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Acidification and Prognosis for Future Recovery of Acid-Sensitive Streams in the Southern Blue Ridge Province

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Abstract This study applied the Model of Acidification of Groundwater in Catchments (MAGIC) to estimate the sensitivity of 66 watersheds in the Southern Blue Ridge Province of the Southern Appalachian Mountains, United States, to changes in atmospheric sulfur (S) deposition. MAGIC predicted that stream acid neutralizing capacity (ANC) values were above 20 μeq/L in all modeled watersheds in 1860. Hindcast simulations suggested that the median historical acidification of the modeled streams was a loss of about 25 μeq/L of ANC between 1860 and 2005. Although the model projected substantial changes in soil and stream chemistry since pre-industrial times, simulated future changes in response to emission controls were small. Results suggested that modeled watersheds would not change to a large degree with respect to stream ANC or soil % base saturation over the next century in response to a rather large decrease in atmospheric S deposition. Nevertheless, the magnitude of the relatively small simulated future changes in stream and soil chemistry depended on the extent to which S emissions are reduced. This projection of minimal recovery in response to large future S emissions reductions is important for designing appropriate management strategies for acid-impacted water and soil resources. Exploratory analyses were conducted to put some of the major modeling uncertainties into perspective.

Keywords Sulfur · Atmospheric deposition · Base cation · Acidification · Modeling

1 Introduction

The USDA Forest Service is concerned about the current and future health of terrestrial and aquatic resources within the Blue Ridge Province of the Southern Appalachian Mountains in western North Carolina, eastern Tennessee, and South Carolina. Soils within these watersheds have developed from

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the slow breakdown of parent rock material that can be inherently low in base cations. Adequate amounts of available calcium, magnesium, and potassium are essential to maintain healthy vegetation, and calcium is sometimes a factor limiting the maintenance of healthy aquatic organisms. These base cations are stored in soil and vegetation and are cycled through the soils as vegetation decomposes. Base cations also become dissolved in the soil water and are transported into streams to be utilized by aquatic organisms.

Ecosystem sensitivity to acidification and the potential effects of sulfur (S) deposition on surface water quality have been well-studied in the southeastern United States, particularly within the National Acid Precipitation Assessment Program (1991), the Fish in Sensitive Habitats project (Bulger et al. 1999), and the Southern Appalachian Mountains Initiative (SAMI; Sullivan et al. 2002a, b). Although aquatic effects from nitrogen deposition have not been studied as thoroughly as those from sulfur deposition, concern has been expressed regarding the role of NO_3^- in acidification of surface waters, particularly during hydrologic episodes (e.g., Cook et al. 1994; Sullivan 1993, 2000; Wigington et al. 1993).

Sulfur is the primary determinant of precipitation acidity and SO_4^{2-} is the dominant acid anion associated with acidic streams throughout most of the southern Appalachian Mountains region (Sullivan et al. 2002a). Although a substantial proportion of atmospherically deposited S is retained in watershed soils, SO_4^{2-} concentrations in many mountain streams have increased as a consequence of acidic deposition. Nitrate concentrations in stream water are also high in some streams, especially at high elevation.

Soil and drainage water acidification developed in this region over a period of many decades in response to high levels of atmospheric sulfur and nitrogen deposition. Many streams in the national forests show signs of acidification from atmospheric deposition, including streams in Class I areas that are administered by the Forest Service—Linville Gorge, Joyce Kilmer-Slickrock, and Shining Rock wilderness areas. These Class I areas are designated to receive special protection against air pollution impacts under the Clean Air Act. However, sulfur deposition has been declining throughout the eastern United States since about the early 1980s and further decreases are expected in the future. More information is needed regarding the watershed responses that should be expected. There is concern that base cations in the soil are being depleted in watersheds where stream acidification is occurring. This could adversely impact terrestrial site productivity (Elliott et al. 2008).

Computer models can be used to predict pollution effects on ecosystems and to perform simulations of future ecosystem response. The Model of Acidification of Groundwater in Catchments (MAGIC) model, a lumped-parameter, mechanistic model, has been widely used throughout North America and Europe to project stream water and soil response. SAMI used MAGIC to assess stream chemistry response to various emission reduction strategies throughout the southern Appalachian Mountains region (Sullivan et al. 2002a). MAGIC has also been used recently by the Shenandoah National Park, VA (Sullivan et al. 2008) and Monongahela National Forest, WV (Sullivan and Cosby 2004), to determine sulfur deposition levels at which unacceptable environmental damage would be expected to occur.

Forest managers are concerned with the following:

1. What will be the future trend in Southern Blue Ridge stream acid neutralizing capacity (ANC) as acid deposition continues to decrease in the eastern United States?
2. What were the historical stream chemistry and watershed soil base saturation levels for acid-sensitive streams in this region?
3. What levels of sulfur deposition would be needed to protect those streams and soils that are not yet heavily impacted and to restore those that are already impacted?

Future stream water and soil chemistry can be projected with MAGIC, given various emissions control scenarios. Future emissions can be estimated on the basis of existing or expected regulations or in response to more aggressive emissions control options.

The principal objectives of the study reported here were to use the MAGIC model to estimate for a group of 66 generally acid-sensitive streams and their watersheds in the southern Blue Ridge region (1) past changes in stream chemistry and soil base saturation since pre-industrial time and (2) future trends for stream chemistry and soil base saturation under a range of future atmospheric deposition scenarios.

2 Methods

2.1 Site Selection and Development of Model Input Data

The USDA Forest Service has, in recent years, collected stream chemistry samples at 256 stream locations in Pisgah and Nantahala National Forests in western North Carolina, Cherokee National Forest in eastern Tennessee, and the Andrew Pickens Ranger District, Sumter National Forest in South Carolina, all within the Southern Blue Ridge Province. This area includes three Class I areas administered by the Forest Service: Joyce Kilmer-Slickrock, Linville Gorge, and Shining Rock wildernesses. Data on additional streams in this region having available water chemistry data were compiled for SAMI by Sullivan et al. (2004).

Soil samples were collected from 40 watersheds that covered the range of site conditions found on National Forest ownership in North Carolina, South Carolina, and Tennessee. At least one watershed was sampled in each wilderness in North Carolina and South Carolina. Also, at least one watershed was sampled in most of the major mountain ranges in the study area. Soil samples were collected from watersheds that covered the range of elevations, stream ANC values, lithologies (siliceous, argillaceous, or felsic), and vegetation types.

Sites were selected for modeling in this project from several data sets. Initially, the following sites were selected as candidates:

- All watersheds recently sampled by the Forest Service for both soil and water chemistry
- Sites in Shining Rock or Joyce Kilmer-Slickrock wilderness areas modeled by Sullivan and Cosby (2002) and Linville Gorge (Elliott et al. 2008)
- All SAMI modeling sites (Sullivan et al. 2004) located in NC, TN, or SC that had both water chemistry and soils input data

Potential modeling sites were pre-screened to remove from consideration streams that had high concentrations of Cl^- (>70 μeq/L) that could potentially have been caused by road salt application, and those that had high concentrations of NO_3^- (>30 μeq/L) that could potentially have been caused by agricultural or silvicultural fertilization within the watershed. The potential for such anthropogenic disturbances, other than air pollution, was determined by stream chemistry and the location within the watersheds of roads, wilderness areas, and agricultural or forestry operations.

