

Critical loads and exceedances for nitrogen and sulfur atmospheric deposition in Great Smoky Mountains National Park, United States

HABIBOLLAH FAKHRAEI,^{1,†} CHARLES T. DRISCOLL,¹ JAMES R. RENFRO,² MATT A. KULP,²
TAMARA F. BLETT,³ PATRICIA F. BREWER,³ AND JOHN S. SCHWARTZ⁴

¹*Department of Civil and Environmental Engineering, Syracuse University, Syracuse, New York 13244 USA*

²*National Park Service, Great Smoky Mountains National Park, Gatlinburg, Tennessee 37738 USA*

³*Air Resources Division, National Park Service, Lakewood, Colorado 80225 USA*

⁴*Department of Civil and Environmental Engineering, University of Tennessee, Knoxville, Tennessee 37996 USA*

Citation: Fakhraei, H., C. T. Driscoll, J. R. Renfro, M. A. Kulp, T. F. Blett, P. F. Brewer, and J. S. Schwartz. 2016. Critical loads and exceedances for nitrogen and sulfur atmospheric deposition in Great Smoky Mountains National Park, United States. *Ecosphere* 7(10):e01466. 10.1002/ecs2.1466

Abstract. Acid deposition has impacted sensitive streams, reducing the amount of habitat available for fish survival in the Great Smoky Mountains National Park (GRSM) and portions of the surrounding Southern Appalachian Mountains by decreasing pH and acid neutralizing capacity (ANC) and mobilizing aluminum dissolved from soil. Land managers need to understand whether streams can recover from the elevated acid deposition and sustain the healthy aquatic biota, and if so, how long it would take to achieve this condition. We used a dynamic biogeochemical model, PnET-BGC, to evaluate past, current, and potential future changes in soil and water chemistry of watersheds of the GRSM in response to the projected changes in acid deposition. The model was parameterized with soil, vegetation, and stream observations for 30 stream watersheds in the GRSM. Using model results, the level of atmospheric deposition (known as a “critical load”) above which harmful ecosystem effects (defined here as modeled stream ANC below a defined target) occur was determined for the 30 study watersheds. In spite of the recent marked decreases in atmospheric sulfur and nitrate deposition, our results suggest that stream recovery has been limited and delayed due to the high sulfate adsorption capacity of soils in the park resulting in a long lag time for recovery of soil chemistry to occur. Model simulations suggest that over the long term, increases in modeled stream ANC per unit decrease in NH_4^+ deposition are greater than unit decreases in SO_4^{2-} or NO_3^- deposition, due to high SO_4^{2-} adsorption capacity and the limited N retention of the watersheds. Watershed simulations were used to extrapolate the critical load results to 387 monitored stream sites throughout the park and depict the spatial pattern of atmospheric deposition exceedances. These types of model simulations inform park managers on the amount of air quality improvement needed to meet the stream restoration goals.

Key words: 303(d) listed streams; critical loads; Great Smoky Mountains National Park; forest watershed biogeochemical model; nitrogen and sulfur deposition; Southern Appalachian Mountains; Special Feature: Science for Our National Parks' Second Century; stream acidification; total maximum daily load.

Received 20 March 2016; **revised** 1 July 2016; **accepted** 5 July 2016. Corresponding Editor: D. P. C. Peters.

Copyright: © 2016 Fakhraei et al. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

† E-mail: hfakhrae@syr.edu

INTRODUCTION

Atmospheric deposition of sulfur and nitrogen compounds (known as acid deposition) has adversely impacted the forest and aquatic ecosystems in North America, Europe, and Asia (Driscoll et al. 2001). Acid deposition originates from the emissions of sulfur dioxide (SO_2), nitrogen oxides (NO_x), and ammonia (NH_3) primarily from electric utilities, industrial processes, mobile sources, and agricultural activities (Driscoll et al. 2001). The spatial and temporal links of atmospheric emissions to transport, deposition, and watershed ecosystem impacts can be investigated using models. An acidification model can provide a comprehensive framework to develop a quantitative understanding of the response of forest ecosystems to atmospheric deposition. Models can be used to test conceptual understanding, provide insight into ecosystem behavior, and quantify and refine the modeling limitations. Models of surface waters can also be applied to determine the extent of historical acidification of watershed ecosystems and evaluate the potential benefits of control on the emissions of acidifying compounds (SO_2 , NO_x , and NH_3). The results from such simulations can inform decision makers on policy related to atmospheric emissions and acid deposition.

In this study, a dynamic model, net photosynthesis evapotranspiration and biogeochemistry (PnET-BGC; Gbondo-Tugbawa et al. 2001), was used to reconstruct the past changes that have occurred and to project the future changes that may occur in the acid–base status of soil and streams in the GRSM in response to the changes in acid deposition. Stream ecosystems in the GRSM are sensitive to acid deposition because of the combination of high elevation (the park elevation ranges from 270 to 2028 m and 51% of the area is above 1000 m), highly weathered base-poor soils, and the presence of coniferous vegetation (Weathers et al. 2006). Elevated deposition raises concern that the biological function of stream ecosystems has been negatively impacted due to the acidification of soils and stream waters (Cook et al. 1994, Kahl et al. 2004). Following the implementation of the Clean Air Act and the subsequent rules (the NO_x Budget Trading Program, the Clean Air Interstate Rule, and the Cross-State Air Pollution Rule) (Burtraw and Szambelan

2009), there has been a marked decline in emissions of acidifying compounds (SO_2 and NO_x) resulting in a concomitant decrease in the concentrations and fluxes of sulfate (SO_4^{2-}) and nitrate (NO_3^-) in wet and dry deposition in the eastern United States (Lehmann et al. 2005, Driscoll et al. 2010). In the GRSM, data from the Elkmont monitoring station indicate a 81% reduction in SO_4^{2-} wet deposition and 53% reduction in NO_3^- wet deposition between 1981 and 2014 (source: NADP; <http://nadp.isws.illinois.edu>). Despite these improvements, there has been a limited recovery in the acid–base status of the streams in the southeastern United States (Kahl et al. 2004, Rice et al. 2014) and in the GRSM (Schwartz et al. 2014, and as we demonstrate in the *Results* section). In this study, we investigated the factors that contribute to the delay in the recovery of watersheds in the GRSM from acid deposition. Intensive ecological monitoring in the GRSM, coupled with diverse physiographical characteristics and a high elevational gradient, makes the park a valuable landscape for this study and a good representative area of the Southern Appalachian Mountains with its other Class I wilderness areas, national parks, and national forests that have been impacted by acid deposition (Fig. 1). Our findings from model applications can guide decision makers with regard to the impacts of acid deposition, not only for the GRSM, but also for other national parks and Class I wilderness areas with similar biophysical characteristics, such as those in the adjacent Southern Appalachian Mountains.

Applying the “critical load” (CL) concept, we estimated the acceptable levels of acid deposition and the period necessary to recover streams in the GRSM from the acidification effects. These results may be used by park resource managers as a guide to the extent of atmospheric deposition reductions that are necessary to protect aquatic integrity of the streams in the park. A CL is defined as “the quantitative estimate of an exposure to one or more pollutants below which the significant harmful effects on specified sensitive elements of the environment do not occur according to the present knowledge” (Nilsson and Grennfelt 1988). Although the CL concept is applicable for the assessment of a variety of pollutants, the focus of our study was on sulfur (S) and nitrogen (N) deposition. CLs have been widely used to set the

policy for resource protection in Europe and North America (e.g., Henriksen et al. 1992, Dupont et al. 2005) and identified as an effective tool for communication between scientists and policy makers (Driscoll et al. 2010). CLs have been applied in the United States to inform the development of ecosystem protection goals and strategies related to the effects of atmospheric deposition, including for national parks and national forests (Burns et al. 2008, Baron et al. 2011, Sullivan et al. 2011, Blett et al. 2014, Zhou et al. 2015). In this study, to be consistent with the conventional nomenclature that has been used in other CL efforts (e.g., Porter et al. 2005, Sullivan et al. 2012), we referred to the modeled time-variant (dynamic) critical loads as “target loads” (TLs). We considered the CL as a TL that will be considered for implementation by managers or policy makers.

Our previous application of PnET-BGC model to several GRSM streams illustrated that modeled preindustrial stream ANC decreased in response to historical acid deposition (mean of modeled stream ANC for the streams decreased by $38 \mu\text{mol}_e/\text{L}$; Zhou et al. 2015). Using the recent observations of meteorological, atmospheric deposition, and stream water chemistry data in the GRSM, previous simulations were updated to take advantage of marked decreases in acid deposition that has occurred in recent years. We also expanded the number of simulated streams to 30 to include watersheds with a wide range of biophysical characteristics and all 303(d) listed streams (TDEC 2010) in the GRSM.

The overarching goal of this research was to evaluate the recent atmospheric deposition and stream chemistry data at the GRSM and to apply the dynamic watershed biogeochemical model PnET-BGC to improve the understanding of the processes controlling temporal trends and spatial patterns in the acid-base status of GRSM streams. Specifically, (1) develop a series of deposition loading scenarios (TLs) that would inform the extent and rate of future recovery of GRSM streams from decades of acidification; (2) use PnET-BGC to evaluate the extent to which park streams have been degraded by acid deposition from preindustrial conditions, and the extent and time to which future recovery to a healthy condition is possible; (3) assess the relative responsiveness of park streams to different types of deposition reductions (sulfate, nitrate,

and ammonium); (4) use data from 30 simulated streams to extrapolate the projections of the response of 387 streams representing the entire park; and (5) evaluate how atmospheric deposition, elevation, soils, and other biophysical characteristics of watersheds in the park influence the historical acidification and the rate of recovery of streams from acid deposition.

METHODS

Study site

Model calculations were made on 30 stream watersheds in the GRSM (Fig. 1). The GRSM is located in the Southern Appalachian Mountains of the United States, in Tennessee and North Carolina, and has a total area of 2074 km^2 (Van Miegroet et al. 2007). The dominant vegetation types in the GRSM include montane oak-hickory (31%), high-elevation hardwood (17%), yellow pine species (16%), cove hardwood (12%), and spruce-fir forest (8%) (Whittaker 1956, Jenkins 2007). The watersheds selected for model simulation cover physiographic and geological variability within the GRSM (Appendix S1: Tables S1 and S2) (Neff et al. 2013). The State of Tennessee identified 12 streams in the GRSM (Appendix S1: Table S1) as not supporting designated use classifications, and subsequently listed these as “303(d) impaired streams” under the Clean Water Act due, in part, to low pH (<6.0) associated with acid deposition. These 12 state-designated impaired streams and 18 additional GRSM streams (i.e., totally $12 + 18 = 30$ sites), most with low ANC and exhibiting chronic or episodic acidification, were selected for model simulations (Appendix S1: Table S1). To conduct a parkwide analysis and extrapolating CL results from the 30 simulated sites, we used stream chemistry data for 387 sampling locations on the streams throughout the park. In a survey of the chemistry of 387 stream locations in the GRSM during 1993–1996, 6% were found to be very sensitive to acid deposition and chronically acidic ($\text{ANC} < 0 \mu\text{mol}_e/\text{L}$). An additional 42% had ANC values between 0 and $50 \mu\text{mol}_e/\text{L}$ and are susceptible to the short-term acidification during hydrological events (data source: EPA-STORET; <https://www.epa.gov/waterdata/storage-and-retrieval-and-water-quality-exchange>). The selection of 18 additional streams was not only based on the stratified ANC classes,

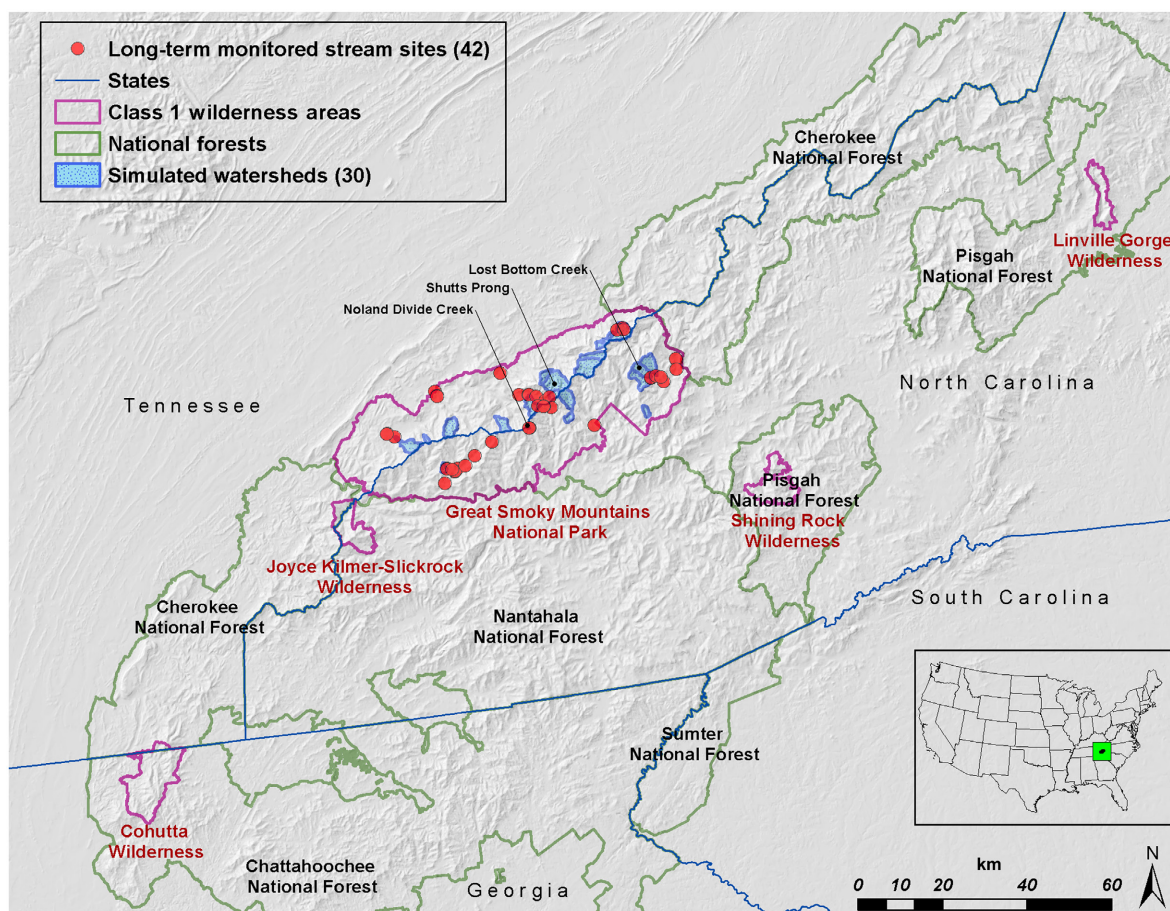


Fig. 1. Location of Great Smoky Mountains National Park, other nearby Class I wilderness areas, national forests, and the 30 watersheds for which the model simulations were conducted. Also shown are 42 stations where the long-term observations of stream chemistry were available for temporal trend analysis.

but also by considering watershed characteristics, particularly elevation, area, and slope (Neff et al. 2013). Streams in watersheds with high sulfidic shale (Anakeesta) geology (>30%) supplying elevated SO_4^{2-} were excluded, as the focus of study was on atmospheric deposition and recovery without being confounded by geologic sulfur sources. Soils in the study area are shallow Inceptisols with spodic characteristics (McCracken et al. 1962). Due to high concentrations of amorphous Al and Fe, Inceptisols can readily adsorb SO_4^{2-} (Harrison et al. 1989). Wet and dry depositions are reported inside and near the park at low elevations (i.e., 640 and 793 m, respectively) through the National Atmospheric Deposition Program (NADP; Elkmont [TN11]) and Clean Air Status and Trends Network (CASTNET; Look

Rock [GRS420]). NADP measures wet deposition, while CASTNET provides an estimate of dry deposition using modeled dry deposition velocity and the measured air quality concentrations. Summing the reported wet and dry deposition at these stations, the current (2012–2014) annual total sulfur (S) and nitrogen (N) depositions are $3.1 \text{ kg S}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ ($19.3 \text{ mmol}_c\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) and $5.1 \text{ kg N}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ ($36.5 \text{ mmol}_c\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$), respectively. The annual mean precipitation is 152.3 cm/yr (range: $47.0\text{--}202.1 \text{ cm/yr}$) for the period of 1981–2014 at the Elkmont station (<http://nadp.isws.illinois.edu/>). In contrast, throughfall measurements (i.e., precipitation drip through canopy) during 1999–2012 beneath the canopy of a high-elevation forest in the GRSM at Noland Divide (1708 m; Schwartz et al. 2014) indicate

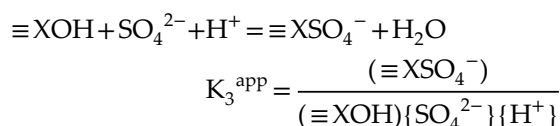
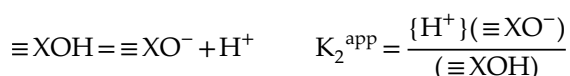
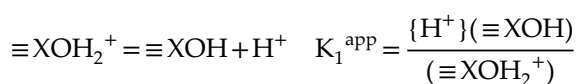
much higher annual precipitation (mean: 204 cm/yr), suggesting greater total deposition (by a factor of 3 for S and 2 for N) than that at low elevation. Previous studies also suggest that elevation plays a critical role in the gradient of deposition across the park (Cook et al. 1994, Shubzda et al. 1995, Weathers et al. 2006, Johnson and Lindberg 2013). As a result of this substantial variation in precipitation and deposition throughout the park, the GRSM has regionally relevant characteristics to study the impact of acid deposition on montane forest and aquatic ecosystems.

