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Streamwater acid-base chemistry and critical loads of atmospheric sulfur deposition in Shenandoah National Park, Virginia

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Abstract A modeling study was conducted to evaluate the acid-base chemistry of streams within Shenandoah National Park, Virginia and to project future responses to sulfur (S) and nitrogen (N) atmospheric emissions controls. Many of the major stream systems in the park have acid neutralizing capacity (ANC) less than 20 μeq/L, levels at which chronic and/or episodic adverse impacts on native brook trout are possible. Model hindcasts suggested that none of these streams had ANC less than 50 μeq/L in 1900. Model projections, based on atmospheric emissions controls representative of laws already enacted as of 2003, suggested that the ANC of those streams simulated to have experienced the largest historical decreases in ANC will increase in the future. The levels of S deposition that were simulated to cause streamwater ANC to increase or decrease to three specified critical levels (0, 20, and 50 μeq/L) ranged from less than zero (ANC level not attainable) to several hundred kg/ha/year, depending on the selected site and its inherent acid-sensitivity, selected ANC endpoint criterion, and evaluation year for which the critical load was calculated. Several of the modeled streams situated on siliciclastic geology exhibited critical loads <0 kg/ha/year to achieve ANC >50 μeq/L in the year 2040, probably due at least in part to base cation losses from watershed soil. The median modeled siliciclastic stream had a calculated critical load to achieve ANC >50 μeq/L in 2100 that was about 3 kg/ha/year, or 77% lower than deposition in 1990, representing the time of model calibration.

Keywords Acidification · Critical load · Sulfur · Stream chemistry · Modeling

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Introduction and objectives

Air pollution and associated acidic deposition have caused documented adverse impacts on water quality, aquatic ecosystems, soils, and some sensitive plant species in Shenandoah National Park (SNP), Virginia. Visibility has been seriously degraded by air pollution, detracting from visitor enjoyment of the vistas accessible from Skyline Drive and the Appalachian Trail within SNP (Sullivan et al. 2003). Visitor complaints about poor visibility are frequent. In addition, ozone concentrations, which are formed in part by nitrogen oxides present in air pollution, cause foliar injury to sensitive plants and have periodically exceeded the air quality standard for human health. Foliar damage attributable to ozone has been documented for sensitive tree species, and there is concern regarding potential effects of ozone on forest growth and health. Key precursor air pollutant concentrations that affect visibility and ozone formation also contribute to acidic deposition. SNP has among the highest levels of acidic atmospheric deposition that impact aquatic systems of all national parks in the United States.

The park contains three widely-distributed classes or types of bedrock which generally reflect their sensitivity to acidification: granitic, basaltic, and siliciclastic (i.e., sedimentary rocks that contain abundant silica or sand). Each type covers approximately one-third of the park (Sullivan et al. 2003). There are also minor amounts of argillaceous and carbonate rock types.

There are about 90 small streams in the park, many of which contain native brook trout (*Salvelinus fontinalis*; Shenandoah National Park 1998). Almost all are headwater, typically first to third order. Headwater streams are often more sensitive to acidification from acidic deposition because they tend to have thinner soils, steeper slopes, higher precipitation, more rapid runoff, more resistant bedrock, and slower weathering rates as compared with low elevation streams.

Chronic and episodic acidification associated with air pollution has adversely impacted streams in SNP and affected in-stream biota (Bulger et al. 1999, 2000). Acidification has been most pronounced in watersheds dominated by base-poor bedrock types that give rise to soils having low base saturation and relatively low S adsorption, and to streams having low ANC. Fish within sensitive streams in the park, including brook trout and blacknose dace (*Rhinichthys atratulus*), have suffered significant impacts at the community, population, and individual levels (Bulger et al. 1999).

Sulfur is the primary determinant of precipitation acidity and SO_4^{2-} is the dominant acid anion associated with acidic streams, both in the central Appalachian Mountains region (Sullivan et al. 2002, 2004) and within Shenandoah National Park (Sullivan et al. 2003). Although a substantial proportion of atmospherically deposited S is retained in watershed soils, SO_4^{2-} concentrations in western Virginia mountain streams have increased over the past two decades as a consequence of acidic deposition. Nitrate concentrations in streamwater are generally negligible, except in association with severe disturbance, such as forest defoliation by the gypsy moth (Webb et al. 1995). In the absence of disturbance, N is generally tightly cycled within SNP watersheds and does not contribute significantly to streamwater acidification. Low streamwater NO_3^- concentrations are likely a consequence of the relatively low levels of N deposition received by SNP, past landscape disturbance, and the prevalence of deciduous forest types, which seem to have a higher N demand than coniferous forests (Aber et al. 1991). Nitrogen inputs can also impact terrestrial and/or aquatic ecosystems via nutrient enrichment and eutrophication processes. Such effects are not considered in this study.

Key questions now facing scientists and policy makers concern the prognosis for future change in streamwater chemistry in SNP and the extent to which S emissions and deposition will need to be reduced to allow ecosystem recovery and prevent further damage (c.f., Jenkins et al. 1998). Critical loads can be calculated for streams, assuming chemical/biological dose–response relationships (Bull 1992). The critical load can be defined as the deposition load below which harmful effects do not occur to sensitive elements of the environment according to present knowledge (Nilsson and Grennfelt 1988). Because different species respond at varying ANC levels, multiple critical loads can be calculated or applied to a given stream. Federal land managers are now beginning to use model-based critical loads calculations for setting resource protection and restoration goals on federal lands (Porter et al. 2005). Process-based watershed acid-base chemistry models can be used in an iterative fashion to calculate critical loads, based on the chemical indicator ANC. This analysis requires specification of the criteria ANC values, below which ecosystem damage would be likely to occur, and the time period in the future at which the critical load evaluation is to be made. Thus, critical load is calculated objectively using a process model, but the results are partly determined by subjective selection of ANC endpoint target value and evaluation year. The target load, in contrast, implies a policy judgment, which can be based on such factors as political decisions, interim goals, or allowance for modeling uncertainty.

The objectives of the research reported here are to summarize the current status of streamwater chemistry within SNP, conduct model simulations to forecast the responses of park streams to future changes in atmospheric S and N deposition, and estimate the critical loads of atmospheric S deposition that would be required to accomplish various ecological objectives regarding protection or recovery of future streamwater chemistry and associated probable biological responses. We do not attempt to quantify critical loads of N deposition to protect streams against acidification because current N deposition is not sufficiently high as to cause substantial NO_3^- leaching and N deposition levels are expected to decrease further in response to existing emissions control regulations.

Materials and methods

Site selection

Fourteen streams were selected for aquatic effects modeling for this study, to represent the range of geologic sensitivity and ANC of the major streams found in SNP. Watershed modeling requires atmospheric deposition and soil and streamwater chemical data for model calibration. The 14 streams chosen are all of the streams in SNP for which existing water quality data were available in sufficient quantity and of sufficient quality for use in calibrating the aquatic effects model to a long-term database of streamwater chemistry.

Soils and streamwater chemistry

Soil samples were collected and analyzed at 79 sites within the 14 study watersheds. Between four and eight soil pits were excavated within each watershed, geographically distributed to account for differences in slope, aspect, land use history, fire history, and forest cover type. Laboratory analyses were conducted by Penn State University and Virginia Tech (Welsch et al. 2001) to provide needed soils input data for the modeling effort.

The selected study streams are routinely sampled as part of the Shenandoah Watershed Study (SWAS; Galloway et al. 1999) and the Virginia Trout Stream Sensitivity Study (VTSSS; Webb et al. 1989). The frequency of sampling ranged from weekly (6 streams) to quarterly (8 streams) and all streams had at least 12 years of monitoring data available. Five streams are underlain by rocks from each of the siliciclastic and basaltic geologic sensitivity classes. Four streams represent the granitic sensitivity class. The siliciclastic watersheds included four streams having median ANC between 0 and 16 μeq/L, and one stream having ANC= 26 μeq/L. The streamwater ANC in the granitic watersheds ranged from 60 to 102 μeq/L, and for the basaltic watersheds ranged from 126 to 258 μeq/L. There are also a number of smaller, typically first order, streams on siliciclastic bedrock that are known to be chronically acidic and have ANC as low as −18 μeq/L (Galloway et al. 1999).

