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ABOUT THIS REVIEW

EPRI is conducting a full review of the elements contained in the Policy Assessment Document (PAD) for the Secondary National Ambient Air Quality Standards for SO_x and NO_x Review. EPRI has brought together a team of experts in ecosystem and atmospheric sciences from Tetra Tech, ENVIRON Corporation and within EPRI. Several key researchers from the National Acid Precitation Assessment Program (NAPAP) and other prominent studies are represented in this team including Steve Gherini, Robert Goldstein, David Grigal, Ralph Morris, Ron Munson and Karen Summers. In conducting the review, the research team has examined the extent to which key variables are adequately represented using the assumptions and models described in the PAD. This analysis illustrates that the uncertainty associated with EPA's approach to estimating critical loads and mapping those to atmospheric concentrations is so large that its use in defining the requisite level of a standard is questionable. The research team is continuing its review of all documents released, including the second draft PAD released on September 15, 2010 and the addendum released on September 23, 2010. EPRI will submit a final report of this review before the November 12, 2010 filing deadline.

ABOUT ELADIO KNIPPING

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Dr. Knipping received his B.S. degree in civil engineering from the Instituto Tecnológico de Santo Domingo (Dominican Republic). He received both his M.S. degree in environmental engineering and his Ph.D. degree in mechanical and aerospace engineering from the University of California, Irvine.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) is considering proposing a new secondary National Ambient Air Quality Standard (NAAQS) that considers the combined effects of oxides of sulfur (SO_x) and oxides of nitrogen (NO_x) on aquatic and terrestrial systems. The proposed approach for developing a combined standard is presented in a policy assessment document (PAD). Two drafts of the PAD have been released, the latest on September 15, 2010 with an addendum released on September 23, 2010. The proposed approach for establishing secondary standards is based on the effects of NO_x and SO_x on surface waters, and to a lesser extent on terrestrial systems.

As the emphasis of the PAD is on the protection of sensitive surface waters, our comments today are focused on the science underlying the Atmospheric Acidification Potential Index and the results of an uncertainty analysis showing the impact on SO_x and NO_x concentrations required to show attainment.

The principal components of EPA's approach include evaluation of critical loads for specific watersheds in different regions of the country, followed by scale-up to determine allowable ambient air concentrations. An example of a tradeoff curve was developed by EPA to show how both SO_x and NO_x can be considered together. Additional comments on the overall approach can be found in **Appendix A1**.

Concerns with EPA's techniques and proposed models will be discussed thoroughly in our full report. The primary concern is that the uncertainty associated with EPA's approach to estimating critical loads and mapping those to atmospheric concentrations is so large that its use in defining the requisite level of a standard is questionable. EPA cites this uncertainty as very small; our computations show otherwise.

COMMENTS

Our key comments are summarized as follows:

1. **[STEADY-STATE ASSUMPTION]** A steady-state approach is inconsistent with ecosystem dynamics, particularly in terrestrial systems.
2. **[ACID NEUTRALIZING CAPACITY: ANC]** With respect to Acid Neutralizing Capacity (ANC), the data shown in the PAD are specific to the Adirondacks. It has been shown that fish respond directly to inorganic aluminum concentrations [Al_i] and, to a lesser extent, the hydrogen ion concentration [H⁺] or pH—not ANC.

Florida lakes with low DOC provide an example of this. Lake Barco and Lake Five-O were evaluated as part of the Hydrology and Acidity of Seepage Lakes study. Both have low ANC and low pH, (i.e.,

elevated [H⁺]). However, because neither lake receives significant inputs from terrestrial sources, both have low aluminum concentrations and thus thriving fisheries (Pollman et al, 1991).

- 3. [BASE CATION DEPOSITION AND BASE CATION UPTAKE]** Non-anthropogenic atmospheric deposition of base cations is an important input to the SSWC model used to calculate critical loads. Measurements of non-anthropogenic atmospheric deposition are not available. Measurements of total deposition of base cations are available, but sampling locations are not evenly distributed nationwide, especially for dry deposition. In addition, techniques for differentiation of anthropogenic versus non-anthropogenic deposition are not described.

Base cation uptake by watershed vegetation is another important model input, but this value is influenced by a wide variety of both natural and anthropogenic disturbances and varies over time even in the absence of disturbances.

Appendix A2 provides a more detailed discussion on these processes.

- 4. [PRE-INDUSTRIAL BASE CATION CONCENTRATION: BC₀]** Determination of the critical deposition load is highly dependent upon historical values of pre-industrial base cation concentrations in 1850-1860. Those values were never measured.

EPA proposes to estimate those values using “hindcasting” with the MAGIC model or using an “F” factor approach. The latter method was developed for Scandinavian countries that have much less diverse bedrock and soils than in the United States.

- 5. [HINDCASTING WITH THE MAGIC MODEL]** Testing of the MAGIC model going forward in time raises doubts about its ability to simulate from far back in the past.

Please see **Appendix A3** for a discussion on hindcasting with the MAGIC model.

The EPA should consider that both deposition and surface water data are available for the last 20-30 years, a period with decreasing SO_x and NO_x deposition. This period must be simulated accurately to gain confidence in the models; only then can one move forward in time with the models to develop an approach for evaluating sensitivities to deposition, rather than trying to hindcast conditions from over 150 years ago that were never measured.

- 6. [CATION EXCHANGE]** Cation exchange is missing completely from the processes leading to the AAPI equation. Moreover, surface water pH is largely determined by the fraction of precipitation that flows laterally through deeper soil horizons and cation exchange in these soils.

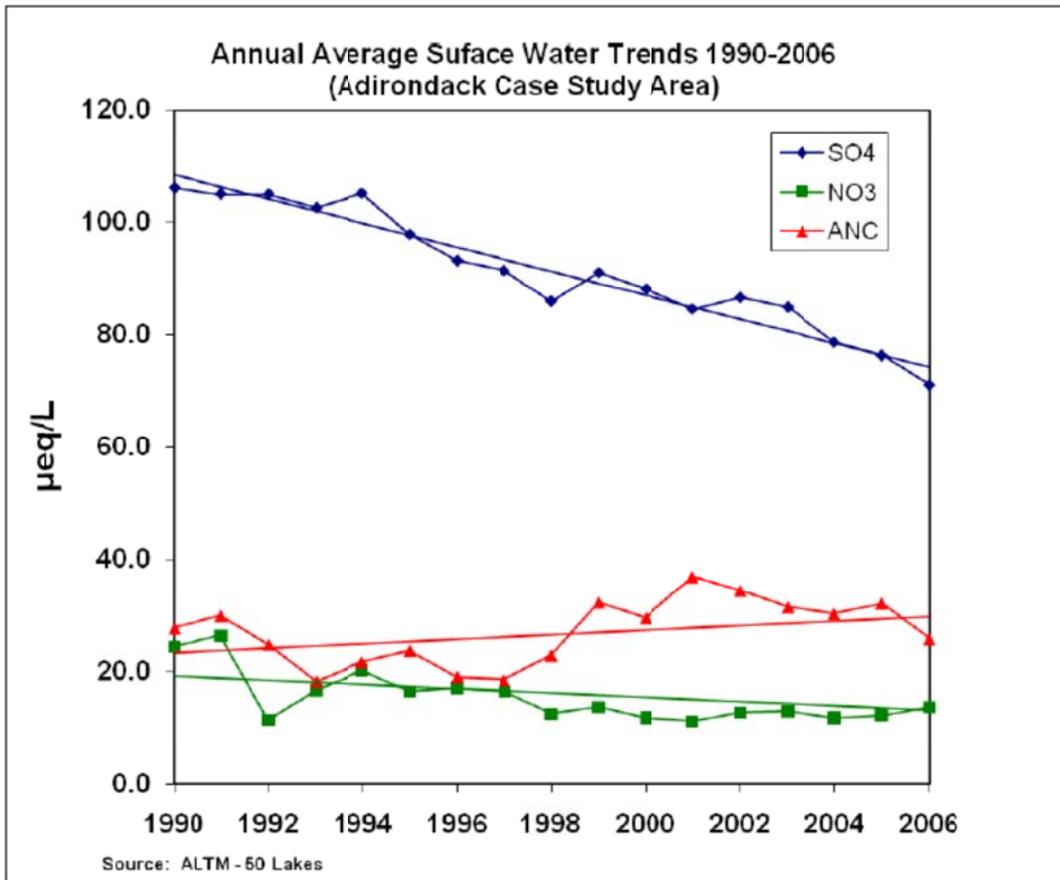


Figure 1. Adirondack Lakes Solute Trends (Source: PAD)

Figure 1 shows how in the Adirondacks, surface water sulfate concentration has decreased with decreasing SO_x deposition from 1990 to 2006. Surface water nitrate concentration has also decreased, though to a lesser degree. Note the ANC, which is the difference between base cation concentrations and strong acid anion concentrations, increased only slightly. This is because the base cation concentration, being largely induced by the strong acids, also decreased. Thus, the predicted increase in ANC by the MAGIC model did not materialize (see Figure 2).

Measured				MAGIC Model			
Solute	1990	2006	Delta	Solute	1990	2006	Delta
SO ₄ ²⁻	107	73	-34	SO ₄ ²⁻	115	68	-47
ANC	25	30	+5	ANC	33	61	+28
NO ₃ ⁻	19	14	-5	NO ₃ ⁻	5	5	0
ΣC _A	126	87	-39	ΣC _A	120	75	-45
ΣC _B	151	117	-34	ΣC _B	153	134	-19

$\Sigma C_B / \Sigma C_A = 0.87$
 $\Sigma C_B / \Sigma C_A = 0.42$

here, $\Sigma C_A = \text{SO}_4^{2-} + \text{NO}_3^-$

A similar comparison for the Shenandoah area shows MAGIC having some trends in the wrong direction, bringing into question the use of MAGIC to extrapolate forward from 150 years in the past

Figure 2. Changes in Solute Concentration in Comparable Adirondack Lakes, 1990-2006, Measured vs. MAGIC

Please see **Appendix A4** for a more detailed discussion on cation exchange.

- [BASE CATION WEATHERING]** Base cation weathering inputs play a critical role in SSWC applications, but are likely to be highly uncertain due to the use of hindcasting, which requires guesses regarding pre-industrial conditions, and the under-constrained nature of the weathering formulations used in the MAGIC model.

Moreover, the method proposed for regional extrapolation of base cation weathering does not properly account for regional differences in mineralogy and could lead to large errors in projected response to changes in deposition.

Please see **Appendix A5** for a more detailed discussion on base cation weathering.

- [ORGANIC ACIDITY]** Organic acids can be components of surface and soil waters, as well as part of both wet and dry deposition. Typically they are mixtures of carboxylic acids. Some are relatively strong; i.e., they readily donate protons to solution and thus occur in dissociated form. They are naturally occurring compounds.

Typically, the contributions of these acids to total acidity in deposition are small but can be large in limited cases. Notwithstanding, the concentration encountered in soil and surface waters are

typically larger than that found in deposition, as these acids are naturally-occurring breakdown products of soil organic matter.