Model description

Models of varying levels of complexity have been used to develop CLs, including steady-state (Ouimet et al. 2006, McNulty et al. 2007), dynamic (Sullivan et al. 2012), and empirical approaches (Bobbink and Hettelingh 2010, Pardo et al. 2011). The steady-state approach is widely used in CL analyses. However, this approach focuses on only a time-invariant mass balance and is inadequate to simulate biotic processes, which are essential to evaluate the role of nitrogen in CL calculations. Furthermore, the steady-state and empirical approaches have limitation in simulating the future ecosystem dynamics in response to the current atmospheric deposition scenarios. Therefore, we used a dynamic model (PnET-BGC) that depicts the major abiotic and biotic processes. PnET-BGC is a biogeochemical model that simulates the long-term effects of land disturbance, climate change, and atmospheric deposition on soil and water chemistry of forest and interconnected aquatic ecosystems (Gbondo-Tugbawa et al. 2001, Pourmokhtarian et al. 2012). The model consists of a forest vegetation submodel, PnET-CN—in which energy, water, carbon, and N dynamics are simulated using physiological processes (Aber et al. 1997)—and an expanded biogeochemical submodel (BGC), which includes the interactions of other major elements (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Al^{3+} , Cl^- , F^- , Si, S, P) with forest vegetation and soil organic matter, abiotic soil processes, and solution speciation (Gbondo-Tugbawa et al. 2001).

An important feature of the model that is relevant to watersheds of the southeast (with high SO_4^{2-} adsorption capacity) is the depiction of pH-dependent SO_4^{2-} adsorption. Laboratory experiments on the soils sampled from a high-elevation watershed in the GRSM and other forest sites

(Nodvin et al. 1986, Cai et al. 2012) and field manipulations (Nodvin et al. 1988) indicate that SO_4^{2-} adsorption is an important solution controlling process and strongly correlated with pH. At low soil solution pH, the soil surfaces adsorb protons resulting in a net positive charge. However, the same surface site can exhibit a negative charge at high water pH due to deprotonation. This amphoteric behavior enhances the adsorption of anions (including SO_4^{2-}) with the decreases in soil pH and enhances the desorption with the increases in soil pH. The PnET-BGC model uses a surface complexation algorithm, which depicts variation in SO_4^{2-} adsorption with pH. The SO_4^{2-} adsorption process is formulated in the model by considering the ionization reactions representing the amphoteric behavior of oxide surfaces, and the specific sorption of SO_4^{2-} via ligand exchange (Dzombak and Morel 1990) as follows:



$$X_T = (\equiv\text{XOH}) + (\equiv\text{XO}^-) + (\equiv\text{XOH}_2^+) + (\equiv\text{XSO}_4^-)$$

where X_T is the total number of surface sites and represents the anion (including SO_4^{2-}) adsorption capacity; $\equiv\text{XOH}_2^+$, $\equiv\text{XOH}$, and $\equiv\text{XO}^-$ represent positively charged, neutral, and negatively charged surface hydroxyl groups; and K^{app} is the apparent equilibrium constant for the reactions; {} represent the concentration; and {} is activity of the species.

In contrast to SO_4^{2-} , N in forest soils is predominantly affected by biological processes. The mechanism of N retention in forest ecosystems is simulated by the uptake of mineral N to organic N that is the dominant pool within soil and vegetation and by the mineralization of organic N and the potential nitrification. In addition, NH_4^+ can also be chemically immobilized directly into the soil by cation exchange. Therefore, both biotic and chemical sinks contribute to N retention (Aber 1992). PnET-BGC incorporates both the

biotic and chemical N sinks in biogeochemical simulation of a forest ecosystem. The degree of N retention in a study ecosystem can be calibrated by, for instance, adjusting the ratio of N immobilization to the N mineralization.

PnET-BGC simulates acid neutralizing capacity (ANC) as an analog to the analytical ANC measurement by Gran plot analysis (Gran 1952), by considering the contributions of dissolved inorganic carbon, organic anions, and aluminum complexes (Driscoll et al. 1994). The ANC is estimated as follows (Driscoll et al. 1994):

$$\begin{aligned} \text{ANC} = & [\text{OH}^-] - [\text{H}^+] + [\text{HCO}_3^-] + 2 * [\text{CO}_3^{2-}] \\ & + [\text{HOrg}^{2-}] + 2 * [\text{Org}^{3-}] + [\text{Al}(\text{OH})_2^+] \\ & + 3 * [\text{Al}(\text{OH})_4^-] + [\text{AlOrg}] \end{aligned}$$

where [] is molar concentration and Org^{3-} is the organic analog anion.

PnET-BGC has been validated and applied to forest watersheds in the northeastern (Gbondotugbawa et al. 2001, Fakhraei et al. 2014) and southeastern United States (Zhou et al. 2015). A detailed description of the model is given by Gbondotugbawa et al. (2001).

Model data preparation

Application of PnET-BGC requires a time series of monthly atmospheric drivers, including precipitation, maximum and minimum air temperature, solar radiation, and atmospheric deposition. Forest vegetation type and soil physical and chemical characteristics are assumed to be constant inputs over time. Users have the ability to impose land disturbance events in model simulation (e.g., forest cutting, fire). Runoff observations and stream chemistry data are used for hydrological and chemical calibration of the model. For application of the model to the GRSM, the sources of these inputs are summarized in Table 1. Data were largely obtained from the National Park Service Inventory and Monitoring (NPS I&M) Program. The NPS I&M Program conducts long-term monitoring of ecological indicators in over 270 national parks with significant natural resources. The GRSM is part of the NPS I&M Program. The ecological monitoring in the park has been implemented in a variety of categories (air quality and climate, water quality and hydrology, soil quality and geology, biological integrity, and landscape) and provides a basis for scientific assessment of the park ecosystem (Emmott et al. 2005).

Detailed temporal precipitation and air temperature data were derived by extrapolating the long-term observations (1933–2012) at a National Climate Data Center (NCDC) station inside the GRSM (Gatlinburg). Spatial extrapolation of climatic data was based on regional regression models that were developed based on point observations at NCDC sites inside and nearby the park (Fakhraei 2016). Solar radiation was determined from the empirical models we developed for the region based on point observations at National Solar Radiation Database (NSRDB) stations close to the park (Fakhraei 2016).

Current (1981–2014) parkwide atmospheric deposition was spatially estimated by applying an empirical model developed by Weathers et al. (2006) to the point measurements at the closest national network monitoring stations that are located inside or near the park (i.e., wet deposition from NADP at Elkmont and dry deposition from CASTNET at Look Rock; Fig. 2). Using digital elevation model (DEM) and National Land Cover Database (NLCD) data layers, the approach developed by Weathers et al. (2006) allows the estimation of total deposition of S and N on a 30-m grid scale capturing the spatial and elevational gradients of the park. To estimate the historical (1900–1980) precipitation chemistry for the region, we initially developed linear regression models (Appendix S1: Figs. S1 and S2) between the observed precipitation chemistry of SO_4^{2-} and NO_3^- and the reported national emissions of SO_2 and NO_x , respectively (for the period of 1981–2014; <https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data>). By applying the historical estimates of national emissions (Nizich et al. 1996) into these regression models, we estimated the precipitation chemistry from 1900 to 1980. Unlike the SO_2 – SO_4^{2-} and NO_x – NO_3^- relationships, we did not observe any significant relationship between NH_3 emissions and concentrations of NH_4^+ in precipitation (Appendix S1: Figs. S1 and S2). This lack of a relationship is likely due to an inadequate emission inventory for NH_3 sources and the minimal changes over the period of record. The primary source of NH_3 emissions is agricultural activities (e.g., manure from livestock and poultry, N fertilizer, crop senescence); however, other sources, which are difficult to measure, may also contribute (e.g., automobile emissions, industrial processes) (Jordan and Weller 1996, Driscoll et al. 2003).

Table 1. Major data sources used in this study.

Database	Publicly available source/reference	Major information provided
United States Department of Agriculture (USDA) – Geospatial Data Gateway (GDG)	http://datagateway.nrcs.usda.gov/	Watersheds boundary and hydrological units
United States Geological Survey (USGS) – Earth Resources Observation and Science (EROS) Center	http://eros.usgs.gov/	DEM 7.5 min (30 m)
USGS – National Land Cover Database (NLCD)	http://www.mrlc.gov/	Land cover 2006
Environmental Protection Agency (EPA) – Clean Air Status and Trends Network (CASTNET)	http://java.epa.gov/castnet/clearsession.do	Dry deposition at GRSM—Look Rock
National Atmospheric Deposition Program (NADP)	http://nadp.sws.uiuc.edu/	Precipitation and wet deposition at GRSM—Elkmont
National Climate Data Center (NCDC)	http://www.climate.gov/maps-data	Climate data
National Solar Radiation Database (NSRDB)	http://rredc.nrel.gov/solar/old_data/nsrdb/	Solar radiation
Direct/Delayed Response Project (DDRP)	Church et al. (1989)	Soil chemistry
EPA-STORET Data Warehouses	https://www.epa.gov/waterdata/storage-and-retrieval-and-water-quality-exchange	Stream chemistry
USGS water data	http://waterdata.usgs.gov/nwis	Stream discharge flow
National Park Service; Gaseous Pollutant Monitoring Program (GPMP)	http://ard-request.air-resource.com/data.aspx#	Ambient temperature, precipitation, and solar radiation for four GRSM sites
EPA CMAQ run (2007)	Schwede and Lear (2014)	Annual dry and wet deposition estimated for 2011 using CMAQ model. This data set allowed comparing the observed and CMAQ model-simulated deposition for year 2011
Future deposition scenarios	Driscoll et al. (2015)	Annual dry and wet deposition projected for year 2020 using CMAQ model under reference and three control scenarios
National Park Service; Aquarius	https://irma.nps.gov/aqwebportal/	Stream discharge flow and pH for Noland Divide flumes

We used the values for the San Carlos site in Venezuela (Galloway et al. 1982) to estimate pre-industrial concentrations of chemical constituents, because it is the closest nonisland site to the GRSM. We estimated preindustrial deposition at Elkmont NADP site in GRSM by multiplying the precipitation concentrations from Galloway et al. (1982) and 10-yr annual average of precipitation quantity recorded at the Elkmont site. Using the same scaling factors that were applied to estimate the current spatial pattern of atmospheric deposition through the park (i.e., Weathers et al.'s 2006 model), the estimated preindustrial wet S deposition spatially ranged from 4.7 to 12.3 $\text{mmol}_c\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ in the park. These values compare with the natural background estimates of 9.3 $\text{mmol}_c\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ by Granat et al. (1976) and 4.4–9.3 $\text{mmol}_c\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ for North America by Husar and

Holloway (1982). The estimated natural wet background deposition of NO_3^- for the GRSM (i.e., 4.5–11.9 $\text{mmol}_c\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) is of the same order of magnitude as the proposed values by Husar and Holloway (1982) (i.e., 2.1–4.2 $\text{mmol}_c\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ for North America). Similar to SO_4^{2-} and NO_3^- , we estimated the background deposition of NH_4^+ for the GRSM (i.e., 4.0–10.5 $\text{mmol}_c\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$); however, these values are considerably less than the reconstructed deposition for Cape Cod region, Massachusetts, in mid-1920s (i.e., 28.6 $\text{mmol}_c\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$; Bowen and Valiela 2001), and recorded values in eastern North America in 1880–1890s (i.e., 19–30 $\text{mmol}_c\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$; Brimblecombe and Stedman 1982). Deposition inputs for the period of 1850–1900 were assumed to increase linearly from the preindustrial levels in 1850 to the reconstructed values in 1900.

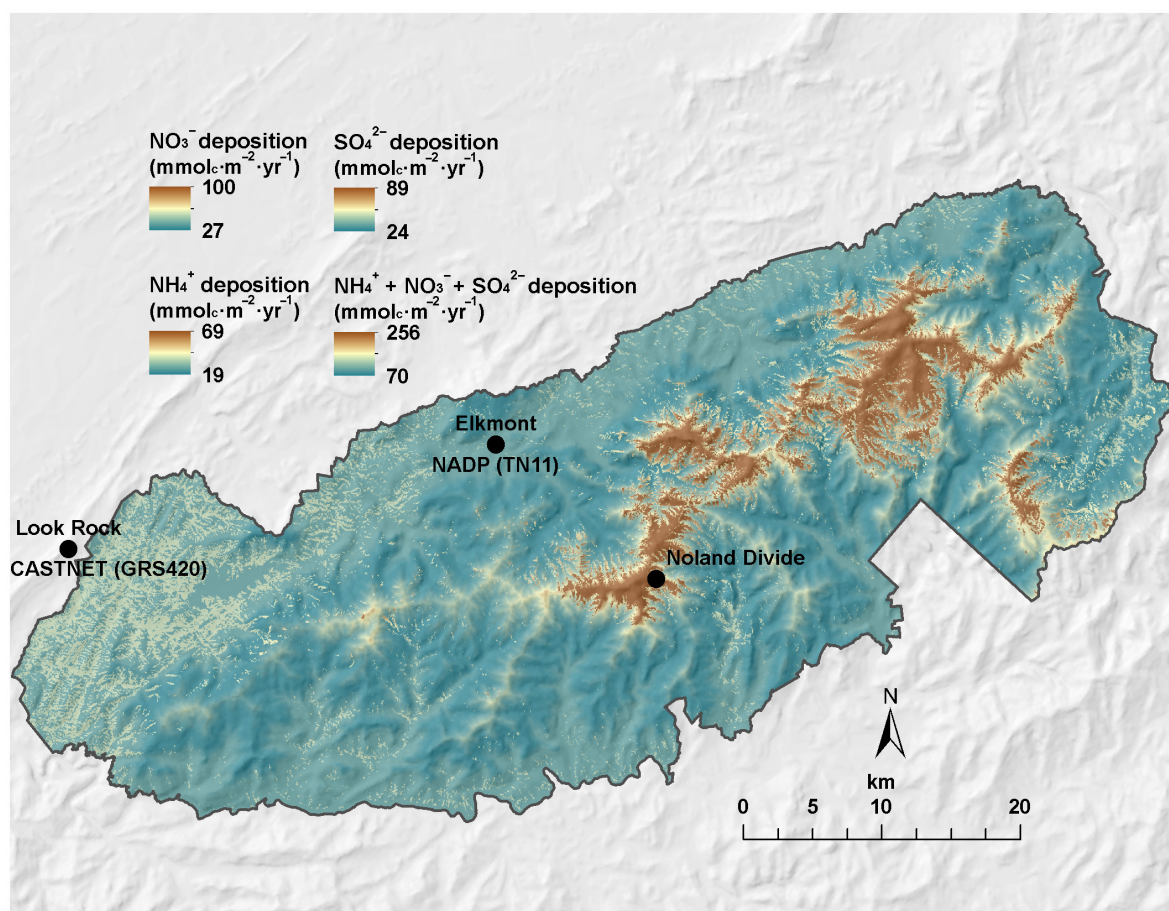


Fig. 2. Spatial pattern of the current (2012–2014) total (dry + wet) atmospheric NH_4^+ , NO_3^- , and SO_4^{2-} deposition ($\text{mmol}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) in Great Smoky Mountains National Park, using the empirical model developed by Weathers et al. (2006). Location of NADP wet (Elkmont; TN11), CASTNET dry (Look Rock; GRS420) and Noland Divide deposition monitoring stations is also shown.