Modeling

Computer models are used to improve understanding of complex ecosystem processes. They can also be used to predict pollution effects on aquatic ecosystems and to perform simulations of future ecosystem response (c.f., Cosby et al. 1985a, b, c). Model projections are valuable to natural resource management agencies which require quantitative predictions of pollution impacts and the likely future benefits of emissions control programs. For this study we used the Model of Acidification of Groundwater in Catchments (MAGIC), which was calibrated to each of the study streams. It is a lumped-parameter mechanistic model which has been used throughout North America and Europe and extensively tested against the results of diatom reconstructions of historic water chemistry and ecosystem manipulation experiments (e.g., Wright et al. 1986; Sullivan et al. 1992; Sullivan and Cosby 1995; Cosby et al. 1995, 1996; Sullivan 2000).

MAGIC requires as atmospheric inputs estimates of the annual precipitation volume (m/year) and the total annual deposition (eq/ha/year) of eight ions: Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, SO_4^{2-}, Cl^-, and NO_3^-. These total deposition data are required at each site for each year of the calibration period (the years for which observed streamwater data are used for calibrating the model to each site). Estimated total deposition data are also required for more than 100 years preceding the calibration period as part of the calibration protocol for MAGIC, and for each year of any future scenario that will be run using MAGIC.

Total deposition of an ion at a particular site for any year can be represented as combined wet and dry deposition. Inputs to the model are specified as wet deposition (the annual flux in meq/m^2/year) and a dry deposition enhancement factor (DDF, unitless) used to multiply the wet deposition in order to estimate total deposition:

$$\text{TotDep} = \text{WetDep*DDF}$$

where:

$$\text{DDF} = 1+\text{DryDep}/\text{WetDep}.$$

Thus, given an annual wet deposition flux (WetDep) and the ratio of dry deposition to wet deposition (DryDep/WetDep) for a given year at a site, the total deposition for that site and year is estimated.

Four inputs are required for each of the eight deposition ions in MAGIC in order to estimate the total deposition for all years required in the calibrations and future simulations:

(1) The absolute value of wet deposition at the site for the Reference Year (meq/m^2/year);
(2) The absolute value of DDF (calculated from the DryDep/WetDep ratio) for the site for the Reference Year (unitless);
(3) Time series of scaled values of wet deposition and scaled values of DDF covering all historical years necessary to calibrate the model (scaled to the Reference Year);
(4) Time series of scaled values of future total deposition covering all future years of interest, scaled to the Reference Year.

The absolute value of wet deposition is time and space-specific, varying geographically and from year to year. The absolute value of the DDF specifies the ratio between the absolute amounts of wet and total deposition. This ratio is less variable in time and space than is the estimate of total deposition. That is, if in a given year the wet deposition goes up, then the total deposition usually goes up also (and conversely). Because the modeling takes a long-term climatological perspective, estimates of DDF used for MAGIC calibrations can be derived from a procedure (model) that has a lower spatial resolution and/or temporally smoothes the data. Similarly, the long-term sequences used for MAGIC simulations do not require detailed spatial or temporal resolution. That is, if for any given year the deposition goes up at one site, it also goes up at neighboring sites.

In order to calibrate MAGIC and run future scenarios or simulate critical loads, time series of the total deposition at each site must be estimated for each year of: (a) the calibration period; (b) the historical reconstructions; and (c) the future scenarios. The procedure used to provide these input data was as follows.

MAGIC was calibrated to each study watershed using wet deposition data collected at Big Meadows by the National Acid Deposition Program/National Trends Network (NADP) and at White Oak Run and North Fork Dry Run by the University of Virginia (UVA). The UVA sites collect bulk samples into open plastic funnels. UVA laboratory analysis protocols are consistent with NADP and include multi-laboratory standards testing. All three of these monitoring stations are located within the park. Wet deposition input data were averaged for the three sites over a 5-year period centered on 1990, which was selected to represent the reference year. Dry deposition was estimated based on a DDF, which was calculated using NADP wet deposition (http://nadp.sws.uiuc.edu/) and CASTNet dry deposition (http://www.epa.gov/castnet) data from Big Meadows (Sullivan et al. 2003), also as a 5-year average, using those years for which a complete record was available (1991, 1992, 1993, 1995, 1997, 1998). These 6-year average estimates of total deposition for S (13 kg/ha/year) and N (7.6 kg/ha/year) were used to calibrate all study watersheds.

Given the Reference Year deposition values, the deposition data for historical and calibration periods were calculated using the Reference Year absolute values and scaled time series of wet deposition and DDF that gave the values for a given year as a fraction of the Reference Year value. The Advanced Statistical Trajectory Regional Air Pollution (ASTRAP) model produced wet and total deposition estimates of S and oxidized N every 10 years starting in 1900 and ending in 1990 (Shannon 1998). The model outputs are smoothed estimates of deposition roughly equivalent to a 10-year moving average centered on each of the output years. The outputs of ASTRAP were used to set up the scaled sequences of past wet deposition and DDF for the calibration of each site. MAGIC modeling sites were assigned the historical sequences of the nearest site having ASTRAP output, considering both distance and elevation. The time series of DDF values from 1900 to 1990 for each site for which ASTRAP estimates were available from the study of Shannon (1998) were normalized to the 1990 values at each site to provide scaled sequences of DDF.

Future deposition

The Regional Acid Deposition Model (RADM, Chang et al. 1987) was used to simulate atmospheric transport and future changes in wet and dry deposition of S and N. The model was originally developed with 80-km grids. For this analysis, we used a 20-km grid created as a one-way nest covering the northeastern United States. The model was extended or enhanced to treat nutrient deposition by adding the capability to represent $SO_4^{2-} - NO_3^- - NH_4^+$–water aerosol composition based on equilibrium thermodynamics by incorporating into RADM a module from the Regional Particulate Model (Binkowski and Shankar 1995; Mathur and Dennis 2003). Scenarios of future emissions for 2010 and 2020 were developed for this study following U.S. EPA methods regarding preparation of emissions inventory input into air quality modeling for policy analysis and rule making purposes. A baseline emissions inventory was created representing the future, with economic assumptions obtained from the Bureau of Economic Analysis and emissions controls representative of the laws, rules, and regulations already on the books and final as of the date of preparation of the inventory. For the 1990 Base Case and the 2010 and 2020 scenario projections, meteorology was held constant, and only the emissions were changed. We did not investigate the extent to which model results might be affected by climate change. Such effects may include altered leaching losses of base cations and changes in forest growth and decomposition, which affect N-saturation processes (Wright et al. 2006).

Four emissions scenarios were selected by the assessment team (Sullivan et al. 2003) and implemented for this study:

Scenario 1. Baseline scenario with reasonable economic growth and emissions limitations according to existing regulations as of summer, 2000; 1990 Clean Air Act (CAA) Title IV acid rain controls on SO_2 and NO_x; NO_x State Implementation Plan (SIP) Call in the Midwestern and Northeastern U.S.; national Tier II Vehicle Standards on cars (U.S. EPA 2002, 2000). Projections of emissions controls are provided to 2010.

Scenario 2. Continuation of Baseline scenario projection to 2020 with additional national Heavy Duty Diesel Vehicle standards to further reduce NO_x emissions. Allows for continued implementation of Tier II Vehicle Standards to realize their full effect. Little further reduction in SO_2 emissions. (U.S. EPA 2000, 2002).

Scenario 3. Stringent Utility Controls in addition to Scenario 2 in the interest of reducing acidic deposition – 90% reduction in utility SO_2 emissions from 1990 levels and utility NO_x emissions at an annual rate of 0.10 lbs/million BTU (81% reduction from 1990 levels).