EPA is proposing that waters with DOCs of greater than 10 mg L⁻¹ be excluded from further analyses and be deemed naturally acidic. However, the selection of this threshold is largely arbitrary.

9. **[NITROGEN UPTAKE]** The biogeochemistry of nitrogen in catchments is quite different than that of sulfur. In many terrestrial systems, nitrogen is the limiting nutrient for vegetation growth; in most systems, nitrogen input from deposition is largely removed by vegetation.

Please see **Appendix A6** for a more detailed discussion on nitrogen uptake.

10. **[USE OF BEDROCK MINERALOGY AS A CLASSIFICATION GUIDE]** EPA calculates the critical acid deposition for a population of lakes and streams, grouped by acid sensitivity using bedrock mineralogy as classification guide. However, there is no single factor that can be used to characterize vulnerability. The flow path of water tributary to a lake or stream is critical. Water bears the chemical characteristics of where it has been; thus, factors influencing flow path are key. In sloping watersheds this would include soil depth. In seepage lakes, a critical factor would be the local hydrologic gradient.

11. **[ATMOSPHERIC TRANSFER FUNCTIONS (VSO_x and VNO_y) AND REDUCED N LOAD LNH_x]** VSO_x and VNO_y are atmospheric deposition transfer functions which are calculated from model simulations by dividing annual average SO_x and NO_y concentrations by the total NO_y and SO_x deposition, **respectively, for each grid cell and then aggregating all grid cells in the area of interest.** LNH_x is the reduced nitrogen loading calculated similarly. Therefore, VSO_x, VNO_y, and LNH_x are key parameters that determine AAPI. The VSO_x and VNO_y parameters, in particular, are important because they link the air quality indicator (SO_x and NO_y) to the adverse effect (AAPI) that the secondary NAAQS is based upon.

To analyze how these parameters vary spatially and between different model simulations, we have calculated them using existing annual atmospheric model simulation outputs. **Table 1** summarizes available modeling outputs (i.e., the scenarios) that were used to examine the variability in these parameters. **Figure 3** illustrates the regions used in this analysis.

Table 1. Existing regional annual atmospheric model output data that are processed to analyze variability in VSOx, VNOy, and LNHx.

Study	Model	Emiss/Met Years	Domain 1		Domain 2		Domain 3	
			km	Local	km	Local	km	Local
VISTAS	CMAQ V4.5.1 SOAmods	2002/2002 2009/2002 2012/2002 2018/2002	36	CONUS	12	SE US		
UBAQS	CMAQ V4.6	2005/2005 2006/2006 2012/2005 2012/2006	36	CONUS	12	UT-CO		
EPRI	CMAQ AMSTERDAM	2002/2002			12	E US		
FCAQTF	CAMx V4.51	2018/2005	36	CONUS	12	SW US	4	4Corners
General	CAMx V5.21	2005/2005 2006/2006	36	CONUS				

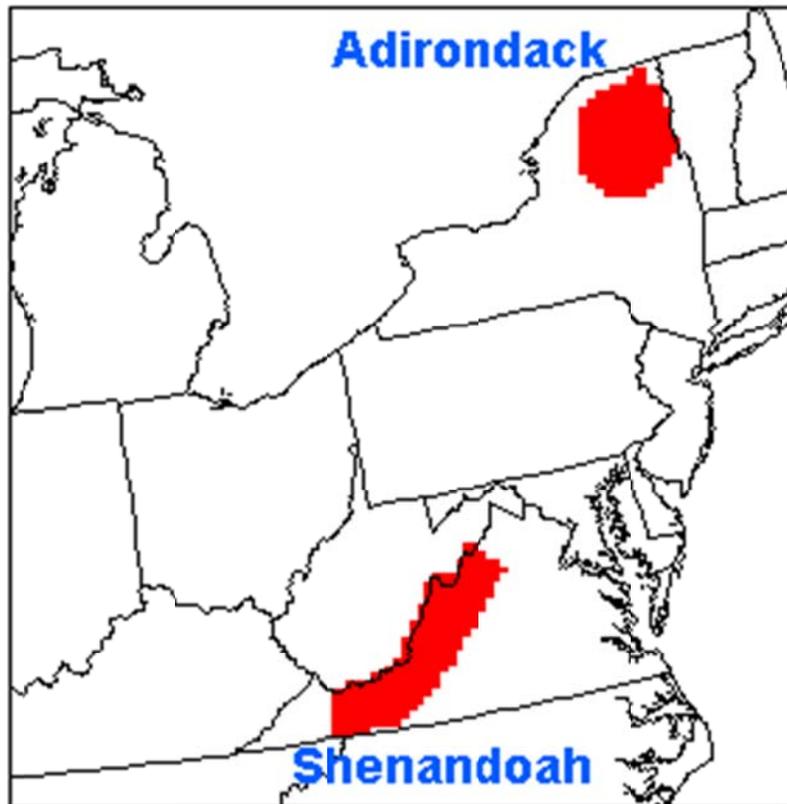


Figure 3: Regions used for analysis of variability in the VSOx, VNOy and LNHx terms. The Adirondack region has 18 cells in a 36-km grid and 164 cells in a 12-km grid. The Shenandoah region has 23 cells in a 36-km grid and 207 cells in a 12-km grid.

The choice of the simulation year, the atmospheric model, and the model configuration (such as the grid resolution) can make a large difference in the calculated VSO_x and VNO_y parameters. This introduces uncertainty in the definition of a secondary NAAQS using EPA's proposed approach. This is illustrated in **Figure 4**.

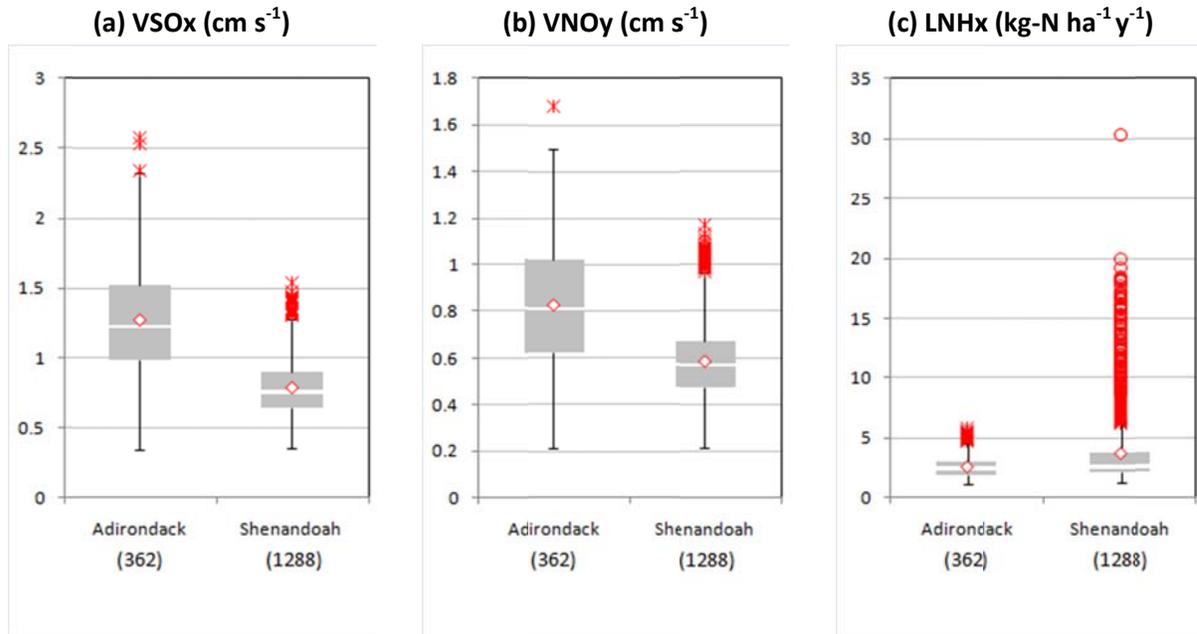


Figure 4. Box and whisker plots for variability of (a) VSO_x, (b) VNO_y, and (c) LNH_x across all the grid cells at each test case area and all the modeling scenarios.

Appendix A7 contains a more detailed evaluation of VSO_x, VNO_y, and LNH_x.

- 12. [UNCERTAINTY ANALYSIS]** EPA in their revised PAD presents a qualitative table on uncertainties. However, EPA does not present calculation examples or show **traceable quantitative uncertainty analyses**. At one point in the previous PAD, EPA claims that their errors are “offsetting” and conducts an uncertainty analysis of critical loads. Although the terms in their equations have uncertainties of 25 to 65 percent each, their overall uncertainty, at least for the 0 and 50 ANC_{lim} cases, are stated to be only 4 and 9 percent, respectively. Not only does this sound unlikely, but by using the theory of variances, **one can show it to be mathematically impossible** (see **Appendix A8**).

We have conducted a suite of uncertainty analyses using EPA's equations/models and the Monte Carlo technique as well as the Kline-McClintock method, and a combination of our and EPA's estimates of uncertainty in the individual terms for an example in the Adirondacks. In every case we found large overall uncertainties that compromise the practical usefulness of the equations and models (see **Figure 5**). When we evaluated cases of EPA's approach for multiple lakes/streams, we found even larger uncertainties.

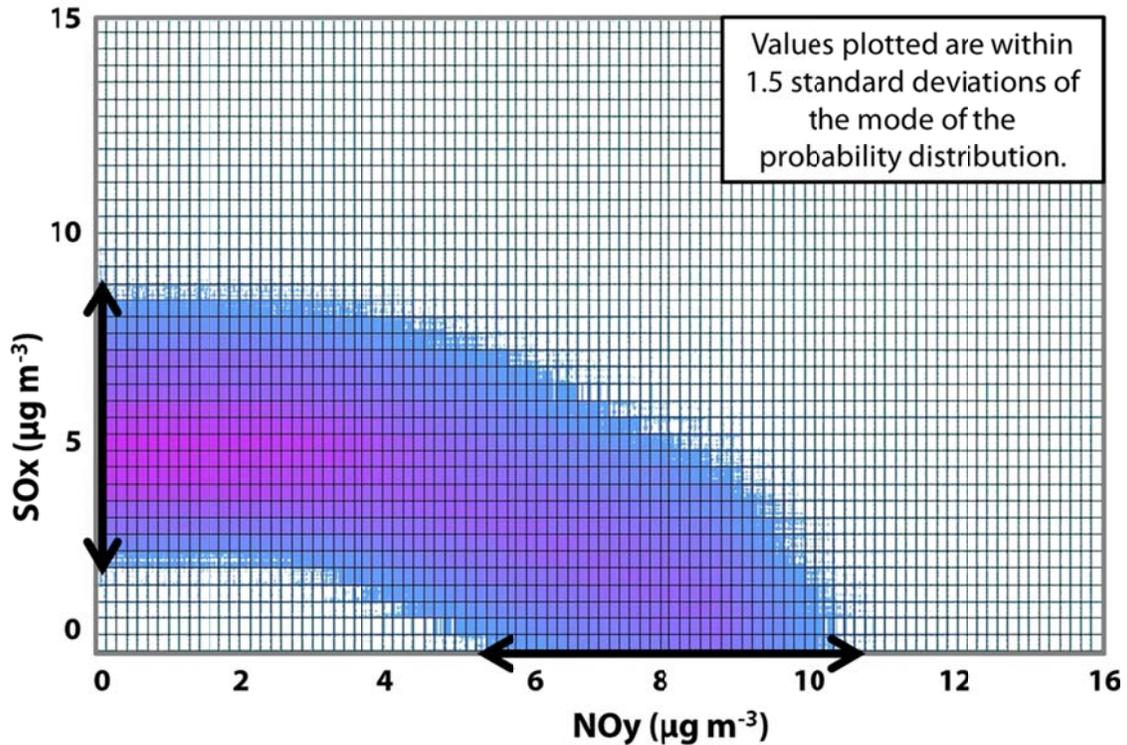


Figure 5. Uncertainty in Atmospheric Standards: Adirondack Example. The effects of uncertainty on ambient air standards for SO_x and NO_y (NO_x). Note that values plotted are within ± 1.5 standard deviations from the mode of the probability distribution (representing an 87% confidence interval). These results also do not include the LNH_x term and its associated uncertainties. These results are for a single lake; multiple lake results (and results in other regions with less available data) will have wider variances and confidence limits.

