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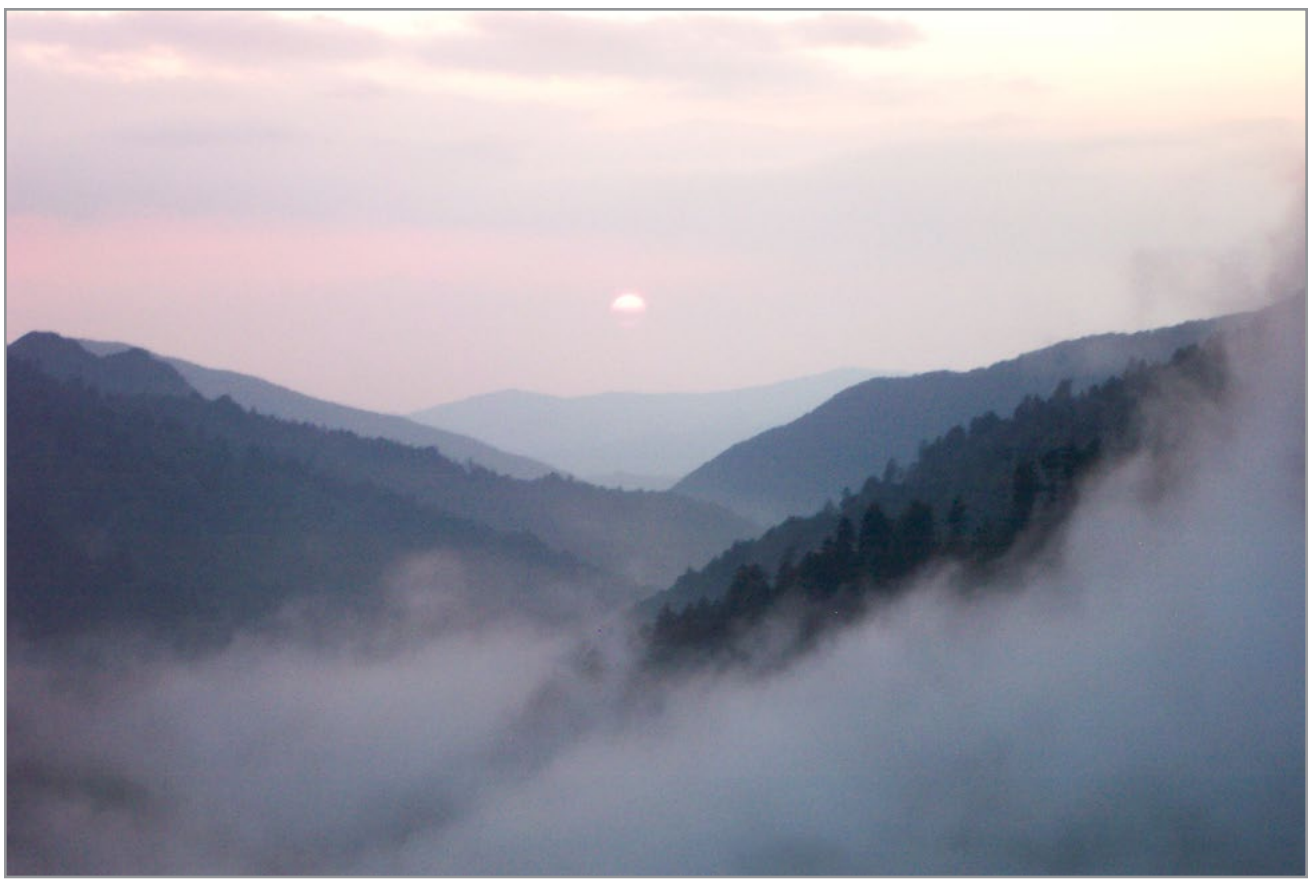
Critical Loads of Sulfur and Nitrogen and Modeled Effects of Deposition Reduction for Forested Ecosystems of Great Smoky Mountains National Park

Linda H. Pardo, Natasha Duarte, Helga Van Miegroet, L. Suzanne Fisher, and Molly J. Robin-Abbott