Scenario 4. Stringent Controls on Utility, Major Industrial, and Light-Duty Mobile Sources to further the reduction of acidic deposition. Adds to Scenario 3 by reducing national non-utility major point source emissions of SO_2 and NO_x by 50% (Pechan & Assoc. 2001) and instituting a super-ultra-low California Car nationwide.

The percent changes in total S and N deposition calculated for the emissions control scenarios using the RADM model are given in Table 1. Major reductions in S, and to a lesser extent N, emissions within the SNP airshed are anticipated as a result of rules and regulatory plans prior to 2003, represented by Scenarios 1 and 2. Under the set of rules prior to the 2005 Clean Air Interstate Rule (CAIR) (http://www.epa.gov/cair/), SO_2 emissions within the SNP airshed would be reduced by an estimated 47% from 1990 levels and NO_x emissions would be reduced by 41%. For this analysis, the airshed was determined as the source region for most emissions that impact the park, based on RADM simulations. The policy emphasis in Scenario 2 is reduction of ground-level ozone levels.

Table 1 Percent changes in sulfur and nitrogen deposition relative to 1990 base, calculated for emissions control scenarios

Constituent	Scenario Year	All 1996	1 2010	2 2020	3 2020	4 2020
Sulfur		−20.2	−33.2	−36.7	−68.7	−74.9
Oxidized nitrogen		+2.7	−35.2	−50.3	−59.0	66.8
Reduced nitrogen		+29.9	+26.1	+25.7	+29.6	+20.0

Scenarios 3 and 4 represent significant additional emissions reductions in order to further reduce acidic deposition. The Federal CAIR rule enacted in 2005 is expected to limit emissions in the latter years of these scenarios to levels that are approximately midway between Scenarios 2 and 3 for both SO_2 and NO_x Future streamwater chemistry was simulated for each site from 1990 to 2100, based first on a scenario of continued constant deposition at 1990 levels and then, following a ramp down, at 2010 levels for Scenario 1 and at 2020 levels for Scenarios 2, 3, and 4 out to 2100.

Two modeling exercises were conducted. The first was based on the series of scenarios of future emissions control. The second was based on reaching specified streamwater ANC targets (or critical levels). For a given model scenario in the first exercise, the deposition in future years was specified as a fraction of the total deposition in the reference year. In that the future deposition changes were specified only as changes in total deposition, these were implemented in MAGIC by assuming that wet and dry deposition change by the same relative amount.

Critical loads calculations

In order to conduct the second modeling exercise, the MAGIC model was used in an iterative fashion (repeated runs based on incremental changes in acidic deposition levels) to calculate the S deposition values that would cause the chemistry of each of the modeled streams to either increase or decrease streamwater ANC (depending on the reference year value) to reach the specified critical levels. The critical ANC levels were set at 0, 20, and 50 μeq/L, the first two of which are believed to approximately correspond with chronic and episodic damage to brook trout populations in park streams (Bulger et al. 2000, Cosby et al. 2006). Other species of aquatic biota may be impacted at ANC near 50 μeq/L (Driscoll et al. 2001). In order to conduct this critical loads analysis for S deposition, it was necessary to specify the corresponding levels of N deposition. Nitrogen deposition accounts, however, for only a minor component of the overall acidification response of streams in the park. For this critical loads analysis, future N deposition was held constant at 1990 levels (7.6 kg N/ha/year). This is a reasonable assumption, given that base flow NO_3^- concentrations in these streams are low, except during periods of tree defoliation from insect infestation. It does not bias our critical loads calculations given the minor importance of N in these streams currently and the expectation that NO_x emissions will decrease in the future.

It was also necessary to specify the times in the future at which the critical ANC values would be reached. We selected the years 2040 and 2100. It must be recognized that streamwater chemistry will continue to change in the future for many decades subsequent to stabilization of atmospheric deposition levels. This is mainly because soils will continue to change in the degree to which they adsorb incoming S and because some watersheds will have become depleted of base cations. The latter process can cause streamwater base cation concentrations and ANC to decrease over time while SO_4^{2-} and NO_3^- concentrations in streamwater maintain relatively constant levels.

Results

Reference conditions

Atmospheric deposition

Some data are available regarding both wet and dry deposition in SNP. An NADP/NTN wet deposition monitoring station has been in operation at Big Meadows (elevation 1,074 m) since 1981. Wet deposition data are also collected at the White Oak Run and North Fork Dry Run watersheds by the University of Virginia. Precipitation volume and the concentrations of major ions in precipitation are reported. Wet deposition of each ion is calculated as the product of the precipitation value and ionic concentration in precipitation. Dry deposition was calculated using NADP and CASTNet data from Big Meadows, also as a 6-year average, using those years for which a complete record was available (1991, 1992, 1993, 1995, 1997, 1998). The estimates derived for total S and N deposition using these methods were each 1.8 times the estimated wet deposition, in general agreement with estimates of wet and total deposition derived at multiple sites throughout the southeastern United States using the ASTRAP model (Shannon 1998; Sullivan et al. 2002). Annual total deposition values for S and N in the Base Year (1990) were estimated to be 13.0 and 7.6 kg/ha/year, respectively, averaged for the three wet deposition monitoring sites over a five-year period centered on 1990.

Streamwater chemistry

The SNP landscape includes three major geologic sensitivity types, each of which influences about one-third of the stream length in the park. All streams on siliciclastic bedrock monitored during the period 1988–1999 had relatively high median SO_4^{2-} concentration (76 to 109 μeq/L), whereas three of four streams monitored on granitic bedrock had sulfate concentration <43 μeq/L. Sulfate concentrations in streams draining basaltic bedrock were more variable, ranging from 52 to 127 μeq/L. Streamwater base cation concentrations and ANC also vary dramatically from site to site. Median streamwater base cation concentrations were generally lowest in the watersheds on siliciclastic bedrock, and this could reflect lower base cation supply from watershed soils and/or greater base cation depletion of soils caused by leaching of SO_4^{2-} to streams. Base cation concentrations were substantially higher (median > 235 μeq/L) in watersheds on basaltic bedrock.

There are many streams on siliciclastic bedrock in the park that have chronic ANC in the range where sensitive aquatic biota cannot exist and/or where episodic acidification to ANC values near or below zero frequently occur during hydrological events. The streams that are most susceptible to adverse chronic or episodic biological effects are those having chronic ANC less than about 50 μeq/L, especially those having chronic ANC less than about 20 μeq/L (Bulger et al. 1999). These occur primarily on siliciclastic bedrock (Table 2).

The observed patterns in streamwater chemistry are strongly related to patterns in bedrock geology within the park. In fact, geological type, soils conditions that developed from underlying geology, and water chemistry conditions are all closely interrelated within SNP. The ANC values of streams in the park associated with siliciclastic bedrock are low. Almost half of the sampled (mostly first order) streams on siliciclastic bedrock in the 1992 survey of small sub-watersheds in SNP had ANC in the chronically acidic range (<0 μeq/L) in which lethal effects on brook trout are probable (Galloway et al. 1999). The balance of the small streams on siliciclastic bedrock had ANC in the episodically acidic range (having chronic ANC between 0 and 20 μeq/L) in which sub-lethal or lethal effects on brook trout are possible. Many of the streams on granitic bedrock were in the indeterminate range (20–50 μeq/L; Bulger et al. 1999). In contrast, the streams on the basaltic bedrock type had ANC values that were well within the suitable range for brook trout (>50 μeq/L). All of the streams associated with siliciclastic bedrock had pH <6, identified by Baker and Christiansen (1991) as too acidic for some acid-sensitive fish species.