It may be argued that these overall uncertainties are large because our estimates of individual parameter uncertainties are large. We would counter that they are huge because of the formulations proposed by EPA, i.e. using BC₀*. Also note that our parameter uncertainties fall within the ranges used in EPA's Monte Carlo simulation.

CONCLUSIONS

In the proposed approach, whatever standard is established will be based on highly uncertain methods, including under-constrained estimates of pre-industrial conditions. However, the best evidence available regarding how surface waters will respond to changes in acidic deposition is the change measured in response to decreased deposition over the past two decades.

Only mechanistic models that can accurately represent this observed response can build confidence in the ability to predict responses to future changes in deposition. Establishment of a standard requires a technically rigorous basis and must not ignore high-quality research regarding the response of surface waters to changes in deposition.

Appendix A1: Additional Comments on the Proposed Approach

Definitive determination of the proposed approach for the establishment of standards based on surface water acidification is difficult. The report contains many contradictory statements and spends a significant amount of time describing assessment methods that it later says are inappropriate for use in a national assessment aimed at establishing secondary standards. However, on page 27 of Appendix B to the PA report, EPA appears to define their approach as follows:

Utilizing a process-based model, which can calibrate BC_w rates to stream or lake chemistry across any number of years, provides a credible long-term estimate of the BC_w rate that can be input into the SSWC in order to obtain the system critical load. The process-based model most widely applied throughout the U.S. to date is the MAGIC model.

In other words, EPA plans to calculate critical loads with a modified version of the Steady-State Surface Water Chemistry Model (SSWC) using base cation weathering rates (BC_w) established by the MAGIC model.

The SSWC is a very simple model, and that simplicity can make it seem attractive to use in establishing a standard with such widespread applicability. However, surface water acidification is dependent on the interaction of a wide variety of extremely complex processes. These include the deposition processes themselves (wet and dry), hydrologic processes that determine where water flows (see Figure A1), and biogeochemical processes that influence the acid-base chemistry of water flowing through a basin. The interaction of all of these processes determines water quality (Munson and Gherini, 1991a). A tool as simple as SSWC cannot capture that complexity and cannot produce an accurate representation of the response of surface waters to changes in acidic deposition.

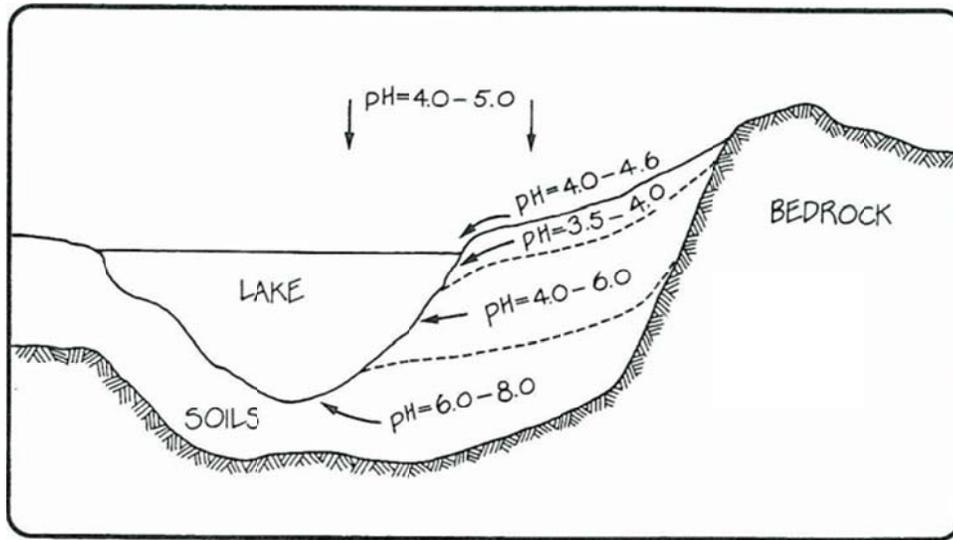


Figure A1. Changes in soil solution pH with vertical distance through the soil profile for an Adirondack lake watershed (after Gherini et al, 1985). Solution in the upper soil horizons is often more acidic than the incident precipitation or throughfall. As one moves down the soil profile more alkaline solution is encountered. The amount of water moving laterally through the soil horizons strongly influences the acidity of surface waters, and this lateral routing can change. Large amounts of water from storms and snow melt can overwhelm the lateral flow carrying capacity of the lower layers and back up lateral flow into the upper layers, resulting in more acidic surface waters.

However, given that application of SSWC is the approach proposed in the PAD, an examination of specific aspects of the approach is warranted. There are several potential pitfalls to the proposed use of SSWC in establishing the NAAQS secondary standard that will be described below.

Appendix A2: Base Cation Deposition and Base Cation Uptake

BC^*_{dep} Estimation

Atmospheric deposition data are more readily available than data for the other components of BC^*_o . For BC^*_{DEP} , the National Atmospheric Deposition Program (NADP) wet deposition data are available from the sampling locations shown in Figure A2 (NADP, 2010). Note that for the Adirondacks and for the Sierra Nevada mountains, there appear to be four sampling locations within each region. However, the land area for the Sierra Nevada mountains region is much larger than for the Adirondacks. Application of data from the same number of stations over a much larger region would have the effect of increasing the uncertainty in deposition estimates in the Sierra Nevada mountains region relative to the Adirondacks. In general, there are more sampling locations per land area in areas thought to be sensitive in the eastern U.S. than in the west. Thus wet deposition estimates in the west are likely to be more uncertain than those in the east.

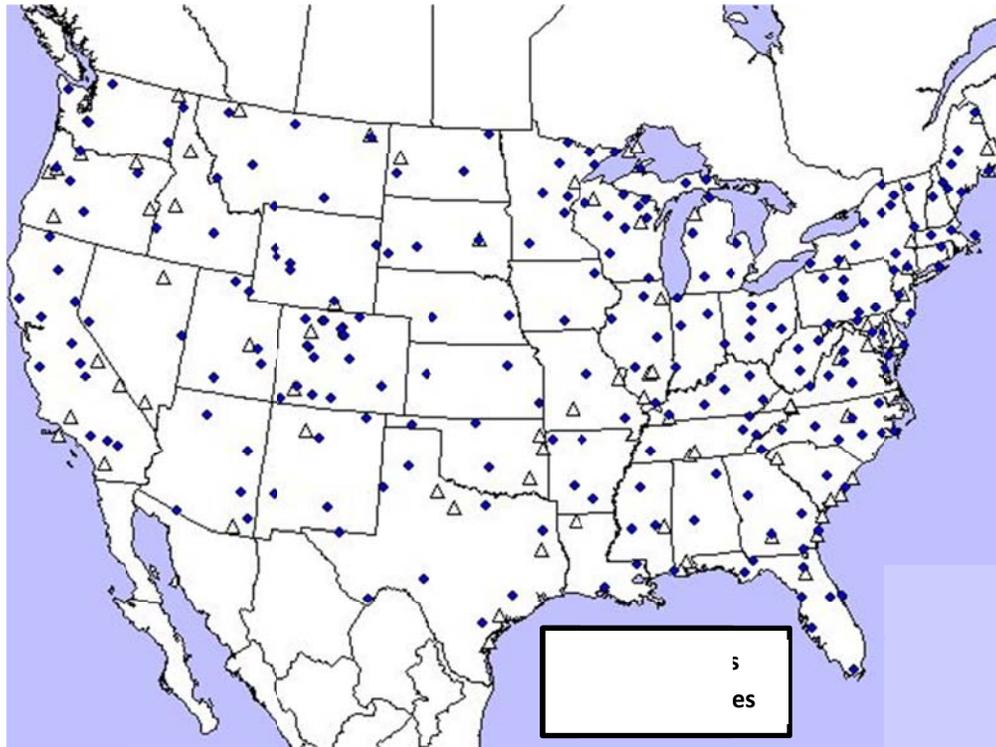


Figure A2. NADP Wet Deposition Sampling Locations (NADP, 2010)

The eastern bias in sampling locations is even more striking for the CASTNET dry deposition network, as shown in Figure A3 (EPA, 2009b). Further, it has been shown previously (by Chen et al, 1983 and Lindberg et al, 1986) that actual deposition to forested ecosystems can be increased considerably by the forest canopy. It is unclear how this will be handled in EPA's approach.

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Another issue is that BC_{dep}^* is defined as the non-anthropogenic deposition flux of base cations. The measurements of wet and dry deposition define the total deposition flux of base cations. Sampling methodologies do not separate anthropogenic flux from non-anthropogenic flux, and anthropogenic flux of base cations is ill-defined at best. Base cation inputs originating from a cement plant would clearly be anthropogenic, but would dust generated from nearby dirt roads be anthropogenic or non-anthropogenic, and how could they be differentiated in at a receptor-location in any case? Estimates of anthropogenic inputs versus non-anthropogenic inputs can be calculated, but the basis for the calculations is unclear and the applicability of any calculation scheme nationwide would not be appropriate due to different processes that come into play in different regions.

These issues illustrate that even for the component of BC_o^* with the most reliable data, the uncertainties are large.



Figure A3. CASTNET Dry Deposition Network Sampling Locations (EPA, 2009b)

BC_u Estimation

The PAD report states that, “Assumptions or estimates for BC_u ... can be made based on attributes of the area of study, including vegetation characteristics.” The U.S. Forest Service (USFS) has data on vegetation characteristics for most parts of the country, including areas that are thought to be sensitive to acidic deposition. However, base cation uptake in forest soils is a highly variable process that is influenced by a wide range of natural processes as well as land management practices.

