring that all the material is summarized in a clear and concise manner.

4) **Gaps in legislative background and history of the current review**
   a) CAIR should be mentioned in the regulation portion of this discussion.

b) Major scientific, multi-state and national surveys and summary reports of the period (i.e., since SO_2 NAAQS 1982) need to be mentioned, included but not limited to the EPA Eastern and Western Lake Surveys, the National Acid Precipitation Assessment Program (NAPAP), the NAPAP Integrated Assessment in 1991, and the EPA Acid Deposition Standard Feasibility Study Report to Congress in 1995. Significant state surveys like the Adirondack Lakes Survey in 1984-1987 and the ongoing Adirondack Long Term Monitoring of lakes and streams should also be included.

c) The recent progression of the importance of N in acidification should be given more attention. For example, the recent chemical recovery signal in Adirondack lakes appears closely linked with N deposition. Recent data show stream acidification is also highly correlated.

d) Section 1.1.3 SO_x. Include the primary standard for SO_x. Fill in the history gap between 1988 and 2006.

e) Section 1.1.4. Include what led to the development of a deposition approach to this secondary standard as opposed to an ambient air standard. Add what other states may have done with respect to 1) more stringent primary standards or 2) proposals of secondary standards or other regulations to protect the environment from NO_x and SO_x.

f) Current levels of ambient and deposition N and S are improved because of all efforts to attain clean air, which should include major state efforts such as New York State's NYS Sulfur Dioxide Control Program in 1985 that evolved into its Acid Deposition Control Program. Several northeast states (NH,VT, CT and ME) have discussed or proposed S and N deposition standards to protect forests.

5) **Particulate of NO_x and SO_x omission**

a) The first paragraph states "The scope of the joint NO_x and SO_x ISA is limited to welfare topics that do not duplicate those addressed by the forthcoming particulate matter (PM) science assessment. The welfare effects of visibility impairment and climate interactions associated with particulate NO_x and SO_x will be addressed within the secondary PM NAAQS.

b) The omission of particulate phase NO_x and SO_x appears to limit the potential for setting standards in the future using both PM and oxides of Nitrogen and Sulfur standards. Furthermore, PM plays a significant role in nitrogen and sulfur deposition.

c) Also, 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_x and SO_x 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.

6) **Implementation of a secondary standard(s)**

a) It is important to state that this document covers the setting of a secondary standard(s) but not, at this point, the implementation of a secondary NAAQS. They would need to be developed or ……This would be very difficult because at present, there are no adequate source-receptor models to provide the level of control that would be required to meet the secondary NAAQS, if the deposition standards were exceeded in any particular area.

Charge Questions

Question #1

To what extent is the evidence on atmospheric chemistry and physics, air quality, and deposition and exposure sufficiently and correctly described, clearly communicated, and relevant to the review of the secondary NAAQS for NO_2 and SO_2?

1) The information on gas-phase chemistry and physics is sufficient and well-presented in Chapters 2 and 3.
2) Since both gas-phase and particulate S/N are involved in deposition, the ISA would benefit from inclusion of more chemistry and physics on the particulate side in these chapters as well.

Question #2

How well characterized are the relevant properties of the ambient air concentrations and deposition of NO_x and SO_x, including policy-relevant background concentrations, spatial and temporal patterns, and the relationships between ambient air concentrations and ecological exposures?

1) There is enough information on urban NO_2 and SO_2 to characterize ambient levels, but not enough information in rural areas and sensitive ecosystems.
2) In general, emission inventories for SO_2, whose sources are well-characterized, are more reliable than estimates for emissions of $NO_{x,}$ and certainly far more reliable than NH_3 emissions.
3) There is more information, in terms of spatial coverage, on wet deposition of SO_4, NO_3, and NH_4 than ambient SO_2, NO_2, or NH_3

Question #3

How sufficient is the information on atmospheric sciences and exposures for the purposes of evaluating and interpreting the ecological effects presented in Chapter 4 of the draft ISA?

1) There is an inherent danger here of assuming that these three areas of ecological effects are equally important or equally developed in the literature, which in my view, they are not. The danger is the inevitable conclusion that the sufficiency of the information will not be adequate for all of them.
    a) A better use of time would be to go to the bigger questions framed above that have to do with the interaction between the primary and the secondary standards, and the value and need for establishing deposition standards.

