Simulated Effects of Sulfur Deposition on Nutrient Cycling in Class I Wilderness Areas

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We predicted the effects of sulfate (SO_4) deposition on wilderness areas designated as Class I air quality areas in western North Carolina using a nutrient cycling model (NuCM). We used three S deposition simulations: current, 50% decrease, and 100% increase. We measured vegetation, forest floor, and root biomass and collected soil, soil solution, and stream water samples for chemical analyses. We used the closest climate stations and atmospheric deposition stations to parameterize NuCM. The areas were: Joyce Kilmer (JK), Shining Rock (SR), and Linville Gorge (LG). They differ in soil acidity and nutrients, and soil solution and stream chemistry. Shining Rock and LG have lower soil solution base cation and higher acidic ion concentrations than JK. For SR and LG, the soil solution Ca/Al molar ratios are currently 0.3 in the rooting zone (A horizon), indicating Al toxicity. At SR, the simulated Ca/Al ratio increased to slightly above 1.5 after the 30-yr simulation regardless of S deposition reduction. At LG, Ca/Al ratios ranged from 1.6 to 2.4 toward the end of the simulation period, the 100% increase scenario had the lower value. Low Ca/Al ratios suggest that forests at SR and LG are significantly stressed under current conditions. Our results also suggest that SO_4 retention is low, perhaps contributing to their high degree of acidification. Their soils are acidic, low in weatherable minerals, and even with large reductions in SO_4 and associated acid deposition, it may take decades before these systems recover from depletion of exchangeable Ca, Mg, and K.

As a consequence of human land use, population growth, and industrialization, wilderness and other natural areas can be threatened by air pollution, climate change, and exotic diseases or pests. Air pollution in the form of acidic deposition is comprised of sulfuric and nitric acids and ammonium derived from emissions of sulfur dioxide, nitrogen oxides, and ammonia. These compounds are largely emitted to the atmosphere by fossil fuel burning and agricultural activities. Once acid compounds enter sensitive ecosystems, they can acidify soil and surface waters, causing a series of ecological changes (Driscoll et al., 2003; Watmough et al., 2005). Acidic deposition has contributed to declining availability of Ca, Mg, and K in the soils of acid-sensitive forest ecosystems by leaching Ca, Mg, and K from foliage and from soil in the primary rooting zone. Acid deposition can also mobilize aluminum in soils affecting soil solution and drainage waters (National Acid Precipitation Assessment Program, 1998).

Forest ecosystems that are potentially sensitive to the adverse impacts of acidic deposition are found throughout the southern Appalachian region, particularly at high elevation and within Class I areas. Class I areas are federally mandated wilderness areas, national parks, or national wildlife refuges according to the Clean Air Act as amended in 1977. Within wilderness areas, old-growth forests may be more sensitive to atmospheric pollution than young forests, because old trees near the end of their life-cycle are typically more susceptible to environmental stressors, either in the form of air pollution or changes in climate (Pregitzer and Euskirchen, 2004). Similarly, differences in nutrient pool sizes and cycling rates between old and young forests (Knoepp and Swank 1994) implies that responses observed in young or aggrading forests may not be applicable to old-growth forests. Sulfur processing within sensitive forest ecosystems is important to understand the acidification of surface waters. Sulfur is the most abundant mobile anion in atmospheric deposition and alters the mobility of other elements, especially acidic (H and Al) and basic (Ca, Mg, Na, and K) cations in soil solutions (Johnson et al., 1982, 1985, 1998; Reuss and Johnson, 1986; Nihlgard et al., 1994; Watmough et al., 2005; Sullivan et al., 2006).

Acidic deposition accelerates Ca, Mg, and K losses. Increased acidity solubilizes Al, which displaces Ca, Mg, and K from soil

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Abbreviations: NuCM, nutrient cycling model; JK, Joyce Kilmer/Slickrock wilderness; SR, Shining Rock wilderness; LG, Linville Gorge wilderness.

exchange sites, which then leach in association with SO_4 (Reuss and Johnson, 1986; Huntington et al., 2000). At current rates of SO_4 deposition, watershed model simulations indicate that SO_4 deposition contributes to chronic soil Ca leaching losses (Huntington et al., 2000; Sullivan et al., 2006). In some eastern deciduous forests, the hydrologic budgets of SO_4 indicated that precipitation inputs exceeded streamflow export, suggesting soil SO_4 adsorption (Johnson et al., 1980; Swank et al., 1985; Mitchell and Lindberg, 1992). Other studies in the eastern United States have found that decreases in SO_4 concentrations in streamwater over the past two decades were linked to decreased S deposition (Driscoll et al., 1989; Lawrence et al., 1999, 2000; Johnson et al., 2000). At Coweeta in the southeastern United States, there has been a decrease in SO_4 dry deposition (Swank and Waide, 1988). However, the rate of decline in stream SO_4 is related to the soil SO_4 adsorption and desorption capacity, which may result in considerable delays in some systems (Reuss and Johnson, 1986). The mobility of anions such as SO_4 and nitrate in acid soils has a direct influence on soil solution and surface water acidity. In acidic soils the counter ions balancing these anions will consist of greater concentrations of H^+ and Al^{3+} being removed from cation exchange sites than would be the case in more neutral soils (Reuss and Johnson, 1986). Although SO_4 concentrations in deposition have steadily declined, SO_4 remains the primary anion associated with acidification of streamwater. Soils with high SO_4 adsorption capacities such as those found in the southeast United States may buffer decreases in S deposition and maintain high SO_4 concentrations for decades by desorption of formerly adsorbed SO_4, thereby resisting improvements to surface water acidification.

Wet deposition (precipitation) and dry deposition of SO_4, aerosol SO_4, and the interception of cloud water or fog droplets containing SO_4 all contribute to the atmospheric deposition of S (Lindberg, 1992). With passage of the 1970 and 1990 Clean Air Act Amendments, S emissions had decreased by 27% in 2000, and are projected to decrease another 7% by 2010 (Baier and Cohn, 1993). However, in areas near heavily industrialized centers, total S deposition may remain high because of the combination of higher SO_4 concentration in rainfall and high rainfall amounts (National Atmospheric Deposition Program, 1998).

One of the responsibilities of land managers is to protect sensitive wilderness and natural resources by evaluating external stressors such as air pollution, and in some cases making recommendations to the appropriate federal, state, or local air regulatory agency. Predicting future response to altered atmospheric environment conditions requires a modeling approach because of the complexities of nutrient cycling processes in forest ecosystems. A major limitation of modeling, especially in wilderness or other natural areas, is having adequate data to parameterize or calibrate models to assure the necessary level of precision and accuracy for valid model output. One option is to focus on the most sensitive or unique locations within wilderness areas, combining intensive field measurements and a modeling approach. In this article, we used such an approach by utilizing the Nutrient Cycling Model (NuCM) to simulate the effects of three S deposition levels (current, 50% decrease, and 100% increase) on three wilderness areas in western North Carolina. As part of the Integrated Forest Study (IFS), NuCM was developed to synthesize current understanding of nutrient cycling in forests and to predict how forests respond to changing S and N atmospheric deposition rates (Johnson and Lindberg, 1991; Liu et al., 1991a, 1991b). The NuCM model links soil–solution chemical components with traditional conceptual models of forest nutrient cycling on a stand level (Liu et al., 1991a).

Three wilderness areas, designated as Class I air quality in western North Carolina, were chosen for this study because of their potential sensitivity to acidic atmospheric deposition. The area modeled within Joyce Kilmer/Slickrock wilderness contains one of the largest old-growth forests in the eastern United States. The area in SR wilderness is a high elevation, highly disturbed former red spruce forest with high deposition inputs, and frigid soils, with low biological activity. Linville Gorge wilderness was chosen because it is a high elevation acidic cove/slope forest with little evidence of human disturbance, contains a large area of old-growth forest, and is located on geologic parent material known to be low in Ca, Mg, and K (Newell and Peet, 1995) and thus sensitive to acidic deposition.

Materials and Methods

Site Descriptions

Joyce Kilmer-Slickrock wilderness, SR wilderness, and LG wilderness are located in the southern portion of the Southern Appalachian Mountains (Fig. 1); and represent three of the five Class I wilderness areas in western North Carolina. Joyce Kilmer/Slickrock and LG contain two of the few remaining large areas of old-growth forest in the eastern United States (Lorimer, 1980, Runkle, 1981, Runkle, 1982). Detailed descriptions of location, vegetation, soils, and geology for the wilderness areas are provided in Table 1. Joyce Kilmer/Slickrock, SR, and LG are part of the oak–chestnut forest region originally described by Braun (1950). Within this broad forest region, Braun (1950) further subdivided moderate elevation forests into three communities; mixed, mesophytic or cove hardwoods, oak–chestnut (now mixed-oak hardwoods), and oak–pine; and high elevation forests into two communities, northern hardwoods and grassy or heath balds.