For example, Figure A4 shows the response of two watersheds in the Hubbard Brook Experimental Forest to clear cutting (Likens et al, 1994). In Watershed 2, growth was suppressed for three years following clear cutting. In Watershed 5, regrowth was allowed to progress immediately after clear cutting. Note that the rate of calcium uptake in Watershed 5 doubled in years 4 to 8 in comparison to years 1 to 3, and in Watershed 2 uptake went from zero during years 1 to 3 (due to a land management practice: growth suppression) to over two kmol ha⁻¹ during years 4 to 8. The results of this analysis demonstrate three important points:

- Changes in uptake occur in response to perturbations
- Uptake rates can change over time
- Uptake rates can vary substantially even in watersheds that are physically close together and have similar characteristics, as reflected in the differences in uptake in the two watersheds during the years 4 to 8 time period.

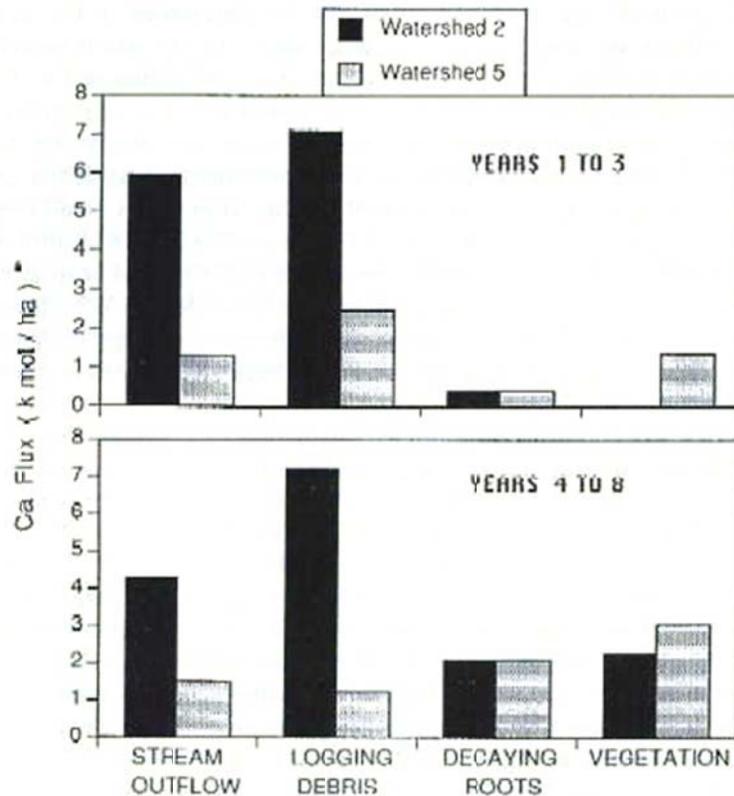


Figure A4. Response of Watersheds in Hubbard Brook Experimental Forest to Clear Cutting (Likens et al, 1994)

Variability in uptake within a region is further illustrated using the results of the Integrated Lake-Watershed Acidification Study (ILWAS) of lakes in the Adirondacks (Goldstein et al, 1984). Woods, Panther, and Sagamore Lakes are located in close physical proximity, receive nearly identical deposition loads, and have similar soil and geologic characteristics. Woods Lake is acidic, Panther is

circumneutral, and Sagamore is in-between. During a three-year study, over 600,000 data points were generated to evaluate the processes influencing the acid-base characteristics of the three lake-watershed systems. A dynamic mechanistic simulation model developed as part of the study, the ILWAS model, was applied to the lakes to evaluate their response to changes in acidic deposition (Gherini et al, 1985). Figure A5 shows the simulated contribution of various processes to the observed ANC in Woods and Panther Lakes. As indicated, plant growth has a much larger impact on the surface water characteristics of Woods Lake than Panther Lake (Munson and Gherini, 1991b). In spite of the significant similarities between the two systems in terms of proximity and acidic inputs, the impact of uptake by vegetation is considerably different. Thus a simplistic treatment of base cation uptake is inappropriate.

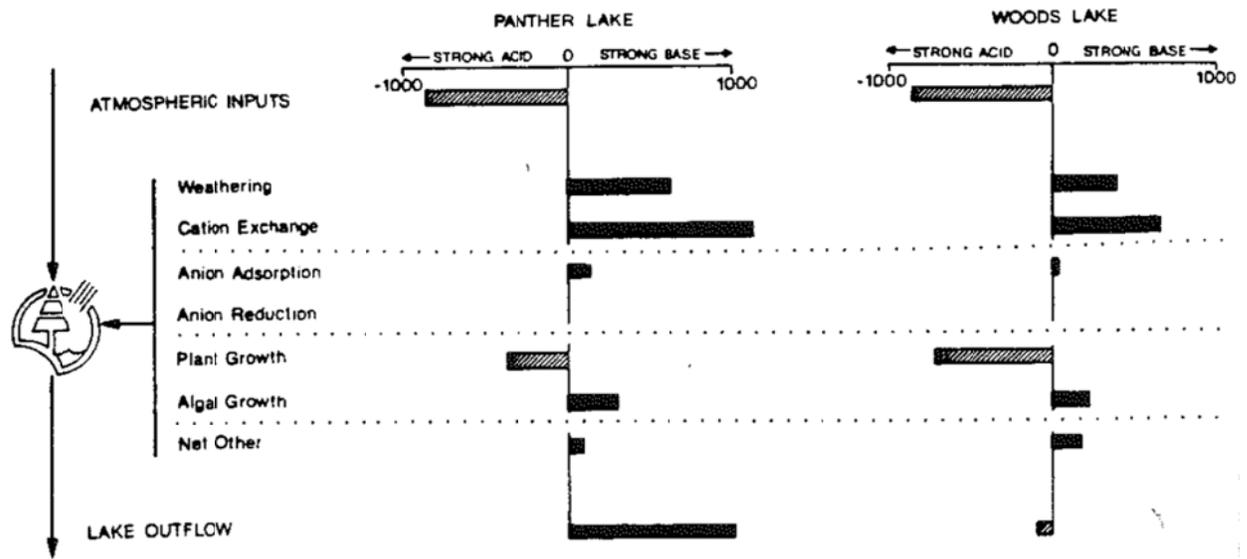


Figure A5. Contribution of various processes to the observed ANC in Woods and Panther Lakes (based on ILWAS model simulations). Note the large difference in acid generation due to plant growth between the two systems. Units are eq ha⁻¹ y⁻¹ (Munson et al, 1987)

The authors of the PAD report try to negate these types of issues by assuming that, “*steady-state conditions exist.*” The assumption of steady state is not appropriate. Ecological processes are never at a truly steady state condition (Sullivan et al, 2009). Climactic variations, fires, forest blowdown, perturbations by biota (e.g., beaver activity and insect infestations) and even processes that take place over geologic time scales (e.g., glaciation) all cause deviations from steady state conditions. Uptake varies considerably depending on the forest successional stage, which is typically characterized by rapid uptake to support early growth, followed by slower maintenance uptake, and finally minimal uptake when the forest is in decline. Perturbations superimpose large variations in uptake on this general successional uptake pattern. To impose a standard with a criterion that it be consistent with steady state conditions is not appropriate.

Appendix A3: Hindcasting with the MAGIC Model

One of the basic principles used in application of the MAGIC model is hindcasting. Application of MAGIC involves starting with assumed historical, or pre-acidification (ca. 1850 – 1860), conditions and running the model forward to see if it matches current observed conditions. If the simulated current concentration comes within a pre-determined range of current observations, that model run is considered “successful” (EPA, 2009a). However, measurements of pre-acidification conditions do not exist. The assumed pre-acidification conditions are really no better than a guess. However, that guess can have serious implications with regard to the ultimate simulation results. It has been demonstrated that using a similar approach in modeling different ecological phenomena results in a wide range of historical conditions that allow for matches with current conditions (Grieb et al, 1999, Spear et al., 1994). The MAGIC model calibration procedure is described in the REA as follows (see Figure A6):

For each of the modeled sites, 10 distinct calibrations were performed with the target values, parameter values, and deposition inputs for each calibration reflecting the uncertainty inherent in the observed data for the individual site. The effects of the uncertainty in the assumptions made in calibrating the model (and the inherent uncertainties in the data available) can be assessed by using all successful calibrations for a site when simulating the response to different scenarios of future deposition.

This is the same procedure that was followed for MAGIC model calibrations done under EPA’s Direct Delayed Response Project (DDRP). During DDRP, MAGIC was used to simulate streams in the Southern Blue Ridge Province, and one of the streams simulated was shown to reach negative ANC values under a particular deposition scenario. Results from this simulation were then scaled to a large number of streams in the region with the implication that these streams would all become acidic under this particular deposition scenario. However, when evaluated more carefully, it was discovered that the calibrated ANC was significantly lower than the observed ANC (approximately 30 $\mu\text{eq L}^{-1}$). Thus in the simulation, the stream lost 30 $\mu\text{eq L}^{-1}$ of ANC in a “calibration event”, and that loss was carried through to the response to the deposition scenario. Without that loss of ANC associated with model calibration, the stream would not have been shown to acidify and thus no other streams in the region would have been projected to acidify (Munson et al, 1990).

This story illustrates the basic problem with using hindcasting as an integral component of the model calibration process. Because pre-acidification conditions are not measured and those pre-acidification conditions play an important role in the model calibration process, the model is highly under-constrained. This lack of constraint is reflected in the large deviation between simulated and observed current conditions that, based upon the standard application procedures built into the model, were allowed to persist and produced a “successful” calibration. Taken to the next level, that obviously inadequate calibration was then allowed to be scaled-up with the result that a large

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number of streams were erroneously assumed to be impacted under a particular deposition scenario.

The REA (EPA, 2009a) reports that for a MAGIC model application to 44 lakes in the Adirondacks, the pre-acidification ANC ranged from 106.8 to 134.0 $\mu\text{eq L}^{-1}$. This range seems relatively small, but the fact that it is based upon a procedure that is highly under-constrained and that there is no means to compare the simulated values to measurements undermines any confidence in the result.

Appendix A4: Cation Exchange

The base cation supply to surface water systems includes inputs from deposition, weathering, and cation exchange. The MAGIC model calculates cation exchange, but its contribution to surface water base supply is ignored in the calculation of critical loads. The justification given for this is provided on page 5 of Appendix A as follows:

Present-day surface water concentrations of base cations are elevated above their steady state preindustrial concentrations because of base cation leaching through ion exchange in the soil due to anthropogenic inputs of SO₄ to the watershed. For this reason, present-day surface water base cation concentrations are higher than natural or preindustrial levels, which, if not corrected for, would result in critical load values not in steady-state condition.

This gets back to two issues noted earlier:

- ecological processes are never at a truly steady state condition (Sullivan et al, 2009), and
- pre-industrial ion concentrations were not measured.