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Abstract

Great Smoky Mountains National Park (GSMNP) is subject to high levels of sulfur (S) and nitrogen (N) deposition, which can adversely affect forest vegetation and aquatic biota. We used multiple chemical criteria to calculate critical loads for S and N deposition (CL (S + N)) and nutrient N ($CL_{nut}N$) and used the Very Simple Dynamic (VSD) model to predict the effects of deposition reduction scenarios on critical thresholds for four forested sites in GSMNP. Critical loads were exceeded for current deposition at three of four sites using critical thresholds of aluminum to base cations (Al:Bc) = 0.1 or no decrease in base saturation but were not exceeded using the chemical criteria of Al = 0.2 meq L^{-1}, Al:Bc = 1.0, and pH = 4.2. With deposition reductions of 48 percent S and 56 percent nitrate (NO_3^-), neither the critical thresholds of acid neutralizing capacity (ANC) = 20 µeq L^{-1} nor a decrease in base saturation was achieved. With deposition reductions of 90 percent S and 90 percent NO_3^-, ANC = 100 µeq L^{-1} was achieved at a single site. Historical ANC values affected a site's ability to achieve ANC critical thresholds. The critical threshold for soil solution NO_3^- was exceeded for all but the most stringent deposition scenarios (–90 percent S and –90 percent NO_3^-). Deposition reductions of 90 percent for NO_3^- and 80 percent for ammonium (NH_4^+) were not sufficient to lower deposition below the $CL_{nut}N$ at all sites. Data indicate that upper sites at GSMNP are N saturated; to protect these sites from acidification, the more protective chemical criteria of no decrease in base saturation and Al:Bc = 0.1 should be used when determining critical loads. When choosing chemical criteria in deposition reduction modeling, care should be taken to ensure that the criteria chosen will protect sensitive ecosystem elements.

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Cover Photo

A typical view of the mountains in the Great Smoky Mountains National Park, North Carolina. Photo by Helga Van Miegroet, used with permission.

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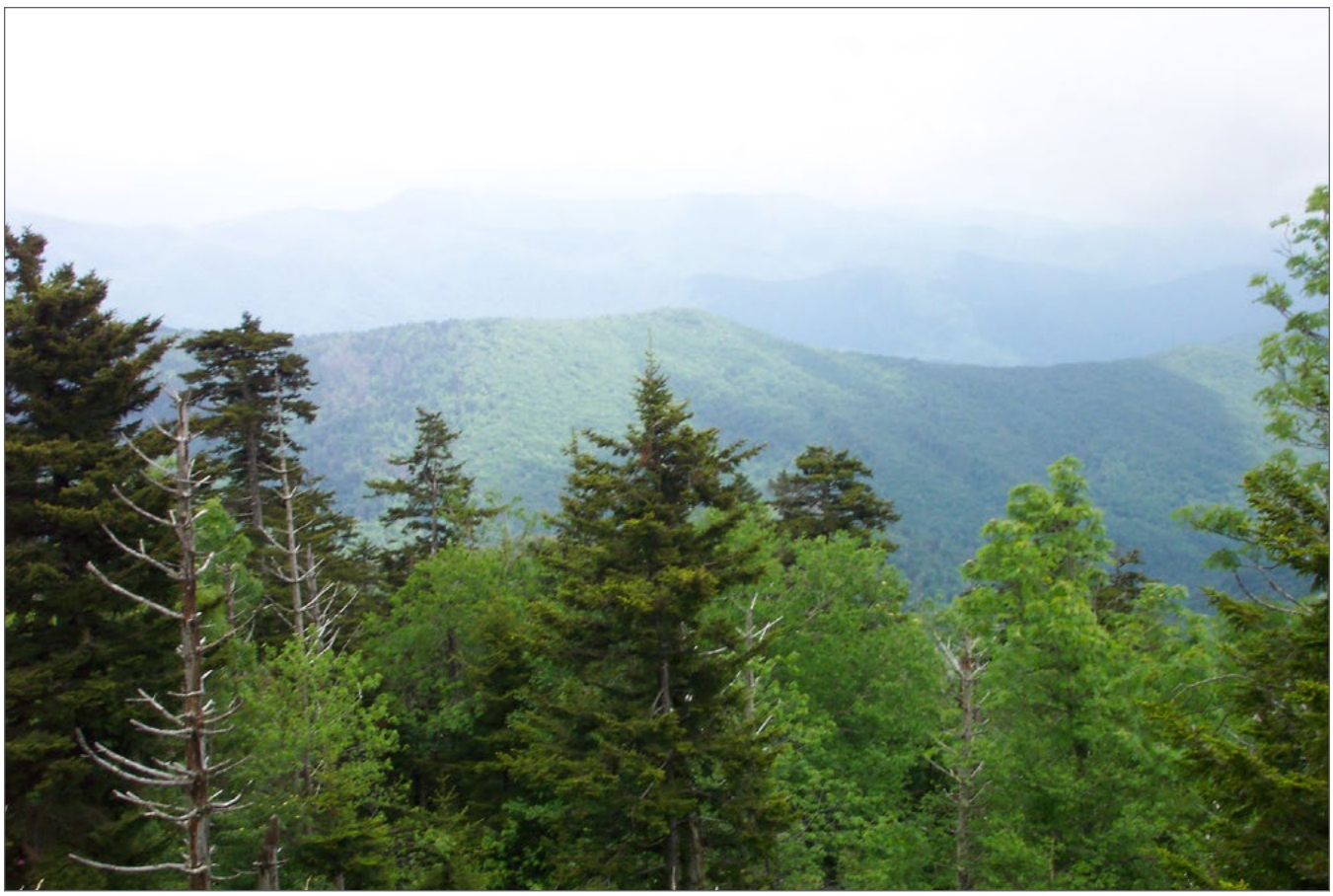