Soils

A common measure of base availability in soils is the percent base saturation, which represents the base cation fraction of total exchangeable acid and base cations. Base saturation values in the range of 10–20% have been cited as threshold values for incomplete acid neutralization and leaching of aluminum from soil to surface waters (Reuss and Johnson 1986; Binkley et al. 1989a, b; Cronan and Schofield 1990). Data from the 2000 soil survey are summarized in Table 3 for each of the study watersheds, stratified by the predominant bedrock class present in each watershed. Median base saturation was less than 10% for mineral soils associated with siliciclastic bedrock and less than about 14% for mineral soils associated with granitic bedrock in the park. The present low base cation availability in soils of watersheds underlain primarily by siliciclastic or granitic bedrock can likely be attributed to a combination of low base cation content of the parent bedrock and depletion by decades of accelerated leaching by acidic deposition.

The soils within watersheds situated primarily on siliciclastic bedrock generally showed the lowest soil pH (median 4.4–4.5), cation exchange capacity (median 3.5–7.5 cmol/kg), and base saturation (median 8–12%). Values for watersheds having soils primarily on granitic bedrock were generally intermediate, and basaltic watersheds were higher in all three parameters (Table 3).

A clear relationship was found between streamwater ANC and median soil base saturation among the SWAS study watersheds (Fig. 1). All watersheds that were characterized by soil base saturation less than 15% had average streamwater ANC<100 μeq/L. Watersheds that had higher soil base saturation (all of which were >22%) were dominated by the basaltic

Table 2 Interquartile distributions of spring quarter acid neutralizing capacity (ANC), sulfate (SO_4^{2-}), and sum of base cations (SBC; Ca^{2+}, Mg^{2+}, K^+, and Na^+) for Shenandoah National Park study streams during the period 1988–1999

Site ID	Watershed	Percent of watershed area			ANC (μeq/L)			SO_4^{2-} (μeq/L)			SBC (μeq/L)		
		Siliciclastic	Granitic	Basaltic	25th	Med	75th	25th	Med	75th	25th	Med	75th
Siliciclastic Bedrock Class													
PAIN	Paine Run	100.0	0.0	0.0	1.9	3.7	5.3	106.6	109.1	112.4	142.6	143.6	149.7
WOR1	White Oak Run	100.0	0.0	0.0	12.8	16.2	22.0	70.3	75.7	81.9	130.1	137.4	145.3
DR01	Deep Run	100.0	0.0	0.0	−0.6	0.3	1.2	100.3	105.3	108.3	129.4	130.2	132.1
VT36	Meadow Run	100.0	0.0	0.0	−4.7	−3.1	−1.3	87.0	89.2	94.0	112.0	112.8	118.1
VT53	Twomile Run	100.0	0.0	0.0	7.8	10.0	12.0	94.9	98.7	101.2	137.1	140.3	143.3
Granitic Bedrock Class													
STAN	Staunton River	0.0	100.0	0.0	73.2	76.8	80.3	40.3	42.6	43.3	154.4	157.4	161.3
NFDR	North Fork of Dry Run	0.0	100.0	0.0	43.5	48.7	51.2	92.6	97.4	101.8	200.4	209.7	216.1
VT58	Brokenback Run	0.0	93.4	6.6	69.2	74.4	81.8	37.1	39.4	41.4	148.0	156.0	162.7
VT62	Hazel River	0.0	100.0	0.0	77.2	86.8	90.0	35.1	36.9	38.6	157.2	167.5	175.3
Basaltic Bedrock Class													
PINE	Piney River	0.0	31.3	69.7	186.7	191.9	205.0	60.6	62.8	67.5	314.8	319.3	340.5
VT66	Rose River	0.0	9.1	90.9	129.2	133.6	137.5	49.8	51.7	57.0	242.5	254.3	271.2
VT75	White Oak Canyon	0.0	14.1	85.9	107.7	119.3	124.9	50.4	52.2	55.3	221.6	235.3	248.3
VT61	North Fork of Thornton River	5.2	27.0	67.8	221.1	249.1	263.5	77.5	83.6	90.0	386.8	392.4	414.3
VT51	Jeremys Run	31.0	0.0	69.0	141.0	158.5	166.6	121.6	127.0	133.1	328.3	336.4	355.6

Spring quarter samples collected over a 12-year period during the last week of April

Twelve years of data are available for all sites except VT75 (9 years)

Table 3 Interquartile distribution of pH, cation exchange capacity (CEC), and percent base saturation for soil samples collected in SNP study watersheds during the 2000 soil survey

Site ID	Watershed	N	pH			CEC (cmol/kg)			Percent Base Saturation		
			25th	Med	75th	25th	Med	75th	25th	Med	75th
Siliciclastic Bedrock Class[a]											
PAIN	Paine Run	6	4.4	4.5	4.7	3.7	5.7	5.7	7.1	10.0	24.9
WOR1	White Oak Run	6	4.3	4.4	4.4	4.8	7.5	7.8	5.3	7.5	8.5
DR01	Deep Run	5	4.3	4.4	4.5	3.9	5.0	5.8	7.2	8.9	10.8
VT36	Meadow Run	6	4.4	4.4	4.5	3.1	3.5	7.6	7.8	8.7	11.3
VT53	Twomile Run	5	4.3	4.5	4.5	4.6	6.0	6.9	11.7	12.3	13.6
Granitic Bedrock Class											
STAN	Staunton River	6	4.7	4.8	4.9	6.5	7.5	9.2	9.1	13.9	29.5
NFDR	NF of Dry Run	5	4.4	4.5	4.7	7.3	8.0	9.2	7.5	10.8	12.4
VT58	Brokenback Run	5	4.6	4.7	4.7	7.3	8.4	9.6	6.0	6.7	9.7
VT62	Hazel River	4	4.5	4.7	4.8	5.3	5.3	6.5	12.3	12.8	21.6
Basaltic Bedrock Class											
PINE	Piney River	6	4.7	5.0	5.3	7.3	7.7	10.0	17.0	24.0	57.0
VT66	Rose River	8	4.8	5.0	5.3	7.3	10.1	10.7	19.1	38.0	63.5
VT75	White Oak Canyon	6	4.9	5.1	5.5	7.1	7.5	9.3	15.6	32.8	43.4
VT61	NF of Thornton River	7	5.1	5.2	5.3	7.7	9.6	10.8	35.6	54.4	71.2
VT51	Jeremys Run	4	4.7	5.0	5.3	6.3	7.6	7.7	15.0	22.8	46.1

Samples collected from mineral soil <20 cm depth

[a] Watersheds are stratified according to the predominant bedrock class present in each watershed

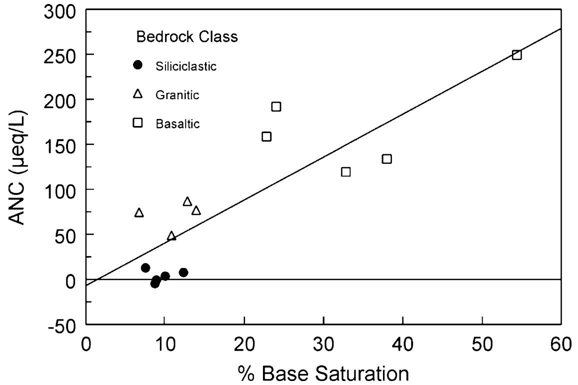

Fig. 1 Median spring acid neutralizing capacity of streams in the Shenandoah Watershed Study watersheds during the period 1988–1999 versus median base saturation of watershed soils

bedrock type and had average streamwater ANC> 100 µeq/L. Lowest base saturation values (7–14%) were found in the siliciclastic and granitic watersheds, with much higher values in the basaltic watersheds.

Model calibrations

The calibration procedure for each site produced summary statistics (mean, standard deviation, maximum and minimum) for the observed values, the simulated values and the differences (simulated minus observed values) of each of the 15 stream variables and each of the 7 soil variables simulated for each of the sites. In addition, plots of simulated versus observed values for stream variables were examined. These analyses allowed us to determine that the model calibration results were not biased and did not contain unacceptably large residual errors (Sullivan et al. 2003). For example, simulated versus observed streamwater ANC for the 13 modeled streams in the reference year is shown in Fig. 2. Calibrated values (5-year averages centered on 1990) showed good agreement with measured values at all sites.