Samples were also pre-screened to remove sites for which the observed percent soil base saturation (% BS) was >60%. Such high values of % BS probably represent a sampling or analysis error or reflect a local (and unrepresentative) heterogeneity in the soil matrix at the sampling site.

Based on these modeling candidates and pre-screening criteria, 37 sites having both soil and water chemistry data available within the watershed were identified for modeling. These were designated as Tier I sites. We examined the characteristics of these 37 sites to determine if they exhibited a range of different stream water ANC, NO_3^- and SO_4^{2-} concentrations, location, bedrock geology, soil type, elevation, and general vegetation type. Based on these analyses, gaps were identified in the variable distributions for these 37 sites. To fill in these gaps in the landscape coverage, additional sites were selected for modeling from among those streams that had recently been surveyed by the Forest Service for stream water chemistry, but not sampled for soil chemistry.

For each stream in this group of sites added to the selection process, soil data for model calibration were derived from nearby watersheds using the methods employed by SAMI (Sullivan et al. 2004), after pre-screening to remove candidate watersheds that showed evidence of watershed impacts other than from air pollution (NO_3^- concentration >30 μeq/L; Cl^- concentration >70 μeq/L). Sites were selected from this screened database in order to maximize the distribution of modeling sites across the gradients of stream water ANC, SO_4^{2-} and nitrate concentrations, and also elevation, geology, and geographic location. A major emphasis was on selection of many acidic and low-ANC (<50 μeq/L) streams, which exhibited varying SO_4^{2-} and NO_3^- concentrations, and which occurred at varying elevation. This selection process identified an additional 29 streams for modeling.

A total of 66 stream sites in NC, TN, and SC were modeled (Fig. 1) from among the 256 stream sites sampled by the Forest Service in recent years and the stream data compiled for the SAMI project and other recent modeling efforts. Site selection was not statistically based, and we do not assume that the selected streams are representative of the overall population of streams within the region. Rather, many of the sites were initially selected for stream sampling

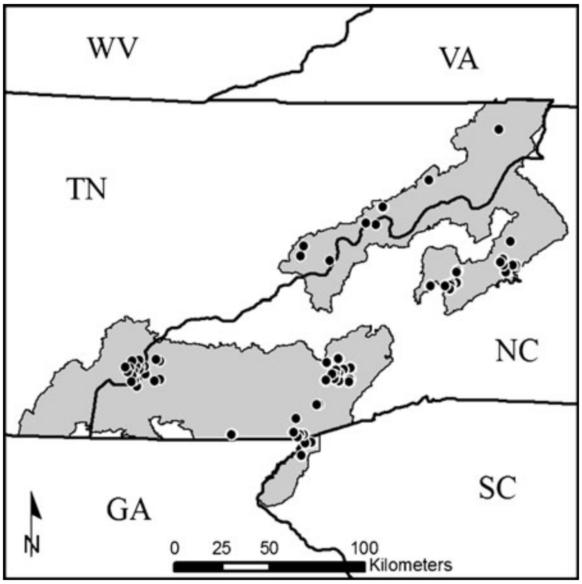


Fig. 1 Map showing locations of 66 stream sites modeled for this project. Forest Service lands within the Blue Ridge province (*shaded*) constitute the study area

because they were suspected of being at least moderately acid-sensitive, based on geology, elevation, and the results of previous studies.

Summary statistics for selected key variables are provided in Table 1. In general, study watersheds were small (median 143 ha), located at high elevation (median 908 m), with low ANC (median 19 μeq/L) and exchangeable soil base cations (median percent base saturation about 10%). Median SO_4^{2-} (31 μeq/L) and NO_3^- (2 μeq/L) concentrations were low. Sulfur and nitrogen deposition were variable among the study watersheds, largely due to topography and orographic effects. In general, atmospheric deposition levels were high for both S and N (Table 1).

Modeled sites were widely distributed across elevation (Fig. 2a) and lithology (Fig. 2b). Sites were relatively evenly distributed across the three most acid-sensitive geologic sensitivity classes (siliceous, argillaceous, and felsic). Only one modeled site was located on the less-sensitive mafic geology (Fig. 2c), and none were located on insensitive carbonate geology. Stream water SO_4^{2-} concentrations were rather widely distributed, with some sites having SO_4^{2-} concentration below 15 μeq/L and some above 65 μeq/L. Several streams had NO_3^- concentration higher than 15 μeq/L, but more than half had NO_3^- concentration less than 4 μeq/L. All modeled streams had calculated ANC below 150 μeq/L, and one third had ANC below 20 μeq/L. Thus, many of these modeled streams are very acid-sensitive. Most (70%) had pH above 6.0, although some modeled sites (7%) had pH below 5.0.

2.2 Modeling Approach

MAGIC is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on soil and surface water chemistry (Cosby et al. 1985a, b). The model simulates soil solution chemistry and surface water chemistry to predict the monthly and annual average concentrations of major ions in these waters. MAGIC

Table 1 Summary statistics for the 66 modeled sites for selected key variables

Parameter	Unit	Min	25th	Median	75th	Max	Mean
Watershed area	ha	9.31	72.97	142.56	358.69	1,357.97	269.24
Stream ANC	μeq/L	−20.60	6.80	19.40	38.65	83.70	24.18
Elevation	m	411.00	740.25	907.50	1,149.75	1,719.00	955.59
Stream nitrate	μeq/L	0.00	0.52	2.14	5.93	24.87	4.90
Stream pH	standard	4.74	5.83	6.30	6.55	6.85	6.14
Stream sulfate	μeq/L	9.79	23.79	31.13	45.13	207.44	37.78
Soil BS	%	2.40	6.00	9.89	12.09	18.04	9.68
Soil exchange Ca^{2+}	%	0.35	1.83	3.01	4.32	9.12	3.58
Soil exchange Ca^{2+} + Mg^{2+}	%	1.06	3.35	5.99	8.28	13.14	6.23
CEC	meq/kg	23.37	30.49	32.47	38.83	105.23	41.33
Sulfur deposition (reference year)	kg/ha/year	6.51	9.96	11.21	13.36	22.17	12.00
Nitrogen deposition (reference year)	kg/ha/year	3.43	5.28	6.12	7.49	12.77	6.52