Information on soil mass and cation exchange capacity was derived from the Direct/Delayed Response Project (DDRP) database (Church et al. 1989). This soil survey included a few watersheds in the park, which are not in the same watersheds used for model simulations. However, we performed one-way analysis of variance (ANOVA) across the soil sites, finding no significant differences among the means of mass-weighted soil characteristics of the sampled sites in the park ($P = 0.8$ for soil mass and $P = 0.5$ for cation exchange capacity). This result suggests that the variation in soil characteristics among the pedons inside the sites is as large as the variation among the soil sampling sites. Therefore, the means of mass-weighted soil characteristics (cation exchange capacity and soil

mass) obtained from the DDRP database were used for modeling the study sites. Other soil characteristics including Ca^{2+} , Mg^{2+} , Na^+ , and Cl^- weathering rates and SO_4^{2-} adsorption capacity were parameterized by model calibration (Appendix S1: Table S3). Those soil parameters were adjusted until a good agreement was achieved between the observed and the predicted stream chemistry of major elements and ANC.

Since the official park dedication in 1940, the GRSM has not been impacted by any appreciable logging or fire (Pyle 1988). However, an exotic insect infestation, the balsam woolly adelgid (BWA; *Adelges picea* Ratz.), caused the death of mature Fraser fir trees (Nicholas et al. 1992, Van Miegroet et al. 2001). The first detection of infestation in the

GRSM occurred at Mt. Sterling in 1963 (Nicholas et al. 1992). The adelgid infestation caused the total dead standing areas ranging from 7 to 27 m²/ha along an elevation gradient (Nicholas and White 1985). A survey in 1985 and 1986 researchers found that 11–44% of the total overstory species were dead depending on elevation (adapted from Table 4 in Nicholas et al. 1992). Due to the abundance of fir, which is more vulnerable to the adelgid, higher tree mortality was observed at higher elevations in the park (Nicholas et al. 1992). We accounted for this incident by using the land disturbance feature of the model for high-elevation watersheds. A few fire and logging incidents before the park establishment are recognized from the GIS data layers and were considered in model simulations (Appendix S1: Table S2).

The model simulates stream ANC by considering the contributions of dissolved inorganic carbon, naturally occurring organic acids, and aluminum complexes (Driscoll et al. 1994). Due to the limited observations of dissolved organic carbon (DOC) in the GRSM, we were not able to refine the organic acid parameters for this application. Therefore, we used the parameters obtained from the calibrated values in the northeastern United States (Fakhraei and Driscoll 2015). However, in the GRSM, organic acids do not appear to contribute significantly to the acid–base chemistry because the concentrations of DOC are low (<2.1 mg/L) (Cook et al. 1994, Martin et al. 2001). The DOC concentrations are comparable to the values observed in the Southern Blue Ridge Province during the National Stream Survey (Sale et al. 1988). Cook et al. (1994) attributed low concentrations of DOC at the GRSM due to the high potential sorption by clay-rich soils.

Stream chemistry data were obtained for 387 monitoring sites through the GRSM, which were monitored by NPS I&M Program during various periods (Schwartz et al. 2014). Of 387 monitoring sites, 42 were intensively monitored and provide the long-term information for stream chemistry in the GRSM. We used these 42 sites for temporal trend analysis. Stream chemistry data for the simulated sites were also obtained from this NPS I&M data set and were used in model calibration. Concentrations of major cations and anions and ANC for 29 study streams were measured over the interval between 1991 and 2014 for 2–23 years; no observations were available for

one stream (Lowes Creek) (Schwartz et al. 2014, data source: EPA-STORET; <https://www.epa.gov/waterdata/storage-and-retrieval-and-water-quality-exchange>).

Modeling procedure

The model was run using soil and vegetation data and a time series of historical meteorological data, atmospheric deposition, and vegetation disturbance as inputs. The hydrological algorithm of the model partitions the precipitation inputs between canopy interception (evaporation), surface runoff, soil water, and plant uptake (transpiration). Water remaining beyond evapotranspiration and soil water holding capacity is drained from watersheds as stream flow (Aber and Federer 1992). Modeled stream flow was compared with the observed stream flow at U.S. Geological Survey (USGS) gauging stations, and any necessary adjustment was made through the calibration of the evaporation coefficient. Stream flow is measured at USGS gauges at five locations inside the park. We calibrated hydrology of each study site by using data from the stream gauge observations of a watershed that is close and downstream of the corresponding study watershed. Stream flow observations for two streams in Noland Divide watershed, obtained from the NPS Aquarius Web Data Portal (<https://irma.nps.gov/aqwebportal>), were used for the hydrological calibration of Noland Divide watershed. Following the hydrological calibration, the modeled stream chemistry (of SO₄²⁻, NO₃⁻, Cl⁻, ANC, Ca²⁺, Mg²⁺, Na⁺, and K⁺) was matched to the observed stream chemistry by calibrating the parameters including soil weathering rates, soil SO₄²⁻ adsorption capacity and a parameter representing a N sink. The model output, the quantity and quality of water at the monitoring stations, was made to coincide with the observed values by the adjustment of calibration parameters. We limited the calibration to those parameters for which the observations were not available in the park. However, the calibration parameters were adjusted within reasonable ranges that are consistent with the observations reported in the literature. For example, weathering rates of Ca²⁺ and Mg²⁺ were adjusted within the reported ranges for granitic soils in North America and Europe (6–115 and 2–45 mol_c·m⁻²·yr⁻¹, respectively; Vadeboncoeur et al. 2014).

Hindcast model simulations were initiated with an extended spin-up period (1000–1850) to allow the watershed to come to steady state with respect to preindustrial meteorology and atmospheric deposition (Pourmokhtarian et al. 2012). Starting in 1850, anthropogenic impacts including the historical changes in atmospheric deposition and land disturbances were considered in model simulations by applying our reconstructed inputs. We continued the simulation for an additional period of ~150 years (until 2150) to assess the recovery of ecosystem from ~150 years of historical acidification (i.e., from 1850 to present). The model simulations were compared with the measured values over the time periods that the stream chemistry data are available to test model performance. In the appendix, we provide a detailed description of three metrics (i.e., normalized mean error (NME), normalized mean absolute error (NMAE), and normalized root-mean-squared error (NRMSE); Janssen and Heuberger 1995) that were used to evaluate the model performance. In general, the modeled stream chemistry was in good agreement with the measured values. A summary of model performance based on evaluating the three statistical criteria is available in Appendix S1: Tables S5 and S6, and a plot of simulated vs. the measured mean concentrations for individual stream sites is depicted in Appendix S1: Fig. S4.

The calibrated model was applied to individual study watersheds to quantify the future projections of soil and water chemistry to evaluate the ecosystem response to controls of SO_4^{2-} , NO_3^- , and NH_4^+ deposition, individually, and under two general deposition control scenarios: (1) control on atmospheric deposition of $\text{SO}_4^{2-} + \text{NO}_3^-$ and (2) control on atmospheric deposition of $\text{SO}_4^{2-} + \text{NO}_3^- + \text{NH}_4^+$. Although there are no regulations in the United States to control NH_3 emissions, we considered the decreases in NH_4^+ deposition along with the decreases in SO_4^{2-} and NO_3^- deposition as a scenario to assess the importance of NH_4^+ in mitigation of streams acidification. Future projections were compared with the simulations of holding current deposition constant until the end of the study period ("business-as-usual" scenario). The model was also run under a control strategy equivalent to the proposed EPA Clean Power Plan (USEPA 2015) for regulating national SO_2 and NO_x

emissions. We adopted this scenario (which is adapted from Driscoll et al. 2015) to represent an "on-the-books" scenario depicting the most reasonable foreseeable future emissions reductions of air pollutants over the next several decades. According to the "on-the-books" scenario, current (i.e., average of 2012–2014) deposition level was ramped linearly down from year 2015 to the Clean Power Plan level in year 2020 and then was held constant until the end of the simulation period (Appendix S1: Fig. S3). The magnitude of change in atmospheric deposition from the current (2012–2014) level to the Clean Power Plan level in year 2020 varies among the study sites largely due to the variation in elevation; on average, 25, 17, and 22% decreases were projected for SO_4^{2-} , NO_3^- , and NH_4^+ deposition, respectively. After this initial ramping period (i.e., 2020), we applied four additional reduction levels (25, 50, 75, and 100% decreases) to characterize other potential emissions reduction scenarios and assess their hypothetical effects on park stream quality. These additional reduction levels were applied linearly for a period of 10 years (2021–2030; Appendix S1: Fig. S3). Note that the 100% decrease in deposition is equivalent to a "preindustrial" deposition.

Following the simulation of stream chemistry at each study site under the aforementioned reduction scenarios, model projections of stream ANC were extracted for two future target years (i.e., 2050 and 2150). Chemical and biological recovery of streams from acidification can take multiple decades to centuries to achieve (Josephson et al. 2014); accordingly in developing TLs, we considered that two long lag times (i.e., targeting years 2050 and 2150) to restoration of streams occur. Using the regression analysis, we developed the relationships between atmospheric deposition and model-projected stream ANCs for each of the 30 study sites. We used these relationships to estimate the reduction in atmospheric deposition necessary to achieve a selected target ANC in 2050 or 2150. Applying these required load reductions to the current atmospheric deposition, we determined the TLs for each of the 30 study sites.

One of the objectives of this study was to estimate TLs for all the monitored streams (i.e., 387 sites for which water chemistry observations are available) in the GRSM. We estimated TLs for

these parkwide sites by extrapolating the calculated TLs for the 30 simulated sites. We observed that the calculated TLs were a linear function of measured stream ANC (i.e., median monitored ANC during 1993–1996 survey) across the 30 modeled sites. This empirical relationship between the observed stream ANC and the TLs for the simulated watersheds was used to extrapolate the parkwide TLs for 387 individual stream sites.

We considered two approaches for ANC targets of streams to establish the values of TLs. First, we used the traditional approach of designating a fixed ANC as a goal for recovery, selecting a value of 20 $\mu\text{mol}_\text{c}/\text{L}$ as a potential target (USEPA 2009). In addition, we developed ANC targets based on our hindcast simulations, estimating preindustrial ANC (~1850) for study watersheds. These values represent the projected natural stream conditions prior to the degradation of stream chemistry by acid deposition. As far as we are aware, this is the first time that this approach has been considered for the determination of CLs. We considered two ANC targets: the estimated preindustrial ANC (i.e., the ANC simulated for 1850) and, because this target was generally not attainable, 20 $\mu\text{mol}_\text{c}/\text{L}$ below the simulated preindustrial ANC (preindustrial ANC–20 $\mu\text{mol}_\text{c}/\text{L}$).

Statistical trend and regression analysis

In addition to our application of PnET-BGC, we investigated the recent observed changes in the chemistry of atmospheric deposition and stream water in the GRSM, using the nonparametric seasonal Kendall's tau test for time-series analysis (Hirsch et al. 1982) on the observed monitoring data (SO_4^{2-} and NO_3^- concentrations, ANC) for 42 streams with the long-term observations from NPS I&M data sets (Schwartz et al. 2014). Water quality trend analysis can reveal how responsive streams are to the temporal variation in atmospheric deposition. Eleven of these 42 sites are among the 30 streams modeled by PnET-BGC.

The trend analysis of precipitation chemistry was conducted using the data from a monitoring station at low elevation in the National Atmospheric Deposition Program (NADP; Elkmont [TN11]) and a bulk deposition site at high elevation located in Noland Divide

watershed (Fig. 2). The bulk deposition (direct precipitation onto ground surface) data for Noland Divide have been collected weekly/biweekly by the National Park Service since 1991 (Cai et al. 2010, Schwartz et al. 2014). Seasonal trend analysis was performed on monthly stream and deposition volume-weighted concentrations calculated from the weekly/biweekly data set. The slopes of trends were estimated by the Sen estimator (Sen 1968). The seasonal Kendall's tau test was modified for the possible autocorrelation of the time-series data (Hirsch and Slack 1984).

Using the model-predicted data for the long-term soil and stream chemistry of 30 study sites, we conducted the regression analysis to evaluate the role of watershed characteristics in the historical acidification and recovery among the study sites in the GRSM. In this regression analysis, the predictors were watershed characteristics including measured elevation, atmospheric deposition, and vegetation land cover, and model-derived SO_4^{2-} adsorption capacity, N retention coefficient, weathering rate of cations. The analysis revealed how these factors influence the extent of historical acidification and future recovery of soil and stream water at the study sites in the GRSM.

The importance of each individual component of acid deposition (SO_4^{2-} , NO_3^- , and NH_4^+) in the recovery of modeled stream ANC was evaluated by calculating the rate of recovery per unit decrease in deposition. The recovery of stream ANC (from the current year to the year 2150) was determined by running the model for the 30 study sites while decreasing a specific component of atmospheric deposition (SO_4^{2-} , NO_3^- , or NH_4^+) to preindustrial levels. All statistical analyses were conducted using R version 3.0.1 (R Core Team 2016).

RESULTS

Recent observed trends in atmospheric deposition and stream chemistry

At the NADP monitoring site in the GRSM (Elkmont—TN11), concentrations of SO_4^{2-} in atmospheric deposition significantly ($P < 0.001$) decreased at the rate of 0.73 $\mu\text{mol}_\text{c}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$ between 1981 and 2014. Nitrate concentrations in precipitation did not show any significant trend between 1981 and 2002, but after the implementation of the NO_x Budget Trading Program (NBP;

established under the NO_x State Implementation Plan [SIP] Call Program in 2003; Burtraw and Szambelan 2009) significantly ($P < 0.001$) decreased at a rate of $0.3 \mu\text{mol}_c\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$. Ammonium in precipitation has not shown any significant change (data source: NADP; <http://nadp.isws.illinois.edu/>).

Observed bulk atmospheric deposition at Noland Divide exhibited a significant ($P < 0.001$) decreasing trend for SO_4^{2-} ($0.51 \mu\text{mol}_c\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$ from 1991 to 2013). There was no significant ($P > 0.05$) change from 1991 to 2002 (i.e., before NBP implementation) in NO_3^- , but again showed a significant ($P < 0.001$) decreasing trend ($1.28 \mu\text{mol}_c\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) from 2003 to 2013. A slight but statistically significant ($P = 0.006$) decrease in NH_4^+ ($0.21 \mu\text{mol}_c\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) was evident during the period 1991–2013.