Future projections

Future streamwater chemistry was simulated for each site throughout the period 1990–2100, based on the scenario of continued constant deposition at 1990 levels and the four emissions control scenarios.

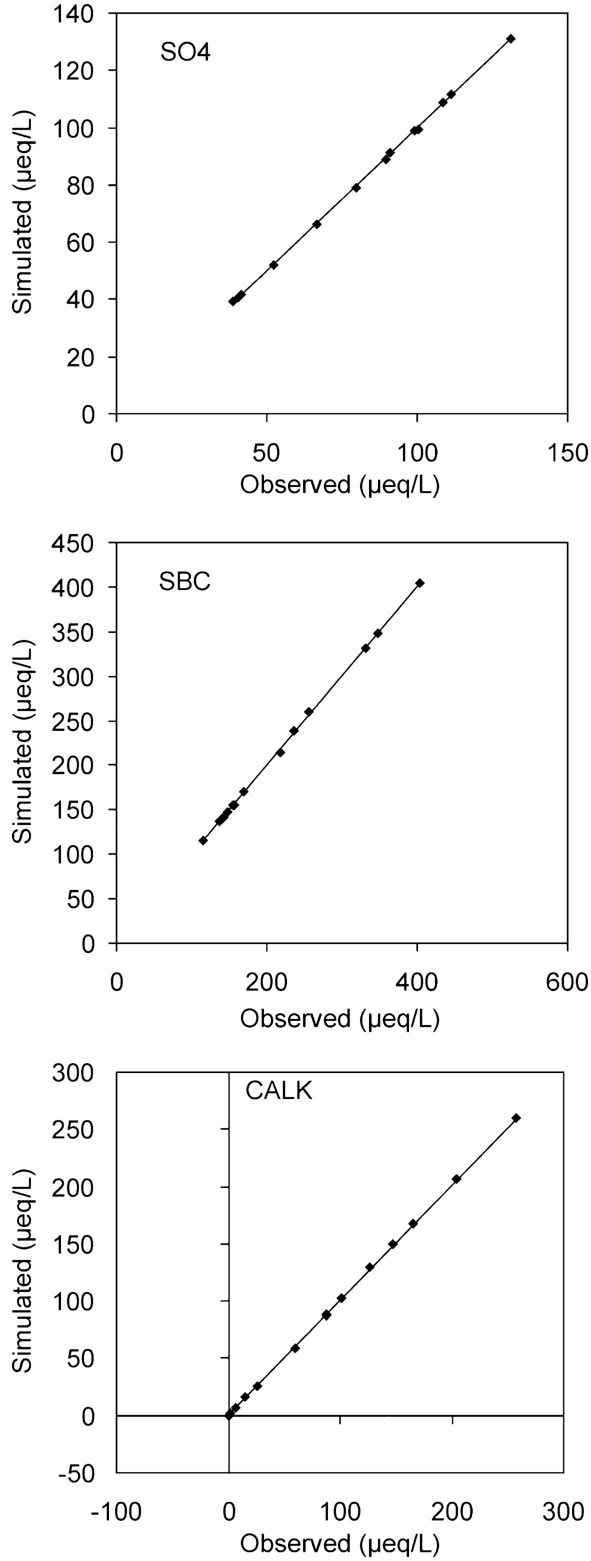

Fig. 2 Calibration results, expressed as predicted versus observed SO_4, sum of base cations, and calculated acid neutralizing capacity (CALK) for the reference year. A 1:1 equity line is added for reference

Hindcast simulation results suggested substantial past acidification (40–84 μeq/L) of the modeling sites that occur on siliciclastic bedrock. Among the modeling sites on granitic bedrock, North Fork Dry Run showed evidence of moderate historic acidification (22 μeq/L), whereas other modeling sites on granitic bedrock and most of the sites on basaltic bedrock showed relatively less historic acidification (<15 μeq/L). The inferred pre-industrial ANC of all of the siliciclastic sites and of North Fork Dry Run granitic site ranged between about 60 and 90 μeq/L, whereas other sites were inferred to have had pre-industrial ANC near or above 100 μeq/L.

Projected future concentrations of SO_4^{2-}, NO_3^-, sum of base cations, and ANC are presented in Table 4 as median values for the modeled sites in each geologic sensitivity class. Sulfate concentrations in streamwater were projected to increase at all sites under the scenario of continued constant deposition. Under the four emissions control scenarios, streamwater SO_4^{2-} concentrations were projected to decrease at all of the sites on siliciclastic bedrock, but results were mixed for the various scenarios applied to sites on granitic and basaltic bedrock. The most stringent emissions control strategy (Scenario 4) resulted in substantial (>25 μeq/L) projected decreases in streamwater SO_4^{2-} concentrations (Table 4). Changes in streamwater NO_3^- concentration in response to the scenarios were either negligible or were projected decreases in concentration that were less than about 12 μeq/L. Changes in streamwater base cation concentrations were projected to be smallest for the siliciclastic sites and largest for the basaltic sites. At a given site, base cation leaching was projected to be largest under continued constant deposition and progressively smaller with increasingly stringent emissions control scenarios (Table 4).

The combined effects of modeled changes in SO_4^{2-} and base cations resulted in projected future changes in streamwater ANC that ranged from less than 10 μeq/L for some siliciclastic sites under Scenarios 1 and 2 to projected ANC increases of more than 40 μeq/L at Deep Run and Paine Run for Scenarios 3 and 4. All siliciclastic sites were projected to become acidic by the year 2040 under continued deposition at 1990 levels. White Oak Run was projected to nearly become acidic under Scenarios 1 and 2 by 2100, but other sites on siliciclastic bedrock were projected to increase ANC in the future under all emissions control scenarios. In contrast, the majority of the sites on granitic and basaltic bedrock showed little pro-

Table 4 Median projected streamwater chemistry (units in μeq/L) using the Model of Acidification of Groundwater in Catchments (MAGIC) model for 14 streams within Shenandoah National Park in response to simulated constant deposition at 1990 levels and to the four emissions control scenarios. Results are presented for the 1990 reference year and projections for 2040 and 2100

Parameters	Median projected streamwater chemistry (μeq/L)										
	1990 ref. yr.	Const. Dep		Scenario 1		Scenario 2		Scenario 3		Scenario 4	
		2040	2100	2040	2100	2040	2100	2040	2100	2040	2100
Sites on Siliciclastic Bedrock (*n*=5)											
SO_4^{2-}	99	112	113	78	75	76	72	59	42	55	36
NO_3^-	3.5	3.5	3.5	2.6	2.6	2.1	2.1	2.0	2.0	1.8	1.8
SBC[a]	142	135	129	126	122	126	121	119	113	118	112
ANC	6.8	−4.8	−19	13	13	14	17	31	43	34	48
Sites on Granitic Bedrock (*n*=4)											
SO_4^{2-}	41	63	85	52	61	52	59	44	41	43	38
NO_3^-	4.3	4.3	4.3	3.7	3.7	2.7	2.7	2.6	2.6	2.3	2.3
SBC[a]	163	176	187	168	171	168	170	163	155	162	151
ANC	88	80	70	83	78	83	78	86	85	86	86
Sites on Basaltic Bedrock (*n*=5)											
SO_4^{2-}	66	99	120	78	82	77	79	62	48	57	44
NO_3^-	26	26	26	20	20	17	17	16	16	15	15
SBC[a]	332	348	343	308	302	304	296	278	262	273	256
ANC	168	163	158	168	166	169	166	173	174	174	175

[a] *SBC* sum of base cations (Ca^{2+}+Mg^{2+}+K^++Na^+) concentrations

jected improvement in ANC under most of the scenarios (Table 4).

Critical loads

As described above, it is well documented that air pollution and acidic deposition have caused environmental degradation of streams in SNP. Recent emissions control efforts have focused on attempts to reduce air pollution and acidic deposition sufficiently to permit ecosystem recovery, if not to pre-industrial levels, at least to ecologically acceptable levels.