Joyce Kilmer/Slickrock is a mixed, deciduous old-growth forest. Shining Rock is a former red spruce forest; it was harvested and then severely burned by wildfires twice (1925 and 1942) (Vanderzanden et al., 1999). Following the fires, there was extensive soil erosion, which had additional negative impacts on base cation availability. Linville Gorge is an oak–pine old-growth forest. All three wilderness areas are within the Blue Ridge Geologic Province and soils are derived from high-grade metamorphosed sedimentary rocks, which are covered by unconsolidated Quaternary-aged colluvial and alluvial deposits (Lesure et al., 1977). The mica gneiss and lower quartzite parent materials at SR and LG result in the formation of soils with low Ca, Mg, and K and potentially sensitive to acid deposition. More detailed descriptions of the vegetation, geology, and soils in these wilderness areas can be found in Newell et al. (1997) (JK wilderness), Newell and Peet (1996) (SR wilderness), and Newell and Peet (1995) (LG wilderness).

In JK, three study plots (20 by 20 m) were placed; one in mesic, cove hardwoods (low-slope), one in mixed-oak hard-

woods (mid-slope), and one in northern hardwoods (higher elevation, ridge), to represent the three major community types present in the wilderness. For SR and LG, study areas were located in small catchments within the wilderness boundaries. The catchment size within SR was 62 ha and the catchment size within LG was 24 ha. In SR, five 20 by 20 m plots were located along a 400-m transect at about 70-m intervals parallel to Greasy Cove Prong Creek. In LG, five 20 by 20 m plots were located along a 400-m transect from near stream to upslope from a first-order stream that drained into the Linville River.

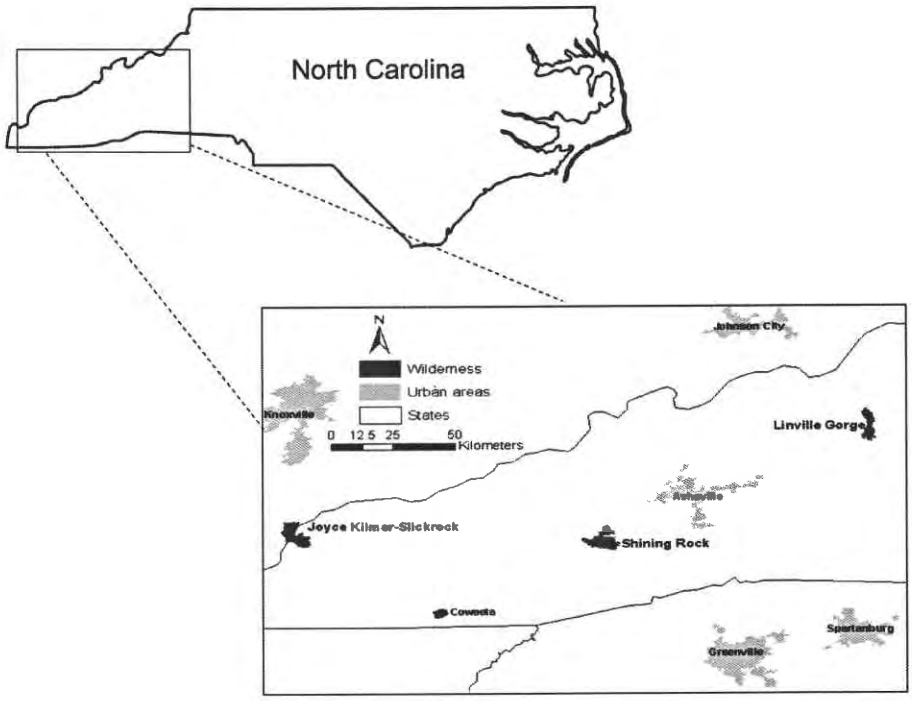

Fig. 1. Locations of three Class I wilderness areas in western North Carolina, USA: Joyce Kilmer/Slickrock wilderness (JK); Shining Rock wilderness (SR); Linville Gorge wilderness (LG); and Coweeta Hydrologic Laboratory Experimental Forest.

Model Parameterization and Data Collection

Most of the model input data were derived from measurements taken within each of the three wilderness areas (JK, SR, or LG). Climate data were obtained from NCDC/NOAA climate stations closest to the corresponding wilderness. Where data were unavailable, we used long-term climate data records from the Coweeta Hydrologic Laboratory located in the Nantahala Mountains of western North Carolina (Swank and Crossley, 1988). For a complete description of data requirements for model parameterization see Munsen et al. (1992). In brief, the NuCM model requires five input data files to parameterize the model for a simulation. These

Table 1. Site descriptions of the three Class I wilderness areas (Joyce Kilmer/Slickrock, Shining Rock, and Linville Gorge) in western North Carolina, United States.

Wilderness area	Joyce Kilmer	Shining Rock	Linville Gorge
Location (county in NC)	Graham	Haywood	Burke
Mountain Range	Unicoi Mountains	Great Balsam Mountains	Grandfather Moutains
Size	6805 ha	7400 ha	4390 ha
Latitude	35.22–35.38	35.17–35.28	35.50–35.58
Longitude	83.55–84.02	82.59–82.47	81.56–81.52
Elevation	250–450 m	1450–1550 m	1090–1160 m
Geology	Arkosic metasandstone	Mica gneiss	Lower quartzite
Soils	Typic Haplumbrepts; Cheoa series and Umbric Dystrochrepts; Jeffrey series	Typic Haplumbrepts; Wayah series	Typic Dystrochrepts; Soco-Ditney series complex
Climate			
Max temperatures	25–30°C	27–30°C	21–27°C
Min temperatures	12–17°C	11–18°C	14–17°C
Annual precipitation	1400 mm	1025–1825 mm	1250–1625 mm
Vegetation†	Low elevation, cove-hardwoods; tulip poplar‡, eastern hemlock, and montane oak (northern red oak, chestnut oak)	High elevation, mixed-hardwood Subtype of northern hardwood forest; yellow birch, red maple	Acidic cove and slope; chestnut oak, red maple
Mean DBH of overstory (range)	22.1 cm (5.0–150.5)	12.8 cm (5.0–44.1)	18.0 cm (5.0–71.1)
Aboveground mass (Mg ha^{-1})	400	119	167
Forest floor mass (g m^{-2})	2600	1900	10,000
Root mass (g m^{-2})	1380	1000	–

† Joyce Kilmer, community types 8.2 and 7.4 (Newell et al., 1997); Shining Rock, community type 5.2 (Newell and Peet, 1996); Linville Gorge, community type 3.1 (Newell and Peet, 1995).

‡ Species latin names are: tulip poplar (*Liriodendron tulipifera* L.), eastern hemlock [*Tsuga canadensis* (L.) Carr.], northern red oak (*Quercus rubra* L.), chestnut oak (*Quercus prinus* L.), yellow birch (*Betula alleghaniensis* Britton), and red maple (*Acer rubrum* L.).

data input files include physiographic, chemistry, meteorologic, deposition, and soil temperature. The meteorologic, deposition, and soil temperature data were created outside the model and input as ASCII files; whereas, the physiographic and chemistry files were created through input menus within the model. The meteorologic data file contains daily values for precipitation, minimum and maximum temperature, cloud cover, dewpoint, atmospheric pressure, and wind speed. For JK, we used climate data from National Oceanic and Atmospheric Administration (1999) National Climatic Data Center for cooperative climate station (no. 318492) located in Tapoco, NC, and Coweeta Hydrologic Laboratory, Climate Station 28 (CS28), located in Otto, NC. Tapoco is located approximately 24 km from JK at 35.45° N lat, 83.94° W long, and 338 m elevation. Coweeta, CS28, is located at 35.02° N lat, 83.28° W long, and 1200 m elevation. Because Tapoca is a cooperative climate station, it records only maximum and minimum temperature and precipitation. Wind speed, relative humidity, atmospheric pressure, cloud cover, and dewpoint temperature were obtained from Coweeta's CS28. We used these combined data sets to calculate average annual daily means for the 10-yr climate record from 1989 to 1998. We used atmospheric deposition data from wet deposition (wetfall) and dry deposition (dryfall) collections taken at Coweeta for the same 10-yr period.

For SR, climate data was obtained from Pisgah, NC (NCDC/NOAA climate station no. 316805), located at 35.16° N lat, 83.42° W long, and 645 m elevation; approximately 16 km southeast of the sample plots. For LG, precipitation data was obtained from Banner Elk, NC (NCDC/NOAA climate station no. 310506), located at 36.09° N lat, 81.52° W long, and 1142 m elevation. Maximum and minimum temperature, wind speed, dew point, and cloud cover were obtained from Jefferson, NC (NCDC/NOAA, climate station no. 314496), located at 36.25° N lat, 81.26° W long, and 845 m elevation. Banner Elk is located about 14 km and Jefferson is about 70 km north of Linville Gorge. Banner Elk only collected precipitation, but its precipitation would be more similar to that received at Linville Gorge. Jefferson was the closest climate station with a full climate record. For SR and LG, we used average annual daily means for the 10-yr climate record from 1992 to 2001.