Climatic variations can lead to soil drying and precipitation of salts. Upon rewetting, these salts can re-dissolve and influence the movement of cations to or from the exchange complex. Forest blowdown can lead to warming of soils and rapid decay of organic matter, releasing acidic compounds that can drive exchange reactions. Insect infestations can have a similar impact. Beaver activity in a watershed can lead to inundation of soils and deposition of reduced sulfur species. Upon drying, these species can re-oxidize to generate acids that promote ion exchange. Soil formation processes themselves (e.g., podsolization) can produce acidic species that alter soil exchange properties. The supposition that ecosystems existed in some form of static state prior to 1850 has no technical basis. This error is compounded by the notion that we have an understanding of what the chemical characteristics of watershed components were in 1850. Measurements of these characteristics simply do not exist. Theoretical constructs of what acid-base characteristics of surface waters were can be attempted, but in the final analysis, they are nothing more than constructs, or informed guesses.

Something tangible that we do have is data collected since the late 1970s. Early research on acid deposition effects was hampered by the fact that there was not a change in signal with regards to acid inputs. However, we now have seen a change in signal to use as a test of our theoretical understanding of the response of ecosystems to changes in acidic deposition inputs. The response to that change in signal integrates the influence of all of the processes that contribute to surface water characteristics, including cation exchange. It would seem prudent to base a standard on available observations as opposed to guesses about conditions in 1850.

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One region that has data reflecting the response of surface waters to the change in signal is the Adirondacks. Changes in lake chemistry for 16 lakes sampled over the period from 1982 through 2004 and for 48 lakes sampled over the period from 1992 through 2004 are shown in Figure A6 (Driscoll et al, 2007). Focusing on the lakes with the longer sampling period (1982 – 2004), all 16 lakes show statistically significant decreases in sulfate concentration, the sulfate plus nitrate concentration, and base cation concentrations. This observation suggests that many of the base cations in solution were induced by acidic inputs. Based upon mean values, the equivalent F factor for these lakes ($F = \text{change in base cations} [-1.97 \mu\text{eq L}^{-1} \text{y}^{-1}] \div \text{the change in the sum of sulfate and nitrate} [-2.31 \mu\text{eq L}^{-1} \text{y}^{-1}]$) would be 0.85. This is significantly higher than the values reported for surface waters in Scandinavia where the F factor model was developed of 0.2 to 0.4 (Henriksen, 1984 and Brakke et al, 1990). With regard to ANC, only 11 of the 16 lakes have statistically significant changes, with a mean value of $0.76 \mu\text{eq L}^{-1} \text{y}^{-1}$. Similar results are seen when evaluating the larger data set (48 lakes) as well. If these observations apply broadly, they imply that even with additional decreases in acid inputs, commensurate increases in ANC are unlikely because base cation concentrations will decrease as well. Will further reductions in SO_x and NO_x have a similarly minimal effect on ANC, H⁺ ion, and Al_i concentrations?

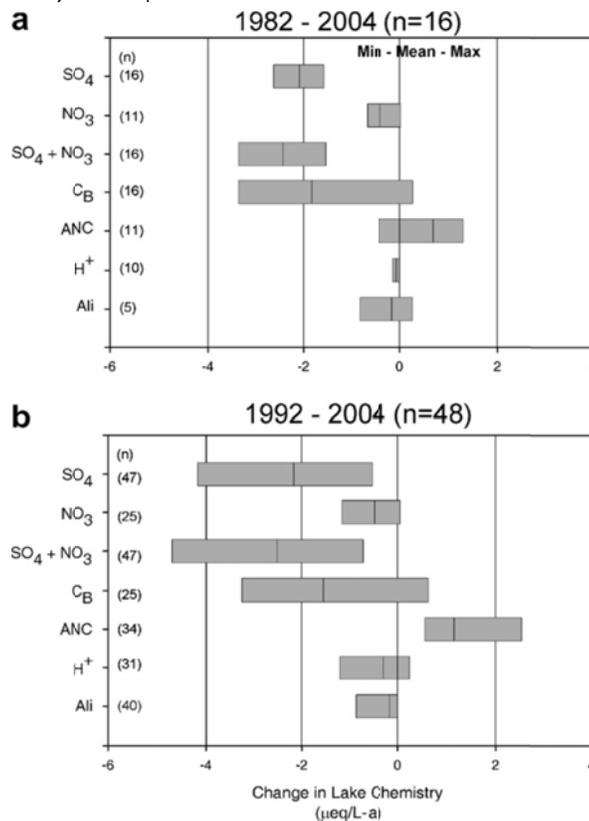


Figure A6. Mean rates of change in solute concentrations in 16 lakes from 1982-2004 (a) and 48 lakes from 1992-2004 (b) of the Adirondack Long-Term Monitoring (ALTM) program (Driscoll et al, 2007). Minimum, mean, and maximum changes in concentrations and number of lakes showing significant trends are shown. All values are in $\mu\text{eq L}^{-1} \text{y}^{-1}$, except for concentrations of inorganic monomeric aluminum (Al_i) which is expressed in $\mu\text{mol L}^{-1} \text{y}^{-1}$.

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This goes to the point made by Sullivan et al (2009) in an analysis of streams in Virginia and West Virginia where they said,

Some acidified lakes and streams are not projected to recover to critical criteria values even if deposition is reduced to zero because they were not that high to begin with.

The complexity embodied in the observed data cannot be captured by the simple critical load model proposed. Cation exchange is an important process in determining the response to changes in deposition inputs, and its influence should be included in determination of the standard.

With specific regard to the longevity of cation exchange, studies have indicated that soils in the northeastern U.S. have adequate sorbed base cations to continue to buffer acid inputs for anywhere from 50 to 200 years (Schnoor and Stumm, 1984) to as many as several hundred years (Gherini et al., 1985; Munson and Gherini, 1991a). Developing a standard that ignores a process that has the potential to continue to influence surface water acid-base characteristics for extended time periods such as these seems inconsistent with the state of the science.

Appendix A5: Base Cation Weathering

MAGIC Model Weathering Formulation

Mineral weathering is a slow process that adds base cations (and thus ANC) to solution in specific stoichiometric ratios (April and Newton, 1985; Munson and Gherini, 1991a and 1993b). The rate of weathering has been reported to have a fractional dependence on hydrogen ion concentration ranging from 0.0 to 0.8 (Bloom, 1988; Schnoor and Stumm, 1984; Drever and Hurcomb, 1986). This is the type of formulation included in models such as PROFILE (Warfvinge and Sverdrup, 1992) and ILWAS (Gherini et al., 1985).

Weathering in the MAGIC model, however, is not tied to any specific minerals, and instead is adjusted on an ion-by-ion basis. The impact of this type of formulation is that weathering estimates generated by MAGIC have the potential to have little or no relationship to the minerals that exist in watershed soils. This is a highly under-constrained condition with the potential to introduce large errors in weathering estimates.

Regional Extrapolation of BC_w Values

One of the components of the proposed approach is extrapolation of calculated weathering rates across a region. This process is described in the report as follows:

Extrapolation of BC_w for modeled streams/lakes to other waterbodies within the region through correlation analysis using stream chemistry data, where available, and landscape parameters in its absence.

This process has the potential to introduce large errors into the analysis.

Using the Adirondacks as an example, it would be conceivable to use the entire Adirondack Park as a single region. That is the approach used in the REA, and seems likely to be used in establishment of secondary standards as well. However, data indicate that weathering rates vary substantially within the Adirondacks (April et al., 1986). Weathering inputs in the western Adirondacks are dominated by amphiboles (hornblende). In the eastern Adirondacks, however, mineral weathering inputs are controlled by a calcium-rich anorthosite. In addition, there are regions within the Adirondacks with calcite minerals. There are lakes in the eastern and western Adirondacks with similar surface water characteristics that would be lumped together using a correlation analysis, but the actual weathering rates and weathering products in the two systems could be substantially different because there are distinctly different minerals controlling weathering inputs. Under the scheme described above, however, they would be treated the same. Correlation based on landscape parameters would be even more problematic. It is likely that landscape characteristics are very similar among watersheds dominated by all three types of minerals, but weathering would be

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extremely different. As an example, Windfall Pond is located in the Big Moose basin of the western Adirondacks and has landscape characteristics very similar to other lakes in basin. However, the surface water chemical characteristics of Windfall Pond are controlled by the small fraction of calcite minerals in the watershed. Correlation based on landscape parameters would not be able to capture the difference between Windfall Pond and the amphibole-dominated watersheds in the Big Moose basin (Newton et al., 1987). The approach noted above has a high likelihood of treating watersheds with very different characteristics as if they were very similar.

Appendix A6: Nitrogen Uptake

Much of the discussion of the adverse effects of nitrogen deposition on both terrestrial and aquatic systems in the PAD is built upon the hypothesis of nitrogen saturation, which is generally defined as a condition wherein inputs of nitrogen to an ecosystem exceed the requirements of terrestrial biota and a substantial fraction of that nitrogen leaches out of the ecosystem as nitrate in groundwater and surface water. Nitrogen saturation is said to contribute to poor forest health and lead to the presence of nitrates in surface waters, contributing to attendant acidification, human health problems, and estuary eutrophication. Although this concept deals with all sources and forms of nitrogen, most of the emphasis has been on atmospheric deposition of nitrate and ammonium. Nitrogen retention, or the fraction of inputs retained by an ecosystem, presumably both defines and measures nitrogen saturation, with retention decreasing as saturation increases.

Nitrogen Saturation Hypothesis

The nitrogen-saturation hypothesis (Aber et al. 1989, Stoddard 1994) conceptually originated in a paper by Vitousek and Reiners (1975), which established the paradigm that nutrients, including nitrogen, are not likely to be lost from growing forests. Nutrient loss is said to be only likely after biomass accumulation has slowed and has approached an approximate steady-state. According to the hypothesis, additions of nitrogen to forests beyond requirements for growth, whether through fertilization or atmospheric deposition, should lead to increased leaching of nitrate or ammonium below the rooting zone of plants (Aber et al. 1989). Because nitrogen is commonly deficient or limiting in ecosystems, **any loss of nitrogen, even if retention is quite high, is said to define a nitrogen-saturated ecosystem.**

Four progressive stages of nitrogen saturation were postulated, with changes in input-output relationships and in plant conditions at each stage (Aber et al., 1989). This was expanded to include an associated change in the magnitude and temporal pattern of nitrate in adjacent aquatic systems at each stage (Stoddard, 1994). The changes that were hypothesized to occur at each stage "fit" the conceptual view of nitrogen dynamics, and hence the concept was initially well-received.