The levels of S deposition that were simulated to cause streamwater ANC to increase or decrease to three specified critical levels or ANC endpoints (0, 20, and 50 μeq/L) are listed in Table 5 for each of the modeled streams. These critical levels have been utilized in critical loads studies elsewhere (c.f., Kämäri et al. 1992; Sullivan and Cosby 2002; Sullivan et al. 2005). Estimated critical loads for S deposition ranged from less than zero (ecological objective not attainable) to several hundred kg/ha/year, depending on the selected site, ANC endpoint, and evaluation year.

It is useful to put the results of this critical loads analysis into the perspective of the population of streams within the park. This cannot be done directly, however, because the modeled streams were not drawn from a statistical frame. This can be done indirectly by quantifying critical load within geologic sensitivity classes and/or as a function of reference year ANC. None of the granitic or basaltic streams exhibited critical loads values lower than the reference year S deposition level (13 kg/ha/year), when evaluated for the endpoint year 2100 using ANC criterion values of either 0 or 20 μeq/L. In marked contrast, all of the modeled siliciclastic streams exhibited critical loads <11 kg/ha/year to protect against acidification to ANC≤0 in the year 2100 (Table 5). The median modeled siliciclastic stream had a calculated critical load to protect against acidification to ANC≤20 μeq/L that was about 31% lower than 1990 deposition.

Table 5 Estimated critical load (kg/ha/year) of sulfur to achieve a variety of acid neutralizing capacity (μeq/L) endpoints in a variety of future years for modeled streams in Shenandoah National Park

Site	BedrockClass	ANC (μeq/L)		Critical Load to Achieve ANC Value[a]								
				ANC=0			ANC=20			ANC=50		
		1990	Pre-1900	2020	2040	2100	2020	2040	2100	2020	2040	2100
VT36	S	0	69	9	9	9	2	5	6	<0	<0	1
DR01	S	2	78	14	13	12	5	8	9	<0	<0	3
VT35	S	7	91	16	15	14	11	11	11	1	4	6
VT53	S	16	81	20	17	15	11	12	11	<0	1	5
WOR1	S	26	66	22	15	10	5	6	6	<0	<0	<0
Median Siliciclastic		7	78	16	15	12	5	8	9	<0	<0	3
NFDR	G	60	82	53	33	17	43	26	13	15	10	7
VT58	G	88	98	119	59	29	109	53	25	83	40	18
VT59	G	88	96	164	86	45	154	79	40	127	62	30
VT62	G	102	116	122	60	29	112	55	26	92	44	20
Median Granitic		88	98	119	60	29	109	53	26	83	40	19
VT75	B	126	143	331	183	78	307	173	76	248	147	69
VT66	B	147	159	155	118	73	143	109	69	127	93	60
VT51	B	166	191	281	151	65	267	145	64	239	134	62
VT60	B	204	218	241	147	72	230	142	70	211	134	67
VT61	B	258	277	502	281	124	487	276	122	459	265	119
Median Basaltic		166	191	281	151	73	267	145	70	239	134	67

Reference year (1990) deposition of S was 13 kg/ha/year

All simulations based on straight-line ramp changes in deposition from 2000 to 2010, followed by constant deposition thereafter.

S Siliciclastic, *G* Granitic, *B* Basaltic

[a] Critical load <0 indicates that the ecological endpoint could not be achieved (no recovery to specified ANC criterion value) even if S deposition was reduced to zero

The calculated S deposition critical load for streams in SNP varied in relation to watershed sensitivity (as reflected in geologic sensitivity class, and soil and streamwater characteristics), the selected chemical criterion (critical ANC value), and the future year for which the evaluation was made. All of these criteria are important. For example, the modeled critical S load to protect the 14 modeled streams in SNP from becoming acidic (ANC=0) in the year 2100 varied from 9 to 124 kg S/ha/year (Table 5). Similarly, for site WOR1 (White Oak Run) in the year 2100, the critical load to protect against ANC≤0 was 10 kg S/ha/year, but this watershed could tolerate only 6 kg S/ha/year to protect against acidification to ANC of 20 μeq/L within the same time period. The model suggested that it would not be possible to achieve ANC=50 μeq/L at this site by 2100, even if S deposition was reduced to zero. The estimated pre-1900 ANC of this stream was 66 μeq/L, which declined to 26 μeq/L by 1990.

The relationships between critical load, selection of ANC criterion value, and selection of evaluation year are important. Higher critical loads can be tolerated if one only wishes to protect against acidification to the year 2020, as compared with more stringent deposition reductions required to protect systems against acidification for a longer period of time. Higher critical loads are allowable if one wishes to prevent acidification to ANC=0 μeq/L (chronic acidification) than if one wishes to be more restrictive and prevent acidification to ANC below 20 μeq/L (possible episodic acidification).

The model suggested that it would not be reasonable to attempt to regain streamwater ANC values during the next century that would be similar to pre-industrial ANC, at least for the most acid-sensitive systems. For example, of the modeled streams that had ANC<100 μeq/L in 1990, only one was projected to reach within 10% of its inferred pre-industrial ANC value anytime between 1990 and 2100, regardless of how much S deposition was reduced. This result is probably largely due to simulated loss of base cations from watershed soils in response to decades of relatively high levels of S deposition.

Some of the streams were projected to be unable even to regain 1990 ANC for some evaluation years. Five of 14 modeled streams were projected to not be able to regain 1990 ANC by the year 2020, regardless of the amount of deposition reduction. All sites except two were projected to be able to regain 1990 ANC by 2100, but S deposition would have to be decreased to below 4 kg S/ha/year at half of the sites to achieve that level of recovery.

The results of these model simulations illustrate that how you phrase the critical load question is extremely important. The estimated deposition change required to achieve certain benchmark streamwater chemistry endpoints can be highly variable depending on how and for what time period the endpoint is defined, and on the starting point chemistry of the watersheds that are selected for modeling. An example critical loads question might be as follows: What is the total sustained sulfur deposition loading, given existing N deposition loading rates, that would cause White Oak Run to decrease to ANC=0 μeq/L in the year 2040?

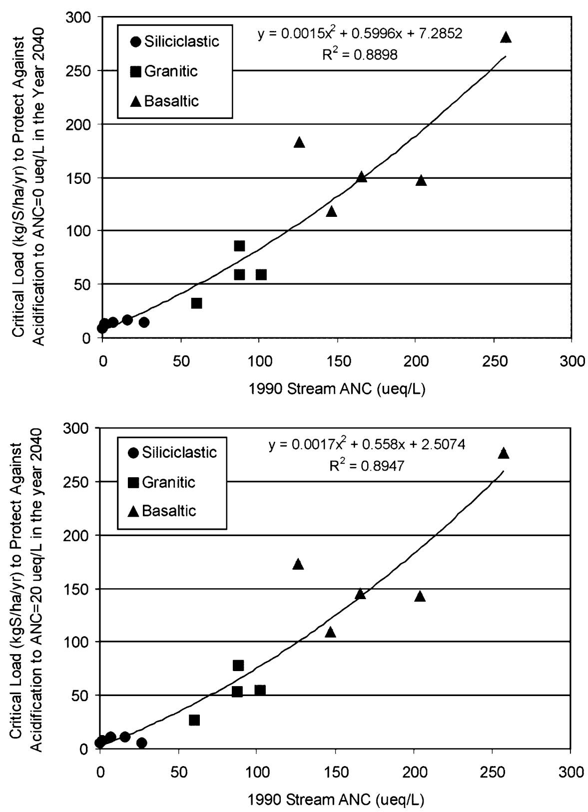

Fig. 3 Critical load simulated by the Model of Acidification of Groundwater in Catchments (MAGIC) to protect streams in Shenandoah National Park against acidification to acid neutralizing capacity below 0 (*top panel*) and 20 μeq/L (*bottom panel*) by the year 2040, as a function of 1990 acid neutralizing capacity and geologic sensitivity class. Reference year (1990) S deposition was 13 kg/ha/year

The calculated critical loads of S deposition required to prevent streamwater acidification to ANC values below 0 and 20 μeq/L varied consistently as a function of measured ANC in 1990, which in turn was separated into rather distinct groupings according to geologic sensitivity class (Fig. 3). These model estimates suggest that all streams within the park that had 1990 ANC≤20 μeq/L would require critical load values between 2.5 and 14.4 kg S/ha/year to maintain ANC above 20 μeq/L in the year 2040. Similarly, a critical load of 7.3 kg S/ha/year would protect all streams that had positive ANC in 1990 from becoming chronically acidic by 2040, and a critical load of 2.5 kg S/ha/year would allow those same streams to achieve or maintain ANC above 20 μeq/L by 2040. Most streams on granitic bedrock, and all streams on basaltic bedrock, had critical loads that were much higher than the current S deposition load.