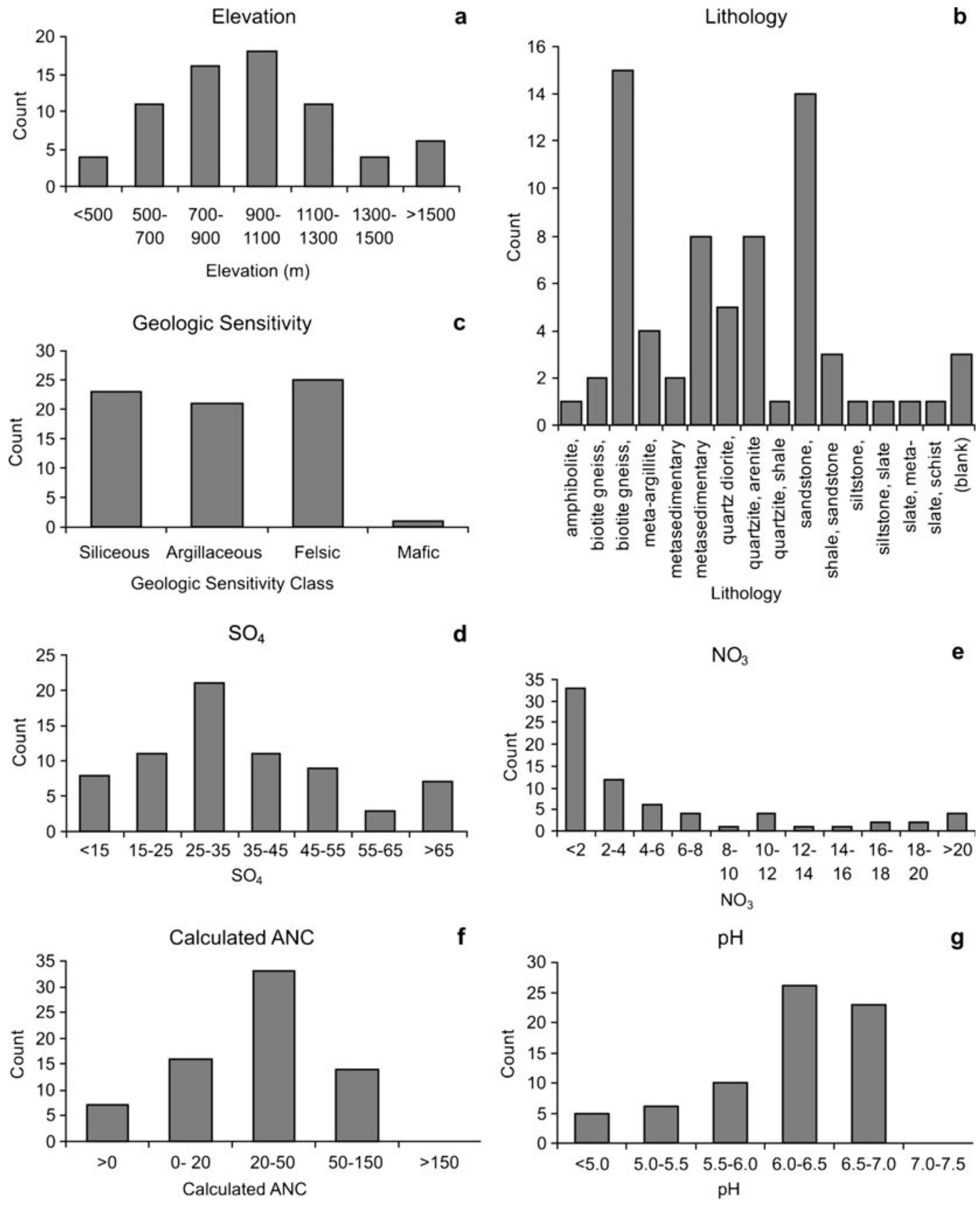


Fig. 2 Distribution of modeling sites across key parameter values. Units are in μeq/L for all ions. The modeling sites were well distributed across these variables that reflect aspects of watershed sensitivity to acidification

consists of (1) a section in which the concentrations of major ions are assumed to be governed by simultaneous reactions involving SO_4^{2-} adsorption, cation exchange, dissolution–precipitation–speciation of Al, and dissolution–speciation of inorganic C and (2) a mass balance section in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering, net uptake and loss in biomass, and loss to runoff. At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time owing to changes in atmospheric deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. The degree and rate of change of surface water acidity thus depend both on flux factors and the inherent characteristics of the affected soils.

Cation exchange is modeled using equilibrium (Gaines–Thomas) equations with selectivity coefficients for each base cation and Al. Sulfate adsorption is represented by a Langmuir isotherm. The only source of S for the soils is assumed to be atmospheric deposition. Aluminum dissolution and precipitation are assumed to be controlled by equilibrium with a solid phase of $Al(OH)_3$. Aluminum speciation is calculated by considering hydrolysis reactions as well as complexation with SO_4^{2-} and F^-. Effects of CO_2 on pH and on the speciation of inorganic C are computed from equilibrium equations. Organic acids are represented in the model as tri-protic analogues. First-order rates are used for biological retention (uptake) of NO_3^- and NH_4^+ in the soils and streams. The rate constants are not varied during the simulation period. Weathering rates for base cations are assumed to be constant. A set of mass balance equations for base cations and strong acid anions are included.

Given a description of the historical deposition at a site, the model equations are solved numerically to give long-term reconstructions of surface water chemistry (for complete details of the model, see Cosby et al. 1985a, b, 1989, 2001). MAGIC has been used to reconstruct the history of acidification and to simulate the future trends on a regional basis and in a large number of individual watersheds in both North America and Europe (e.g., Cosby et al. 1989, 1990, 1996; Hornberger et al. 1989; Jenkins et al. 1990a, b, c; Wright et al. 1990, 1994; Norton et al. 1992; Sullivan and Cosby, 1998; Sullivan et al. 2004).

The aggregated nature of the MAGIC model requires that it be calibrated to observed data from a system before it can be used to examine potential system response. Calibration is achieved by setting the values of certain parameters within the model that can be directly measured or observed in the system of interest (called fixed parameters). The model is then run (using observed and/or assumed atmospheric and hydrologic inputs) and the outputs (stream water and soil chemical variables—called criterion variables) are compared to observed values of these variables. If the observed and simulated values differ, the values of another set of parameters in the model (called optimized parameters) are adjusted to improve the fit. After a number of iterations adjusting the optimized parameters, the simulated-minus-observed values of the criterion variables usually converge to zero (within some specified tolerance). The model is then considered calibrated.

The weathering and selectivity coefficient of each of the four base cations are optimized. Field measurements are used to drive the estimates of the current soil exchangeable pool size and current output flux of each of the four base cations.

Estimates of the fixed parameters, the deposition inputs, and the target variable values to which the model is calibrated all contain uncertainties. A “fuzzy optimization” procedure was used to provide explicit estimates of the effects of these uncertainties. The procedure consists of multiple calibrations at each site using random values of the fixed parameters drawn from a range of fixed parameter values, representing uncertainty in knowledge of these parameters, and random values of reference year deposition drawn from a range of total deposition estimates, representing uncertainty in these inputs. The final convergence of the calibration is determined when the simulated values of the criterion variables are within a specified acceptable window around the nominal observed value. This acceptable window represents uncertainty in the target variable values being used to calibrate the site.