In spite of the recent decreases in atmospheric SO_4^{2-} and NO_3^- deposition at these sites, stream chemistry in the GRSM has not shown widespread changes in acid–base chemistry. Our time-series analysis indicates that of the 42 sites with the long-term observations, only nine have shown a significant increase in ANC with an average rate of $1.19 \mu\text{mol}_c\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$ (ranging from 0.13 to $3.03 \mu\text{mol}_c\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$), one had a significant declining trend ($-0.4 \mu\text{mol}_c\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$), and the remaining 32 sites did not exhibit any significant change (at a significance level of 0.05).

Of the 42 sites with the long-term observations, just two streams exhibited significant declines in SO_4^{2-} (-0.56 and $-1.44 \mu\text{mol}_c\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$), while 13 streams showed significant increases with an average rate of $0.53 \mu\text{mol}_c\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$ (ranging from 0.13 to $2.53 \mu\text{mol}_c\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) and the remaining 27 streams did not exhibit any significant trend (at a significance level of 0.05). The concentration of NO_3^- in eight streams had a significant increasing trend with an average rate of $0.36 \mu\text{mol}_c\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$ (ranging from 0.01 to $0.85 \mu\text{mol}_c\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$), five showed a significant decreasing trend with an average rate of $-0.84 \mu\text{mol}_c\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$ (ranging from -0.3 to $-1.18 \mu\text{mol}_c\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$), and the remaining 29 streams did not exhibit any significant change (at a significance level of 0.05).

Watershed response to historical deposition

Median model-predicted stream ANC for the preindustrial period (~1850) at the simulated sites (30 watersheds) was $50.3 \mu\text{mol}_c/\text{L}$ (ranging

from 27.8 to $79.7 \mu\text{mol}_c/\text{L}$). Coinciding with increases in atmospheric deposition, simulated concentrations of SO_4^{2-} and NO_3^- increased in the streams; consequently, the median modeled stream ANC decreased to $18.9 \mu\text{mol}_c/\text{L}$ (ranging from -10.9 to $76.4 \mu\text{mol}_c/\text{L}$) in the 1993–1996 period (Fig. 3). None of the study streams are estimated to have preindustrial ANC less than $20 \mu\text{mol}_c/\text{L}$; 14 of the sites on the streams are estimated to have preindustrial ANC between 20 and $50 \mu\text{mol}_c/\text{L}$, and the remaining 16 sites are estimated to have $\text{ANC} > 50 \mu\text{mol}_c/\text{L}$.

The variability in ANC response among the stream sites to historical acid deposition can partially (i.e., 42%) be explained by the variation in elevation (Eq. 1 in Table 2). Note, however, model-calibrated soil SO_4^{2-} adsorption capacity and atmospheric acid deposition, which are correlated with elevation, together can also be used to empirically estimate the magnitude of the historical stream acidification (Eq. 2 in Table 2). Historical increases in atmospheric acid deposition to the watersheds not only acidified the streams, but also acidified the soil. Hindcast simulations of soil chemistry suggest that soil acidification due to the historical acidic deposition is manifested through the increases in soil pools of adsorbed SO_4^{2-} (from median preindustrial value of 20.2 g/m^2 to the current median of 145.6 g/m^2) and the decreases in soil base saturation (from preindustrial median of 17.8% to the current median of 12.6%; Fig. 3). Other researchers, either by modeling (e.g., Johnson et al. 1993) or based on the field observations (e.g., Johnson and Todd 1990, Joslin et al. 1992, Huntington et al. 2000, Warby et al. 2009), have reported the decreases in soil base saturation for other acid-impacted regions. Johnson et al. (1993) have predicted the substantial increase in soil adsorbed SO_4^{2-} under an increase in S deposition scenario in a nearby forest ecosystem at Coweeta, North Carolina. Historical depletion of exchangeable base cations from the soil estimated by hindcast simulations with PnET-BGC is related to soil SO_4^{2-} adsorption capacity and atmospheric acid deposition across the modeled watersheds at the GRSM (Eq. 5 in Table 2).

Although physiographical and geological characteristics influence the soil acidification (Driscoll et al. 2001, Fenn et al. 2006), model simulations generally suggest that the soil at higher

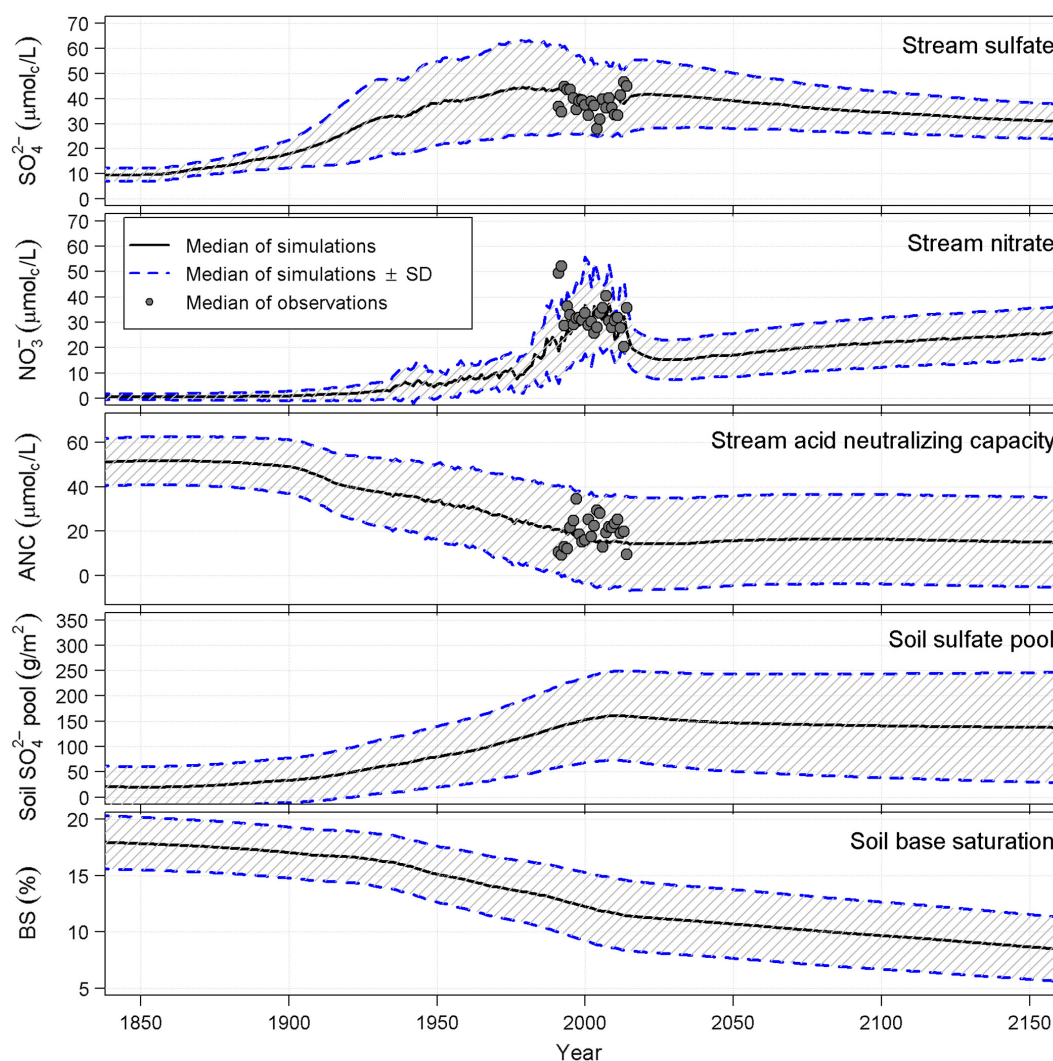


Fig. 3. Median ($\pm$ standard deviation) of model-predicted stream and soil chemistry for the 30 simulated streams in GRSM during 1850–2150. Future projections are shown under “business-as-usual” scenario. Median values of annual volume-weighted observed concentrations of SO_4^{2-} , NO_3^- , and ANC are shown for comparison.

elevation in the GRSM has experienced greater impacts by the historical acid deposition than the sites at lower elevation (Eq. 6 in Table 2). Soil SO_4^{2-} adsorption capacity and atmospheric acid deposition can be used to empirically estimate the magnitude of the historical accumulation of SO_4^{2-} on soil (Eq. 7 in Table 2).

Future projections under different emissions control scenarios

Simulations of the response of streams to future deposition scenarios suggest that projected increases in ANC are a function of the reduction

in deposition load and watershed characteristics (Fig. 4). Moreover, over time (e.g., 2150 vs. 2050), modeled stream ANC becomes more responsive to the reductions in deposition (Fig. 4). For example, a decrease in $\text{SO}_4^{2-} + \text{NO}_3^-$ deposition from the current (2012–2014) to a preindustrial deposition value in the future at Shutts Prong watershed, a site with low SO_4^{2-} adsorption capacity and low N retention, is projected to increase the current simulated stream ANC by 18.2 and 39.3 $\mu\text{mol/L}$ by the years 2050 and 2150, respectively (Fig. 5). In contrast, the ANC of stream water draining the Lost Bottom Creek—a watershed

Table 2. Regression models for estimating the historical acidification and the future recovery of soil and streams in GRSM (coefficients are significant at $P < 0.001$).

Equation	Variables	Constant	Elevation (m)	Deposition scaling factor [†]	Logarithmic sulfate adsorption capacity (mol/kg)	(Logarithmic sulfate adsorption capacity [mol/kg]) ²	Observed stream SO_4^{2-} ($\mu\text{mol}_\text{c}/\text{L}$) [‡]	(Observed stream SO_4^{2-} [$\mu\text{mol}_\text{c}/\text{L}$]) ²	Observed stream ANC ($\mu\text{mol}_\text{c}/\text{L}$) [‡]	R^2 or Adjusted R^2
1	Historical decrease in modeled stream ANC ($\mu\text{mol}_\text{c}/\text{L}$)	-31.843	0.044							0.42
2	Historical decrease in modeled stream ANC ($\mu\text{mol}_\text{c}/\text{L}$)	17.613		13.289	-17.412					0.92
3	Historical increase in modeled stream SO_4^{2-} ($\mu\text{mol}_\text{c}/\text{L}$)	23.214			-10.069					0.86
4	Historical increase in modeled stream NO_3^- ($\mu\text{mol}_\text{c}/\text{L}$)	34.668			-11.801					0.47
5	Historical decrease in modeled soil BS (%)	3.868		1.937	-2.246					0.81
6	Historical decrease in modeled soil BS (%)	-2.462	0.006							0.37
7	Historical increase in modeled soil sulfate pool (g/m^2)	-99.725		91.497	73.843					0.91
8	Recovery of modeled stream ANC ($\mu\text{mol}_\text{c}/\text{L}$)	6.725			-9.056	3.838				0.85
9	Recovery of modeled stream ANC ($\mu\text{mol}_\text{c}/\text{L}$)	7.867					-0.676	0.029		0.86
10	Future change in modeled soil BS (%)	0.007			-0.700	0.202				0.74
11	Logarithmic calibrated sulfate adsorption capacity (mol/kg)	1.798					-0.055		0.007	0.95
12	Rate of modeled ANC change per control on NH_4^+ deposition ($\mu\text{mol}_\text{c}/\text{L}$)/($\text{mmol}_\text{c}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$)	0.650			-0.670	0.266				0.76
13	Rate of modeled ANC change per control on NO_3^- deposition ($\mu\text{mol}_\text{c}/\text{L}$)/($\text{mmol}_\text{c}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$)	0.525			-0.523	0.218				0.77
14	Rate of modeled ANC change per control on SO_4^{2-} deposition ($\mu\text{mol}_\text{c}/\text{L}$)/($\text{mmol}_\text{c}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$)	0.5418			-0.5850	0.2090				0.77

[†] Ratio of the total atmospheric deposition at interested watershed to the total atmospheric deposition observed at NADP (Elkmont) and CASTNET (Look Rock) stations.

[‡] Based on the observed stream chemistry during 1993–1996.

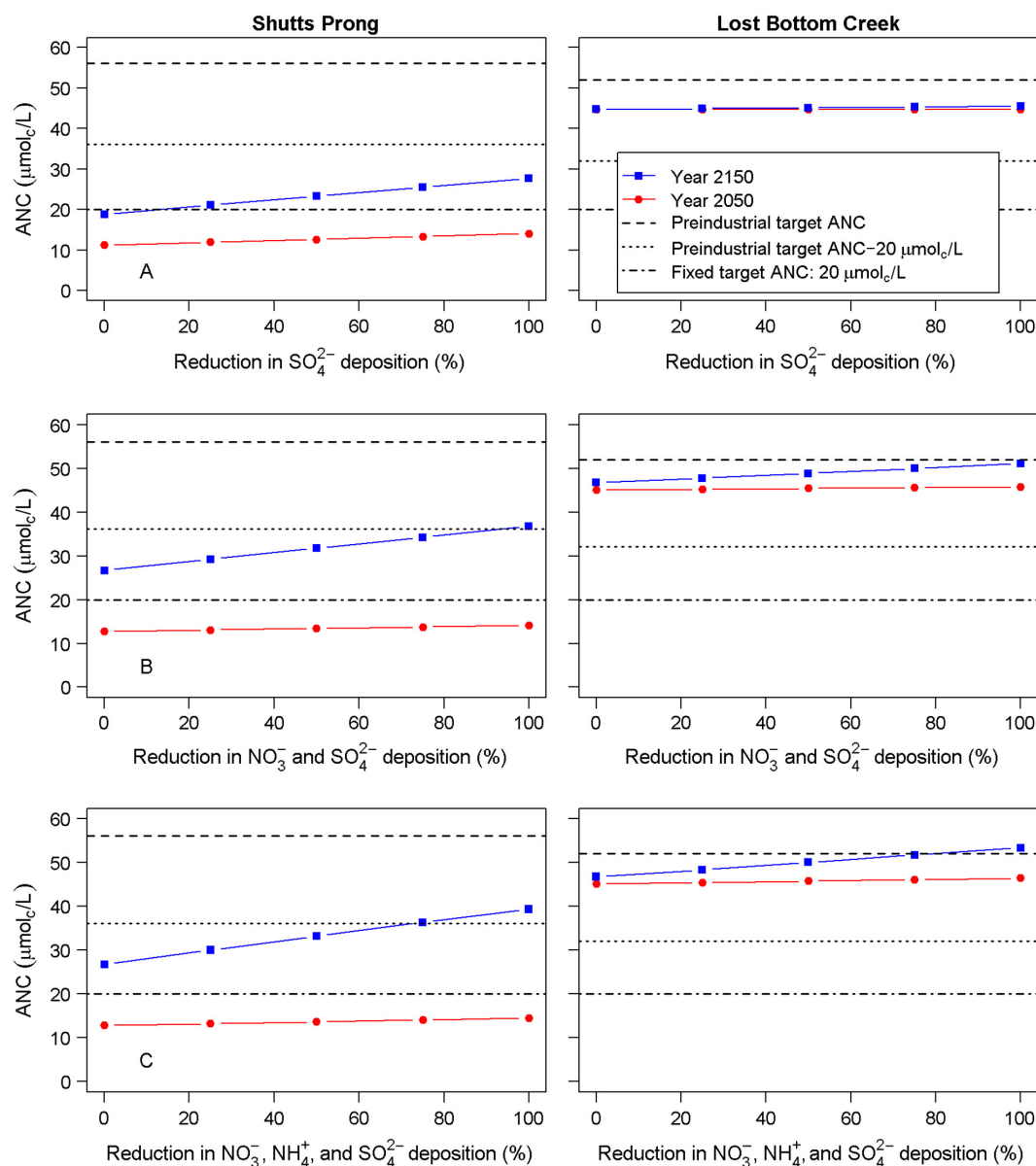


Fig. 4. Projections of ANC of Shutts Pong (left panels) and Lost Bottom Creek (right panels) in response to the different load reduction scenarios: (A) SO_4^{2-} load reduction, (B) SO_4^{2-} and NO_3^- load reduction, and (C) SO_4^{2-} , NO_3^- , and NH_4^+ load reduction, for two different target years (i.e., 2050 and 2150). Also shown are two preindustrial target ANC's (i.e., preindustrial ANC and preindustrial ANC-20 $\mu\text{mol}_e/\text{L}$) and a fixed target ANC of 20 $\mu\text{mol}_e/\text{L}$.

that has as similar deposition as Shutts Prong watershed, but exhibits high SO_4^{2-} adsorption capacity and high N retention—is projected to increase only 2.9 and 10.1 $\mu\text{mol}_e/\text{L}$ by years 2050 and 2150, respectively, in response to a similar decrease in $\text{SO}_4^{2-} + \text{NO}_3^-$ deposition (Fig. 5).