For both SR and LG, we used atmospheric deposition data, bulk deposition wetfall and dryfall, for a 10-yr period (1992–2001), supplied from National Atmospheric Deposition Program (National Atmospheric Deposition Program, 1998) site NC45 located at Mt. Mitchell, NC. Mt. Mitchell is the closest NADP site to these two wilderness areas and it is also a high elevation site (1900 m). Wet deposition (wetfall) and dry deposition (dryfall) were calculated from a ratio of wetfall/dryfall based on the long-term record at Coweeta Hydrologic Laboratory. Soil temperature data were calculated from air temperature data using a model developed for the Coweeta Basin (Vose and Swank, 1991); monthly average values were calculated for each of the soil depths used in the simulations. Physiographic data included stand physical characteristics, soil physical characteristics, soil chemistry, and stream chemistry and characteristics. In NuCM, mineral weathering is calculated based on the dissolution of primary minerals when they react with hydrogen ions to form secondary minerals plus cations and silica. These are slow reactions that depend on the mass of the mineral and solution-phase of hydrogen-ion concentration taken to a fractional power (Munsen et al., 1992). For the mineral composition and mass, we used generalized values for all three wilderness areas that represented the most common metamorphic geology of the region (Velbel, 1992). Once compiled, these data were input using the format outlined in the NuCM user's manual (Munsen et al., 1992).

Stream, Soil Solution, and Soil Chemistry

At all three study areas, water samples were collected from streams that drain study plot locations. At JK, we collected samples from four first-order streams that drain into Little Santeetlah Creek. At SR, we collected samples at five first order streams that drain into Greasy Cove Prong Creek. At LG, we collected samples at five locations along a first-order stream that drains into the Linville River. Calcium, K, Mg, Na, and NH_4, and extractable SO_4, HPO_4, NO_3, and pH were analyzed at the Coweeta Hydrologic Analytical Lab, Otto, NC. Concentrations of Ca, Mg, K, and Na were determined using a PerkinElmer Analyst 300 atomic absorption spectrophotometer (PerkinElmer Corp., Norwalk, CN). Nitrate, SO_4, and HPO_4 were determined using a Dionex ion chromatograph (Dionex Corp., Sunnyvale, CA). Ammonium-N was determined with an Alpkem Perstorp autoanalyzer (Alpkem Corp., Wilsonville, OR) using the alkaline phenol (USEPA, 1983a) techniques, respectively. Aluminum and dissolved organic carbon (DOC) were analyzed at the Riverbend Analytical Laboratory of University of Georgia, Athens. For Al, water samples were composited monthly and preserved with HCL acid to a pH of 2.0. Analysis was performed on a VG Inductively Coupled Plasma Mass Spectrometer (PerkinElmer SCIEX, Norwalk, CT) using Standard Methods (APHA, 2000). For DOC, stream water samples were filtered through 0.45 μm-pore-diameter-filters, and analysis was performed on an Ol-Analytical TOC analyzer (College Station, TX) using standard methods (APHA, 2000).

Soil solution samples were obtained by installing porous cup tension lysimeters on each plot at each of the sites (i.e., three plots at JK; five plots at SR; and five plots at LG). Lysimeters were placed at depths representing the bottom of the dominant soil horizons of each site, generally the A, AB or BA, and B horizons. Horizon depths were identified from Natural Resources Conservation Service soil survey information (USDA-NRCS, 1996) and by soil probe reconnaissance at each site (Jennifer Knoepp, personal observations, 2000). Lysimeters were installed at 10, 60, and 90 cm for JK; 20, 60, and 90 cm for SR; and 15, 35, and 65 cm for LG. Two sets of lysimeters were installed on each plot at all sites at randomly selected locations (i.e., a total of 18 lysimeters at JK, and 30 lysimeters at SR and LG). Soil water and stream water samples were collected weekly and composited to obtain a monthly sample. Samples were collected for a 6 to 8 mo period in 1999–2000 for JK, 2000 for SR, and 2001–2002 for LG. Analytical procedures for soil water were the same as described for stream water samples.

Composite soil samples were collected from all plots within JK, SR, and LG. Soils on each plot were collected by depth, using an Oakfield soil probe. Depths correspond to major soil

horizons as described above. Actual sample depths were 0 to 10, 10 to 30, and 30 to 90 cm for JK; 0 to 20, 20 to 60, and 60 to 90 cm for SR; and 0 to 15, 15 to 35, and 35 to 65 cm for LG. Composite samples were made up of six to eight individual samples. Soils were kept cool until returned to the laboratory and then stored at 4°C. Within 24 h, soils were moist sieved to <6 mm and extracted with 2 M KCl for determination of NO_3– and NH_4–N. One 5-g subsample was shaken with 20 mL of 2 M KCl for 1 h to extract NH_4– and NO_3–N. The soil/KCl mixture was then centrifuged for 15 min at 6000 rpm. The supernatant was analyzed for NH_4– and NO_3–N on an Alpkem Perstorp autoanalyzer (Alpkem Corp., Wilsonville, OR) using alkaline phenol (USEPA, 1983a) and cadmium reduction (USEPA, 1983b) techniques, respectively. One subsample (10 g) was placed in a 105°C oven for >12 h to obtain oven-dry weight. All soil N data are reported on an oven dry weight basis. All soil data are presented for sample depth and horizon designations as described above but are referred to as A, AB, and B horizons.

Soil samples were air-dried and sieved to <2 mm before chemical analysis. Exchangeable cations were extracted from 10 g of soil on a mechanical vacuum soil extractor using 50 mL of 1 M NH_4Cl. Solution concentrations of Ca, Mg, K, and Na were determined using a PerkinElmer atomic absorption spectrometer (PerkinElmer Corp., Norwalk, CN). Aluminum was determined with a Thermo Jarrell-Ash Enviro 36 Inductively Coupled Argon Plasma (standard methods; APHA, 2000) at the University of Georgia, Chemical Analysis Laboratory, Athens, GA. Following the initial 12-h extraction excess NH_4Cl was removed from the soil interstitial spaces with 95% EtOH. Ammonium–N on the soil exchange sites was then extracted with 2 M KCl as a measure of effective soil cation exchange capacity (ECEC). The NH_4–N concentration in the KCl solution was determined using the alkaline phenol method described above. Soil pH was determined in a 1:1 soil/0.01 M $CaCl_2$ solution slurry. We used analysis of variance (PROC GLM, SAS Institute, 2002–2003) to determine significant differences for stream, soil solution, and soil chemistry among the three wilderness areas.

Langmuir SO_4 adsorption isotherms were generated for each soil sample using the method outlined by Harrison et al. (1989), with slight modifications. We used 5 g of air-dry soil placed in a mechanical soil extractor and 50 mL of solution for both desorption and adsorption phases. For native SO_4 desorption, soil was extracted repeatedly with deionized H_2O to remove native SO_4 and obtain a desorption curve. The desorption phase continued until the SO_4 concentrations in the extract solution was <0.005 $mmol_c\ L^{-1}$, about 10 extractions. Irreversibly adsorbed native SO_4 was then extracted from the same soil sample with five 50-mL aliquots of 5.26 $mmol_c\ L^{-1}$ K_2HPO_4 solution. The SO_4 desorbed from the soil plus the K_2HPO_4 extracted SO_4 was summed to determine native SO_4 concentrations. For SO_4 adsorption, 50 mL of $CaSO_4$ solution was repeatedly leached through 5.0-g soil aliquots to obtain data for calculating a SO_4 adsorption curve.

Solution concentrations ranged from 0.05 to 0.25 mM $CaSO_4$ and differed for each site: Shining Rock, 0.05, 0.08, and 0.25 mmol; Linville Gorge, 0.08, 0.15, and 0.25 mmol; and Joyce Kilmer, 0.08, 0.15, and 0.25 mmol. Initially, we used the 0.25 mmol solution recommended by Harrison et al. (1989) for isotherm determination using one 5-g soil sample, conducting a minimum of 10 extractions. The amount of SO_4 adsorbed increased slowly; however, solution concentrations equilibrated quickly, often after only two extraction cycles leaving few points to generate the Langmuir isotherm. Therefore, we applied two lower concentration solutions (see concentrations above); on a second 5-g soil sample, to SO_4 define the lower portion of the adsorption curve. The second soil sample was leached sequentially, five times with the lowest and five times with the middle solution concentration. Sulfate concentrations in all solutions were determined on a Dionex ion chromatograph (Dionex Corp., Sunnyvale, CA). All equilibrium solution concentrations were corrected for interstitial solution SO_4–S.

We calculated the Langmuir isotherms using both desorption and adsorption data with PROC NLIN (SAS Institute, 2002–2003), to solve the equation $X = ABC/(1 + BC)$, where X = SO_4 adsorbed ($\mu mol_c\ kg^{-1}$) by the soil; A = adsorption maximum ($\mu mol_c\ kg^{-1}$); B = adsorption coefficient; and C = equilibrium SO_4–S concentration ($\mu mol_c\ L^{-1}$) in solution.

Biomass

We estimated biomass of the overstory, understory, forest floor, and roots from 20 by 20 m plots located in each of the wilderness areas. In the plots, diameter of all woody stems was measured to the nearest 0.1 cm. To estimate aboveground biomass, diameter measurements were converted to biomass using species-specific allometric equations from Martin et al. (1999) for the hardwoods and Jenkins et al. (2003) for the pines. Four forest floor samples were collected within each plot at each site using a 0.3 by 0.3-m wooden sampling frame. Material within the 0.09-m^2 quadrat was separated into three components: small wood (<7.5 cm diameter), litter (Oi), and a combined fermentation and humus layer (Oe + Oa). Small wood within the sampling frame was cut using pruning shears, and forest floor was removed by component (i.e., Oi, Oe + Oa) after cutting along the inside of the sampling frame with a knife. Forest floor materials were placed in a paper bag and transported to the laboratory. Root mass was estimated by taking five cores from each plot. Root cores were 5.1 cm in diameter and samples were collected from mineral soil to 30 cm. Forest floor and root samples were dried at least 72 h at 60°C, to a constant weight, and weighed to the nearest 0.1 g. Aboveground live biomass and root biomass estimated values were then input into the NuCM model for simulations for each site.