Discussion

Sulfur retention reduces the potential for the acidification of surface waters because it decreases the mobility of sulfate. However, S retention by adsorption on soils is largely a capacity-limited process. As the finite adsorption capacity of watershed soils is exhausted, SO_4^{2-} concentration can increase in surface waters, potentially contributing to greater acidification.

Despite the fact that a high percentage of the S deposited in SNP watersheds does not currently enter the streams, SO_4^{2-} is still the chemical species with the highest concentration among all the solutes in many streams. Given the absence of significant S-bearing minerals in the park (Gathright 1976), it is clear that most of this S is derived from the atmosphere. It is also clear that without the delaying effect of S retention in watershed soils, many more streams in the park would now be acidic. This relationship can be seen in the lower left portion of Fig. 1. The siliciclastic and granitic watersheds had similar values of soil base saturation, ranging from about 7 to 14%. However, streamwater ANC was considerably lower in the siliciclastic watersheds, and this can be attributed, at least in part, to lower S retention in the soils of siliciclastic watersheds.

Although baseline, pre-industrial resource conditions are not precisely known, it is probable that none of the streams modeled within SNP were acidic in pre-industrial times and the number of streams having ANC≤20 μeq/L was much lower than it is currently. MAGIC model estimates suggested that streams that currently exhibit streamwater ANC≤20 μeq/L experienced, on average, a decrease in ANC of 73 μeq/L since pre-industrial times. Of the 14 streams modeled for this assessment, none had simulated pre-industrial streamwater ANC≤50 μeq/L, compared with five that currently have ANC≤26 μeq/L. Most streams that occur on siliciclastic bedrock now exhibit periodic episodic decreases in streamwater ANC to values near or below zero during hydrological events. Model estimates suggest that the chronic (base flow) ANC of streams was not sufficiently low for this to have been the case in pre-industrial times. In the most acid-sensitive streams, such episodic ANC depressions are accompanied by pulses of increased acidity (decreased pH) and inorganic aluminum, which are toxic to many species of aquatic biota. Although episodic acidification is partly a natural process, it is also partly driven by S of atmospheric origin, and it is superimposed on baseflow chemistry that is substantially more acidic than it was previously. This chronic and episodic loss of ANC has been accompanied by a loss of some fish species and other species of aquatic biota. Many streams have lost the more acid-sensitive species of fish and invertebrates. Species richness has declined, as has the condition of some remaining species. In some streams, these impacts have been sufficiently large as to eliminate or reduce the population of brook trout, a rather acid-tolerant species.

As illustrated in the analysis of critical loads of sulfur deposition presented here for Shenandoah National Park, there exists a range of important issues that should be considered in developing and implementing a critical loads approach. Key issues include the following:

- What is the environmental response indicator, and what does it tell us about the system?
- What is/are the selected critical endpoint criterion value(s) for the response indicator?
- What constitutes "recovery" in the context of this indicator?
- What is the time period of evaluation of the critical load?
- How representative of the broader region are the water bodies selected for modeling and/or how many waters are represented by the modeled sites?
- What are the major sources and levels of uncertainty?

Although process-based watershed models such as MAGIC entail uncertainty (c.f., Sullivan et al. 2004), results of model simulations and critical loads calculations presented here will help to inform the development of the critical loads approach as a potential assessment and policy tool in the United States. This could aid the management of aquatic resources in Shenandoah National Park and elsewhere. The approach may also be useful for addressing transboundary air pollution issues affecting Canada and Mexico. Additional logical steps in the process could include extrapolation of modeling results to additional streams in the park and selection of interim (politically-determined) target loads of S deposition which would allow acid-sensitive streams in the park to begin the process of chemical recovery and move toward the long-term critical load values that would sustain sensitive aquatic life forms. There is also a continuing need to monitor atmospheric deposition, streamwater chemistry, and aquatic biota to document future improvements in response to emissions reductions.

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References

Aber, J. D., Melillo, J. M., Nadelhoffer, K. J., Pastor, J., & Boone, R. D. (1991). Factors controlling nitrogen cycling and nitrogen saturation in northern temperate forest ecosystems. *Ecological Applications, 1*(3), 303–315.

Baker, J. P., & Christensen, S. W. (1991). Effects of acidification on biological communities. In D. F. Charles (Ed.), *Acidic deposition and aquatic ecosystems* (pp. 83–106). New York: Springer.

Binkley, D., Driscoll, C., Allen, H. L., Schoeneberger, P., & McAvoy, D. (1989a). *Acidic deposition and forest soils: Context and case studies in the southeastern U.S.* Ecological studies no. 72, New York: Springer.

Binkley, D., Valentine, D., Wells, C., & Valentine, U. (1989b). An empirical model of the factors contributing to 20-year decrease in soil pH in an old-field plantation of loblolly pine. *Biogeochemistry, 8*, 39–54.

Binkowski, F. S., & Shankar, U. (1995). The Regional Particulate Matter Model. 1. Model description and preliminary results. *Journal of Geophysical Research, 100*(26), 191–209.

Bulger, A. J., Cosby, B. J., Dolloff, C. A., Eshleman, K. N., Webb, J. R., & Galloway, J. N. (1999). *An integrated assessment of fish community responses to stream acidification*. The Shenandoah National Park: Fish in Sensitive Habitats (SNP: FISH) Project final report, National Park Service.

Bulger, A. J., Cosby B. J,. & Webb, J. R. (2000). Current, reconstructed past and projected future status of brook trout (*Salvelinus fontinalis*) streams in Virginia. *Canadian Journal of Fisheries and Aquatic Sciences, 57*, 1515–1523.

Bull, K. R. (1992). An introduction to critical loads. *Environmental Pollution, 77*, 173–176.

Chang, J. S., Brost, R. A., Isaksen, I. S. A., Madronich, S., Middleton, P., Stockwell, W. R., et al. (1987). A three-dimensional Eulerian acid deposition model: Physical concepts and formation. *Journal of Geophysical Research, 92*(14), 681–700.

Cosby, B. J., Hornberger, G. M., Galloway, J. N., & Wright, R. F. (1985a). Time scales of catchment acidification: A quantitative model for estimating freshwater acidification. *Environmental Science & Technology, 19*, 1144–1149.

Cosby, B. J., Norton, S. A., & Kahl, J. S. (1996). Using a paired-catchment manipulation experiment to evaluate a catchment-scale biogeochemical model. *Science of the Total Environment, 183*, 49–66.

Cosby, B. J., Webb, J. R., Galloway, J. N., & Deviney, F. A. (2006). *Acidic deposition impacts on natural resources in Shenandoah National Park*. Technical report NPS/NER/NRTR-2006/066. (Philadelphia: U.S. Department of the Interior, National Park Service, Northeast Region).

Cosby, B. J., Wright, R. F., & Gjessing, E. (1995). An acidification model (MAGIC) with organic acids evaluated using whole-catchment manipulations in Norway. *Journal of Hydrology, 170*, 101–122.