Spruce -fir forest near Clingman's Dome, North Carolina. Photo by Helga Van Miegroet, used with permission.

INTRODUCTION

The Eastern United States has been severely affected by elevated atmospheric deposition of sulfur (S) and nitrogen (N) over many decades (Driscoll et al. 2001, Eagar and Adams 1992, Reuss and Johnson 1986). Atmospheric S and N deposition have contributed to acidification of soils and surface waters, with harmful effects on forest vegetation and aquatic biota (Driscoll et al. 2001). Sulfur dioxide (SO_2) emissions peaked in the United States in 1973 and declined ~67 percent between 1980 and 2009 because of the Clean Air Act (Burns et al. 2011). This pattern has not, however, coincided with widespread recovery of soil and surface waters from acidic deposition (Bailey et al. 2004, 2005; Rice et al. 2014; Stoddard et al. 2003; Warby et al. 2005, 2009). Acidification may deplete soils of base cations and can mobilize aluminum (Al) in soils (Elliott et al. 2008, Reuss 1983, Reuss and Johnson 1985), resulting in toxicity to plants and other biota. Nitrogen deposition poses a threat to forest health beyond the impacts of acidification; it can lead to N saturation, the condition where available N exceeds biotic demand (Aber et al. 1989). Detrimental responses to elevated N deposition, which occur with N saturation, include elevated surface water nitrate (NO_3^-) concentration (Aber et al. 2003, Brookshire et al. 2007); biotic responses include increases in tissue N chemistry and shifts in understory and overstory species composition (Boggs et al. 2005, Pardo et al. 2011a), which have been observed across the Eastern United States.

The Great Smoky Mountains National Park (GSMNP), designated an International Biosphere Reserve in 1976 and a World Heritage Site in 1983, has long been considered a center of vascular plant biodiversity in North America (Jenkins 2007). In addition to a diverse assemblage of plant communities, GSMNP is home to many plants that are endemic to the southern Appalachians and large tracts of primary forest. These communities are subject to multiple threats to forest health, including exotic pests and pathogens and airborne pollutants (Jenkins 2007). Great Smoky Mountains National Park has received among the highest levels of N and S deposition in the Eastern United States (Johnson et al. 1991, Lovett and Lindberg 1993, Weathers et al. 2006). For 2000, Weathers et al. (2006) modeled deposition hotspots of 42 kg ha^{-1} y^{-1} (2,600 eq ha^{-1} y^{-1}) S and 31 kg ha^{-1} y^{-1} (2,200 eq ha^{-1} y^{-1}) N. Soils, especially at high elevations, have low base saturation and therefore little capacity for buffering acidic inputs (Cai et al. 2012, Johnson and Lindberg 1992). High-elevation soils and runoff show signs of N saturation (Nodvin et al. 1995, Van Miegroet et al. 2001). Some tree species in the park, for example, red spruce (*Picea rubens* Sarg.), are sensitive to elevated N inputs and acidification (Sullivan et al. 2001, Webster et al. 2004). Thus, some areas of GSMNP may be susceptible to the adverse impacts of N and S deposition.