Each of the multiple calibrations at a site begins with (1) a random selection of values of fixed parameters and deposition and (2) a random selection of the starting values of the adjustable parameters. The adjustable parameters are then optimized using an algorithm to minimize errors between simulated and observed criterion variables. Calibration success is judged when all criterion values simultaneously are within their specified acceptable windows. This procedure is repeated ten times for each site. For this project, the acceptable windows for base cation concentrations in streams were specified as ±2 μeq/L around the observed values. Acceptable windows for soil exchangeable base cations were taken as ±0.2% around the observed values. Fixed parameter uncertainty in soil depth, bulk density, cation exchange capacity, stream discharge, stream area, and total deposition of each ion were assumed to be ±10% of the estimated values.

This procedure produced multiple simulated values of each variable in each year, all of which are acceptable in the sense of the calibration constraints applied in the fuzzy optimization procedure. The median of all the simulated values within a year represents the most likely response for the site in that year. For any year in a given scenario, the largest and smallest values of a simulated variable define the upper and lower confidence bounds for that site's response for the scenario under consideration. Thus, for all variables and all years of the scenario, a band of simulated values can be produced from the ensemble simulations at a site that encompasses the likely response (and provides an estimate of the simulation uncertainty) for any point in the scenario.

2.3 Specification of Stream and Soil Input Data

The water chemistry data used for model calibration are the concentrations of the individual base cations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) and acid anions (Cl^{-}, SO_4^{2-}, NO_3^{-}) and the stream pH. For the 66 streams selected for modeling, at least one complete stream water chemical sample was available for each site during the period 1999 through 2005. No stream had samples taken in all years, and no single year was sampled in all streams. Multiple samples at a site within a given year (four streams) were averaged. For 59 sites, a single water sample was available, and it was used to calibrate MAGIC, regardless of the year that it was taken. The remaining seven streams had samples available for multiple years; all were sampled in 2000, and that year was used for calibration of MAGIC at those sites. The uncertainty arising from using 2000 rather than another year to calibrate those sites was examined in an exploratory analysis.

The soil data used in the model calibration include soil depth and bulk density, soil pH, soil cation exchange capacity, and exchangeable bases on the soil (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}). Soils data for model calibration were derived as vertically averaged values of soil parameters determined from the two soil layers sampled at each Tier I site. Soil samples represent the top 10 cm of mineral soil and an integrated sample taken at depth 10 cm to either bedrock or 50 cm, whichever came first. The soils data for the deep and shallow layers at each sampling site were averaged based on layer thickness and bulk density to obtain single vertically aggregated values for each soil pit. The vertically aggregated data were then spatially averaged to provide a single value for each soil variable in each watershed.

Soil data were assigned to modeling sites using protocols developed for the SAMI aquatic assessment (Sullivan et al. 2002a, 2004). For the Tier I sites (n=37), soils chemistry data were available from within the watershed to be modeled, most commonly from three soil pits. Data from multiple soil sampling sites were aggregated on an area-weighted basis to reflect the distribution of mapped soil types within each Tier I watershed. For a second group of sites (Tier II, n=6), soils data within the watershed were missing but were taken from a nearby (<5 km) watershed underlain by similar geology. For a third group of sites (Tier III, n=23), soils data were neither available from within the watershed nor from a nearby watershed on similar geology, but were obtained using a surrogate approach. Each watershed that lacked soil data was paired with a watershed for which all input data were available. This pairing was accomplished by comparing watershed similarity on the basis of stream water characteristics (ANC, sulfate and base cation concentrations), physical characterization (location, elevation), and bedrock geology data. The missing data were then taken from the paired watershed judged to be most similar. The uncertainty associated with this surrogate soil data assignment procedure was examined in an exploratory analysis.

2.4 Specification of Atmospheric Deposition Input Data

2.4.1 Historical Deposition

The total historical atmospheric deposition into the watershed must be provided as input to MAGIC. Recent wet deposition estimates were based on observed wet deposition at National Atmospheric Deposition Program/National Trends Network (NADP/NTN) monitoring stations (http://nadp.sws.uiuc.edu/). The spatial extrapolation model of Grimm and Lynch (1997) was used to derive a spatially interpolated value of wet deposition at each site, correcting for changes in precipitation volume with elevation. The NADP data (and thus the estimates provided by Grimm's model) covered the period 1983 to 2005. This period includes the MAGIC reference year (2005) and the calibration years for all of the modeling sites in this project.

The ASTRAP model (Shannon 1998) was used to provide historical estimates of wet, dry, and cloud deposition of sulfur and nitrogen oxide at 33 sites in and around the SAMI region sites using a nearest-neighbor approach that included correction for elevation, as described by Sullivan et al. (2004). Shannon (1998) produced wet, dry, and cloud deposition estimates of sulfur and nitrogen oxide every 10 years starting in 1900 and ending in 1990. The model outputs were smoothed estimates of deposition roughly equivalent to a 10-year moving average centered on each of the output years. To estimate total deposition from wet deposition, the wet, dry, and cloud deposition estimates provided by ASTRAP for each year were used to calculate dry plus cloud deposition enhancement factors (DDF) for each year and each site. This provided time series of DDF for sulfur and nitrogen oxide for each site extending from 1900 to 1990. The value of DDF for 1990 was used as the absolute value of DDF for the reference year and was assumed to remain constant in the future.

At high elevation, the inputs of ions from cloud water can be large. In the SAMI project (see Sullivan et al. 2002a, b, 2004), high elevation sites in the Great Smoky Mountain National Park were determined to have DDF values (reflecting dry and cloud, but particularly cloud water inputs) that were approximately twice as large as those specified by the ASTRAP model. Accordingly, Sullivan et al. (2004) used the larger DDF values for any site over 1,500 m elevation. In this project, the five sites that were over 1,500 m elevation were assigned the higher DDF values used by Sullivan et al. (2004). The potential bias and uncertainty associated with the use of this high elevation DDF correction was examined in an exploratory analysis.

2.4.2 Future Deposition Scenarios

We used atmospheric modeling results developed by the Visibility Improvement State and Tribal Association of the Southeast (VISTAS) to specify the base case emissions control scenario and associated levels of future acidic deposition at modeling site locations. VISTAS recently performed a technical analysis for the state, local, and tribal air quality agencies for ten southeastern states (http://vistas-sesarm.org/documents/FinalDocs.asp). VISTAS is evaluating pollution control strategies that currently exist or could be implemented to achieve reasonable progress to attain, by 2064, natural (not impacted by human activities) visibility conditions on the days having poorest visibility at the federally mandated Class I areas within the southeastern states. The year 2018 is the first year for which the affected states have evaluated whether air pollution emission reductions will provide reasonable progress to attain the visibility goal in 2064. There are three Class I areas in eastern Tennessee and western North Carolina that VISTAS included in their analysis and are relevant to this study: Great Smoky Mountains National Park (which also represents the adjacent Joyce Kilmer-Slickrock Wilderness), Linville Gorge Wilderness, and Shining Rock Wilderness.