We evaluated the watershed response to changing deposition loads of SO_4^{2-} , NO_3^- , and NH_4^+ deposition individually and in combination. Model simulations across the study watersheds suggest that over the long term, increases in modeled stream ANC per equivalent decrease

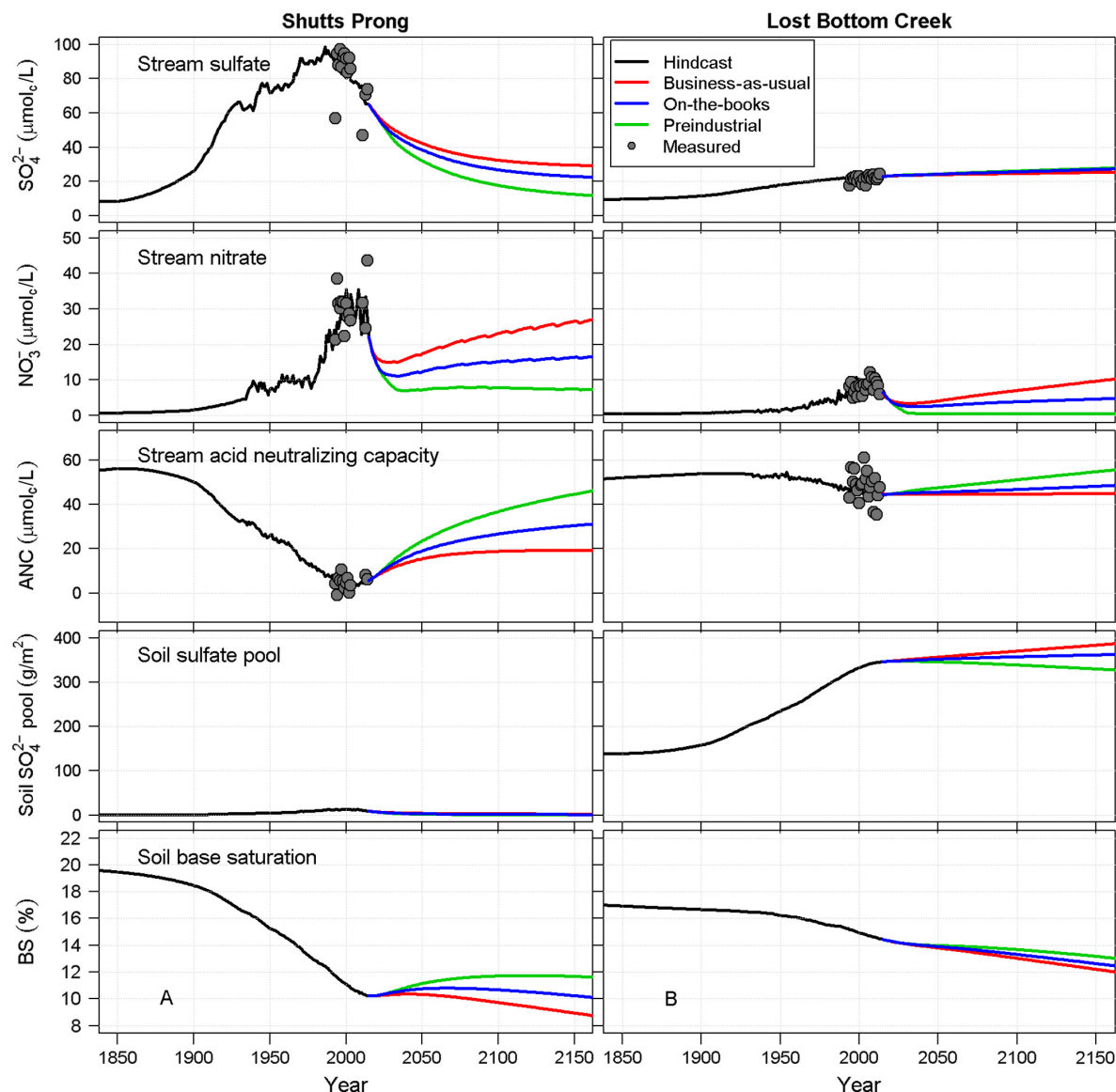


Fig. 5. Comparison of model-simulated annual volume-weighted concentrations of SO_4^{2-} , NO_3^- , ANC; soil sulfate pool; and soil base saturation for (A) Shutts Prong and (B) Lost Bottom Creek during 1850–2150. Model projections are shown for three future atmospheric deposition scenarios (i.e., business-as-usual, on-the-books [EPA Clean Power Plan], and preindustrial deposition). Preindustrial scenario is invoked by controlling $\text{SO}_4^{2-} + \text{NO}_3^-$ deposition.

in NH_4^+ deposition are greater than the equivalent decreases in SO_4^{2-} deposition, due to high SO_4^{2-} adsorption capacity and the limited N retention. In the GRSM, all simulated streams showed greater increases in modeled stream ANC in response to the control of NH_4^+ deposition compared with the equivalent control on

SO_4^{2-} deposition. The mean rate of increase in ANC for the 30 study sites, by year 2150, per unit decrease in NH_4^+ or SO_4^{2-} deposition was 0.37 and 0.27 ($\mu\text{mol}_c/\text{L})/(\text{mmol}_c\cdot\text{m}^{-2}\cdot\text{yr}^{-1})$, respectively. Control of NH_4^+ deposition individually is also more effective in terms of improving modeled stream ANC compared with the control of

only NO_3^- deposition. The mean rate of increase in ANC of the simulated sites in response to unit decrease in NO_3^- deposition was $0.32 \text{ } (\mu\text{mol}_\text{c}/\text{L})/(\text{mmol}_\text{c}\cdot\text{m}^{-2}\cdot\text{yr}^{-1})$. The rate of increase in ANC in response to the decreases in deposition of SO_4^{2-} , NO_3^- , or NH_4^+ is a function of the soil SO_4^{2-} adsorption capacity; the lower the SO_4^{2-} adsorption capacity, the greater the increase in ANC (Eqs. 12–14 in Table 2). The model simulations also suggest that for sites with low SO_4^{2-} adsorption capacity, the control of SO_4^{2-} deposition is more effective and resulted in a greater rate of ANC recovery than the control of NO_3^- deposition. Although there is a variation in stream recovery of ANC from the contribution of individual components of acid deposition, the overall recovery of watersheds is maximized if a combined load reduction of $\text{SO}_4^{2-} + \text{NO}_3^-$ or $\text{SO}_4^{2-} + \text{NO}_3^- + \text{NH}_4^+$ is implemented.

The extent of recovery of modeled stream ANC by the year 2150 was evaluated in the context of factors identified as drivers of historical acidification, under the scenario in which atmospheric $\text{SO}_4^{2-} + \text{NO}_3^-$ deposition was decreased to preindustrial levels. The recovery period (from present to 2150) was selected because this interval is nearly equivalent to the period (i.e., from 1850 to present) of historical acidification (~150 years). Although the model does not come to steady state (i.e., modeled stream ANC is still increasing at the end of the simulation period), this extended period allows for exploration of the conditions required for recovery from the acidification. The recovery of modeled stream ANC following the decreases in atmospheric $\text{SO}_4^{2-} + \text{NO}_3^-$ to preindustrial values is negatively related to the soil SO_4^{2-} adsorption capacity (Eq. 8 in Table 2). This pattern suggests that the greater the SO_4^{2-} adsorbed to soil during the historical acidification period, the greater the tendency for the watershed to release this previously adsorbed SO_4^{2-} under the conditions of lower deposition and delay recovery. Our analysis also indicates that the observed stream SO_4^{2-} is a good predictor for estimating the extent of recovery of modeled stream ANC in future (Eq. 9 in Table 2). No recovery was observed for soil base saturation of the simulated sites under the “preindustrial” scenario. Base cations continue to leach from the soil exchange complex despite the decrease in SO_4^{2-} and NO_3^- deposition to preindustrial conditions

due to the release of legacy SO_4^{2-} from soil to drainage waters as watersheds come to steady state with respect to lower atmospheric deposition. Soils with higher SO_4^{2-} adsorption capacity showed a greater degree of depletion of base saturation (Eq. 10 in Table 2).

Empirical relationship between ANC and target load

Model-projected stream ANC values under deposition reduction scenarios were estimated for the year 2050 and 2150 to determine the allowable load (TL) of $\text{SO}_4^{2-} + \text{NO}_3^-$ or $\text{NH}_4^+ + \text{NO}_3^- + \text{SO}_4^{2-}$ to achieve the fixed target ANC (i.e., $20 \text{ } \mu\text{mol}_\text{c}/\text{L}$) and the site-specific ANC (i.e., preindustrial ANC and preindustrial ANC– $20 \text{ } \mu\text{mol}_\text{c}/\text{L}$). Evaluating various stream chemistry measurements against TLs, we found that the observed stream ANC was a good predictor of TLs, indicating that the streams with lower ANC are more sensitive and will need a lower TL (required greater deposition reductions) to recover ANC to a given target value (e.g., Fig. 6 depicts the relationship for achieving the target ANC of $20 \text{ } \mu\text{mol}_\text{c}/\text{L}$, and Table 3 includes the relationships for other targets). For a given measured stream ANC, the atmospheric deposition load (TL) is lower to achieve the higher target ANC (e.g., preindustrial ANC) than to achieve the lower target ANC (e.g., preindustrial ANC– $20 \text{ } \mu\text{mol}_\text{c}/\text{L}$). Of the 30 study sites, 26 sites did not achieve the preindustrial target ANC by

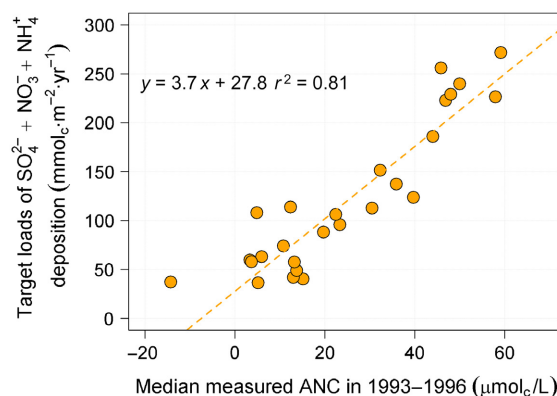


Fig. 6. Empirical relationships between the target loads of deposition and the median of observed ANC in 1993–1996 for 30 streams in GRSM to achieve the target ANC of $20 \text{ } \mu\text{mol}_\text{c}/\text{L}$ by year 2150 based on control on $\text{NH}_4^+ + \text{NO}_3^- + \text{SO}_4^{2-}$ deposition ($\text{mmol}_\text{c}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$).

Table 3. Linear regression equations for predicting the target loads of acidity as a function of median observed stream ANC in 1993–1996 (i.e., $TLs = \text{slope} \times \text{ANC} + \text{intercept}$) for various target years, target ANC, and deposition scenarios (coefficients are significant at $P < 0.001$).

Controlled deposition	Target year	Target ANC	Linear regression coefficients		
			Slope	Intercept	R^2
$\text{NH}_4^+ + \text{NO}_3^- + \text{SO}_4^{2-}$	2050	20 $\mu\text{mol}_c/\text{L}$	19.48	−370.61	0.91
		Preindustrial ANC	13.06	−919.96	0.52
		Preindustrial ANC−20 $\mu\text{mol}_c/\text{L}$	12.85	−427.06	0.63
	2150	20 $\mu\text{mol}_c/\text{L}$	3.70	27.79	0.81
		Preindustrial ANC	1.62	−72.49	0.45
		Preindustrial ANC−20 $\mu\text{mol}_c/\text{L}$	2.06	19.50	0.68
$\text{NO}_3^- + \text{SO}_4^{2-}$	2050	20 $\mu\text{mol}_c/\text{L}$	23.42	−453.73	0.9
		Preindustrial ANC	14.80	−1071.53	0.5
		Preindustrial ANC−20 $\mu\text{mol}_c/\text{L}$	15.10	−505.62	0.64
	2150	20 $\mu\text{mol}_c/\text{L}$	3.99	24.36	0.81
		Preindustrial ANC	1.53	−72.89	0.37
		Preindustrial ANC−20 $\mu\text{mol}_c/\text{L}$	2.18	17.56	0.66

2150 even under the condition in which atmospheric $\text{NH}_4^+ + \text{NO}_3^- + \text{SO}_4^{2-}$ is decreased to the natural preindustrial levels. As a result, we also considered a site-specific ANC target that is 20 $\mu\text{mol}_c/\text{L}$ below the estimated preindustrial levels (preindustrial ANC−20 $\mu\text{mol}_c/\text{L}$).