The concept of critical loads was introduced in Europe more than two decades ago as a tool for negotiating reductions in air pollution to protect sensitive ecosystems (Posch et al. 2001). A critical load is the estimate of exposure to pollutants below which harmful effects on sensitive elements of the environment do not occur over the long term based on present knowledge (UBA 2004). Critical loads can be determined using empirical approaches, steady-state mass-balance calculations, and dynamic modeling for aquatic or terrestrial systems. Terrestrial critical loads for acidity (CL (S + N)) are used to estimate the level of N + S deposition that will lead to soil acidification and the subsequent detrimental effects to the forest ecosystem; aquatic critical loads for acidity determine the deposition that will maintain an acid neutralizing capability (ANC) level that will protect aquatic biota from acidification (Scheffe et al. 2014). Steady-state mass-balance critical loads for nutrient N ($CL_{nut}N$) for terrestrial ecosystems designate the N deposition level in excess of potential biological and abiotic retention within the ecosystem. The exceedance, the extent to which current deposition exceeds the critical load (exceedance = current deposition – critical load), is a simple way of quantifying the risk from atmospheric deposition for an ecosystem.

The purpose of this assessment was to calculate critical loads for S and N deposition at forest ecosystem sites in GSMNP based on available data and using four chemical criteria. Our approach to critical load

Table 1.—Site description

Site	Upper Spruce-Fir	Lower Spruce-Fir	Beech Gap	Mixed Hardwood
Elevation (m)	1800	1740	1600	635
Forest type	spruce-fir	spruce-fir	American beech	mixed hardwood
Additional site information	Red Spruce; Becking site IFS (SS) [a]	Red Spruce; Noland Divide Tower site IFS (ST) [a]	American Beech site IFS (SB) [a]	NADP/NTN [b] Elkmont site (TN11)
Total S deposition (eq ha^{-1} y^{-1})	1958	1958	983	625
Total S deposition (kg ha^{-1} y^{-1})	31	31	16	10
Total N deposition (eq ha^{-1} y^{-1})	2313	2313	1162	607
Total N deposition (kg ha^{-1} y^{-1})	32	32	16	8.5
Total base cation deposition (eq ha^{-1} y^{-1})	1713	1713	860	173
N sequestration rate (eq ha^{-1} y^{-1})	321	45	0	0
Base cation sequestration rate (eq ha^{-1} y^{-1})	562	79	0	0
Weathering rates (eq ha^{-1} y^{-1})	770	2632	682	971
Weathering rate source	IFS	IFS	Substrate type–clay % [c]	Substrate type–clay % [c]

[a] Sites included in the Integrated Forest Study (Johnson and Lindberg 1992).
[b] National Atmospheric Deposition Program/National Trends Network.
[c] Sverdrup et al. 1990.

calculation differs from recent studies (Fakhraei et al. 2016, Zhou et al. 2015), which focused primarily on impacts of surface water acidity (ANC) on aquatic biota. We focus on the potential impacts on soil and vegetation and incorporate the effect of disturbance on stand dynamics in the high-elevation spruce-fir ecosystems. A simple mass-balance model comparing ecosystem inputs (including N or S deposition) to ecosystem outputs was used to calculate CL (S + N) and $CL_{nut}N$. We used the Very Simple Dynamic (VSD) model (Posch and Reinds 2009, Posch et al. 2003) to predict when an ecosystem parameter (e.g., soil solution chemistry) may achieve a critical value, or when the ecosystem may recover. We used dynamic modeling to evaluate various deposition scenarios to assess emission control strategies. Resource managers and policy makers require this information to assess the impact of additional pollution sources and to determine the level of deposition reduction necessary to protect national parks and other protected lands. We used the steady-state model to assess critical thresholds in critical loads calculations and the dynamic model to assess changes in chemical criteria over time.