The hypothesis of nitrogen saturation, however, has not yet been clearly demonstrated; it is a hypothesis without definitive proof. The Austrian and British philosopher Popper famously argued that it is easy to obtain evidence in favor of virtually any theory, and he consequently discounted such 'corroboration'. Instead, he advocated testing a scientific theory by attempting to refute or to falsify it, with a single counter-instance falsifying the whole theory. The scientific literature is filled with reports of corroboration of the theory of nitrogen saturation. **Although nitrogen, in the form of nitrates, is being leached from some forest systems, the developmental history of these forest systems and the progression of processes that have led to this leaching have not been fully documented.**

Using the criterion that defines nitrogen saturation, virtually all terrestrial ecosystems are calcium-, magnesium, and potassium-saturated. Although all are essential elements for plants, they apparently are not limiting because they are lost by leaching from nearly all terrestrial ecosystems, sometimes well in excess of inputs by atmospheric deposition and weathering (retention is negative). This phenomenon even occurs in ecosystems that are said to be in poor health because of base cation deficiency. Most terrestrial ecosystems therefore demonstrate at least the early stages of base cation saturation. **Only in the case of nitrogen does any loss by leaching indicate an ecosystem problem.**

Although not everything is understood about nitrogen behavior in ecosystems, there is considerable information available. Nitrogen has long been recognized as an important controller of plant productivity, and because of that fact, it is a widely-used fertilizer in both agriculture and forestry. Its importance in ecosystem dynamics has led to abundant research on nitrogen in forested systems in the U.S. A number of mechanisms retain nitrogen in forests. Possible storage pools for nitrogen include the living trees, the soil, the forest litter, and the coarse woody debris (CWD), which includes dead standing trees and boles on the ground. Although the hypothesis of nitrogen saturation has focused on living trees (Aber et al., 1989), much less attention has been paid to the other storage pools. Forests that undergo periodic harvest have little opportunity to become saturated with nitrogen. The removal of forest products inescapably leads to the removal of nitrogen in that product. In fact, such periodic depletions of ecosystem nitrogen have been a cause of concern for continuing productivity of intensively-managed forests in the Southern Hemisphere (Keeves 1966, Whyte 1973).

Observations

Forests are also continuously disturbed, not only by harvest but also by fires, windstorms, insect infestations and disease. Forests are in a continual state of change, and an assumption of forests persisting for decades without any disturbance is unrealistic. All changes that forests undergo can be expected to alter nitrogen dynamics, and lead to changes in amounts of nitrogen moving within and from those forests. As a result, many factors in addition to the hypothesized role of atmospheric deposition have been reported as strongly influencing the capacity of forest systems to retain nitrogen. These include historic land-use (Lovett et al., 2000, Aber et al., 2003), forest composition (Lovett et al., 2002, Zak et al., 1986), climatic extremes such as drought (Aber and Driscoll, 1997) and soil frost (Mitchell et al., 1996, Groffman et al., 1999; Fitzhugh et al., 2001), insect defoliation (Eshleman et al., 1998), groundwater sources (Burns et al., 1998), and water flow paths (Creed et al., 1996).

There are numerous examples in the literature demonstrating that nitrogen saturation is not the universal phenomenon that its advocates claim. For example, as forest ecosystems continue to receive atmospherically-deposited nitrogen over time, increasing the total amount of nitrogen in those systems, the hypothesis of nitrogen saturation would predict that nitrate levels in adjacent

aquatic systems would increase. The Adirondack Region of New York “probably exhibits the most severe ecological impacts from acidic deposition of any region in North America” (Driscoll et al., 2003a). However, monitoring of 17 lakes in the Adirondack Region over the period from 1982 to 2000 found that 8 lakes had significant declines in nitrate concentration, 8 lakes showed no trend, and only one lake showed a “small” significant increase (Driscoll et al., 2003a). This occurred in spite of the fact that NO_x emissions, and presumably NO_x deposition, had remained relatively constant since 1980. This is not the only observation of declines in nitrate concentration in aquatic systems in the Northeast. Streams on Mount Moosilauke and Mount Washington, New Hampshire, had lower nitrate concentrations in 1996-97 relative to 1973-74 (Goodale et al., 2003). Nitrate concentrations in four streams in and near an old-growth forest watershed of the Bowl Research Natural Area in the White Mountains of New Hampshire “declined markedly” between the periods 1973-74 and 1994-97 (Martin et al., 2000).

Nitrogen Fertilization

Much of the data on anthropogenic additions of nitrogen to forests were summarized by Johnson (1992a). He thoroughly discusses the issue of nitrogen retention and points out the many confusing results with respect to such retention. Forest fertilization studies report relatively low accumulation of the fertilizer nitrogen in the growing trees but substantial retention in the litter and soil, so that total retention from fertilizer applications ranges into the hundreds of kg of nitrogen per hectare (Johnson, 1992a). With respect to atmospherically-deposited nitrogen, he reports that data from 31 forest sites, representing systems varying widely in geography and composition, indicate that “ecosystem retention of atmospherically deposited N ranges from -266% to 99%, with no apparent relationship to atmospheric input” (Johnson, 1992a). In experimental work in the northeast U.S. specifically designed to test the hypothesis of nitrogen saturation, extraordinarily high annual inputs of nitrogen (atmospheric deposition of 8 kg N ha⁻¹ y⁻¹ supplemented by 50 or 150 kg N ha⁻¹ y⁻¹ over a nine-year period) were added to two forest stands in Massachusetts (Magill et al., 2000). Total additional nitrogen added over the experimental period was equivalent to 55 and 165 years of ambient acid deposition. Nitrogen retention over the 9-year experimental period was 98% in the plots receiving the lower amounts of additional nitrogen, and ranged from 85% to 96% in those receiving higher amounts of nitrogen (Magill et al., 2000). These studies illustrate the limited nitrate leaching that exists with even high levels of added nitrogen.

Leaching Loss

All of this is not meant to suggest that nitrate does not leach from some forests. Nitrate leaching has been documented in high-elevation spruce-fir forests in the southern Appalachians (Joslin and Wolfe, 1992; Joslin et al., 1992; Van Miegroet et al., 1992a,b; and Nodvin et al., 1995). In those cases, it has been attributed to a combination of very high nitrogen deposition associated with cloud water (Lovett and Kinsman, 1990) and low nitrogen uptake by the slow-growing trees. The Catskill Mountains of New York receive relatively high rates of atmospheric nitrogen deposition, and

streams in the area have been reported to have high nitrate levels, presumably because of excess nitrogen in their forested watersheds (Stoddard, 1994). An analysis of streams from 39 small watersheds in the Catskills showed a 2 to 36 micromolar variation in the concentrations of stream nitrate, in spite of the fact that all the watersheds were on similar geology and had similar rates of atmospheric deposition (Lovett et al., 2000). Neither did variation in stream nitrate result from differences in watershed topography or groundwater influx to streams (Lovett et al., 2000). The cause of the differences in nitrate in streams was speculated to be differences in forest composition and history. Nitrogen retention was measured in 13 forested catchments in the headwaters of the Upper Susquehanna River (Goodale et al., 2009). Nitrogen deposition in the region was approximately 8.5 kg N ha⁻¹ y⁻¹, a fairly high value. Over a two-year period, the average retention of inorganic nitrogen was 96%, with trivial differences among catchments (standard deviation = 2%). Similarly, retention of atmospherically-deposited nitrogen in nine undisturbed forested watersheds in the mid-Appalachian region of the U.S. ranges from 50% to 100% (Williard et al., 1997). Loss of nitrogen from these watersheds was not related to atmospheric deposition of nitrogen, but instead to the amount of soil nitrogen and its dynamics (Williard et al., 1997). Munson and Gherini (2010), in detailed dynamic simulations of over 40 hydrologic basins across the US, using ILWAS and NuCM, found nitrogen retention values all above 95%.

Threshold

A variety of thresholds or levels of atmospheric deposition have been proposed, above which nitrogen saturation is said to occur. For example, Driscoll et al. (1989a) suggested that data from sites primarily in eastern North America indicated nitrogen leaching at atmospheric deposition (wet only) greater than approximately 5.6 kg N ha⁻¹ y⁻¹. Total deposition, which includes both wet plus dry, ranges from about 1.5 to 2 times wet deposition (Boyer et al., 2002), and so this threshold is approximately 8 to 11 kg ha⁻¹ y⁻¹ wet plus dry. Analysis of those data and additional data not considered by Driscoll et al. (1989a) led Stoddard (1994) to conclude that the threshold value for wet deposition is about 4.2 kg ha⁻¹ y⁻¹ (about 6 to 8 kg ha⁻¹ y⁻¹ wet plus dry). Similarly, Aber et al. (2003) reported a steep increase in nitrogen leaching at total nitrogen deposition above about 6.8 kg ha⁻¹ y⁻¹ at low elevation sites (base of watersheds) in the northeastern U.S.; they inferred that was equal to about 10 kg ha⁻¹ y⁻¹ for the whole watershed. Castro et al. (2001) presented a curvilinear relationship between wet deposition of nitrogen and leaching for upland forests of the eastern U.S., with an increase in leaching above about 6 kg ha⁻¹ y⁻¹ (about 10 kg ha⁻¹ y⁻¹ wet plus dry). Finally, Johnson (1992a), in an analysis of data from 31 forested sites throughout the northern hemisphere, concluded that vegetation affects the relationship between atmospheric inputs and retention of nitrogen. Inputs in excess of those required for the vegetation result in nitrogen leaching (Johnson 1992a); the average required nitrogen in the 26 studies for which data were available was 10 kg N ha⁻¹ y⁻¹.

Input-output budgets from European forests have shown that above a threshold of approximately 10 kg N ha⁻¹ y⁻¹ in throughfall (a surrogate for wet plus dry deposition), many sites appear N

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saturated and have nitrate-leaching rates above 5 kg N ha⁻¹ y⁻¹. Below 10 kg N ha⁻¹ y⁻¹ in throughfall elevated nitrate leaching is rare in all data compilations from Europe (Dise and Wright, 1995; Gundersen et al., 1998a; Kristensen et al., 2004; MacDonald et al., 2002; and Nilsson et al., 1998). The N input thresholds for elevated nitrate leaching found on both continents may therefore nearly be identical at approximately 10 kg ha⁻¹ y⁻¹ (Gunderson et al., 2006).

The congruency of the threshold for nitrogen leaching, about 10 kg ha⁻¹ y⁻¹ wet plus dry, should not be interpreted as a discrete value above which leaching uniformly occurs, but instead as a value above which the probability of leaching increases. Actual rates of leaching are affected by all the other factors previously discussed.

Average wet deposition of nitrate-nitrogen in 2008 for the areas of the U.S. identified as containing ecosystems sensitive to acidifying deposition (excluding Florida -- PA, Figure 6-1, p. 202), was approximately 2.2 kg N ha⁻¹ y⁻¹, with higher levels in New York-Pennsylvania and lowest levels in the Midwest. Average wet deposition of ammonium-N in 2008 for those areas was approximately 2.0 kg N ha⁻¹ y⁻¹. Even if those values are doubled to approximate total nitrogen deposition, they do not exceed the 10 kg N ha⁻¹ y⁻¹ "threshold". If time trends continue, they indicate a further 10% reduction in nitrate deposition by 2015. Even if total deposition were at the threshold 10 kg ha⁻¹ y⁻¹, average estimated retention is greater than 80%. Only a small fraction of nitrogen leaves watersheds.