Parkwide target loads and exceedances

Empirical relationships developed between TLs and the observed stream site ANC (for the 30 simulated sites; Table 3) were applied to estimate TLs for the 387 sites based on their observed ANC during 1993–1996. To estimate the exceedance levels for the 387 stream sites, we initially calculated the site-specific current (2012–2014) atmospheric deposition by scaling the values based on the point observation of deposition at Elkmont/Look Rock using Weathers et al.'s (2006) model (Fig. 2). We then compared the current site-specific deposition with the projected TLs, and the exceedance levels were estimated for a given target ANC and a given future year. The number of park streams with the current atmospheric loads exceeding their calculated TLs indicates the extent to which streams are unable to achieve park management goals for recovery to the levels targeted to support the healthy aquatic biota. The cumulative frequency of streams that exceed TLs is shown in Fig. 7 for the two target endpoint (fixed and stream-specific) approaches and for the two recovery periods evaluated (2050 and 2150). These cumulative frequency diagrams represent two potential combinations of deposition

scenarios (one with NH_4^+ and one without NH_4^+) to examine the influence of the types of emissions sources contributing to acidification and recovery of park streams. This approach allows park resource managers to evaluate a CL that justifies an acceptable exceedance level. Implementing greater control on atmospheric deposition (which means selecting a lower TL) to the park would result in more streams achieving an ANC target (Fig. 7). With a longer period following the decreases in acid deposition (2150 vs. 2050), a smaller fraction of streams are projected not to meet the target ANC particularly at low TLs (Fig. 7). For example, keeping the current (2012–2014) deposition load (i.e., using the observed total deposition of $\text{NO}_3^- + \text{SO}_4^{2-}$ equal to 41.1 $\text{mmol}_c \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ at Elkmont/Look Rock monitoring stations and scaling to the other sites by Weathers et al.'s 2006 model) results in 17% of the 387 stream sites that are projected to fail to meet a target ANC of 20 $\mu\text{mol}_c/\text{L}$ by 2050, with this value only decreasing to 14% by 2150 (Fig. 7B). The projected TL needed for streams to achieve a target ANC is increased by shifting the target date from 2050 to 2150 because targeting to a later date provides more time for watershed to provide weathering materials from bedrock to neutralize legacy acidification and to allow for leaching of SO_4^{2-} that accumulated in the soil from the historical acid deposition. However, the fact that only 3% more park streams (from 17% exceedance to 14% exceedance) achieve the 20 $\mu\text{mol}_c/\text{L}$ ANC target by waiting for an additional 100 years (from 2050

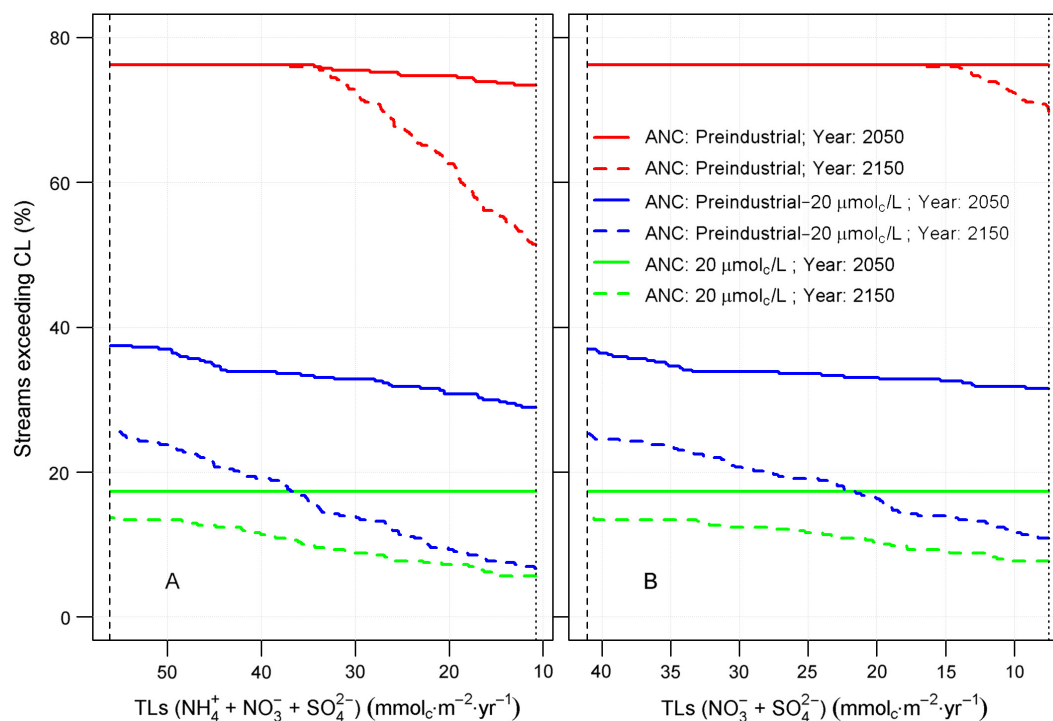


Fig. 7. Percentile of sampled streams (387 sites) with exceedance of atmospheric deposition from two target loads (TLs; $\text{mmol}_c\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) of (A) $\text{NH}_4^+ + \text{NO}_3^- + \text{SO}_4^{2-}$ and (B) $\text{NO}_3^- + \text{SO}_4^{2-}$ to achieve a fixed and two site-specific preindustrial target ANCs by years 2050 and 2150. Vertical lines indicate the current (i.e., dotted lines) and preindustrial (i.e., dashed lines) atmospheric deposition at Elkmont/Look Rock monitoring stations.

to 2150) indicates that if acid deposition is not reduced below the existing levels, the recovery of park streams from acidification effects will be very slow.

The TLs and deposition exceedances were also examined to determine the extent to which stream-specific ANC targets could be met at each projected loading level (Fig. 7). Model calculations indicate that if a $\text{NO}_3^- + \text{SO}_4^{2-}$ loading equal to the preindustrial deposition (i.e., $7.5 \text{ mmol}_c\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ at Elkmont/Look Rock monitoring stations) were achieved by the year 2030, 32% of the 387 sites would fail to achieve a theoretical target goal of preindustrial ANC ($20 \mu\text{mol}_c/\text{L}$) by year 2050. This rate of failure to achieve the ANC goal of preindustrial ANC ($20 \mu\text{mol}_c/\text{L}$) decreases to 11% by year 2150 (Fig. 7B).

Implementation of decreases in NH_4^+ deposition in addition to $\text{NO}_3^- + \text{SO}_4^{2-}$ does not appreciably accelerate the rate of watershed response from acidification over shorter timescales (e.g., 2050). Rather, the decreases in NH_4^+ deposition

are manifested over longer timescales. For example, if $\text{NO}_3^- + \text{SO}_4^{2-}$ deposition were reduced to levels equal to the preindustrial deposition, 76% and 70% of the 387 streams sites would be in exceedance of the preindustrial target ANC by 2050 and 2150, respectively (Fig. 7B). However, if $\text{NH}_4^+ + \text{NO}_3^- + \text{SO}_4^{2-}$ deposition were reduced to levels equivalent to the preindustrial deposition, then it is projected to result in an additional 3% and 19% decrease in the number of stream sites exceeding the target by year 2050 and 2150 (i.e., 73% and 51% of the streams being in exceedance of the preindustrial target ANC by year 2050 and 2150; Fig. 7A).

Even if natural background deposition (i.e., preindustrial levels) were possible to achieve, model calculations suggest that the recovery of ANC levels that is safe for healthy fisheries ($50 \mu\text{mol}_c/\text{L}$; USEPA 2009) would not be achieved for 39% of the 387 sampled stream sites by 2150. However, we found from hindcast simulations that 14 of the 30 simulated sites had preindustrial

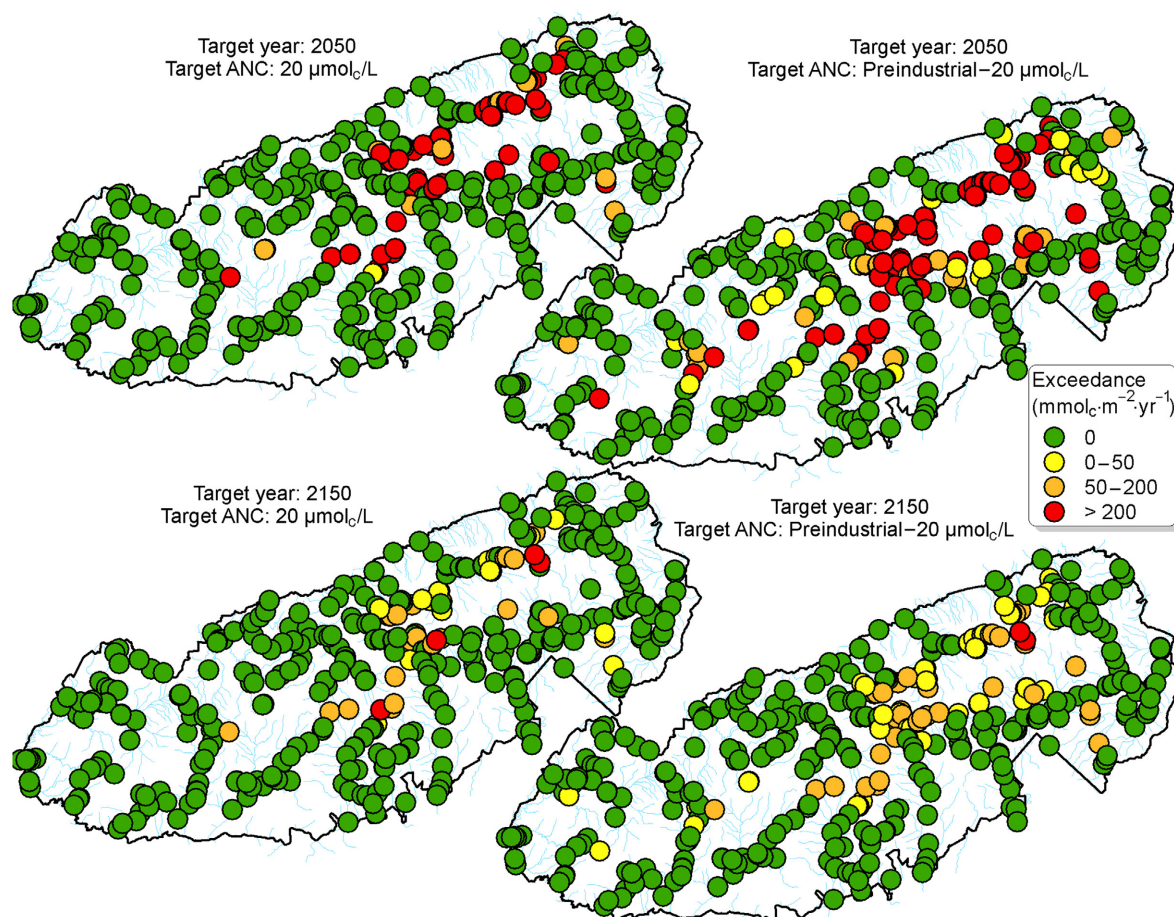


Fig. 8. Exceedance level of current $\text{NO}_3^- + \text{SO}_4^{2-}$ atmospheric deposition for 387 stream sites in GRSM. Exceedances were calculated for the year 2050 and 2150 using two targets for modeled stream ANC recovery of 20 $\mu\text{mol}_c/\text{L}$ and 20 $\mu\text{mol}_c/\text{L}$ less than the preindustrial ANC.

ANC below 50 $\mu\text{mol}_c/\text{L}$; therefore, expectation to increase the modeled stream ANC to a level that is greater than the values estimated for the period prior to the advent of acid deposition is likely not an attainable goal. Accordingly, we examined the recovery of streams to site-specific preindustrial targets in addition to the fixed ANC targets.

The spatial patterns of the condition of 387 park stream sites relative to achieving two potential ANC recovery goals are depicted for the years 2050 and 2150 (Fig. 8). The stream sites exceeding the TL largely depend on the target ANC. High-elevation sites in the east-central area of the GRSM are in exceedance for the target ANC of 20 $\mu\text{mol}_c/\text{L}$ (a target to protect the brook trout health) and the target ANC of 20 $\mu\text{mol}_c/\text{L}$ below the preindustrial ANC. A significant decrease in

the distribution of stream sites in exceedance to these targets was obtained over the longer simulation period (up to 2150) (Fig. 8).

DISCUSSION

ANC targets of acidification recovery

Restoration goals for streams in the GRSM likely include a return of the chemistry and biology of these ecosystems to preindustrial conditions. Bioassessment is one approach to evaluate the recovery of fisheries or other important groups of aquatic organisms from acidification stress. However, as biological monitoring data are limited, the recovery of streams is typically assessed by the analysis of biologically relevant chemical indicators such as pH, ANC, and Al

concentrations. Selected toxicity thresholds and an Index of Biological Integrity are presented in Appendix S1: Table S4. In this study, we used ANC as an indicator of acid–base status of the streams and evaluated the fixed and site-specific ANC targets for the determination of TLs. At levels below ANC of 0 $\mu\text{mol/L}$, streams are chronically acidic and cannot support the populations of brook trout (*Salvelinus fontinalis*) or other fish species and only acidophilic species are present (Bulger et al. 1998, USEPA 2009). Streams with ANC between 0 and 20 $\mu\text{mol/L}$ experience episodic acidification at the levels harmful to brook trout with the limited persistence of other tolerant fish species (USEPA 2009). The ANC target (20 $\mu\text{mol/L}$) is based on a study of 36 streams in the western Adirondacks, which concluded that this ANC value may be protective of brook trout health by guarding against the elevated concentrations of dissolved inorganic Al (Baldigo et al. 2009). This target value is also reported as a threshold for lethal effects on brook trout in a study of Virginia streams (Bulger et al. 1998). An ANC of 50 $\mu\text{mol/L}$ provides a suitable habitat for brook trout reproduction (Bulger et al. 1998).

Although the fixed ANC targets have the advantage of being well-defined values, they also have drawbacks. First, studies (e.g., Charles 1990), including this work (see *Results: Watershed response to historical deposition*), suggest that preindustrial ANC values were below 50 $\mu\text{mol/L}$ in highly sensitive stream sites. Goals to achieve the future ANC values that are greater than preindustrial values are therefore likely unattainable. Second, the depletion of exchangeable base cations and the accumulation of SO_4^{2-} in soil associated with the historical acid deposition compromise the ability of a watershed to achieve preindustrial ANC values over policy-relevant time periods (e.g., decades). Finally, in some regions (North America and northern Europe), a compensatory increase in naturally occurring organic acids appears to be occurring in response to the decreases in acid deposition (Driscoll et al. 2007, Driscoll et al. 2016, Monteith et al. 2007, Fakhraei and Driscoll 2015). This response limits the ANC recovery that may be achievable in response to the decreases in acid deposition.

To attempt to address these limitations, we also examined the recovery of streams and developed the target loads of acidity based on two

site-specific ANC targets: a simulated preindustrial ANC (i.e., simulated ANC in the year 1850) and an ANC of 20 $\mu\text{mol/L}$ below preindustrial estimates. These targets are derived from model hindcasts for individual study sites of ANC prior to the increases in acid deposition (~1850). These site-specific ANC targets attempt to address the natural variability in surface water ANC due to watershed biophysical characteristics and may be a useful alternative to the fixed ANC values, although there is uncertainty associated with hindcast projections of preindustrial ANC. The empirical relationships that developed between TLs and the measured stream ANC for the site-specific target ANCs are not as strong as the correlations that were developed for the fixed target ANC (Table 3). This is likely due to the uncertainties that are embedded in the hindcasts of preindustrial ANC targets. Uncertainties in these estimates are due to a variety of factors, but primarily uncertainty in the estimates of historical deposition, soil SO_4^{2-} adsorption capacity, and Ca^{2+} weathering rate. Park managers are interested in determining the amount of deposition reductions theoretically needed to return streams to their preindustrial conditions; therefore, developing the critical loads of acidity based on the site-specific preindustrial ANC targets provides basis for these decisions.

Effectiveness of control in emissions

Observed trends in atmospheric deposition at both a low- and a high-elevation site in the GRSM (i.e., Elkmont and Noland Divide deposition stations, respectively) revealed significant decreases in the deposition of SO_4^{2-} and NO_3^- . These trends indicate the effectiveness of controls in emissions of acidifying compounds (SO_2 and NO_x) on the decreases in acid deposition. However, a few (nine of 42) streams in the park demonstrated the improvements in ANC, concurrent with the significant decreases in acid deposition at both low- and high-elevation deposition monitoring sites. The slow pace of recovery or even continued acidification of stream sites in the GRSM is most likely due to the desorption of previously adsorbed soil SO_4^{2-} (Rice et al. 2014) and the long-term depletion of exchangeable base cations from the soil (Huntington et al. 2000, Bailey et al. 2005, Lawrence et al. 2015). The depletion of base cations from forest soils occurs when the rates of

leaching base cation exceed the rates of resupply from mineral weathering and atmospheric inputs (Likens et al. 1996).

It is important to consider what types of emissions reductions (and consequently the deposition reduction) would provide the greatest effectiveness in promoting stream recovery. Regression models developed for controls on $\text{NH}_4^+ + \text{NO}_3^- + \text{SO}_4^{2-}$ (Table 3) indicate that for a given measured ANC, higher values of $\text{NH}_4^+ + \text{NO}_3^- + \text{SO}_4^{2-}$ deposition will achieve the same target ANC than those of $\text{NO}_3^- + \text{SO}_4^{2-}$ deposition. The influence of controls in NH_4^+ deposition in addition to $\text{NO}_3^- + \text{SO}_4^{2-}$ reduction scenarios is manifested over long timescales. For a target year of 2050, ANC recovery is not appreciably different under a $\text{NH}_4^+ + \text{NO}_3^- + \text{SO}_4^{2-}$ control scenario compared with controls for $\text{NO}_3^- + \text{SO}_4^{2-}$ only (Fig. 7).