MATERIALS AND METHODS

Site Description

Great Smoky Mountains National Park covers 2114 km^2 in eastern Tennessee and western North Carolina. We used four sites in the park with available data to assess the critical loads (Table 1, Figure 1). These sites represent three forest types at different elevations:

- High-elevation spruce-fir. This forest type is represented by two sites included in the Integrated Forest Study (IFS) (Johnson and Lindberg 1992). Both sites have Fraser fir as a component of the understory. The soils at both sites are classified as Umbric Dystrochrepts derived from Thunderhead sandstone (Johnson and Lindberg 1992). Soils have a silt loam to sandy loam texture, are acidic, and are characterized by high organic matter content, low base saturation, and high N mineralization and nitrification capacity (Cai et al. 2012, Garten and Van Miegroet 1994, Johnson et

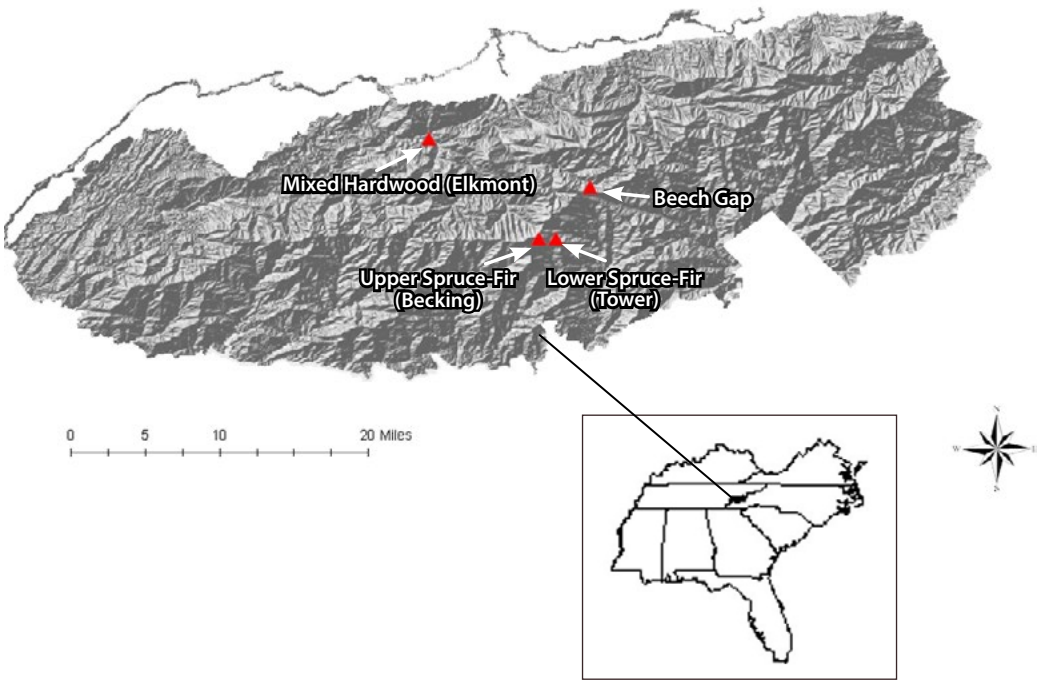

Figure 1.—Map of site locations within Great Smoky Mountains National Park. The four sites represent three forest types at different elevations: (1) high-elevation spruce-fir, (2) mid- to high-elevation American beech, and (3) lower-elevation hardwood. The high-elevation spruce-fir forest type is represented by two sites included in the Integrated Forest Study (IFS) (Johnson and Lindberg 1992): the Upper Spruce-Fir site (called the Becking site in the IFS), and the Lower Spruce-Fir site. The mid- to high-elevation American beech forest type is represented by the IFS Beech Gap site. The Mixed Hardwood site is near the National Atmospheric Deposition Program station in Elkmont. The inset shows the eastern region of the United States.

al. 1991). Both sites have a long-term mean annual precipitation of 200 cm (Vose and Swank 1992).