Cosby, B. J., Wright, R. F., Hornberger, G. M., & Galloway, J. N. (1985b). Modelling the effects of acid deposition: Assessment of a lumped parameter model of soil water and streamwater chemistry. *Water Resources Research, 21*, 51–63.

Cosby, B. J., Wright, R. F., Hornberger, G. M., & Galloway, J. N. (1985c). Modelling the effects of acid deposition: Estimation of long-term water quality responses in a small forested catchment, *Water Resources Research, 21*, 1591–1601.

Cronan, C. S., & Schofield, C. L. (1990). Relationships between aqueous aluminum and acidic deposition in forested watersheds of North America and northern Europe. *Environmental Science & Technology, 24*, 1100–1105.

Driscoll, C. T., Lawrence, G. B., Bulger, A. J., Butler, T. J., Cronan, C. C., Eager, C., et al. (2001). Acidic deposition in the northeastern United States: Sources and inputs, ecosystem effects, and management strategies. *Bioscience, 51*, 180–198.

Galloway, J. N., Deviney, Jr., F. A., & Webb, J. R. (1999). *Shenandoah Watershed Study Data Assessment 1980–*

1993. Project final report, submitted to National Park Service, Luray, VA.
Gathright, T. M. II. (1976). *Geology of the Shenandoah National Park, Virginia*. Bulletin 86, Charlottesville, VA: Virginia Division of Mineral Resources.
Jenkins, A., Helliwell, R. C., Swingewood, P. J., Seftron, C., Renshaw, M., & Ferrier, R. C. (1998). Will reduced sulphur emissions under the Second Sulphur Protocol lead to recovery of acid sensitive sites in UK? *Environmental Pollution, 99*, 309–318.
Kämäri, J., Amann, M., Brodin, Y.-W, Chadwick, M. J., Henriksen, A., Hettelingh, J. P., et al. (1992). The use of critical loads for the assessment of future alternatives to acidification. *Ambio, 21*, 377–386.
Mathur, R., & Dennis, R. L. (2003). Seasonal and annual modeling of reduced nitrogen compounds over the eastern United States: Emissions, ambient levels, and deposition amounts. *Journal of Geophysical Research, 108*(D15), 2201–2219. doi 10.1029/2002JD002794.
Nilsson, J., & Grennfelt, P. (Eds.) (1988). *Critical loads for sulphur and nitrogen*. Report 1988:15. Copenhagen: Nordic Council of Ministers.
Pechan, E. H. & Associates, Inc. (2001). *NO_x and SO_2 Emissions Reduction Assessment Revised Report.* Report prepared for the Clean Air Markets Division, U.S. Environmental Protection Agency. (Pechan report no. 01.06001/9008.413, Springfield, VA).
Porter, E., Blett, T., Potter, D. U., & Huber, C. (2005). Protecting resources on federal lands: Implications of critical loads for atmospheric deposition of nitrogen and sulfur. *BioScience, 55*(7), 603–612.
Reuss, J. O., & Johnson, D. W. (1986). *Acid deposition and the acidification of soil and water*. New York: Springer.
Shannon, J. D. (1998). *Calculation of trends from 1900 through 1990 for sulfur and NOx-N deposition concentrations of sulfate and nitrate in precipitation, and atmospheric concentrations of SOx and NOx species over the Southern Appalachians*. Report to the Southern Appalachian Mountains Initiative.
Shenandoah National Park (1998). *Backcountry & wilderness management plan.* U.S. Dept. of Interior, National Park Service.
Sullivan, T. J. (1993). Whole ecosystem nitrogen effects research in Europe. *Environmental Science & Technology, 27*(8), 1482–1486.
Sullivan, T. J. (2000). *Aquatic effects of acidic deposition.* Boca Raton, FL: Lewis.
Sullivan, T. J., & Cosby, B. J. (1995). Testing, improvement, and confirmation of a watershed model of acid-base chemistry. *Water, Air and Soil Pollution, 85*, 2607–2612.
Sullivan, T. J., & Cosby, B. J. (2002) *Critical loads of sulfur deposition to protect streams within Joyce Kilmer and Shining Rock wilderness areas from future acidification*. Report prepared for USDA Forest Service, Asheville, NC. Corvallis, OR: E&S Environmental Chemistry, Inc.
Sullivan, T. J., Cosby, B. J., Herlihy, A. T., Webb, J. R., Bulger, A. J., Snyder, K. U., et al. (2004). Regional model projections of future effects of sulfur and nitrogen deposition on streams in the Southern Appalachian Mountains. *Water Resources Research 40*(2), W02101 doi: 10.1029/2003WR001998.
Sullivan, T. J., Cosby, B. J., Lawrence, J. A., Dennis, R. L., Savig, K., Webb, J. R., et al. (2003). *Assessment of air quality and related values in Shenandoah National Park*. Technical report NPS/NERCHAL/NRTR-03/090. (Philadelphia: U.S. Department of the Interior, National Park Service, Northeast Region).
Sullivan, T. J., Cosby, B. J., Tonnessen, K. A., & Clow, D. W. (2005). Surface water acidification responses and critical loads of sulfur and nitrogen deposition in Loch Vale Watershed, Colorado. *Water Resources Research, 41*, W01021, doi: 10.1029/2004WR003414.
Sullivan, T. J., Cosby, B. J., Webb, J. R., Snyder, K. U., Herlihy, A. T., Bulger, A. J., et al. (2002). *Assessment of the effects of acidic deposition on aquatic resources in the Southern Appalachian Mountains*. (Report prepared for the Southern Appalachian Mountains Initiative (SAMI). Corvallis, OR: E&S Environmental Chemistry, Inc.; Available at http://www.esenvironmental.com/sami_download.htm).
Sullivan, T. J., Turner, R. S., Charles, D. F., Cumming, B. F., Smol, J. P., Schofield, C. L., et al. (1992). Use of historical assessment for evaluation of process-based model projections of future environmental change: Lake acidification in the Adirondack Mountains, New York, U.S.A. *Environmental Pollution, 77*, 253–262.
U.S. Environmental Protection Agency (2000). *Procedures for developing base year and future year mass and modeling inventories for the heavy-duty engine and vehicle standards and highway diesel fuel (HDD) rulemaking.* EPA report no. EPA420-R-00-020. Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards.
U.S. Environmental Protection Agency (2002). *Documentation of EPA Modeling Applications (V.2.1) using the integrated planning model*. EPA report no. EPA430/R-02-004. Washington, D.C.: U.S. Environmental Protection Agency, Office of Air and Radiation (620N), Clean Air Markets Division.
Webb, J. R., Cosby, B. J., Deviney, F. A., Eshleman, K. N., & Galloway, J. N. (1995). Change in the acid-base status of Appalachian Mountain catchments following forest defoliation by the gypsy moth. *Water, Air and Soil Pollution, 85*, 535–540.
Webb, J. R., Cosby, B. J., Galloway, J. N., & Hornberger, G. M. (1989). Acidification of native brook trout streams in Virginia. *Water Resources Research, 25*, 1367–1377.
Welsch, D. L., Webb, J. R., & Cosby, B. J. (2001). *Description of Summer 2000 Field Work.* Collection of Soil Samples and Tree Corps in the Shenandoah National Park with Summary Soils Data. Charlottesville, VA: Dept. of Environ. Sci., Univ. of Virginia.
Wright, R. F., Aherne, J., Bishop, K., Camarero, L., Cosby, B. J., Erlandsson, M., et al. (2006). Modelling the effect of climate change on recovery of acidified freshwaters: Relative sensitivity of individual processes in the MAGIC model. *Science of the Total Environment, 365*, 154–166.
Wright, R. F., Gjessing, E. T., Christophersen, N., Lotse, E., Seip, H. M., Semb, A., et al. (1986). Project RAIN: Changing acid deposition to whole catchments. The first year of treatment. *Water, Air and Soil Pollution, 30*, 47–64.