Calibration of The Nutrient Cycling Model

The NuCM was calibrated using data collected from JK, SR, and LG, the NCDC/NOAA climate records, and long-term records at Coweeta according to the procedures outlined in the user's manual (Munsen et al., 1992) and guidelines presented by Johnson et al. (1993) for a mixed deciduous forest in the Coweeta Basin. During the process of calibration, soil hydraulic conductivity, the "evapotranspiration coefficient," and saturated hydraulic conductivities were used to match model output with known evapotranspiration rates, soil water flux, and lateral flow values from Coweeta Hydrologic Laboratory (Johnson et al., 1993). In

Table 2. Species composition, density (stems ha^{-1}) and basal area (BA; m^2 ha^{-1}) of the overstory (stems ≥5.1 cm dbh) and understory (stems <5.1 cm dbh, >0.5 m height) for three Class I wilderness areas (Joyce Kilmer/Slickrock, Shining Rock, and Linville Gorge) in western North Carolina, United States. Species are ordered by descending basal area.

Overstory†	Density	BA	Understory†	Density	BA
		Joyce Kilmer‡			
Tulip poplar	29	12.28	Black birch	65	0.069
Northern red oak	42	8.18	Eastern hemlock	47	0.057
Sugar maple	120	8.14	American beech	38	0.040
Eastern hemlock	236	6.68	Sugar maple	33	0.030
Red maple	71	5.83	Striped maple	13	0.022
Chestnut oak	20	5.52	Red maple	18	0.016
Sourwood	22	4.33	Fraser magnolia	9	0.013
Hickory	9	3.62	Ironwood	13	0.009
Black birch	91	3.48	Yellow birch	7	0.006
Silverbell	89	3.23	Cucumber tree	4	0.004
American beech	67	2.02	Mountain holly	4	0.003
Cucumber tree	9	1.52	Silverbell	2	0.002
Basswood	7	1.01	Buckeye	2	0.001
Yellow birch	38	0.73	Serviceberry	2	0.001
Striped maple	20	0.32			
Fraser magnolia	20	0.10			
Serviceberry	2	0.06			
Flowering dogwood	2	0.01			
Ironwood	2	0.01			
		Shining Rock			
Yellow birch	280	4.22	Rose bay	715	1.42
Red maple	45	2.64	Highbush blueberry	225	0.16
Mountain holly	700	2.40	Mountain holly	380	0.14
Pin cherry	245	2.37	Flame azalea	220	0.07
Serviceberry	55	0.75	Mountain rosebay	90	0.08
Red spruce	5	0.53	Pepperbush	170	0.05
Sugar maple	5	0.38	Yellow birch	55	0.02
Black birch	5	0.12	Mountain laurel	10	0.04
Mountain maple	5	0.02	Witherod	20	<0.01
			Highbush blackberry	20	<0.01
			Pin cherry	10	<0.01
		Linville Gorge			
Chestnut oak	90	6.15	Rose bay	450	0.42
Pitch pine	50	5.26	Mountain laurel	380	0.36
White pine	35	4.15	Maleberry	245	0.07
Red maple	110	2.54	Eastern hemlock	40	0.01
Sourwood	185	2.51	Sourwood	35	0.01
Blackgum	135	2.30	Horsesugar	20	0.01
Sassafras	190	2.10	White pine	5	0.01
Eastern hemlock	25	2.01	Blackgum	5	0.01
Fraser magnolia	10	0.36	Serviceberry	5	0.01
Scarlet oak	10	0.30	Sassafras	15	<0.01
Witch hazel	55	0.22	Red maple	5	<0.01
Serviceberry	15	0.19	Mountain rosebay	5	<0.01
American chestnut	15	0.09	Witch hazel	5	<0.01
Horsesugar	10	0.04			
Northern red oak	5	0.02			

this study, we compared NuCM model simulation results for the three wilderness areas to a mixed deciduous forest in the Coweeta Basin (35°04′ N lat, 83°26′ W long). The Coweeta site is representative of most southern Appalachian forests, which are aggrading mixed deciduous vegetation, moderately acidic and low N soils that have a high SO_4 adsorption capacity (Swank and Waide, 1988, Johnson et al., 1993). The Coweeta system strongly retains both S and N from atmospheric deposition (Swank and Waide, 1988; Johnson and Lindberg, 1991). Deposition of acidic ions (SO_4^{2-} and NO_3^-) is lower at Coweeta compared with other high-elevation sites such as Nolan Divide in the Smoky Mountains National Park (National Atmospheric Deposition Program, 1998; Johnson et al., 1999) or other industrialized regions in the eastern United States (National Atmospheric Deposition Program, 1998). Simulated effects of altered acidic atmospheric deposition on nutrient cycling at Coweeta have been summarized in previous papers (Johnson et al., 1993, 1995, 1999).

Results and Discussion

The three wilderness areas differed in forest structure, species composition (Table 2), and disturbance history. Joyce Kilmer/Slickrock was dominated by tulip poplar (*Liriodendron tulipifera* L.), northern red oak (*Quercus rubra* L.), sugar maple (*Acer saccharum* Marshall), and eastern hemlock [*Tsuga canadensis* (L.) Carrière] with a sparse understory (Table 2), that has remained undisturbed during the past century. Shining Rock was dominated by yellow birch (*Betula alleghaniensis* Britton), red maple (*Acer rubrum* L.), mountain holly [*Ilex montana* (T.&G.) A. Gray], and pin cherry (*Prunus pensylvanica* L.) with a dense understory of evergreen and deciduous *Rhododendron* species. For SR, the last large-scale disturbance in 1942, a stand replacing fire, initiated the conversion from a red spruce–dominated forest to the present forest composition and structure (Vanderzanden et al., 1999). Currently, the forest is comprised of northern hardwoods species that have a windswept character, low stature and multiple branching pattern, and red spruce is only a minor component of the forest community (Table 2). Linville Gorge was dominated by chestnut oak (*Quercus prinus* L.), pitch pine (*Pinus rigida* Miller), white pine (*Pinus strobus* L.), red maple, and sourwood [*Oxydendrum arboreum* (L.) DC.] with a less dense understory of evergreen rosebay rhododendron (*Rhododendron maximum* L.) and mountain laurel (*Kalmia latifolia* L.) than SR (Table 2). Joyce Kilmer/Slickrock had the greatest aboveground live biomass; LG had the second greatest aboveg-

† Latin names for species are: red maple (*Acer rubrum* L.), striped maple (*Acer pensylvanicum* L.), sugar maple (*Acer saccharum* Marshall) , mountain maple (*Acer spicatum* Lam.), buckeye (*Aesculus octandra* Marshall), serviceberry (*Amelanchier laevis* Wieg.), yellow birch (*Betula alleghaniensis* Britton), black birch (*Betula lenta* L.), iron wood (*Carpinus caroliniana* Walter), hickories (*Carya* spp.), American chestnut [*Castanea dentata* (Marshall) Borkh.], pepperbush (*Clethra acuminata* Michx.), flowering dogwood (*Cornus florida* L.), American beech (*Fagus grandifolia* Ehrh.), silverbell (*Halesia carolina* L.), witch hazel (*Hamamelis virginiana* L.), mountain holly [*Ilex montana* (T. & G.) A. Gray], mountain laurel (*Kalmia latifolia* L.), tulip poplar (*Liriodendron tulipifera* L.), maleberry [*Lyonia ligustrina* (L.) DC.], cucumber tree (*Magnolia acuminata* L.), fraser magnolia (*Magnolia fraseri* Walter), blackgum (*Nyssa sylvatica* Marshall), sourwood [*Oxydendrum arboretum* (L.) DC.], red spruce (*Picea rubens* Sarg.), pitch pine (*Pinus rigida* Miller), white pine (*Pinus strobus* L.), pin cherry (*Prunus pensylvanica* L.), scarlet oak (*Quercus coccinea* Muenchh.), chestnut oak (*Quercus prinus* L.), northern red oak (*Quercus rubra* L.), flame azalea [*Rhododendron calendulaceum* (Michx.) Torr.], mountain rosebay (*Rhododendron catawbiense* Michx.), rose bay (*Rhododendron maximum* L.), blackberry (*Rubus argutus* Link.), sassafras [*Sassafras albidum* (Nutt.) Nees.], horsesugar [*Symplocus tinctoria* (L.) L'Hér], basswood (*Tilia americana* L.), eastern hemlock [*Tsuga canadensis* (L.) Carr.], highbush blueberry (*Vaccinium simulatum* L.), and witherod [*Viburnum cassinoides* (L.) T. & G.].

‡ For Joyce Kilmer, only understory stems >1.4 m in height were measured (dbh range 2.5–5.0 cm).

Table 3. Soil chemistry for three Class I wilderness areas: Joyce Kilmer/Slickrock wilderness (JK), Shining Rock wilderness (SR), and Linville Gorge wilderness (LG) in western North Carolina, United States. All concentrations are in $cmol_c\ kg^{-1}$ except soil pH.