- The Upper Spruce-Fir site (called the Becking site in the IFS) is located at an elevation of 1800 m on a southwesterly slope west of Noland Divide near Clingmans Dome. This site is characterized by abundant large sandstone boulders on top of and within the soil profile. The vegetation is dominated by old-growth red spruce (*Picea rubens* Sarg.) with occasional Fraser fir (*Abies fraseri* Pursh (Poir.).
- The Lower Spruce-Fir site (called the Tower site in the IFS) is located at an elevation of 1740 m on a southerly slope near Noland Divide. The vegetation here is also dominated by old-growth red spruce and occasional yellow birch (*Betula alleghaniensis* Britton) (Johnson et al. 1991).

Historical logging has affected the western part of GSMNP; however, no further logging activity occurred after the park was established in 1934, and there is no evidence of fire disturbance. The Spruce-Fir sites included in this study have remained largely undisturbed by logging (Pyle 1988). Starting in the 1970s, the balsam woolly adelgid (*Adelges piceae* Ratz.) caused dieback of mature Fraser fir in the Upper Spruce Fir site. This major disturbance, in conjunction with ice storms and hurricane-induced windthrows, led to changes in the forest structure by creating gaps of standing dead fir and fallen spruce (Moore et al. 2008, Pauley et al. 1996). Post-disturbance recruitment of understory trees contributed to increased productivity of these forests from 1993 to 2003 (Moore et al. 2008, Van Miegroet et al. 2007).

- Mid- to high-elevation American beech (*Fagus grandifolia* Ehrh.). This forest type is represented by the IFS Beech Gap site, located at an elevation of 1600 m on a southerly slope, 1 km west of Newfound Gap. The vegetation consists primarily of American beech with occasional buckeye (*Aesculus flava* Aiton) and red spruce (Lindberg et al. 1992). The soils are Umbric Dystrochrepts derived from the Anakeesta Formation (shale parent material), which is sulfide-bearing and may thus lead to release of sulfate (SO_4^{2-}) in soil solution/stream water that is not of atmospheric origin (Johnson and Lindberg 1992).
- Low- to mid-elevation hardwoods. This forest type is represented by the Mixed Hardwood site, which is near the National Atmospheric Deposition Program (NADP) station in

Elkmont (elevation 635 m) and is mapped as the Ditney-Unicoi soil complex, consisting typically of 40–50 percent moderately deep Ditney soils, 25–36 percent shallow Unicoi soils, and about 5 percent rock outcrop (Khiel and Thomas 2007). These soils are well drained and are weathered from metasedimentary rock such as arkose, metagraywacke, metasandstone, and quartzite (USDA, n.d.). The dominant vegetation comprises oak (*Quercus* spp.), hickory (*Carya* spp.), and yellow pine (*Pinus*). The Mixed Hardwood site has a long-term mean annual precipitation of 162 cm.

Methods for Calculating Steady-state Mass-balance Critical Loads

The critical load is based on a mass balance equation—the total amount of acidifying deposition that the ecosystem can tolerate must be balanced by the net input of neutralizing base cations in the ecosystem. Therefore, we calculate the sum of the base cation inputs (from atmospheric deposition and mineral weathering) and outputs (from removal of biomass and leaching losses of ANC) for an ecosystem to determine the net input of base cations per year. Sulfate and NO_3^- deposition is accompanied by hydrogen ions (H^+), which are acidifying. Per the European protocol (UBA 2004), we assume that all ammonium (NH_4^+) entering the ecosystem via deposition is nitrified to NO_3^- within the ecosystem. This assumption is supported by field data (Cai et al. 2010). As this process liberates two H^+ ions, NH_4^+ deposition can be more acidifying than NO_3^- deposition (Nihlgård 1985). These mobile H^+ ions can displace base cations from the soil exchange complex and lead to depletion of the base cation pool in the soil, which ultimately leads to acidification of soils (Reuss and Johnson 1986). This phenomenon has been widely observed across the Eastern United States (Bailey et al. 2004, 2005; Warby et al. 2005, 2009).