The greater response of modeled stream ANC in response to the decrease in NH_4^+ deposition rather than SO_4^{2-} deposition suggests that decreases in NH_3 emissions (or NH_4^+ deposition) would be more effective than the equivalent reductions in SO_2 emissions (or SO_4^{2-} deposition) in terms of GRSM stream recovery over the long term. Although NH_3 is an alkaline component in the atmosphere, when it is deposited nitrification can occur and this input contributes to the acidification of soil and water (van Breemen et al. 1983, Asman et al. 1998, Driscoll et al. 2001).

Preindustrial “background” ANC and historical acidification

Historical model simulations indicated a wide range of variability in preindustrial ANC (~1850) for study sites in the GRSM. Several factors can control this variability, including the variation in rates of mineral weathering, internal bedrock source of sulfur (pyrite), inputs of naturally occurring organic acids (Cook et al. 1994, Driscoll et al. 2001).

Soil acidification due to historical acidic deposition was evident at all simulated sites. The depletion in soil base saturation in response to the historical deposition is attributed to the enhanced leaching of base cations from soil exchange sites due to the elevated concentrations of SO_4^{2-} and NO_3^- from the historical atmospheric deposition (Driscoll et al. 2001, Warby et al. 2009). However, because of the heterogeneity in SO_4^{2-} adsorption

capacity and N retention among the study watersheds, the magnitude of historical impacts from the elevated atmospheric deposition on the modeled stream ANC is highly variable across the GRSM landscape.

Influence of watershed characteristics on stream recovery

The extent of future increases in ANC is also highly dependent on the characteristics of the watershed, particularly the SO_4^{2-} adsorption capacity of soil and the N retention of the watershed. Watersheds with low capacity to adsorb SO_4^{2-} and the limited N retention were found to be relatively responsive to the variation in atmospheric deposition. Further control on SO_4^{2-} and/or NO_3^- deposition increases ANC of the stream water draining the watershed due to the decreases in SO_4^{2-} and NO_3^- concentrations in stream water. In contrast, watersheds with high SO_4^{2-} adsorption capacity and the limited N retention are relatively unresponsive to the decreases in SO_4^{2-} deposition, resulting in the limited increase in modeled stream ANC. In these watersheds, although the decreases in NO_3^- deposition theoretically should improve ANC, the associated increases in pH of soil solution facilitate the desorption of accumulated SO_4^{2-} from soil, which offsets the increases in modeled stream ANC. In watersheds with high SO_4^{2-} adsorption capacity and high N retention, the ecosystem is strongly buffered against the decreases in SO_4^{2-} and NO_3^- deposition and does not show a significant increase in the modeled stream ANC. These watersheds are relatively insensitive, typically have higher ANC ($>50 \mu\text{mol/L}$), and are not responsive to the decreases in acid deposition.

Spruce-fir forests, which dominate vegetation at high elevation (above 1890 m; Jenkins 2007) in the GRSM, have shown symptoms of N saturation (Nodvin et al. 1995, Van Miegroet et al. 2001). Nitrogen saturation occurs when N inputs to an ecosystem are in excess of the N retention capacity of that ecosystem (Aber et al. 1989). Based on the ranking system for N saturation proposed by Aber et al. (1989), high-elevation spruce-fir forests in the GRSM have been designated at an advanced stage (stage 2) of N saturation, which indicates the limited N retention by the ecosystem (Nodvin et al. 1995, Van Miegroet

et al. 2001). As a result, high-elevation watersheds in the GRSM are responsive to the decrease in atmospheric NO_3^- deposition in contrast to the ecosystems in other regions that more strongly retain N (Stoddard 1994).

Our study indicated that streams in the east-central portion of the park are currently in exceedance of the TLs designated for recovery by 2050 (Fig. 8). This area of the park is not only exposed to the highest atmospheric deposition due to higher elevations, but also characterized by lower soil SO_4^{2-} adsorption capacity, which allows for the acidification of streams. However, a substantial number of these streams would not be in exceedance if the target year of recovery is delayed to 2150, indicating that acid-impacted GRSM streams will have the limited response to $\text{NO}_3^- + \text{SO}_4^{2-}$ deposition control and need more time to be recovered.

Irreversibility of adsorbed sulfate

Based on the model simulations, the recovery of GRSM streams to conditions that would be suitable for an intact fishery would take decades, if not centuries. This long delay in watershed recovery is largely due to the large pools of SO_4^{2-} that have accumulated in soil under the historical acid deposition (Rice et al. 2014). Note that model calculations of watershed recovery assume a worst-case condition that adsorbed SO_4^{2-} is completely available to be released under the decreases in deposition and the delayed increases in ANC. If some fraction of SO_4^{2-} is irreversibly adsorbed, recovery would be more rapid. For example, Harrison et al. (1989) postulated that on average 36% of adsorbed SO_4^{2-} was retained irreversibly in subsoils from forest sites in United States, Canada, and Norway. If atmospheric SO_4^{2-} deposition was permanently retained in soil, this condition would allow for more rapid recovery than would be achieved for completely reversible SO_4^{2-} adsorption. Unfortunately, little is known about the reversibility of soil SO_4^{2-} adsorption.

Regional implications

This study should provide insights into the response of other forests in the Southern Appalachian Mountains to the decreases in acid deposition. This region is a highly valued resource, with several protected areas including

Class I wilderness areas, national parks, and national forests (Fig. 1). In addition to the GRSM, considerable research has been conducted in nearby Shenandoah National Park (Webb et al. 2004, Deviney et al. 2006). The montane landscape and heterogeneous soils of the GRSM are typical of the Southern Appalachian Mountains and pose challenges to model applications. There are climatic and edaphic variations across the region that influence the recovery from acid deposition (Rice et al. 2014). Nevertheless, a useful step would be to build on analysis of this study and make projections of the response of the broader Southern Appalachian Mountains to the anticipated changes in air pollution.

CONCLUSIONS

Streams at the GRSM (1993–2014) have not experienced strong recent trends in ANC recovery (only nine of 42 sites have significant increases), despite the marked recent decreases in SO_4^{2-} and NO_3^- deposition. This lack of recovery of the chemistry of acidified streams in the GRSM is likely due to soil conditions characteristic of this area, which have previously adsorbed soil SO_4^{2-} and have experienced depletion of exchangeable base cation concentrations associated with the historical acid deposition. Our model calculations illustrate that at the GRSM, the most important biophysical factors that influence the recovery of streams are SO_4^{2-} adsorption capacity, N retention, depletion of exchangeable base cations of soils, and the level of atmospheric deposition. High-elevation spruce-fir forests at GRSM are in an advanced stage of N saturation as a result of limited N retention and elevated N deposition. Similar to other national parks in United States (Baron et al. 2011), atmospheric deposition in the GRSM increases markedly with the increases in elevation, making streams at high elevation at greater risk of acidification. Furthermore, soils at high-elevation sites with low SO_4^{2-} adsorption capacity are more susceptible to acidification by elevated SO_4^{2-} deposition; however, those sites are also more responsive to the decreases in atmospheric loads. The extent of recovery of the streams of the GRSM from acidification is projected to increase if all three components of acid deposition (SO_4^{2-} , NO_3^- , and NH_4^+) are reduced

in the future. Modeling demonstrates that targeting a later date for the recovery of park streams allows a greater number of streams to meet goals (target ANC levels). Implementing various control scenarios of SO_4^{2-} , NO_3^- , and NH_4^+ deposition suggests that the future increases in modeled stream ANC per equivalent decrease in NH_4^+ deposition are somewhat greater than those per equivalent decreases in SO_4^{2-} or NO_3^- deposition. This pattern suggests that control on NH_4^+ deposition could be a focus of future air pollution control strategies to achieve greater recovery of streams. We conducted a TL analysis considering two approaches for target ANC values. A fixed ANC target of $20 \mu\text{mol}_\text{c}/\text{L}$ is based on the previously established relationships between stream chemistry and the recovery of biotic life in streams. We also selected the stream-specific target ANC values based on the inherent site sensitivity by hindcasting preindustrial ANC values of individual stream. There may be some advantages of using a stream-specific ANC target because in acid-sensitive sites like GRSM, preindustrial ANC values may be lower than some fixed ANC targets (e.g., $50 \mu\text{mol}_\text{c}/\text{L}$) used to set the policy goals for regional or national recovery of large numbers of streams (USEPA 2009), but there is also uncertainty in determining preindustrial ANC values. Our analyses reveal that unlike streams in other areas of the northeastern United States, such as the Adirondacks, most GRSM watersheds retain the majority of historically deposited S, with relatively low SO_4^{2-} leaching to the streams. This accumulation of SO_4^{2-} in soil delays the recovery of the streams and illustrates that a combination of emissions reductions and patience will be needed to allow the recovery of the most sensitive park streams.

ACKNOWLEDGMENTS

We would like to thank E. William Schweiger, Joe DeVivo, and two anonymous reviewers for providing constructive comments on this manuscript. We also thank Donna B. Schwede of the USEPA for providing the estimates of wet and dry deposition from atmospheric model (CMAQ) simulations. Support for this work was provided by the National Park Service through a cooperative agreement H54711000900015 with Syracuse University.

LITERATURE CITED

- Aber, J. D. 1992. Nitrogen cycling and nitrogen saturation in temperate forest ecosystems. *Trends in Ecology and Evolution* 7:220–224.
- Aber, J. D., and C. A. Federer. 1992. A generalized, lumped-parameter model of photosynthesis, evapotranspiration and net primary production in temperate and boreal forest ecosystems. *Oecologia* 92:463–474.
- Aber, J. D., K. J. Nadelhoffer, P. Steudler, and J. M. Melillo. 1989. Nitrogen saturation in northern forest ecosystems. *BioScience* 39:378–386.
- Aber, J. D., S. V. Ollinger, and C. T. Driscoll. 1997. Modeling nitrogen saturation in forest ecosystems in response to land use and atmospheric deposition. *Ecological Modelling* 101:61–78.
- Asman, W. A., M. A. Sutton, and J. K. Schjørring. 1998. Ammonia: emission, atmospheric transport and deposition. *New Phytologist* 139:27–48.
- Bailey, S. W., S. B. Horsley, and R. P. Long. 2005. Thirty years of change in forest soils of the Allegheny Plateau, Pennsylvania. *Soil Science Society of America Journal* 69:681–690.
- Baldigo, B. P., G. B. Lawrence, R. W. Bode, H. A. Simonin, K. M. Roy, and A. J. Smith. 2009. Impacts of acidification on macroinvertebrate communities in streams of the western Adirondack Mountains, New York, USA. *Ecological Indicators* 9:226–239.
- Baron, J. S., C. T. Driscoll, J. L. Stoddard, and E. E. Richer. 2011. Empirical critical loads of atmospheric nitrogen deposition for nutrient enrichment and acidification of sensitive US lakes. *BioScience* 61:602–613.
- Blett, T. F., J. A. Lynch, L. H. Pardo, C. Huber, R. Haeuber, and R. Pouyat. 2014. FOCUS: a pilot study for national-scale critical loads development in the United States. *Environmental Science & Policy* 38:225–236.
- Bobbink, R., and J.-P. Hettelingh. 2010. Review and revision of empirical critical loads and dose-response relationships. *Proceedings of an expert workshop, Noordwijkerhout, The Netherlands*.
- Bowen, J. L., and I. Valiela. 2001. Historical changes in atmospheric nitrogen deposition to Cape Cod, Massachusetts, USA. *Atmospheric Environment* 35:14.
- Brimblecombe, P., and D. H. Stedman. 1982. Historical evidence for a dramatic increase in the nitrate component of acid rain. *Nature* 298:460–462.
- Bulger, A., J. Cosby, and R. Webb. 1998. Acid rain: current and projected status of cold water fish communities in the southeastern US in the context of continued acid deposition. *Trout Unlimited, Arlington, Virginia, USA*.

- Burns, D. A., T. Blett, R. Haeuber, and L. H. Pardo. 2008. Critical loads as a policy tool for protecting ecosystems from the effects of air pollutants. *Frontiers in Ecology and the Environment* 6: 156–159.
- Burtraw, D., and S. J. F. Szambelan. 2009. US emissions trading markets for SO₂ and NO_x. Resources for the Future Discussion Paper, Washington, D.C., USA.
- Cai, M., J. S. Schwartz, R. B. Robinson, S. E. Moore, and M. A. Kulp. 2010. Long-term effects of acidic deposition on water quality in a high-elevation Great Smoky Mountains National Park Watershed: use of an ion input-output budget. *Water, Air, and Soil Pollution* 209:143–156.
- Cai, M., A. M. Johnson, J. S. Schwartz, S. E. Moore, and M. A. Kulp. 2012. Soil acid-base chemistry of a high-elevation forest watershed in the Great Smoky Mountains National Park: influence of acidic deposition. *Water, Air, and Soil Pollution* 223:289–303.
- Charles, D. F. 1990. Effects of acidic deposition on North American lakes: palaeolimnological evidence from diatoms and chrysophytes. *Philosophical Transactions of the Royal Society of London Series B: Biological Sciences* 327:403–412.
- Church, M. R., et al. 1989. Future effects of long-term sulfur deposition on surface water chemistry in the Northeast and Southern Blue Ridge Province: results of the DDRP. EPA/600/3-89/061. United States Environmental Protection Agency, Corvallis, Oregon, USA.
- Cook, R. B., J. W. Elwood, R. R. Turner, M. A. Bogle, P. J. Mulholland, and A. V. Palumbo. 1994. Acid-base chemistry of high-elevation streams in the Great Smoky Mountains. *Water, Air, and Soil Pollution* 72:331–356.
- Deviney, F. A., K. C. Rice, and G. M. Hornberger. 2006. Time series and recurrence interval models to predict the vulnerability of streams to episodic acidification in Shenandoah National Park, Virginia. *Water Resources Research* 42:W09405.
- Driscoll, C. T., M. D. Lehtinen, and T. J. Sullivan. 1994. Modeling the acid-base chemistry of organic solutes in Adirondack, NY, lakes. *Water Resources Research* 30:297–306.
- Driscoll, C. T., G. B. Lawrence, A. J. Bulger, T. J. Butler, C. S. Cronan, C. Eagar, K. F. Lambert, G. E. Likens, J. L. Stoddard, and K. C. Weathers. 2001. Acidic deposition in the northeastern United States: sources and inputs, ecosystem effects, and management strategies. *BioScience* 51:180–198.
- Driscoll, C. T., K. M. Driscoll, K. M. Roy, and J. Dukett. 2007. Changes in the chemistry of lakes in the Adirondack region of New York following declines in acidic deposition. *Applied Geochemistry* 22:1181–1188.
- Driscoll, C. T., E. B. Cowling, P. Grennfelt, J. Galloway, and R. Dennis. 2010. Integrated assessment of ecosystem effects of atmospheric deposition: lessons available to be learned. *EM Magazine* November 2010:6–13.
- Driscoll, C. T., J. J. Buonocore, J. I. Levy, K. F. Lambert, D. Burtraw, S. B. Reid, H. Fakhraei, and J. Schwartz. 2015. US power plant carbon standards and clean air and health co-benefits. *Nature Climate Change* 5:535–540.
- Driscoll, C. T., K. M. Driscoll, H. Fakhraei, and K. Civerolo. 2016. Long-term temporal trends and spatial patterns in the acid-base chemistry of lakes in the Adirondack region of New York in response to decreases in acidic deposition. *Atmospheric Environment*. <http://dx.doi.org/10.1016/j.atmosenv.2016.08.034>
- Driscoll, C. T., K. M. Driscoll, K. M. Roy, and M. J. Mitchell. 2003. Chemical response of lakes in the Adirondack region of New York to declines in acidic deposition. *Environmental Science & Technology* 37:2036–2042.
- Dupont, J., T. A. Clair, C. Gagnon, D. S. Jeffries, J. S. Kahl, S. J. Nelson, and J. M. Peckenhams. 2005. Estimation of critical loads of acidity for lakes in northeastern United States and eastern Canada. *Environmental Monitoring and Assessment* 109:275–292.
- Dzombak, D. A., and F. M. Morel. 1990. Surface complexation modeling: hydrous ferric oxide. John Wiley & Sons, New York, New York, USA.
- Emmott, R. G., N. Murdock, J. Ranney, and P. Flaherty. 2005. Appalachian highlands inventory and monitoring network vital signs monitoring plan. National Park Service, Asheville, North Carolina, USA, 207 pp. https://science.nature.nps.gov/im/monitor/plans/APHN_MonitoringPlan.pdf
- Fakhraei, H. 2016. Modeling the effects of acid deposition and natural organic acids on surface waters. Dissertations – ALL. Paper 432. Syracuse University, Syracuse, New York, USA.
- Fakhraei, H., and C. T. Driscoll. 2015. Proton and aluminum binding properties of organic acids in surface waters of the northeastern US. *Environmental Science & Technology* 49:2939–2947.
- Fakhraei, H., C. T. Driscoll, P. Selvendiran, J. V. DePinto, J. Bloomfield, S. Quinn, and H. C. Rowell. 2014. Development of a total maximum daily load (TMDL) for acid-impaired lakes in the Adirondack region of New York. *Atmospheric Environment* 95:277–287.
- Fenn, M. E., T. G. Huntington, S. B. McLaughlin, C. Eagar, A. Gomez, and R. B. Cook. 2006. Status of soil acidification in North America. *Journal of Forest Science* 52:3–13.
- Galloway, J. N., G. E. Likens, W. C. Keene, and J. M. Miller. 1982. The composition of precipitation in