General Comments

1) **Deposition-based Standard**
   a) The draft ISA demonstrates a strong interrelationship between deposition data and effects to ecosystems as shown in Table 5.7-1.
   b) Concentration-based standards are not biologically relevant to most resources at risk from air pollution (surface waters, groundwater, soils, etc).
   c) It is important that other EPA programs (i.e. CAMD) are reviewing or participating in this ISA. All programs should be aware of the proposed move forward to a multi-pollutant approach and this new pathway.

2) One or multiple secondary standard
   a) One secondary standard for the US or several according to various sensitive receptor areas in the country? Primary standards protect only one organism, people, and they are distributed throughout the country, so generally one size does fit all. Secondary standards protect sensitive ecological receptor areas (ER) which are not evenly distributed and have multiple sensitive components within them. Are we setting one secondary standard for the country? Have we identified all of the sensitive environments that we wish to track and to protect?

   b) Within each sensitive environment, have the ecological assessments identified a single or multiple deposition targets? Shouldn't each ecological area have one targeted? Have the major eutrophication-stressed estuaries picked a limit for NO_x and NH_x?

   c) Critical loads may be an area of interest. Need discussion on the state of knowledge of critical loads. While there may not be a high resolution understanding (small blocks) areas can be defined by forest or east vs west. The EU has critical loads in place.

3) **Climate change**
   a) There may be a need for analysis of the effects of the SO_x and NO_x deposition on climate change. In addition, the effects of climate change on SO_x and NO_x pollution.

4) **Adequacy of existing air monitoring network**
   a) The density of SO_2 and NO_2 monitors is adequate to track the primary standard, but is not adequate for the secondary standard.
   b) The bulk of the ambient SO_2 and NO_2 monitors, as well as the Speciation Trend Network for fine particulate SO_4 and NO_3, are located in urban and suburban areas.
   c) There is no national NH_3 monitoring program, and what little information is available for ambient concentrations is research-oriented.
   d) There is information on fine particulate SO_4 and NO_3 at >100 Class I areas through the IMPROVE program, but this is probably not adequate to characterize all sensitive ecosystems across the nation.
   e) The major deposition networks (CASTNet, NADP/NTN) were generally established to track the effects of emissions reductions from the energy generation sector.
   f) In terms of data coverage, there are more wet deposition monitors measuring SO_4, NO_3, and NH_4 than there are ambient NO_2 monitors, however these networks are not generally

capable of characterizing deposition in urban areas or many rural areas (especially in the western US).

    g) Dry deposition of S/N is inferred rather than measured directly by routine networks like CASTNet, but even so there are far fewer dry deposition sites compared to wet.

5) **Transformation Products**
    a) Clarify which N pollutants are being discussed.
    b) Research which oxidized N compounds are relevant and feasible to monitor
        i) While NO_y may be more appropriate, there is a need to discuss the difficulty of measuring individual compounds.
        ii) Chapter 2 does describe some of the heterogeneous chemistry between NO_y and halogens, but does not really cover ammonium nitrate/sulfate formation. Halogen chemistry plays an important role in urban coastal settings, but ammonium nitrate/sulfate chemistry is important over vast regions of the continent.

6) **NO_x as a precursor**
    a) Ozone
    b) Ambient nitrates
    c) N deposition
    d) Fine particulates

7) **Inclusion of N_2O**
    a) N_2O is certainly a greenhouse gas, but is not a component of NO_y, nor is it relevant to O_3/PM/haze formation or N deposition (and subsequent acidification or nutrient enrichment). More information on particulate N would be favored over N_2O analysis.

8) **Dry deposition**
    a) Different monitoring networks for sulfur and nitrogen.
    b) Monitoring network not adequate for dry deposition

9) **Emissions inventories**
    a) Are they adequate for each, SO_x, NO_x and NH_x? For the primary and secondary standard? In general, emission inventories for SO_2, whose sources are pretty well-characterized, are more reliable than estimates for emissions of $NO_{x,}$ and certainly far more reliable than NH_3 emissions.