	Depth 1 (A-horizon)‡			Depth 2† (AB-horizon)‡			Depth 3† (B-horizon)‡		
Soil chemistry	JK†	SR	LG	JK	SR	LG	JK	SR	LG
pH	4.27a	3.41 b	3.45 b	4.36 a	3.85 b	3.91 b	4.44 a	4.11 b	3.95 b
	(0.14)§	(0.14)	(0.15)	(0.03	(0.06)	(0.09)	(0.03)	(0.08)	(0.07)
NO_3^-–N	0.0013	0.0031	0.0003	0.0002	0.0009	0.0003	0.0002	0.0003	0.0002
	(0.0004)	(0.0018)	(0.0003)	(0.0001)	(0.0005)	(0.0003)	(0.0001)	(0.0002)	(0.0001)
NH_4^+–N	0.016 ab	0.024 a	0.005 b	0.009 b	0.018 a	0.006 b	0.004 b	0.013 a	0.004 b
	(0.0025)	(0.0079)	(0.0006)	(0.0011)	(0.0052)	(0.0008)	(0.0008)	(0.0024)	(0.0004)
HPO_4^{2-}	0.004	0.010	0.011	0.003	0.003	0.004	0.004	0.003	0.003
	(0.0009)	(0.0028)	(0.0028)	(0.0002)	(0.0005)	(0.0009)	(0.0007)	(0.0007)	(0.0006)
K^+	0.402 a	0.162 b	0.116 b	0.169 a	0.090 b	0.082 b	0.113	0.059	0.063
	(0.038)	(0.021)	(0.013)	(0.020)	(0.014)	(0.008)	(0.024)	(0.006)	(0.006)
Na^+	0.080 a	0.018 b	0.009 b	0.018	0.016	0.007	0.013	0.014	0.006
	(0.018)	(0.003)	(0.0006)	(0.012)	(0.001)	(0.0004)	(0.009)	(0.001)	(0.0005)
Ca^{2+}	2.310 a	0.451 b	0.039 b	0.433 a	0.161 b	0.022 b	0.155 a	0.099 ab	0.018 b
	(0.717)	(0.070)	(0.005)	(0.168)	(0.030)	(0.004)	(0.047)	(0.020)	(0.006)
Mg^{2+}	0.933 a	0.303 b	0.093 c	0.146 a	0.109 a	0.043 b	0.087 a	0.060 ab	0.030 b
	(0.216)	(0.068)	(0.007)	(0.027)	(0.006)	(0.003)	(0.016)	(0.004)	(0.004)
SO_4^{2-}	0.200	0.187	0.305	0.521	0.328	0.556	0.946 a	0.437 b	0.404 b
	(0.044)	(0.006)	(0.104)	(0.129)	(0.012)	(0.156)	(0.188)	(0.008)	(0.134)
Al^{3+}	3.357	5.490	5.935	3.109 a	5.329 b	4.760 b	2.996	3.588	4.430
	(1.157)	(1.316)	(0.658)	(0.390)	(0.408)	(0.473)	(0.350)	(0.757)	(0.571)
ECEC	17.98 a	11.06 b	6.84 b	11.03 a	10.29 a	6.81 b	8.69 a	7.85 a	5.46 b
	(2.37)	(1.64)	(0.23)	(0.79)	(0.66)	(0.40)	(0.70)	(0.56)	(0.62)

† Within a soil depth, values followed by different letters denote a significant difference ($p < 0.05$) among sites (SAS Institute, 2002–2003).

‡ Standard errors are in parentheses.

§ For JK, soil depths were 0–10 cm, 10–30 cm, and 30–90 cm; for SR, soil depths were 0–20 cm, 20–60 cm and 60–90 cm; and for LG, soil depths were 0–15 cm, 15–35 cm, and 35–65 cm.

round live biomass with *Pinus* species contributing a large proportion of the biomass; and SR had the least aboveground live biomass (Table 2). The presence of the *Pinus* species at LG contributed to the accumulation of forest floor mass (Table 1). The recalcitrant evergreen litter at both SR and LG may have contributed to the soil and soil solution acidity at these sites (Tables 3 and 4).

Table 4. Mean soil solution and stream chemistry for three Class I wilderness areas: Joyce Kilmer/Slickrock wildness (JK), Shining Rock wilderness (SR), and Linville Gorge wilderness (LG) in western North Carolina, United States. All values are in $\mu mol_c\ L^{-1}$ except for pH, Al ($mg\ L^{-1}$) and DOC ($mg\ L^{-1}$).

	Soil solution chemistry											
	Depth 1† (A-horizon)‡			Depth 2† (AB-horizon)‡			Depth 3† (B-horizon)‡			Stream†		
Soil chemistry	JK	SR	LG	JK	SR	LG	JK	SR	LG	JK	SR	LG
pH	5.75 a	4.35 b	4.22 b	5.43 a	4.80 b	4.40 b	5.44 a	5.04 b	4.51 c	6.66 a	6.08 b	4.74 c
	(0.25)§	(0.15)	(0.12)	(0.22)	(0.11)	(0.12)	(0.14)	(0.09)	(0.11)	(0.08)	(0.08)	(0.04)
NO_3^-–N	4.76	1.60	2.07	16.46 a	5.03 ab	0.48 b	5.85	5.68	0.62	2.69 a	0.71 b	2.06 a
	(2.40)	(0.75)	(0.89)	(12.96)	(1.75)	(0.12)	(2.31)	(3.19)	(0.23)	(0.64)	(0.12)	0.62)
NH_4^+–N	1.20	0.93	1.10	1.47	1.67	0.36	0.41	0.57	0.44	0.31 b	0.35 b	0.74 a
	(0.58)	(0.24)	(0.49)	(0.50)	(0.79)	(0.05)	(0.06)	(0.16)	(0.15)	(0.03)	(0.05)	(0.18)
HPO_4^{2-}	0.12	0.17	0.23	0.09	0.09	0.08	0.10	0.06	0.12	0.09	0.12	0.10
	(0.07)	(0.04)	(0.08)	(0.06)	(0.02)	(0.01)	(0.06)	(0.01)	(0.01)	(0.03)	(0.02)	(0.01)
Cl^-	38.44	55.38	41.64	45.73	43.16	37.16	25.23	21.56	32.81	11.88 b	7.99 c	25.44 a
	(3.23)	(26.04)	(5.97)	(6.41)	(18.19)	(4.12)	(3.47)	(5.91)	(2.82)	(0.27)	(0.22)	(2.34)
K^+	58.44 a	13.71 b	42.74 a	21.82 a	6.08 b	17.16 ab	6.44	4.17	9.68	9.82 a	5.29 c	7.35 b
	(15.08)	(2.84)	(8.05)	(9.70)	(1.04)	(2.98)	(1.16)	(0.68)	(2.39)	(0.69)	(0.12)	(0.47)
Na^+	13.03	20.19	23.82	13.54 b	16.47 b	23.60 b	14.74	17.15	17.69	41.54 a	25.62 b	18.36 b
	(0.91)	(3.47)	(2.58)	(1.73)	(1.06)	(2.26)	(0.79)	(1.21)	(1.55)	(4.41)	(0.81)	(0.99)
Ca^{2+}	73.05 a	22.74 b	17.56 b	67.08 a	22.32 b	9.17 b	59.99a	17.66 b	4.81 b	39.13 a	15.28 b	13.80 b
	(21.24)	(5.26)	(4.60)	(22.22)	(4.04)	(2.56)	(16.48)	(2.99)	(1.98)	(2.70)	(2.03)	(3.01)
Mg^{2+}	40.44	29.89	30.76	41.81 a	20.46 b	22.45 b	34.79 a	19.50 b	15.81 b	21.97 a	12.15 b	15.14 b
	(5.10)	(6.73)	(3.84)	(2.83)	(1.83)	(4.13)	(6.01)	(2.56)	(3.45)	(2.13)	(0.79)	(1.16)
SO_4^{2-}	117.9	64.18	99.98	98.72 a	42.34 b	113.1 a	97.99 a	38.79 b	91.80 a	24.33 b	19.82 b	51.95 a
	(20.77)	(22.50)	(7.63)	(10.34)	(5.06)	(11.23)	(17.24)	(4.16)	(12.26)	(3.01)	(0.62)	(0.44)
Al	0.187	1.266	1.063	0.047 b	0.342 ab	0.802 a	0.028 b	0.220 b	0.622 a	0.013	0. 279	0. 159
	(0.110)	(0.455)	(0.166)	(0.015)	(0.105)	(0.180)	(0.015)	(0.056)	(0.133)	(0.004)	(0.158)	(0.011)
DOC	4.38	15.54	26.52	1.10	2.47	11.21	0.74	1.61	6.64	0.68 b	1.47 a	1.37 a
	(0.78)	(4.75)	(6.97)	(0.11)	(0.54)	(4.23)	(0.21)	(0.32)	(2.45)	(0.10)	(0.17)	(0.20)

† Values within a soil depth are significantly different ($p < 0.05$) among sites (SAS Institute, 2002–2003).

‡ Standard errors are in parentheses.

§ For JK, soil depths were 0–10, 10–30, and 30–90 cm; for SR, soil depths were 0–20, 20–60, and 60–90 cm; and for LG, soil depths were 0–15, 15–35, and 35–65 cm.