- remote areas of the world. *Journal of Geophysical Research: Oceans* (1978–2012) 87:8771–8786.
- Gbondo-Tugbawa, S. S., C. T. Driscoll, J. D. Aber, and G. E. Likens. 2001. Evaluation of an integrated biogeochemical model (PnET-BGC) at a northern hardwood forest ecosystem. *Water Resources Research* 37:1057–1070.
- Gran, G. 1952. Determination of the equivalence point in potentiometric titrations. Part II. *Analyst* 77:661–671.
- Granat, L., H. Rodhe, and R. O. Hallberg. 1976. The global sulphur cycle. *Ecological Bulletins* 22: 89–134.
- Harrison, R. B., D. W. Johnson, and D. E. Todd. 1989. Sulfate adsorption and desorption reversibility in a variety of forest soils. *Journal of Environmental Quality* 18:419–426.
- Henriksen, A., J. Kämäri, M. Posch, and A. Wilander. 1992. Critical loads of acidity: Nordic surface waters. *Ambio* 21:356–363.
- Hirsch, R. M., and J. R. Slack. 1984. A nonparametric trend test for seasonal data with serial dependence. *Water Resources Research* 20:727–732.
- Hirsch, R. M., J. R. Slack, and R. A. Smith. 1982. Techniques of trend analysis for monthly water quality data. *Water Resources Research* 18:107–121.
- Huntington, T. G., R. P. Hooper, C. E. Johnson, B. T. Aulenbach, R. Cappellato, and A. E. Blum. 2000. Calcium depletion in a southeastern United States forest ecosystem. *Soil Science Society of America Journal* 64:1845–1858.
- Husar, R. B., and J. M. Holloway. 1982. Sulfur and nitrogen over North America. *Ecological Effects of Acid Deposition*. Report PM 1636:95–115.
- Janssen, P. H. M., and P. S. C. Heuberger. 1995. Calibration of process-oriented models. *Ecological Modelling* 83:55–66.
- Jenkins, M. A. 2007. Vegetation communities of Great Smoky Mountains National Park. *Southeastern Naturalist* 6:35–56.
- Johnson, D. W., and S. E. Lindberg. 2013. Atmospheric deposition and forest nutrient cycling: a synthesis of the integrated forest study. Vol 91. Springer Science & Business Media, New York, New York, USA.
- Johnson, D. W., and D. E. Todd. 1990. Nutrient cycling in forests of Walker Branch watershed, Tennessee: roles of uptake and leaching in causing soil changes. *Journal of Environmental Quality* 19:97–104.
- Johnson, D. W., W. T. Swank, and J. M. Vose. 1993. Simulated effects of atmospheric sulfur deposition on nutrient cycling in a mixed deciduous forest. *Biogeochemistry* 23:169–196.
- Jordan, T. E., and D. E. Weller. 1996. Human contributions to terrestrial nitrogen flux: assessing the sources and fates of anthropogenic fixed nitrogen. *BioScience* 46:655–664.
- Josephson, D. C., J. M. Robinson, J. Chiotti, K. J. Jirka, and C. E. Kraft. 2014. Chemical and biological recovery from acid deposition within the Honnedaga Lake watershed, New York, USA. *Environmental Monitoring and Assessment* 186:4391–4409.
- Joslin, J. D., J. M. Kelly, and H. Van Miegroet. 1992. Soil chemistry and nutrition of North American spruce-fir stands: evidence for recent change. *Journal of Environmental Quality* 21:12–30.
- Kahl, J. S., et al. 2004. Have U.S. surface waters responded to the 1990 Clean Air Act Amendments? *Environmental Science and Technology* 38: 484A–490A.
- Lawrence, G. B., P. W. Hazlett, I. J. Fernandez, R. Ouimet, S. W. Bailey, W. C. Shortle, K. T. Smith, and M. R. Antidormi. 2015. Declining acidic deposition begins reversal of forest-soil acidification in the northeastern US and eastern Canada. *Environmental Science and Technology* 49:13103–13111.
- Lehmann, C. M. B., V. C. Bowersox, and S. M. Larson. 2005. Spatial and temporal trends of precipitation chemistry in the United States, 1985–2002. *Environmental Pollution* 135:347–361.
- Likens, G. E., C. T. Driscoll, and D. C. Buso. 1996. Long-term effects of acid rain: response and recovery of a forest ecosystem. *Science* 272:244–246.
- Martin, L. A., P. J. Mulholland, J. R. Webster, and H. M. Valett. 2001. Denitrification potential in sediments of headwater streams in the southern Appalachian Mountains, USA. *Journal of the North American Benthological Society* 20:505–519.
- McCracken, R. J., R. E. Shanks, and E. E. C. Clebsch. 1962. Soil morphology and genesis at higher elevations of the Great Smoky Mountains. *Soil Science Society of America Journal* 26:384–388.
- McNulty, S. G., E. C. Cohen, J. A. M. Myers, T. J. Sullivan, and H. Li. 2007. Estimates of critical acid loads and exceedances for forest soils across the conterminous United States. *Environmental Pollution* 149:281–292.
- Monteith, D. T., et al. 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature* 450:537–540.
- Neff, K. J., J. S. Schwartz, S. E. Moore, and M. A. Kulp. 2013. Influence of basin characteristics on base-flow and stormflow chemistry in the Great Smoky Mountains National Park, USA. *Hydrological Processes* 27:2061–2074.
- Nicholas, N. S., and P. S. White. 1985. The effect of balsam woolly aphid infestation on fuel levels in spruce-fir forests of Great Smoky Mountains National Park. Uplands Field Research Laboratory, Atlanta, Georgia, USA.

- Nicholas, N. S., S. M. Zedaker, and C. Eagar. 1992. A comparison of overstory community structure in three southern Appalachian spruce-fir forests. *Bulletin of the Torrey Botanical Club* 119:316–332.
- Nilsson, J., and P. Grennfelt. 1988. Critical loads for sulphur and nitrogen. UNECE/Nordic Council workshop report, Skokloster, Sweden. March 1988. Nordic Council of Ministers, Copenhagen, Denmark. 418 pp.
- Nizich, S. V., D. Misenheimer, T. E. Pierce, A. Pope, and P. Carlson. 1996. National air pollutant emission trends, 1900–1995. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, USA.
- Nodvin, S. C., C. T. Driscoll, and G. E. Likens. 1986. The effect of pH on sulfate adsorption by a forest soil. *Soil Science* 142:69–75.
- Nodvin, S. C., C. T. Driscoll, and G. E. Likens. 1988. Soil processes and sulfate loss at the Hubbard Brook Experimental Forest. *Biogeochemistry* 5:185–200.
- Nodvin, S. C., H. Van Miegroet, S. E. Lindberg, N. S. Nicholas, and D. W. Johnson. 1995. Acidic deposition, ecosystem processes, and nitrogen saturation in a high elevation Southern Appalachian Watershed. *Water, Air, and Soil Pollution* 85:1647–1652.
- Ouimet, R., P. A. Arp, S. A. Watmough, J. Aherne, and I. DeMerchant. 2006. Determination and mapping critical loads of acidity and exceedances for upland forest soils in eastern Canada. *Water, Air, and Soil Pollution* 172:57–66.
- Pardo, L. H., et al. 2011. Effects of nitrogen deposition and empirical nitrogen critical loads for ecoregions of the United States. *Ecological Applications* 21:3049–3082.
- Porter, E., T. Blett, D. U. Potter, and C. Huber. 2005. Protecting resources on federal lands: implications of critical loads for atmospheric deposition of nitrogen and sulfur. *BioScience* 55:603–612.
- Pourmokhtarian, A., C. T. Driscoll, J. L. Campbell, and K. Hayhoe. 2012. Modeling potential hydrochemical responses to climate change and increasing CO₂ at the Hubbard Brook Experimental Forest using a dynamic biogeochemical model (PnET-BGC). *Water Resources Research* 48:W07514.
- Pyle, C. 1988. The type and extent of anthropogenic vegetation disturbance in the Great Smoky Mountains before National Park Service acquisition. *Castanea* 53:183–196.
- R Core Team. 2016. R: a language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. <https://www.R-project.org/>
- Rice, K. C., T. M. Scanlon, J. A. Lynch, and B. J. Cosby. 2014. Decreased atmospheric sulfur deposition across the southeastern US: When will watersheds release stored sulfate? *Environmental Science and Technology* 48:10071–10078.
- Sale, M. J., P. R. Kaufmann, H. I. Jager, J. M. Coe, K. A. Cougan, A. J. Kinney, M. E. Mitch, and W. S. Overton. 1988. Chemical characteristics of streams in the mid-Atlantic and southeastern United States. Volume II: streams sampled, descriptive statistics, and compendium of physical and chemical data. EPA/600/3-88/021b. U.S. Environmental Protection Agency, Washington, D.C., USA.
- Schwartz, J. S., M. Cai, M. A. Kulp, S. E. Moore, B. Nichols, and C. Parker. 2014. Biological effects of stream water quality on aquatic macroinvertebrates and fish communities within Great Smoky Mountains National Park. Natural Resource Report NPS/GRSM/NRR—2014/778. National Park Service, Fort Collins, Colorado, USA.
- Schwede, D. B., and G. G. Lear. 2014. A novel hybrid approach for estimating total deposition in the United States. *Atmospheric Environment* 92:207–220.
- Sen, P. K. 1968. On a class of aligned rank order tests in two-way layouts. *Annals of Mathematical Statistics* 39:1115–1124.
- Shubzda, J., S. E. Lindberg, C. T. Garten, and S. C. Nodvin. 1995. Elevational trends in the fluxes of sulphur and nitrogen in throughfall in the southern Appalachian mountains: some surprising results. *Water, Air, and Soil Pollution* 85:2265–2270.
- Stoddard, J. L. 1994. Long-term changes in watershed retention of nitrogen. Pages 223–284 in L. A. Baker, editor. *Environmental chemistry of lakes and reservoirs*. American Chemical Society, Washington, D.C., USA.
- Sullivan, T. J., B. J. Cosby, W. A. Jackson, K. U. Snyder, and A. T. Herlihy. 2011. Acidification and prognosis for future recovery of acid-sensitive streams in the southern Blue Ridge Province. *Water, Air, and Soil Pollution* 219:11–26.
- Sullivan, T. J., B. J. Cosby, C. T. Driscoll, T. C. McDonnell, A. T. Herlihy, and D. A. Burns. 2012. Target loads of atmospheric sulfur and nitrogen deposition for protection of acid sensitive aquatic resources in the Adirondack Mountains, New York. *Water Resources Research* 48:W01547:16 pp.
- TDEC. 2010. Proposed total maximum load (TMDL) for low pH in the Great Smoky Mountains National Park. Tennessee Department of Environment and Conservation, Nashville, Tennessee, USA.
- USEPA. 2009. Risk and Exposure Assessment for Review of the Secondary National Ambient Air

- Quality Standards for Oxides of Nitrogen and Oxides of Sulfur.
- USEPA. 2015. Clean power plan for existing power plants. Policies and Guidance. <http://www2.epa.gov/cleanpowerplan/clean-power-plan-existing-power-plants>
- Vadeboncoeur, M. A., S. P. Hamburg, R. D. Yanai, and J. D. Blum. 2014. Rates of sustainable forest harvest depend on rotation length and weathering of soil minerals. *Forest Ecology and Management* 318:194–205.
- van Breemen, N., J. Mulder, and C. T. Driscoll. 1983. Acidification and alkalization of soils. *Plant and Soil* 75:283–308.
- Van Miegroet, H., et al. 2001. Is there synchronicity in nitrogen input and output fluxes at the Noland Divide Watershed, a small N-saturated forested catchment in the Great Smoky Mountains National Park? Conference Proceedings: Optimizing Nitrogen Management in Food and Energy Production and Environmental Protection: Proceedings of the 2nd International Nitrogen Conference on Science and Policy. *Scientific World Journal* 1(S2):480–492. <http://dx.doi.org/10.1100/tsw.2001.384>
- Van Miegroet, H., P. T. Moore, C. E. Tewksbury, and N. S. Nicholas. 2007. Carbon sources and sinks in high-elevation spruce–fir forests of the southeastern US. *Forest Ecology and Management* 238: 249–260.
- Warby, R. A. F., C. E. Johnson, and C. T. Driscoll. 2009. Continuing acidification of organic soils across the northeastern USA: 1984–2001. *Soil Science Society of America Journal* 73:274–284.
- Weathers, K. C., S. M. Simkin, G. M. Lovett, and S. E. Lindberg. 2006. Empirical modeling of atmospheric deposition in mountainous landscapes. *Ecological Applications* 16:1590–1607.
- Webb, J. R., B. J. Cosby, F. A. Deviney, J. N. Galloway, S. W. Maben, and A. J. Bulger. 2004. Are brook trout streams in western Virginia and Shenandoah National Park recovering from acidification? *Environmental Science and Technology* 38: 4091–4096.
- Whittaker, R. H. 1956. Vegetation of the Great Smoky Mountains. *Ecological Monographs* 26: 1–80.
- Zhou, Q., C. T. Driscoll, S. E. Moore, M. A. Kulp, J. R. Renfro, J. S. Schwartz, M. Cai, and J. A. Lynch. 2015. Developing critical loads of nitrate and sulfate deposition to watersheds of the Great Smoky Mountains National Park, USA. *Water, Air, and Soil Pollution* 226:1–16.

SUPPORTING INFORMATION

Additional Supporting Information may be found online at: <http://onlinelibrary.wiley.com/doi/10.1002/ecs2.1466/supinfo>