VISTAS used the U.S. Environmental Protection Agency's Models-3 Community Multiscale Air Quality (CMAQ) Modeling System (Byun and Ching 1999) to examine how fine particulate and ozone concentrations, visibility, and dry and wet sulfur and nitrogen depositions will change between 2002 and 2018 in the southeastern United States in response to changes in emissions. For example, North Carolina's Clean Smoke Stacks Act will reduce sulfur dioxide emissions compared with current levels, which will result in improved visibility conditions and simultaneously reduce sulfur and nitrogen deposition at downwind locations.

CMAQ deposition values represent the centers of 12 km by 12 km grid cells across the region. Average dry and wet sulfur and nitrogen deposition were calculated from the grid cells for each of the 66 watersheds included in the MAGIC simulations. The CMAQ results produced by VISTAS provided the basis for estimating the base case sulfur, nitrate–nitrogen, and ammonia–nitrogen deposition for the years 2002, 2009, and 2018. To examine longer-term responses for the 66 study watersheds beyond 2018 in response to future changes in sulfur and nitrogen deposition, VISTAS visibility simulation results were used to estimate the sulfur and nitrogen deposition levels that would be consistent with assumed compliance with the long-term (2064) national visibility goal. We calculated the required slope of continued visibility improvement between 2018 and 2064 for each of the three Class I areas. Future emissions scenarios were based on the average visibility for the three Class I areas in 2018 and 2064 to estimate the slope describing the required change in visibility conditions over time to meet the national goal.

Based on these calculations, MAGIC simulations were performed for three different future deposition scenarios:

1. Base case scenario—visibility goal achieved through 2018 (scenario 1). Deposition expected to occur through 2018 in conjunction with the emissions glide path needed to attain the national visibility goal; no further sulfur or nitrogen reductions were expected beyond those predicted to occur by CMAQ for 2018. For this base case scenario, deposition levels were assumed to remain constant from 2018 to 2100.
2. Aggressive additional emissions controls—visibility goal achieved through 2064 (scenario 2). Assuming that percent changes in sulfur and nitrogen deposition will mimic visibility improvements needed to reach the 2064 visibility goal, the 2018 CMAQ deposition estimates were reduced by 50% to estimate 2064 wet and dry deposition of sulfur and nitrogen. After 2064, the deposition was held constant until 2100.
3. Moderate additional emissions controls—visibility goals missed by 25% (scenario 3). There is a possibility that the regional haze visibility goal may not be achieved in 2064 either due to the cost of controls or international transport of pollutants. The third scenario addresses the possibility that the 2064 goal of natural visibility will be missed by 25%. For this scenario, the 2018 CMAQ results were reduced by 37% to estimate the 2064 wet and dry deposition of sulfur and nitrogen. After 2064, the deposition was held constant until 2100.

Thus, the base case (scenario 1) only considers emission reductions required to take effect through 2018. Under the most aggressive additional emissions control scenario (scenario 2), both wet and dry deposition of S, NO_x, and NH_4 were reduced by 50% in a linear fashion from 2018 to 2064. This level of deposition reduction corresponded approximately with CMAQ estimates of the amount of ambient air pollution reduction that would need to occur in order to meet the national visibility goal. Under the more moderate additional emissions control scenario beyond 2018 (scenario 3), both wet and dry deposition of S, NO_x, and NH_4 were also reduced in a linear fashion from 2018 to 2064. In this scenario, however, the deposition was reduced by 37% as compared with 2018 values.

2.5 Exploratory Simulations

Four major uncertainties that relate directly to the aims of this project were explored: (1) the assignment of soils data to specific watersheds, (2) inter-annual variability in water chemistry data used for calibration, (3) assumptions regarding high elevation cloud deposition, and (4) overall model simulation uncertainty (as described in section 2.2). Although it is not possible to rigorously quantify the overall uncertainty in the assessment results, analyses were conducted to evaluate and put into perspective these four major sources of uncertainty. Additional discussion of uncertainty in MAGIC model projections within this region is provided by Sullivan et al. (2004).

2.5.1 Uncertainty Due to Specification of Soils Data

The uncertainty associated with borrowing soils data for Tier II and Tier III watersheds was examined by calibrating seven selected Tier I watersheds twice, once using the appropriate site-specific soils data and a second time using borrowed soils data from an alternate site, using either Tier II or Tier III protocols. Both sets of calibrations for a site were applied to historical and future simulations. Results were compared to determine the magnitude of the differences in future simulated values resulting from the way soils data were supplied.

2.5.2 Uncertainty Due to Specification of Stream Water Data for Calibration

There were seven streams for which stream water samples were available for multiple years at the site. All seven of these streams had samples available in 2000, and that year was chosen for calibration of MAGIC at those sites. The uncertainty arising from using 2000 rather than another year to calibrate the model at these sites was examined by recalibrating each of the seven sites using stream water data from another of the sampled years at the site. Three of the seven sites had one more year of data available and that year was the adjacent year 1999. Four of the seven sites had one more year of data available in 2004. Two of the sites had an additional year of data available in 2002.

This allowed nine recalibrations using different observed stream water chemistry to examine the effects of inter-annual variability in stream water chemistry on calibration of MAGIC (five sites with one more year for recalibration and two sites with two more years for recalibration). The various calibrations were then applied to historical and future simulations. Results were compared to determine the magnitude of the differences in future simulated values and to derive estimates of the bias and/or variance introduced to the assessment results because of selection of the calibration year.

2.5.3 Uncertainty Due to Specification of High Elevation Cloud Deposition

There were five modeled sites at elevations over 1,500 m for which the DDF values were increased in model calibration to account for assumed cloud water deposition. The uncertainty associated with lack of observed data for high elevation cloud deposition was examined by recalibrating a number of modeled sites. The five highest elevation sites (1,591 to 1,719 m) originally calibrated using the increased high elevation DDF values were recalibrated using the lower ASTRAP DDF values. The next five highest sites (1,245 to 1,453 m), which were originally calibrated using the lower ASTRAP DDF values, were recalibrated using the high elevation increased DDF values. Both sets of calibrations for the ten sites were then used for running historical or future simulations. The simulated results for the ten sites were compared to determine the magnitude of the differences in future simulated values and to derive estimates of the bias and/or variance introduced in the assessment results because of the inclusion (or lack thereof) of cloud water deposition at high elevation. This analysis reflects the uncertainty associated with the sites for which cloud deposition estimates contained maximum potential error. Uncertainties associated with assumed cloud deposition would be lower at most sites because they are located at lower elevation where cloud deposition is much less important.

3 Results and Discussion

The model results presented here are based on the median values of the simulated water and soil chemistry variables from the multiple modeled calibrations at each site using the MAGIC fuzzy optimization procedure. The use of median values for each watershed helps to assure that the simulated responses approximate the most likely behavior of each watershed, given the assumptions inherent in the model and the data used to constrain and calibrate the model.

3.1 Calibration Results

The multiple calibration procedure for each site produced summary statistics (mean, standard deviation, maximum and minimum) for observed values, simulated values and differences (simulated–observed values) for each of the stream variables and soil variables. Plots of simulated versus observed values for selected stream variables are shown in Fig. 3. These analyses document that the model calibration results were not biased and did not contain unacceptably large residual errors.