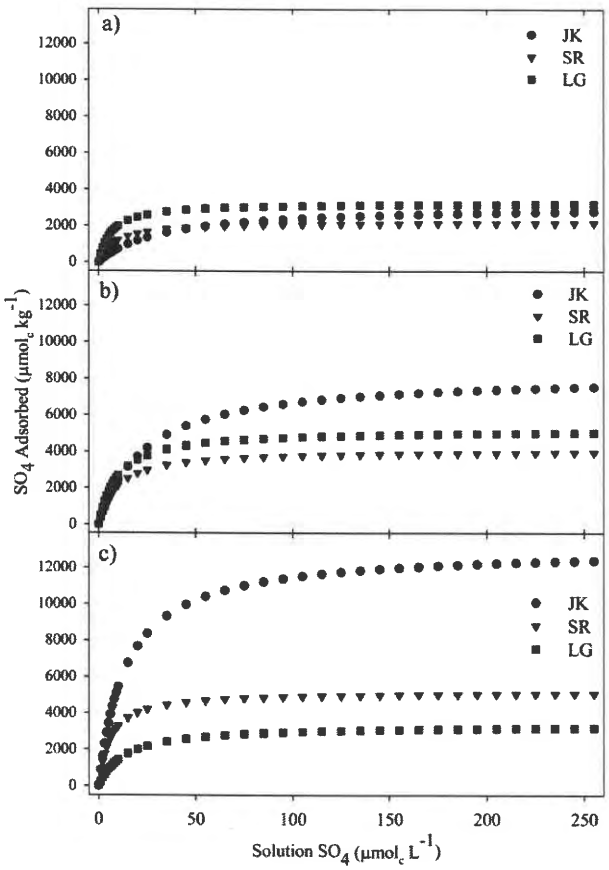

Fig. 2. Langmuir sulfur (S) isotherms for three Class I wilderness areas at the soil depth/horizons: (a) A horizon (rooting zone), (b) AB horizon, and (c) B horizon. For JK, soil depths were 0–10, 10–30, and 30–90 cm; for SR, soil depths were 0–20, 20–60, and 60–90 cm; and for LG, soil depths were 0–15, 15–35, and 35–65 cm. Symbols are Joyce Kilmer/Slickrock wilderness (JK), Shining Rock wilderness (SR), and Linville Gorge wilderness (LG).

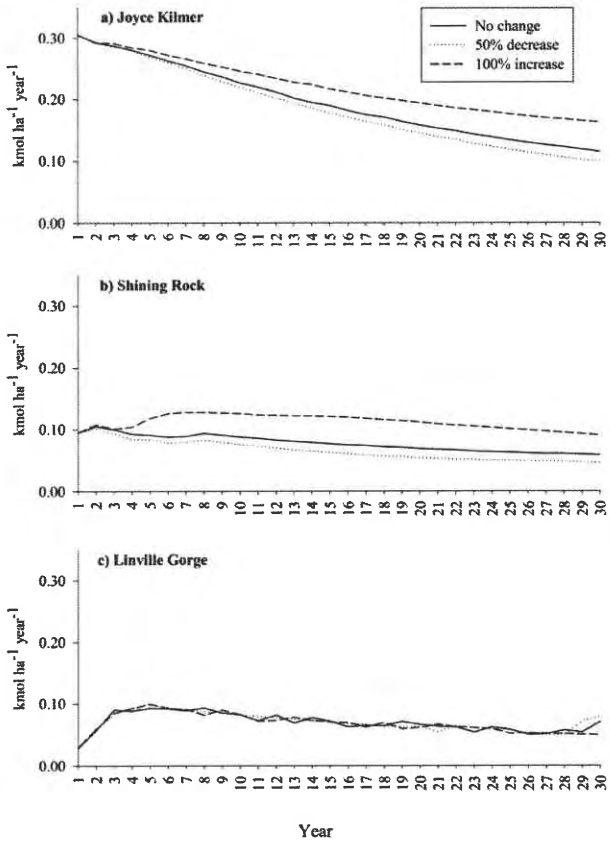

Fig. 3. Simulated calcium (Ca) leaching for three Class I wilderness areas in western North Carolina, United States: (a) Joyce Kilmer/Slickrock wilderness; (b) Shining Rock wilderness; and (c) Linville Gorge wilderness.

The three wilderness areas differed in their S adsorption capacities within the soil profile (Fig. 2). There was little variation in the maximum adsorption capacity in the surface A horizon soils among the three wilderness areas, ranging from 2100 $\mu mol_c\ SO_4\ kg^{-1}$ soil for SR to 3200 $\mu mol_c\ SO_4\ kg^{-1}$ soil for LG. These values suggest that A horizon soils have little capacity for additional SO_4 adsorption. For JK, current concentrations for native SO_4 in A horizon soils are 64% of the maximum SO_4 adsorption capacity; SR and LG are currently at 91 and 94% of the maximum. The differences among sites increased with soil depth. Joyce Kilmer/Slickrock had the greatest adsorption capacity in both the AB and B horizon soils (Fig. 2). Maximum adsorption capacity was 8200 and 13,000 $\mu mol_c\ SO_4\ kg^{-1}$ soil for the AB and B horizon, respectively. There was little difference between SR and LG in the AB or B horizon soils. For example, the maximum adsorption capacities for LG ranged from 3300 $\mu mol_c\ SO_4\ kg^{-1}$ soil for the AB horizon to 5200 $\mu mol_c\ SO_4\ kg^{-1}$ soil for the B horizon (Fig. 2). Native SO_4 concentrations in the AB and B horizon for SR and LG were close to these maximum values, averaging 87% in SR and just over 100% in LG. This suggests that both SR and LG are close to SO_4 equilibrium under current conditions.

The three wilderness areas also differed in soil acidity and chemical characteristics, factors that could influence their susceptibility to altered atmospheric deposition. Shining Rock and LG had significantly lower soil pH, concentrations of Ca, Mg, and K, and ECEC than JK (Table 3). The SR and LG sites were surprisingly low in soil exchangeable Ca, <1.0 $cmol_c\ kg^{-1}$ (Table 3). Model predictions suggest there is more Ca stored in the aboveground vegetation and forest floor than in the soil. Soil exchangeable Ca at JK was about 50% lower than in a nearby mixed-deciduous forest in the Coweeta Basin (Johnson et al., 1993). For SR and LG, soil exchangeable Ca was 80% less than the Ca found in A horizon soils at JK (Table 3). Simulated Ca leaching at JK was 300% greater than SR or LG (Fig. 3). While Ca leaching rates at Coweeta (Johnson et al., 1993) were in between the leaching rates of the three wilderness areas, JK, SR, and LG (Fig. 3). During the 30-yr simulation period, the Ca leaching at LG was not responsive to the 100% increase or 50% decrease SO_4 deposition scenarios (Fig. 3). At JK and SR, simulated Ca leaching was higher with the 100% increase scenario, but only marginally influenced with the 50% decrease SO_4 deposition (Fig. 3). Magnesium and K leaching followed similar trends as Ca leaching for the three wilderness

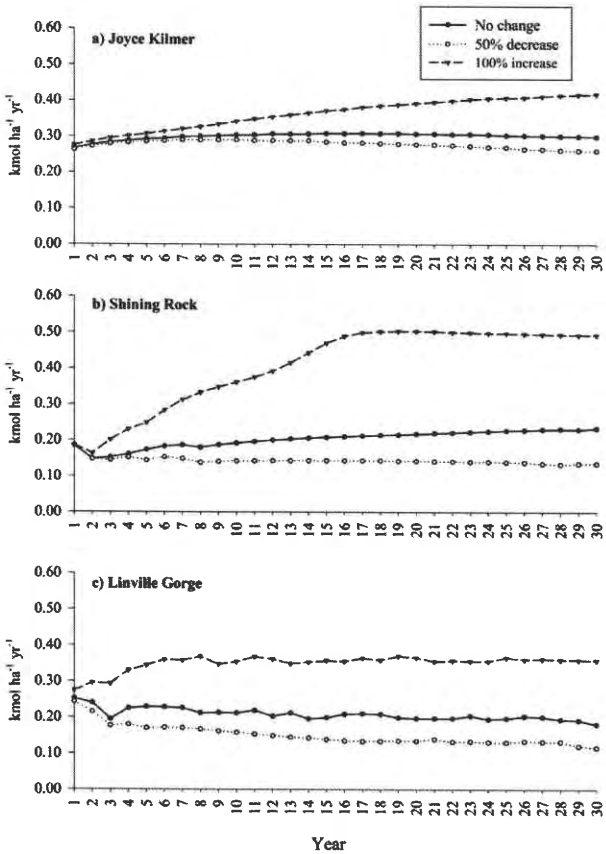

Fig. 4. Simulated sulfate (SO_4) leaching for three Class I wilderness areas in western North Carolina, United States: (a) Joyce Kilmer/Slickrock wilderness; (b) Shining Rock wilderness; and (c) Linville Gorge wilderness.