In summary, while increased nitrogen concentration in forest soils may be caused, in part, by atmospheric deposition, the evidence for the role of atmospheric deposition in nitrogen loss via leaching to streams is equivocal. The issue of nitrogen retention/saturation is much more complex than that encompassed by a simple input-output balance, with myriad factors influencing nitrogen retention in forest systems.

Appendix A7: Variability in VSO_x, VNO_y and LNH_x

To examine variability of VSO_x, VNO_y, and LNH_x, we first focused on the two case study areas that have been extensively studied by EPA for their review of the secondary NAAQS for SO_x and NO_x: the Adirondack Mountains and Shenandoah National Park (NP). Figure A7 presents “box and whisker” plots for the VSO_x, VNO_y, and LNH_x values across the grid cells within each case study area calculated by all the scenarios considered in this study (For details of a box and whisker plot, refer to Figure 1 caption).

Both VSO_x and VNO_y vary considerably in the Adirondack region. Here, the VSO_x values range from 0.56 to 2.6 cm s⁻¹ (changing by a factor of ~5) and VNO_y values range from 0.24 to 1.7 cm s⁻¹ (changing by a factor of ~7).

VSO_x and VNO_y at Shenandoah show similar variability: The VSO_x values spans from 0.35 to 1.5 cm s⁻¹ (by a factor of ~4) and VNO_y from 0.22 to 1.2 (by a factor of ~5). The LNH_x values show even higher variability: At Shenandoah, LNH_x changes its value by a factor of 23.

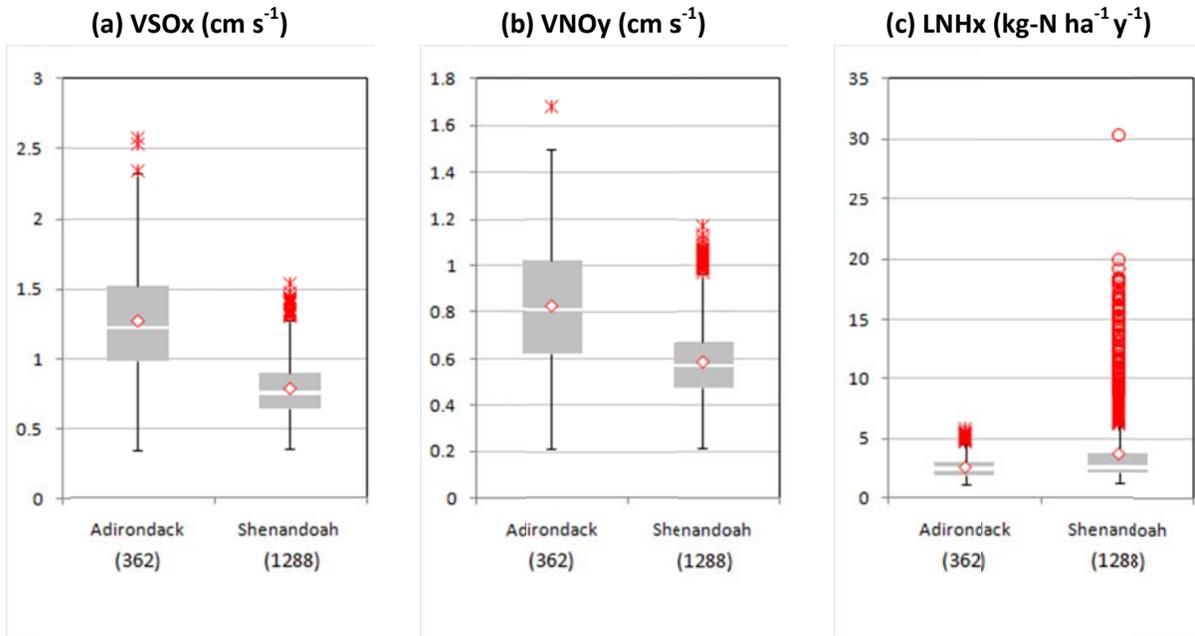


Figure A7. Box and whisker plots for variability of (a) VSO_x, (b) VNO_y, and (c) LNH_x across all the grid cells at each test case area and all the modeling scenarios. The number in parentheses represents the number of each sample data. The inner quartiles of each data sample are represented by light gray boxes, separated at the median by a thin line. The height of the gray boxes together makes up the interquartile range (IQR). The range of data falling within 1.5 IQRs of the median is represented by whiskers. Any outliers that fall between 1.5 and 3 IQRs from the median are represented by asterisk markers, while any outliers falling beyond 3 IQRs from the

median are represented by circular markers. The average of each sample is represented by a diamond marker overlying the box and whisker for that sample.

Figures A8 to A11 show spatial variability of VSO_x, VNO_y, and LNH_x, respectively, at each of the two case study areas for each modeling scenario.

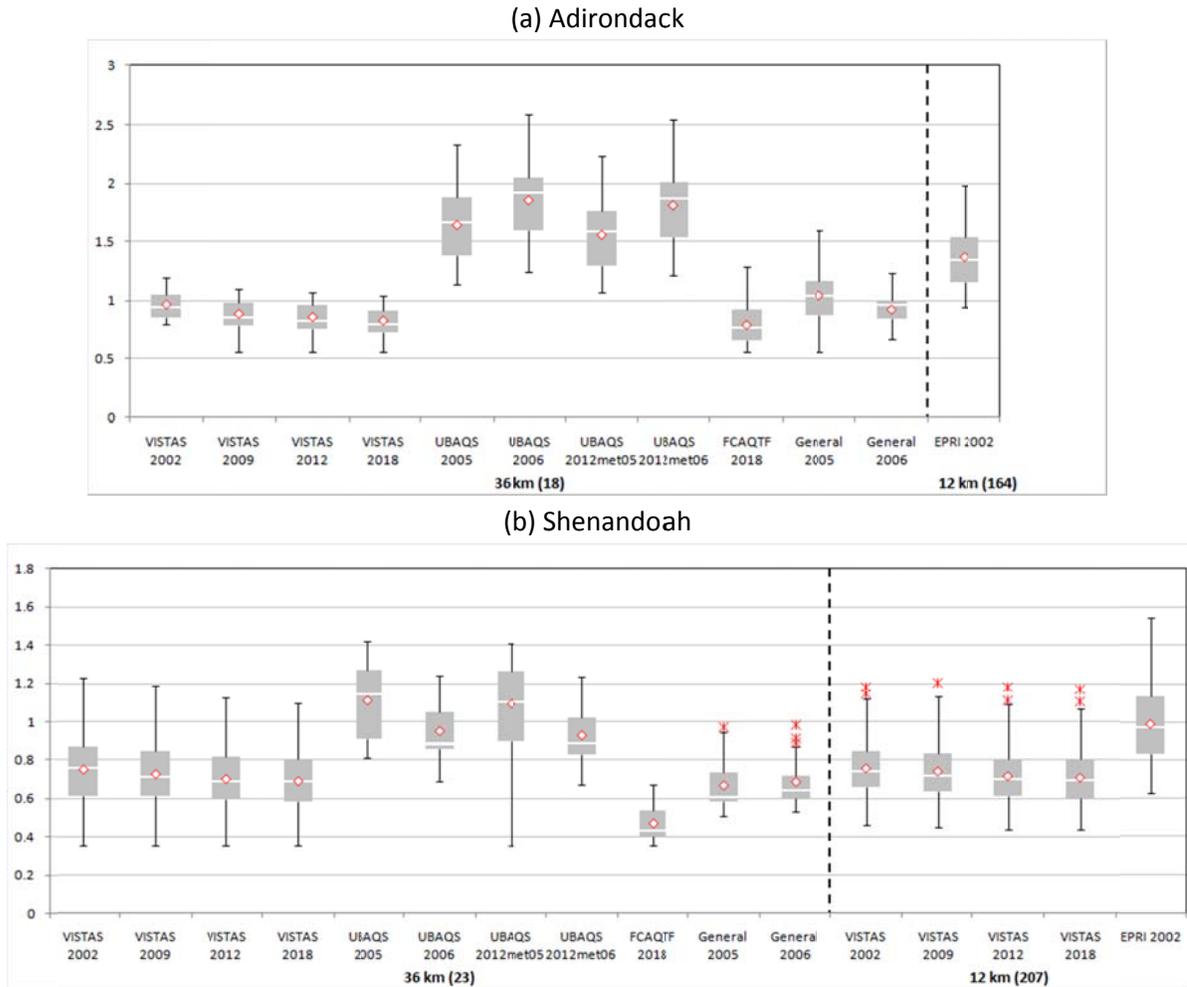
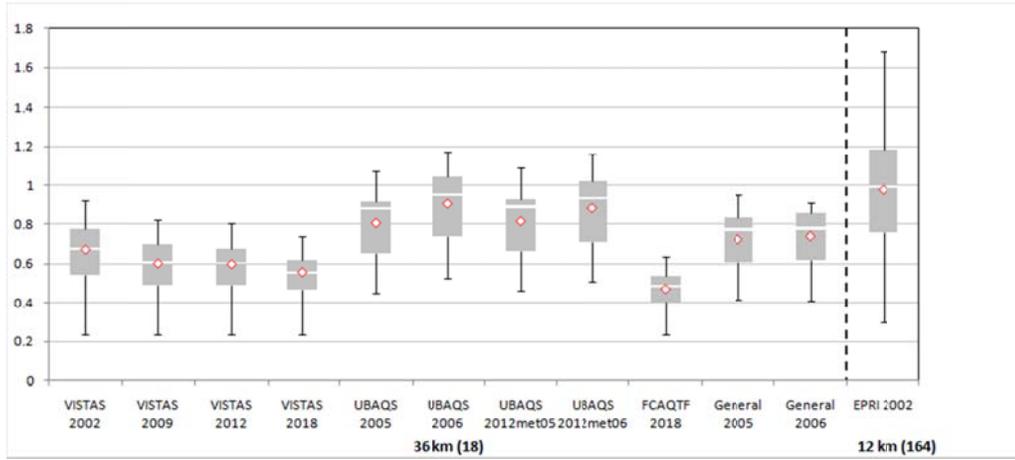


Figure A8. Box and whisker plots for variability of VSO_x (cm s⁻¹) at (a) Adirondack and (b) Shenandoah across all the modeling scenarios. The number in parentheses represents the number of each sample data.