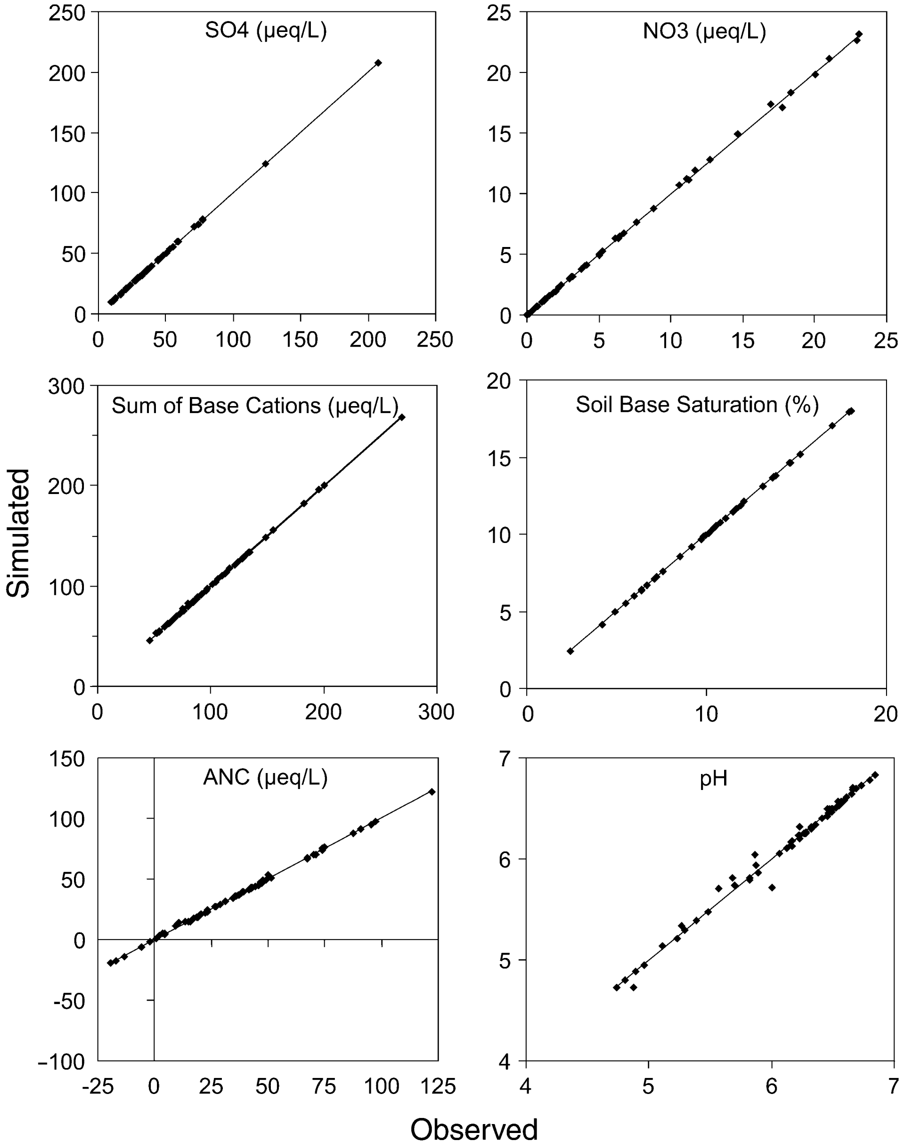
3.2 Hindcast Simulations

MAGIC model simulations predicted that stream ANC values were above 20 μeq/L in all modeled watersheds in pre-industrial time, but below 50 μeq/L in 38% of the watersheds and below 100 μeq/L in 86% of the watersheds at that time (Fig. 4, Table 2). The minimum simulated ANC in 1860 among the modeled streams was 30 μeq/L (Fig. 4). The hindcast simulation results suggested that the average of the modeled streams was acidified from ANC=65 μeq/L in 1860 to ANC=36 μeq/L in 2005. The lowest simulated ANC in 2005 was −19 μeq/L, which was 49 μeq/L lower than the minimum simulated value under pre-industrial conditions. The amount of simulated historical acidification was relatively small for streams having high current ANC, but greater for streams having low current ANC (Fig. 4). Slightly more than half (52%) of the modeled streams had soil % base saturation below 10% in 2005. This contrasts with 40% of the sites simulated by MAGIC to have had % base saturation below 10% in 1860.

3.3 Future Simulations in Response to Emissions Control Scenarios

Future changes in stream chemistry for the modeled sites in response to changes in acidic deposition were simulated to be driven mainly by changes in stream water SO_4^{2-} concentration. For the reference year

Fig. 3 Calibration results for the MAGIC model. Predicted versus observed values of selected stream water and soil variables for the 66 sites in the calibration year (1:1 lines added)



(2005), SO_4^{2-} concentrations in the study streams varied, with half of the modeled streams having SO_4^{2-} concentration between 24 and 45 µeq/L (Table 1). In response to the emissions controls scenarios, some of the modeled streams were projected to exhibit future decreases in SO_4^{2-} concentration, which were largest in more distant future years and under greater emissions reductions.

In response to these simulated changes in stream SO_4^{2-} concentrations, stream base cation concentrations and ANC, and also soil percent base saturation, were projected to change in the future. The majority of the modeled sites (79% to 94%, depending on emissions scenario) were projected to acidify further in the future even under the reduced deposition levels under all three emissions control scenarios. Few sites were simulated to show chemical recovery of stream water ANC, even under aggressive additional emissions reductions (Fig. 5). Simulated future acidification was generally more pronounced under the base case scenario, with 52 of 66 sites (79%) projected to show decreases in stream ANC between 2005 and 2100 of between 5 and 10 µeq/L. Scenario results suggested that the major benefit of the more stringent emissions controls scenarios to projected future stream chemistry would be that more sites

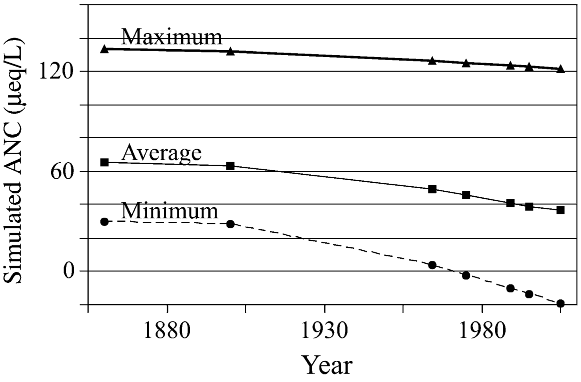


Fig. 4 MAGIC estimates of historical change in ANC for the 66 modeled sites for multiple points in time, represented as maximum, average, and minimum simulated values

would likely acidify in the future by 0 to 5 μeq/L, rather than 5 to 10 μeq/L as was commonly found for the base case scenario (Fig. 5). In general, the model projected that soil and stream chemistry have changed substantially since pre-industrial times, but that future changes in response to different levels of emissions controls will be small.