Critical Loads of S + N

Calculations of critical loads of S + N are based on a simple mass balance model described in detail elsewhere (Pardo 2010, UBA 2004):

$$CL\ (S + N) = BC_{dep} - Cl_{dep} + BC_w - Bc_u + N_i + N_u + N_{de} - ANC_{le,crit} \quad [1]$$

where:

BC_{dep} = sum of base cations (Ca + Mg + Na + K) deposition rate (eq $ha^{-1}\ y^{-1}$)

Cl_{dep} = chloride deposition

BC_w = soil weathering rate of base cations (Ca + Mg + K + Na) (eq $ha^{-1}\ y^{-1}$)

Bc_u = net Ca + Mg + K uptake rate (eq $ha^{-1}\ y^{-1}$) ultimately removed by harvest or fire (*Bc* denotes that Na is not included)

N_i = acceptable net N immobilization (or accumulation) rate in the soil (eq $ha^{-1}\ y^{-1}$)

N_u = net N removed via biomass removal (eq $ha^{-1}\ y^{-1}$)

N_{de} = soil denitrification rate (eq $ha^{-1}\ y^{-1}$)

$ANC_{le,crit}$ = acceptable ANC leaching rate (eq $ha^{-1}\ y^{-1}$).

Equation 1 assumes that the stand is mature and at steady state; for the ecosystem as a whole there is no net change in standing biomass and therefore no net annual nutrient requirement. Nutrient uptake and storage by vegetation are accounted for only when vegetation biomass is removed from the ecosystem; e.g., by harvesting (UBA 2004). We altered equation 1 to reflect the net N sequestration (N_{se}) and net base cation sequestration (Bc_{se}) for the Upper and Lower Spruce-Fir sites, where site disturbance (see Site Description, page 2) reduced the number of mature spruce trees in the overstory (Pauley et al. 1996, Van Miegroet et al. 2001) and led to significant regrowth in the gaps (Moore et al. 2008). These aggrading forest conditions cause the assumption of steady-state to be violated. Equation 2 takes into account the transient assimilation and retention of N by the ecosystem over the period for which the critical load was calculated (~100 years). Not accounting for this N sink would cause us to underestimate the critical load.

$$CL\ (S + N) = BC_{dep} - Cl_{dep} + BC_w - Bc_u - Bc_{se} + N_i + N_u + N_{se} + N_{de} - ANC_{le,crit} \quad [2]$$

Input parameters for calculating steady-state mass-balance critical loads at GSMNP are described below and summarized in Table 2. Pardo and Duarte (2007) provide additional details about the methods, data sources, and assumptions.

Table 2.—Input for VSD calculations

Parameters	Comments[a]	Units	High elevation Noland Divide: Upper Spruce-Fir	High elevation Noland Divide: Lower Spruce-Fir	Mid- to high-elevation Beech Gap	Lower elevation Mixed Hardwood[b]
Elevation		m	1800	1740	1600	635
Forest type			Fraser fir red spruce	Fraser fir red spruce	beech	mixed hardwood
Time frame			1860–2150	1860–2150	1860–2150	1860–2150
Soil depth	Measured	m	0.46	0.57	0.74	0.83
Bulk density	Measured	g cm^{-3}	0.92	0.92	1.13	1.09
Soil moisture	Estimated[c]	M m^{-1}	0.12	0.12	0.12	0.15
CEC	Measured	meq kg^{-1}	180	293	239	132
Base saturation (obs)	Measured	%	7.6	9	21	11
C pool (obs)	Measured	g m^{-2}	5500	9500	9250	2409
C:N (obs)	Measured		10	12	11	16
Q	Modeled	m	1.16	1.16	1.16	0.79
Weathering	Modeled	eq m^{-2} y^{-1} eq ha^{-1} y^{-1}	0.0770 770	0.2632 2632	0.0682[d] 682	0.0971[d] 971
cRCOO	Estimated[e]	0	0.0317	0.0317	0.0317	0.0317
lgKAlBC[f]	VSD		-0.86345	8.0427	3.3423	7.0982
lgKHBC[g]	VSD		3.5317	6.4225	4.781	6.1211
lgKAlox[h]	Constant[i]		8.77	8.77	8.77	8.77
Soil solution PCO_2	Constant[i]		17	17	17	17
Nim_acc[j]	Constant[i]	eq m^{-2} y^{-1} kg ha^{-1} y^{-1}	0.0036 0.5	0.0036 0.5	0.0036 0.5	0.0036 0.5