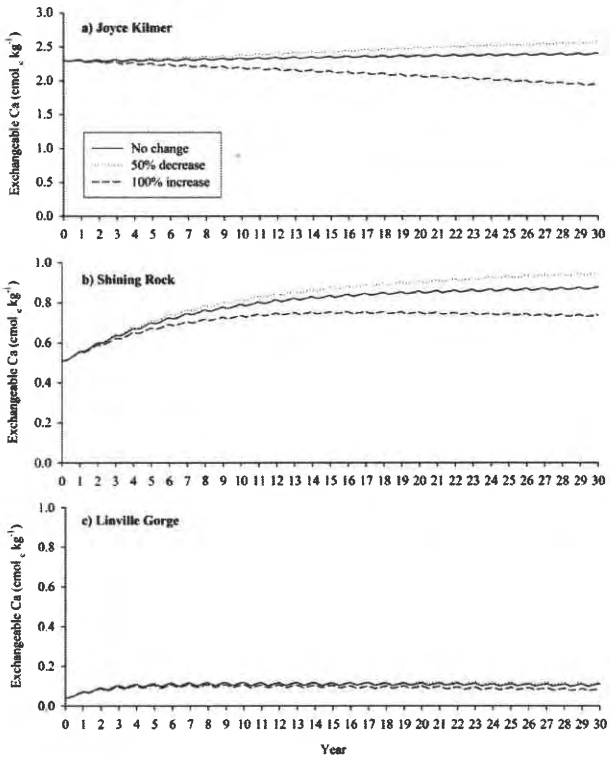

Fig. 5. Rooting zone (A-horizon) soil exchangeable calcium (Ca) for three Class I wilderness areas in western North Carolina, United States: (a) Joyce Kilmer/Slickrock wilderness; (b) Shining Rock wilderness; and (c) Linville Gorge wilderness. Note difference in *y* axis units.

areas (data not shown). For LG, with higher SO_4 leaching and no response in Ca leaching and a small increase in Mg and Al leaching (0.04 to 0.08 kmol ha^{-1} yr^{-1} over the 30-yr simulation) at the 100% increase SO_4 deposition scenario, the additional cation that accompanied this increased SO_4 was hydrogen. The pH was quite low and the Al concentration was high in the soil solution and stream water at this wilderness (Table 4).

For JK, simulated SO_4 leaching decreased over the 30-yr simulation period for all SO_4 deposition scenarios and was higher than the other two wilderness areas for the no change and 50% decrease scenarios (Fig. 4). Under the no change and 50% decrease scenarios, SO_4 leaching for SR and LG remained relatively constant through time because they had already reached equilibrium. With the 100% increase scenario for SR and LG, SO_4 leaching increased through time. Simulated SO_4 leaching at SR and LG were much closer to those projected for a mixed deciduous forest at Coweeta (Johnson et al., 1993).

Soils do not become SO_4 saturated, but reach equilibrium with respect to current inputs; thus, an increase in input concentration results in increased adsorption (Fig. 2). During the 30-yr simulation, soil adsorbed SO_4 for the three wilderness areas, under the no change SO_4 deposition scenario, was about 50 kmol ha^{-1} yr^{-1} for JK, 20 kmol ha^{-1} yr^{-1} for SR, and 10 kmol ha^{-1} yr^{-1} for LG compared with only 2 to 4 kmol ha^{-1} yr^{-1} for Coweeta (Johnson et al., 1993). The 100% increase SO_4 deposition at Coweeta resulted in substantial increases in soil adsorbed SO_4 to16 kmol ha^{-1} yr^{-1} by the end of the simulation (Johnson et al., 1993). In contrast, the 100% increase SO_4 deposition at SR and LG resulted in an increase to 23 and 12 kmol ha^{-1} yr^{-1}, respectively, in less than 10 yr (i.e., only a 2–3 kmol ha^{-1} yr^{-1} increase over the 30-yr simulation), which suggests that these two wilderness areas cannot adsorb more SO_4.

Initial soil exchangeable Ca concentrations significantly differed among the three wilderness areas (Table 3) and exchangeable soil Ca did not show much response to the altered SO_4 deposition scenarios (Fig. 5). Calcium replenishment at these sites is not likely because soils have developed from base-poor igneous and metamorphic parent materials; consequently, contributions from weathering are negligible (Velbel, 1992). In addition, current input from Ca deposition is low (<0.8 kg ha^{-1} yr^{-1}). Even with a 50% decrease in SO_4 deposition, exchangeable soil Ca would increase only marginally at SR and no change was obvious at LG; Ca decreased slightly in JK during the 30-yr simulation (Fig. 5). In fact, rooting zone (A horizon) base saturation was only 4% at LG and projected to increase by <1% with a 50% reduction in SO_4 deposition (Fig. 6). Therefore, sustainability of forest productivity at LG without Ca amendments is clearly in question.

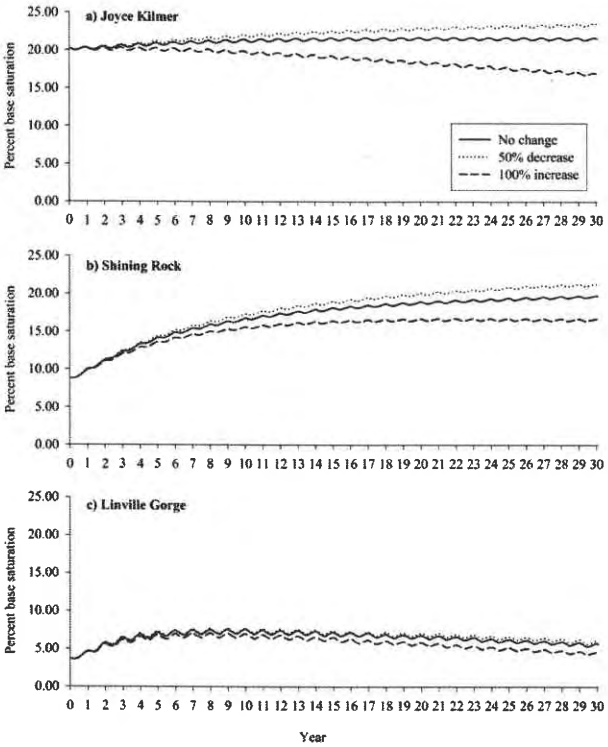

Fig. 6. Rooting zone (A-horizon) soil percent base saturation for three Class I wilderness areas in western North Carolina, United States: (a) Joyce Kilmer/Slickrock wilderness; (b) Shining Rock wilderness; and (c) Linville Gorge wilderness, western North Carolina.

Soil solution and stream chemistry were significantly different among the three wilderness areas (Table 4). In general, SR and LG had much lower soil solution Ca, Mg, and K and higher acid ion concentrations than JK (Table 4). In particular, Ca, Mg, and K were significantly lower and Al concentrations were significantly higher at SR and LG than JK. Simulations of soil solution Ca/Al molar ratios were much higher at JK compared with the other two wilderness areas (Fig. 7) and continued to increase for all SO_4 deposition scenarios. Simulated Ca/Al ratios in A horizon solutions for SR and LG were similar to ratios found at Noland Divide, a high-elevation, spruce–fir forest in the Smoky Mountain National Park (Johnson et al., 1999). A-horizon soil solution Ca/Al ratios at both SR and LG were <0.3, well below the toxicity threshold of 1 (Cronon and Grigal, 1995). These values showed some recovery, to values >1, after 8 yr for LG and 18 yr for SR, regardless of deposition reduction (Fig. 7). At Coweeta, soil solution Al concentrations (<1 $\mu mol_c\ L^{-1}$) were much lower than those at JK and soil solution Ca/Al molar ratios remained at least an order of magnitude above the nominal toxicity threshold of 1 (Johnson et al., 1999). In this study, the low values of Ca/Al ratio suggest that the forest communities at SR and LG are significantly stressed under current conditions. In the southern Appalachians, high elevation spruce–fir forests tend to have thick organic horizons, high organic matter content in the mineral horizons, and low pH (Johnson et al., 1999). Because these sites have largely unreactive bedrock, base-poor litter, organic acid anions produced by the conifers, high precipitation, and high leaching rates, soil base saturation in these forests tends to be <10% and the soil cation exchange complex is generally dominated by aluminum (Johnson and Fernandez 1992). In this study, rooting zone (A horizon) base saturation at LG was <4%; whereas, rooting zone base saturation was 8% at SR and 20% at JK (Fig. 5). The SR and LG sites were more similar to the high elevation spruce forest at Nolan Divide (Johnson et al., 1999) than to JK. Shining Rock and LG had low soil base saturation and soil pH; LG also had high forest floor mass (Oi + Oe + Oa layers) primarily due to the litter contribution from conifers (i.e., white pine and pitch pine).