3.4 Exploratory Simulations

The MAGIC model, like any process model of acid–base chemistry, is a simplification of an array of physical, chemical, and biological processes. Such simplification invariably results in uncertainty with respect to model structure and performance. Unfortunately, models of ecosystem behavior can never truly be validated because environmental systems are not closed and some processes might assume importance only under particular circumstances. Furthermore, with any model, it is possible to get the right answer for the wrong reason (cf., Oreskes et al. 1994). Nevertheless, the MAGIC model has been extensively tested against independent measurements of chemical acidification and recovery. These tests have included many comparisons between model projections of ANC or pH and the results of whole-watershed manipulation experiments and comparisons between model hindcasts of pH and diatom-inferred pH. In general, the MAGIC model has shown good agreement with these independent measurements or estimates of chemical change (Sullivan 2000).

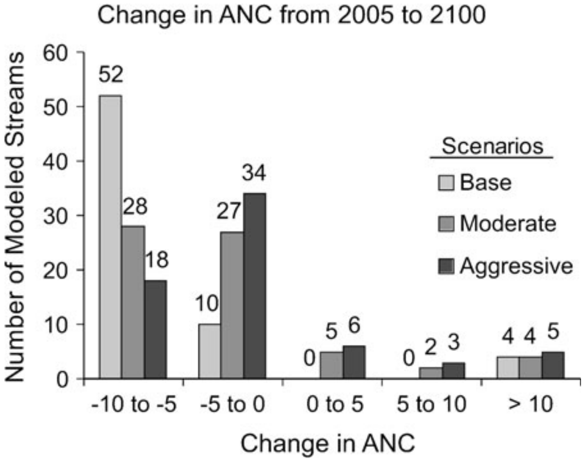


Fig. 5 MAGIC projections of future changes in ANC (2005 to 2100) under three scenarios of emissions control: base case, moderate, and aggressive additional controls. Results are presented by response classes, ranging from estimates of future acidification of −5 to −10 μeq/L (*left side*) to estimates of future recovery in excess of +10 μeq/L (*right side*). Number of sites is indicated above each bar

Table 2 Model estimates of number and percentage of study streams (n=66) below ANC (μeq/L) levels at three different points in time

	ANC ≤0		ANC ≤20		ANC ≤50		ANC ≤100	
	No.	%	No.	%	No.	%	No.	%
1860	0	0	0	0	25	38	57	86
1975	2	3	9	14	43	65	64	97
2005	5	8	20	30	51	77	66	100

Percentages (%) are expressed as the percent of the modeled streams (n=66) that were simulated to have ANC below the target level in the selected year

3.4.1 Uncertainty Due to Specification of Soils Data

Changing the soil data used for calibrating the model produced pronounced offsets in the simulated values of the soil variable % BS while having little effect on simulated values of stream water variables (SO_4^{2-}, sum of base cations (SBC), and ANC; cf., Fig. 6a for ANC response). If the alternate soil chemistry data contained higher observed base saturation in the calibration year, the optimization routine adjusted the selectivity coefficients to produce a higher simulated base saturation in the calibration year (and conversely). Simulated base saturation values in all future years of all scenarios reflected the offset in base saturation values in the calibration

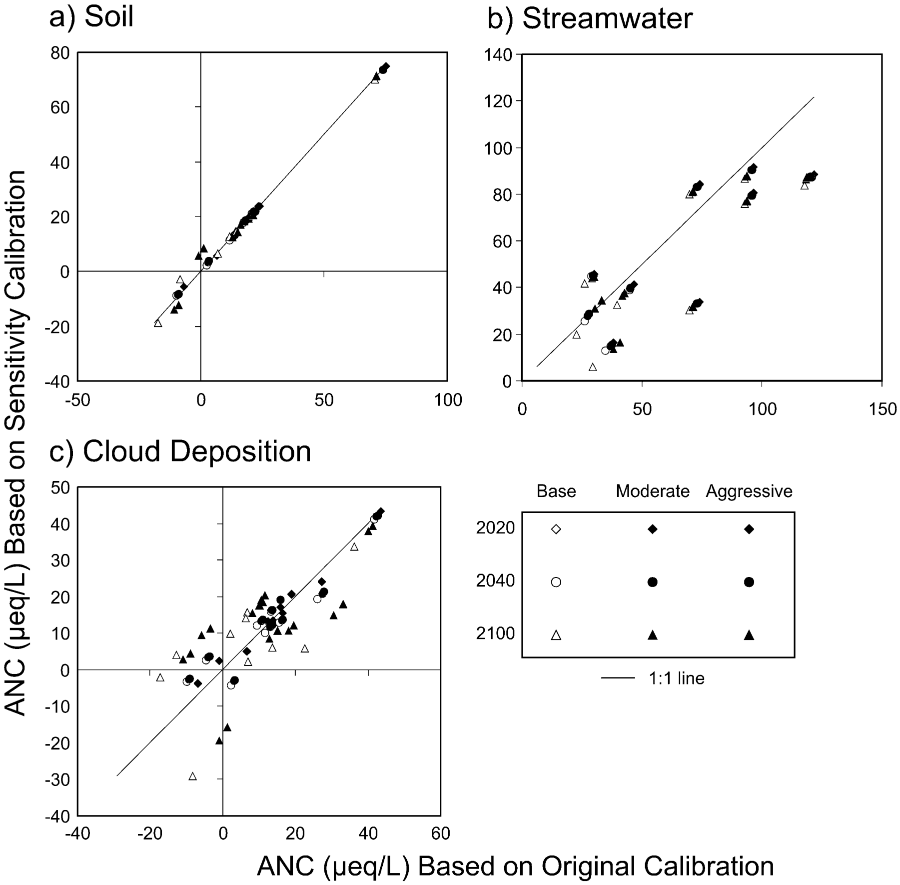


Fig. 6 Sensitivity of model simulations of stream water ANC to specification of **a** soil data, **b** stream water calibration data, and **c** cloud deposition data. MAGIC model projections of ANC are presented for the years 2020 (*diamond*), 2040 (*circle*), and 2100 (*triangle*) for three future deposition scenarios. Values on the *x*-axis are based on the original model calibrations of each site. Values on the *y*-axis are based on the sensitivity recalibration of each site using data as explained in the text. The 1:1 line is shown

year. Because the stream water variables used to calibrate the sites were not changed in this analysis, there was no appreciable offset produced in these variables and their values in future years were essentially unchanged (Fig. 6a for ANC response).

The average changes in variable values ($n=7$) that resulted from changing the soil data used for calibrating the model were greatest for soil %BS ~40% (Table 3). Average changes in simulated stream water SO_4^{2-} (~1%) and SBC (~1%) were very small. Even though individual stream water ions showed little sensitivity to changed soil input data, the average change in future simulated stream ANC (~6%) did show some effect of changing the soil buffer pools (% BS). The average changes in simulated stream water variables appear to be of about the same size in all 3 years and for all three future scenarios. The average change in simulated soil BS, however, appears to decrease as the length of the simulation increases for all three scenarios (Sullivan et al. 2007).