10) **Multiple indicators and multiple sensitive areas.**
    a) States may contain several sensitive regions. And sensitive regions like the Adirondack Mountains will have multiple natural resources with different indicators and/or critical thresholds (see Figure 4.1.-1, page 4.4).
    b) Have all the sensitive areas within the US been identified (Alaska and Hawaii have none?) ? Will each state be responsible for verifying these areas? Is there is enough data to do that in each area? Or whether there will be a blanket single indicator for each sensitive region? What is the more quantifiable indicator of ecological health?

Has the effects literature (for the case study areas where the literature is more complete) identified the most representative indicator to protect the whole area.

Dr. Kathleen Weathers

Chapter 4: Effects of Acidification and Nitrogen Enrichment on Ecosystems and Other Welfare Effects

This chapter was rather unbalanced in writing style as well as analysis and synthesis. It was often difficult to identify the salient points (bottom lines) in much of the first part of the document (until 4.3). There were inaccuracies and/or used unqualified, value-laden language in parts (see specific comments, below). Consider reorganizing and rewriting the chapter, using one voice, and organizing the chapter around a conceptual model. The integrative tables that are at the end of the document could be used to guide a discussion about the overarching effects of acidification and nitrogen enrichment on ecosystems. Supporting information could then be revised, condensed and used to underpin this synthesis.

4a How well are the major effects of SOx and NOx on ecological acidification identified and characterized?
4b To what extent do the discussion and the integration of evidence across scales (e.g., species, communities and ecosystems and regions) correctly represent and clearly communicate the state of the science?

The major acidification effects, which have been indirectly or directly linked to the (wet, sometimes wet + dry) deposition of sulfur and nitrogen, have been identified and characterized in this draft chapter. The relative importance and certainty of various effects was less well characterized.

Categorization of biological and chemical effects is a useful way to partition.

Again, I suggest adding a conceptual model to the beginning of this section. The table (identified as Fig. 4.1-1) and its associated description, is a start. However, I do think that it is more logical to consider deposition as a driving variable and various ecosystem (i.e., export rates, nutrient or pollutant cycling, acidification process, productivity) or ecological properties as response variables rather than the other way around, despite the suggestion that working from top to bottom is inherent in the critical load approach.

Much of the text details studies that have explored the effects of acidification on the various foci of ecological studies (as listed above). The coverage of the literature is reasonably good,. That said, there is much supporting literature in this chapter from past decades. It is very useful to cite these foundational studies, but also important to note what the relevant (to this time period) bottom lines are, especially in situations where the environmental conditions have changed significantly in the interim,. One suggestion is to identify what is new (recent results, or synthesis efforts) and what has been known for some time. I am concerned that studies whose results, for example, point to how ecosystems responded to the depositional regime in the 1980s and 1990s may be dismissed, or questioned as relevant in 2008. However, there have been a number of integrated studies over the past several years, both modeling efforts and synthesis whose results are cited. Thus, It would be useful to identify which class of results is timeless (and therefore avoid questions about whether the findings still hold despite significant changes in emissions and/or deposition over time, for example). Integration and synthesis is difficult to do.

5. How well has the ISI characterized the relationship between acidifying deposition levels of NOx and SOx and ecological effects.

The characterization could be made more direct. As one example, studies that highlight deposition, whether estimated across the landscape or to a site, or controlled through experimental additions, were not highlighted or cited well throughout the text.

The ecosystem approach was underscored in the first part of the chapter. Thus framing the relationships of deposition and ecological responses using a mass balance approach would be another logical way to organize the discussion. Consider including a table or a section that summarizes the relationships between deposition and ecological effects toward the beginning of the chapter.

I appreciated the introduction of critical loads as a way that the EU and others have considered successfully the relationship between atmospheric deposition and environmental effects; it is an important approach to explore in this document.

The word/concept “thresholds” is used in numerous cases. It should be (re) defined in this section. A summary section or table identifying ecological thresholds that have been documented (the response variable and the actual threshold) would be very useful. Even if it turns out that few have been defined, it would be useful exercise.