Stream SO_4 concentrations at LG were significantly higher than the other two sites, but there was no difference between JK and SR (Table 4). At LG, the pH of streamwater was significantly lower than the other two wilderness areas and much less than pH values recorded at reference watersheds streams at Coweeta (Swank and Waide 1988). At LG, stream SO_4 concentration was higher than the mean values observed at Noland Divide in the Great Smoky Mountains National Park (Robinson et al., 2003), but stream NO_3 concentrations were an order of magnitude lower for all three wilderness areas than that reported for Noland Divide (Robinson et al., 2003). Low pH and high aluminum concentrations have been shown to diminish species diversity and the abundance of invertebrates and fish in acid-impacted surface waters in the Northeast (Driscoll et al., 2003). The extremely low pH and high Al concentrations of the first-order streams at LG may place some aquatic life at risk for this wilderness. For example, in the Adirondack region of New York, lakes with pH between 4.0 and 4.5 supported seven species of fish, whereas lakes with pH ranging from 5.0 to 8.0 supported more than 100 species of fish (Driscoll et al., 2001). Low stream acid neutralizing capacity (ANC) also can adversely impact aquatic biota and fisheries, especially native brook trout (*Salvelinus fontinalis* Mitchill). Joyce Kilmer/Slickrock has an ANC value of 73.6 $\mu mol_c\ L^{-1}$ suggesting continued S deposition is unlikely to threaten brook trout populations; while the ANC value of 28.8 $\mu mol_c\ L^{-1}$ for SR suggests extreme sensitivity to further acidification and may adversely affect brook trout. The ANC value of −24.8 $\mu mol_c\ L^{-1}$ for LG indicates that this stream is no longer able to support brook trout or any fish species because acid inputs can no longer be neutralized (Bulger et al., 1999).

Decreases in streamwater Ca have been reported at several long-term monitoring studies (Swank and Waide, 1988; Likens et al., 1996; Clow and Mast, 1999; Gbondo-Tugbawa and Driscoll, 2003; Murdoch and Shanley, 2006) and have been associated with soil Ca depletion through vegetation uptake, soil leaching (Watmough et al., 2005; Duchesne and Houle, 2006), and declines in Ca deposition (Knoepp and Swank, 1994; Likens et al., 1998). In cases where there have been decreases in streamwater SO_4, however, the decreases in streamwater Ca could be due either in part or exclusively to charge balance considerations and have little or nothing to do with changes in soils. Streamwater Ca was significantly lower at SR and LG than at JK, and streamwater Al was significantly higher at LG than at JK (Table 4). Throughout the northeastern United States, recent trends in surface water chemistry indicate that even with decreases in acidic deposition, recovery of sensitive lakes and streams is slow

(Stoddard et al., 1999; Driscoll et al., 2001; Eimers et al., 2004). Three factors were attributed to the slow recovery: Ca, Mg, and K in streams were low due to declines in soil exchangeable Ca, Mg, and K and to a lesser extent reduction in atmospheric inputs of these ions; atmospheric N inputs resulted in elevated concentrations of nitrate in surface waters, contributing to acidification; and even though SO_4 deposition had decreased, S has accumulated in soil and is now being released to surface water as SO_4. In this study, soil-extractable SO_4 was significantly higher at JK and LG compared with SR (Table 3) but stream SO_4 concentrations at JK were significantly lower than at LG (Table 4).

At Coweeta, 68% of the total precipitation anions were contributed by SO_4 (Swank et al., 1984). In addition, high SO_4/NO_3 ratio concentrations in streamwater for the wilderness areas in this study (Table 4) indicate that most leaching of soil Ca, Mg, and K into drainage waters was balanced by SO_4. Soil SO_4 adsorption may account for some of the observed S retention (Strickland et al., 1986, Johnson et al., 1982), incorporation of inorganic SO_4 into soil organic matter also plays an important role in S retention (Strickland et al., 1986; Nihlgard et al., 1994). Thus, SO_4 retention in soils can delay the onset of stream acidification by reducing the flux of SO_4 through the soil. The SO_4 adsorption isotherms and the simulation scenarios from this study suggests that SO_4 retention for the SR and LG wildernesses is low, which may have contributed to more rapid soil acidification than at JK. The extremely low concentrations of exchangeable Ca, Mg, and K are a primary concern for all three wilderness areas, but most alarmingly at SR and LG. The soils at the latter sites are very acidic, low in weatherable minerals, and even with large reductions in SO_4 and associated acid deposition, it may take decades before these systems recover from depletion of exchangeable Ca, Mg, and K.

Shining Rock and LG are the two most sensitive wilderness areas examined in this study, soils in these two areas have experienced prolonged base cation leaching and sequestration by vegetation to such an extent that soils have been depleted of their Ca, Mg, and K reserves. Such depletion would greatly prolong the recovery of these watersheds under conditions of reduced SO_4 deposition and may adversely impact forest productivity (Likens et al., 1998; Duchesne and Houle, 2006) and other ecosystem processes (Driscoll et al., 2003; Fenn et al., 2006; Sullivan et al., 2006).

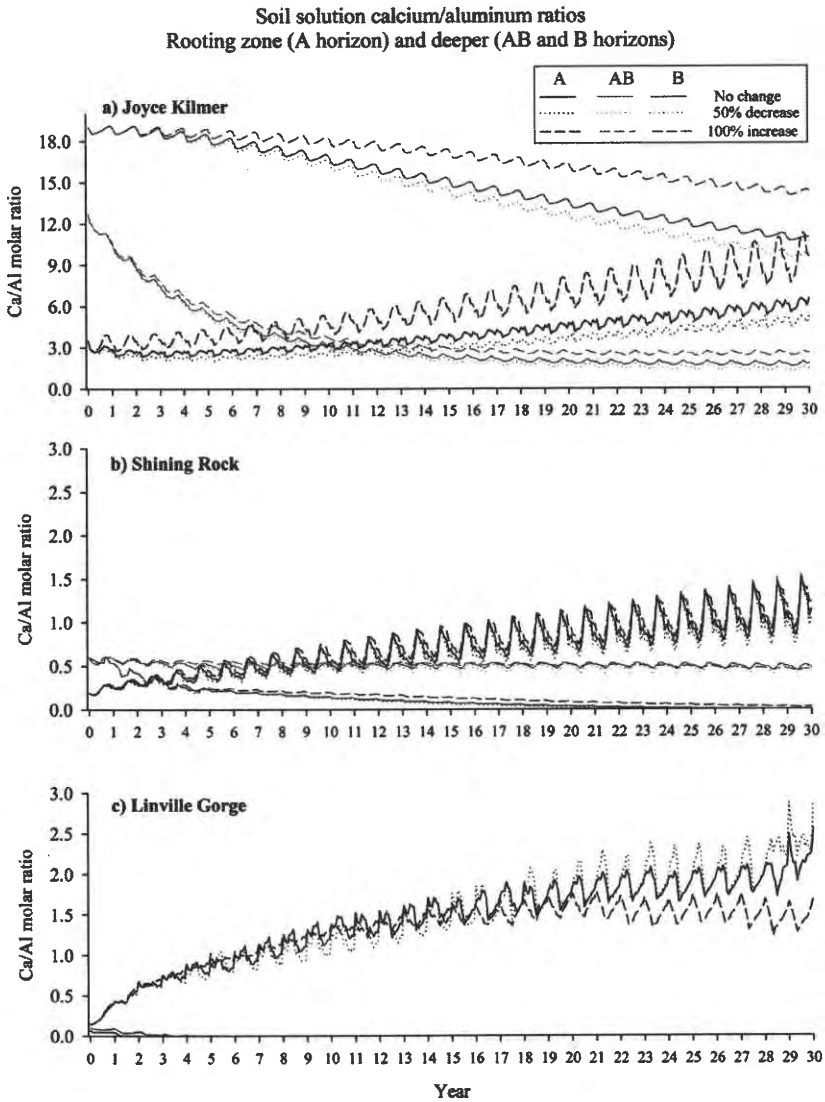

Fig. 7. Simulated soil solution molar Ca/Al ratios for three Class I wilderness areas in western North Carolina, United States: (a) Joyce Kilmer/Slickrock wilderness; (b) Shining Rock wilderness; and (c) Linville Gorge wilderness, western North Carolina. Soil depth/horizons were A horizon (rooting zone), AB horizon, and B horizon. For JK, corresponding soil depths were 0–10, 10–30, and 30–90; for SR, soil depths were 0–20, 20–60, and 60–90; and for LG, soil depths were 0–15, 15–35, and 35–65 cm. Note difference in *y* axis units.

Conclusions

Even within a relatively small geographic area in western North Carolina, Class I wilderness forest ecosystems vary considerably in their current condition and predicted susceptibility to future changes in atmospheric deposition. Due to the complexity of biogeochemical cycling processes, predicting the susceptibility to (or recovery from) changes in long-term chronic or acute deposition requires a modeling approach that is sufficiently mechanistic to represent the interactions among vegetation, soils, and hydrologic fluxes. In our model-based analyses, the SR and LG wildernesses were considerably more sensitive to increased SO_4 deposition than JK. Most of this increased sensitivity was related to inherent soil factors (e.g., low pH; low Ca, K, and Mg concentrations; and low

effective CEC) that reduce the soils ability to neutralize chronic and acute acidic deposition. This variation in susceptibility among wildernesses will require land managers faced with protecting wilderness and natural resource areas from anthropogenic disturbances to understand and quantify key pools and processes regulating biogeochemical cycling within sites of interest. Interestingly, model results also suggested that all three wildernesses will recover very slowly and only modestly to reductions in SO_4 deposition. For example, SO_4 and Ca leaching under the 50% SO_4 reduction scenario were only slightly less than ambient levels; even after 30 yr of reduced SO_4 inputs. For Joyce Kilmer/Slickrock, Shining Rock, and Linville Gorge, the results from this study provide information for the Federal land managers on how changes in acidic deposition might impact these three wilderness areas.

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