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(a) Adirondack



(b) Shenandoah

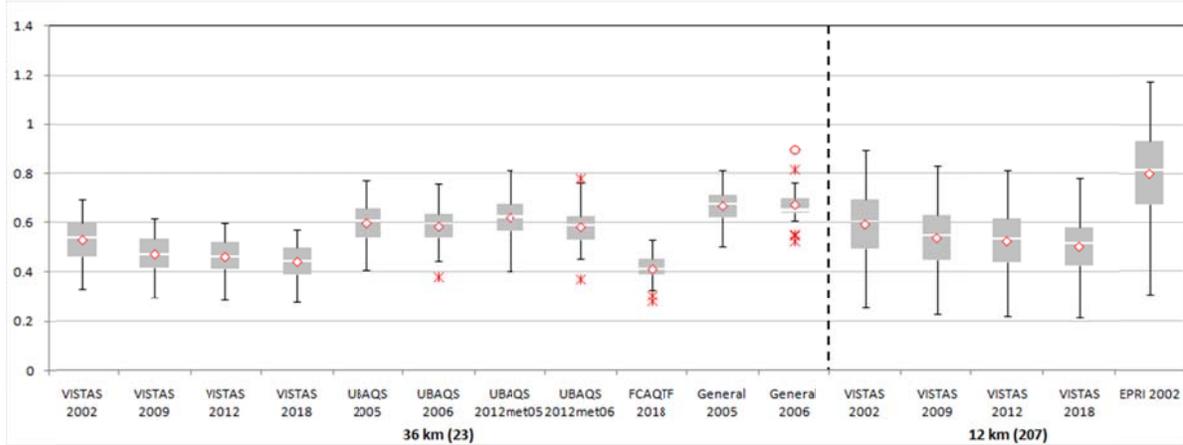
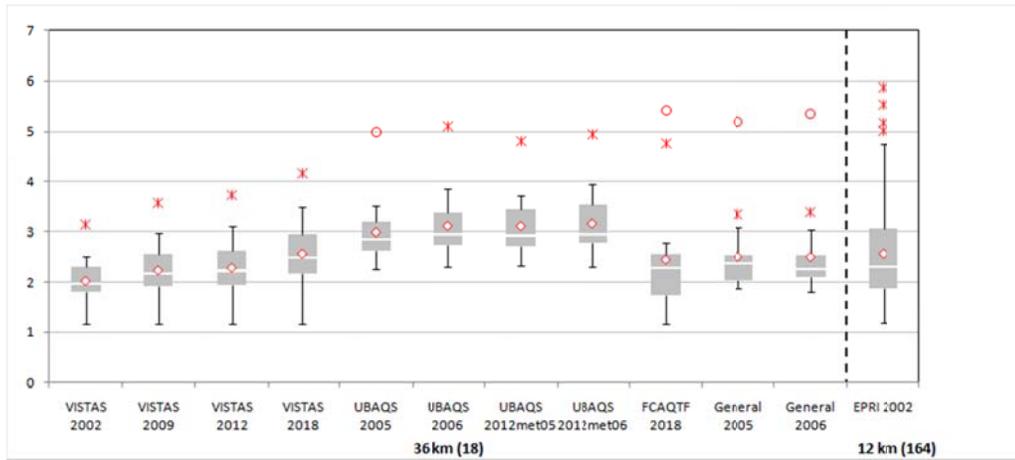


Figure A9. Box and whisker plots for variability of VNO_y (cm s⁻¹) at (a) Adirondack and (b) Shenandoah across all the modeling scenarios. The number in parentheses represents the number of each sample data.

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(a) Adirondack



(b) Shenandoah

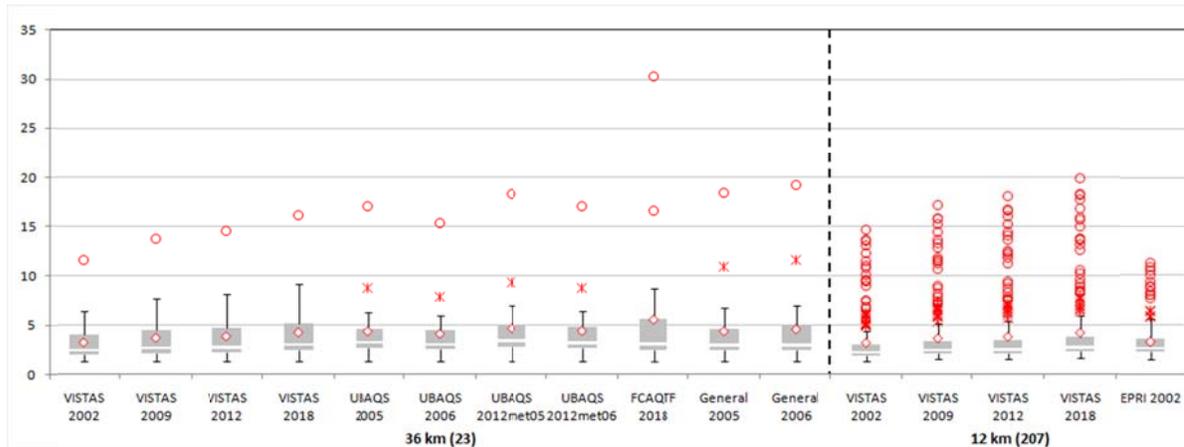


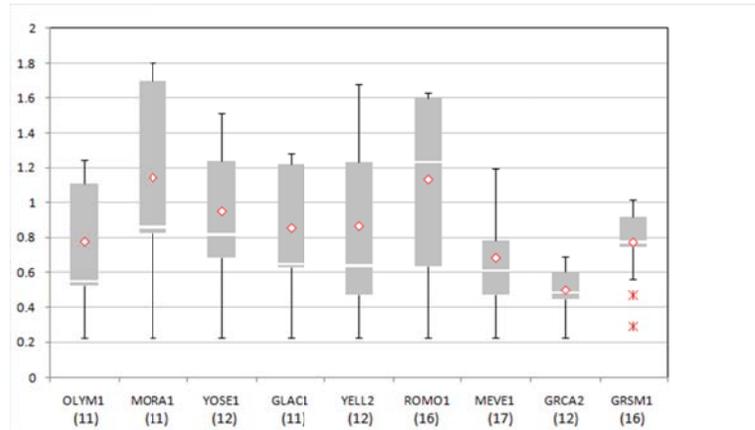
Figure A10. Box and whisker plots for variability of LNHx (kg N ha⁻¹ y⁻¹) at (a) Adirondack and (b) Shenandoah across all the modeling scenarios. The number in parentheses represents the number of each sample data.

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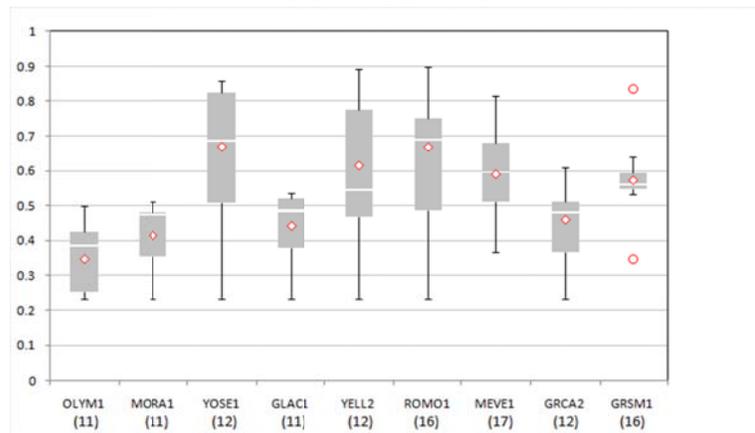
We also looked at variability in these parameters at several Class I areas: Olympic NP (OLYM1); Mount Rainier NP (MORA1); Yosemite NP (YOSE1); Grand Canyon NP (GRCA2); Glacier NP (GLAC1); Yellowstone NP (YELL2); Rocky Mountain NP (ROMO1); Mesa Verde NP (MEVE1); Great Smoky Mountains NP (GRSM1). Unlike the Adirondack and Shenandoah areas discussed above, these Class I areas are represented as single grid cells (at the IMPROVE monitoring sites), therefore only the variability across the modeling scenarios are shown in Figure A12. Again, VSO_x, VNO_y, and LNH_x show large variances. VSO_x spans from 0.2 to 1.8 cm s⁻¹ with higher variability at Mount Rainier NP, Yellowstone NP, and Rocky Mountain NP. The VNO_y values range from 0.2 to 0.9 with higher variability at Yosemite NP, Yellowstone NP, and Rocky Mountain NP. The LNH_x values also varies much and Great Smoky Mountains NP shows quite different LNH_x than those at the western US sites.

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(a) VSO_x (cm s⁻¹)



(b) VNO_y (cm s⁻¹)



(c) LNH_x (kg N ha⁻¹ y⁻¹)

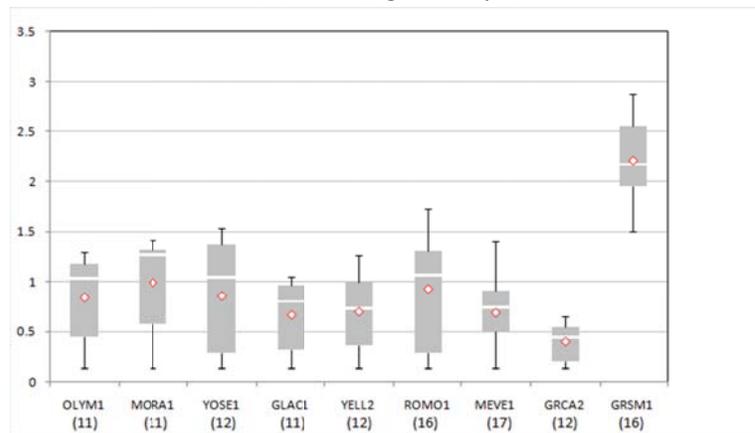


Figure 12. Box and whisker plots for variability of (a) VSO_x, (b) VNO_y, and (c) LNH_x across all the modeling scenarios at each IMPROVE site. The number in parentheses represents the number of each sample data.

Appendix A8: Proof on CV Lower Bound

$$CL(A) = (Q + \varepsilon_1) \left([BC_0^*] + \varepsilon_2 - [ANC]_{lim} \right)$$

This is the equation for critical load from EPA's PA with error terms added (the epsilons) to Q and BC_0^* to represent uncertainty

$$V[CL(A)] = \left([BC_0^*] - [ANC]_{lim} \right)^2 V[\varepsilon_1] + Q^2 \cdot V[\varepsilon_2] + V[\varepsilon_1 \varepsilon_2]$$

Take the variance of the above expression and expand

$$V[CL(A)] \geq \left([BC_0^*] - [ANC]_{lim} \right)^2 V[\varepsilon_1]$$

Variance is positive by definition, so omitting the last two terms above gives this inequality

$$\frac{\sqrt{V[CL(A)]}}{E[CL(A)]} = CV[CL(A)] \geq \frac{\sqrt{\left([BC_0^*] - [ANC]_{lim} \right)^2 V[\varepsilon_1]}}{Q \left([BC_0^*] - [ANC]_{lim} \right)}$$

CV is standard deviation (square root of variance) over expected value. This is just expressing the above variance as a CV

$$CV[CL(A)] \geq \frac{\sqrt{\left([BC_0^*] - [ANC]_{lim} \right)^2 Q^2 (CV[Q])^2}}{Q \left([BC_0^*] - [ANC]_{lim} \right)} = CV[Q]$$

This expresses $var(\varepsilon_1)$ in terms of Q, giving CV(CL) in terms of CV(Q)

The result is that the coefficient of variation of the critical load must be at least that of one of the input parameters, Q. This same conclusion can be reached for all input parameters.

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