An introductory paragraph about the (legitimate/defensible) use of models and a brief characterization (i.e., table about the nature and utility of the various models, and their results, that are cited throughout this chapter) would be a useful addition. Also, wherever there are multiple model results for an ecosystem or region, a summary of the similarities (e.g., page 4-87 for the Adirondacks) as well as the differences in model results and whether there has been any independent validation or verification of the models should accompany the comparison.

6. How well characterized are the oxidized and reduced forms of nitrogen on acidification

The N cascade section was good. Consider including the first part of the N cascade section and a parallel sulfur section at beginning of this chapter.

Make clear that in addition to HNO3 wet and dry deposition, some areas of the country are experiencing a rise in NH3 emissions and NH4 wet deposition (NADP data show this increase). Although there are fundamental differences in ecological processing when reduced vs oxidized nitrogen is added to an ecosystem, it would be useful to point out that there may be downstream acidification/eutrophication effects if nitrogen demand is exceeded and nitrogen is leached as a result of NH4-N deposition (in addition to the brief mention on page 4-145).

A few overarching comments:

Total deposition, wet+snow+dry+fog, in places where it matters, is still poorly characterized for most places on the planet, especially in non-homogeneous terrain. Getting reasonable estimates of total deposition, especially across space, and relating emissions to deposition are still active areas of research. These facts can be problematic when deposition is used as the independent variable or treatment for any of a suite of ecological responses. I do not think that this challenge—obtaining and using reasonable estimates of deposition— renders specific studies either inadequate or wrong. However, it does underscore the need for multiple lines of evidence to identify, with some confidence, the effects of N and S loading on ecosystems, species and communities. These multiple lines of evidence often come through the use of experimentation (especially loading studies), modeling, theory, long-term analyses, and use of deposition gradients (where there are surely large differences in deposition even if the absolute numbers are have large uncertainties associated with them). I think that pointing out the importance and power of multiple lines of evidence in supporting current understanding about the effects of NOx and SOx on ecological systems would be a useful thing to do at the beginning of this section.

I like the case studies, but they could be used more effectively, perhaps to highlight parts of a conceptual model.

Some details:

The charge on sulfate is incorrectly identified throughout the text: sulfate is an anion, not a cation, and it's divalent, not monovalent. I note, however, that there is correct inference for sulfate's behavior throughout the text (i.e. it is listed/included in discussions about mobile anions).

Decomposition should be added as an important process in section 4.1.1 and food webs vs food chains are more realistic descriptions of energy movement within ecosystems.

There are many places in the text where references are missing, but necessary.

Correct the text for reduction/oxidation reactions and products (the transformation from ammonium to nitrate is oxidation, for example).

Figures 4.2-1 and 4.2-2 are transposed.

Y axis on Fig. 4.2-6: "Bad?" death?

Do the colors mean anything on Fig. 4.2-12?

It seems to me that much of the fish data that include abundance, biodiversity, and total numbers of species present as response variables are potentially confounded by freshwater stocking activities. Perhaps stocking did not influence the results or was not practiced in many of the focal surface waters. If that is true, it would help to say so, if it is not, it may still be worth mentioning this confounding point.

I believe that the original reference to N saturation was Agren and Bosatta (sp 1988) (page 4-106).

Equating throughfall N flux with atmospheric N deposition is not warranted in many locations in the US because of variable uptake and leaching in the canopy (page 4-110). Throughfall deposition or flux is often considered to be a good indicator of what is deposited to the forest floor, but not necessarily what is deposited from the atmosphere to canopies when the nutrient, ion or element of interest is biologically reactive/active. Sulfur, however, has often been considered an exception. In regard to sulfur in throughfall, research that has suggested its utility as an indicator of total deposition should be included as well as the one on page 4-162 (Cape) that questions it. For example, Garten and Lindberg, Lindberg and Johnson, Lovett, Weathers et al., etc. have pointed to its utility.

Words such as “harmful” or “negative effects” without qualification should be avoided; if used they should be qualified with specific environmental terms (e.g., harmful physiological effects of acidity on fish biota). Also “ecosystem or ecological health” is ill defined and often a lightning rod-word. I suggest defining it, or better yet, don’t use it.

Consider doing a publication count by year on the topic of acidification/critical loads.