3.4.2 Uncertainty Due to Specification of Stream Water Data for Calibration

Three of the nine sites recalibrated with altered stream water inputs had higher ANC in the calibration year; six sites had lower ANC values in the calibration year. The average changes in variable values ($n=9$) that resulted from changing the stream water data used for calibrating the model were greatest for SBC (~12%), SO_4^{2-} (~15%), and ANC (~27%; Fig. 6b). The changes in % BS (~1%) were relatively small compared to the changes in stream water variables. The average changes in all simulated variables appear to be of about the same size in all 3 years examined (2020, 2040, 2100) and for all three future scenarios.

3.4.3 Uncertainty Due to Specification of High Elevation Cloud Deposition

Changing the cloud deposition data used for calibrating the model produced offsets in the simulated values of

Table 3 Sensitivity analysis scenario results for soil inputs

	Average percent change in simulated chemistry			
	ANC	SO_4	SBC	BS
Base scenario				
2020	6	0	1	45
2040	3	1	1	43
2100	13	1	2	35
Moderate scenario				
2020	6	0	1	45
2040	3	1	1	43
2100	7	0	2	36
Aggressive scenario				
2020	6	0	1	45
2040	3	1	1	43
2100	9	0	3	36

Average percent change in simulated values (for seven sites) resulting from recalibration of the model using alternate soil data. Average changes are presented for selected variables in selected years for the three future deposition scenarios

SBC sum of base cations, *BS* soil % base saturation

SO_4^{2-} and ANC (Fig. 6c) but had a much smaller effect on SBC and % BS. The effect on simulated stream water SO_4^{2-} values is less than straightforward, with competing effects occurring. For those sites recalibrated with higher cloud SO_4^{2-} deposition, the optimization procedure calibrated a higher SO_4^{2-} adsorption capacity to maintain the same target SO_4^{2-} value in stream water in the calibration year. The converse is true for those sites recalibrated with lower cloud SO_4^{2-} deposition.

When forecasts were run into the future, the stream water SO_4^{2-} simulated by sites with higher cloud deposition and higher SO_4^{2-} adsorption capacity were affected by two factors: (1) the scaled future deposition of SO_4^{2-} was higher and (2) the higher SO_4^{2-} adsorption meant either greater adsorption or greater desorption of SO_4^{2-} from the adsorbed soil pool (depending on the calibration year stream water SO_4^{2-} concentration). The converse of these effects applies to streams with lower cloud deposition used for recalibration. As a result, the future simulated values of SO_4^{2-} show both increases and decreases.

The stream water SBC values and soil BS values were essentially unchanged as a result of changing the cloud SO_4^{2-} deposition. This is because the optimization routine was using the same stream water and soil targets for the base cation variables. The optimization routine calibrated different base cation weathering and selectivity coefficients to match these base cation targets even though cloud SO_4^{2-} deposition (and adsorption) had changed. With stream water SO_4^{2-} altered and steam water SBC essentially unchanged, the simulated ANC values show the same magnitude (but opposite direction) of changes as those in stream water SO_4^{2-}.

The average changes in variable values ($n=10$) that resulted from changing the cloud deposition data used for calibrating the model were greatest for stream water SO_4^{2-} and ANC, with patterns across both the future scenarios and future years. In general, changing cloud deposition produced average changes in stream water SO_4^{2-} that increased into the future, starting at 6% in 2020 and increasing about fivefold (to ~30%) by 2100. A similar pattern was noted for average changes in ANC, starting at 13% in 2020 and increasing into the future. Unlike SO_4^{2-}, however, the average changes in ANC for the year 2100 also showed an effect of the scenario, with the average changes in ANC being largest for the base scenario (the scenario with the highest SO_4^{2-} deposition in

Table 4 Sensitivity analysis scenario results for occult deposition inputs

	Average percent change in simulated chemistry			
	ANC	SO_4	SBC	BS
Base Scenario				
2020	13	6	1	0
2040	24	12	2	1
2100	104	28	3	5
Moderate Scenario				
2020	13	6	1	0
2040	24	13	2	1
2100	85	30	3	5
Aggressive Scenario				
2020	13	6	1	0
2040	24	13	2	1
2100	60	31	3	5

Average percent change in simulated values (for ten sites) resulting from recalibration of the model using either increased or decreased occult deposition data. Average changes are presented for selected variables in selected years for the three future deposition scenarios

SBC sum of base cations, *BS* soil % base saturation

2100). Average changes in the base cation variables SBC and % BS were relatively small (1% to 5%; Table 4) compared to the changes in stream water variables, primarily because the target values used to calibrate these variables were not changed in this sensitivity analysis.

4 Conclusions

Model hindcast projections suggest substantial acidification of soils and stream water within the Southern Blue Ridge province since pre-industrial times. The median historical decreases (1860 to 2005) among the modeled sites in soil BS and stream ANC were 1% and 25 μeq/L, respectively. These estimates of historical acidification of soils and stream water occurred in response to large historical increases in atmospheric S deposition, ranging from about 6 to 20 kg S/ha/year depending on watershed location and elevation. Stream water SO_4^{2-} concentration increased to a median (and interquartile range) value of 31 (24 to 45) μeq/L. Increases in stream water NO_3^- concentrations were much smaller, with a median concentration in 2005 of only 2 μeq/L and an interquartile range of 1 to 6 μeq/L. As a consequence of this historical acidification, 30% of the modeled streams had ANC less than 20 μeq/L in 2005, compared with none having such low ANC in 1860.

Despite the estimates of substantial historical acidification, model projections did not suggest widespread chemical recovery from acidification in the future in response to assumed rather large reductions in future S deposition. Rather, under the base case emissions control scenario (approximately 50% decrease in S deposition between 2002 and 2018, with constant deposition thereafter), most (94%) of the modeled streams were projected to decrease in ANC over the next century. Even under the most extreme emissions reduction scenario (additional ~50% decrease in S deposition), more than three fourths (79%) of the modeled streams showed simulated future acidification. Less than 8% of the modeled streams showed projected ANC recovery by more than 10 μeq/L over the next century under any of the emissions control scenarios. These model results were caused by two ongoing processes in these acid-sensitive watersheds. First, simulated soil BS is continuing to decline. Thus, soils likely continue to acidify even under deposition loading rates that are much lower than those observed in the recent past. Second, the extent of S adsorption on soil is simulated to be decreasing over time. Thus, the concentration of SO_4^{2-} in stream water was projected to increase in the future in most streams under all scenarios, even with large additional (~37% to 50%) reductions in S deposition inputs. Chemical recovery from acidification will require reductions in S deposition input to values low enough to counteract the influences of ongoing soil acidification and diminished soil capacity to adsorb S. These model projections suggest that the decrease in S deposition will have to exceed about 50% beyond the base case in many acid-sensitive watersheds for such chemical recovery to occur. This finding is important for the development of management plans for acid-sensitive soil and stream resources in this region.

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