[a] All measured values are from IFS (Johnson and Lindberg 1992) unless otherwise noted.
[b] Measured values are from the Natural Resources Conservation Service.
[c] Based on texture (Brady 1990).
[d] Substrate type-clay% method.
[e] Estimated based on total organic carbon and average carboxyl content from Oliver et al. (1983).
[f] Selectivity constant for Al:Bc exchange.
[g] Selectivity constant for H^+:Bc exchange.
[h] Gibbsite equilibrium constant: Kgibb.
[i] Based on values from the literature.
[j] Acceptable N accumulation in soil, N_i.

Base Cation Deposition. Base cation deposition (BC_{dep}) was calculated for Ca + Mg + Na + K deposition. Total BC_{dep} of 1713 eq ha^{-1} y^{-1} for the Upper and Lower Spruce-Fir sites was estimated using the total deposition: throughfall base cation ratio from the IFS (0.79:1) (Johnson and Lindberg 1992) and throughfall BC_{dep} of 2159 eq ha^{-1} y^{-1} collected under canopy at the Lower Spruce-Fir site from 1999 to 2004 (B. Robinson, personal communication[1]). Total BC_{dep} of 860 eq ha^{-1} y^{-1} for the Beech Gap site (mid- to high-elevation) was estimated using year 2000 Beech Gap: Upper Spruce-Fir total deposition ratio (0.50) (Weathers et al. 2006 and K. Weathers, personal communication[2]) and Spruce-Fir BC_{dep} estimates. Total BC_{dep} for the Mixed Hardwood site of 173 eq ha^{-1} y^{-1} was estimated using annual wet deposition data from the NADP site at Elkmont (NADP site # TN-11) from 1999 to 2004, using a scaling factor of 1.4:1 for total BC_{dep}: wet BC_{dep}. The factor of 1.4 was derived from the ratio of wet + dry S deposition: wet S deposition reported at the

[1] Bruce Robinson, Emeritus Professor, Department of Civil and Environmental Engineering, University of Tennessee.

[2] Kathleen Weathers, Senior Scientist, Cary Institute of Ecosystem Studies.

CASTNET site at Look Rock. Cloud and fog contributions were not included in deposition estimates for this site, because their inputs at this low elevation are negligible.

Base Cation Weathering. Base cation weathering (BC_w) was calculated for Ca + Mg + Na + K weathering. We used mineral weathering rates for the Upper and Lower Spruce-Fir sites as reported in the IFS (April and Newton 1992). We used the substrate type/clay content method to estimate soil mineral weathering (Ouimet 2006, Sverdrup et al. 1990) for the Mixed Hardwood site, which is not an IFS site and therefore did not have reported weathering rates, as well as for the Beech Gap site, which had an anomalously low weathering rate reported in IFS (289 eq ha^{-1} y^{-1}). Weathering rates shown in Table 2 were calculated using depth-weighted data weighted by area for all the soil series that make up the components of the Natural Resources Conservation Service GSMNP order 2 map unit ID (Khiel and Thomas 2007) for the sites. Mineral soil depth was defined as the depth from the top of the mineral soil (A or E horizon) through the bottom of the B horizon (excluding BC and Bx horizons, if present); this depth was selected to represent the rooting zone. Average clay content was calculated as the depth-weighted average of clay content in the mineral soil in the rooting zone (based on horizon-level data).

Base Cation Uptake, Nitrogen Immobilization, and Nitrogen Uptake. No harvesting is permitted in GSMNP, so base cation uptake (Bc_u) and N uptake (N_u) through biomass removal were 0 kg ha^{-1} y^{-1}. We used an acceptable soil N immobilization of 0.5 kg ha^{-1} y^{-1}; this is the upper end of the range, 0.2–0.5 kg ha^{-1} y^{-1}, suggested in the European critical loads protocol (UBA 2004).

Nitrogen and Base Cation Sequestration. We estimated net overstory N_u at the sites based on stand inventory data for the period 1993–2003 (Barker et al. 2002, Van Miegroet et al. 2007). First, we estimated the N increment in wood for 1993–2003 by taking the mean of the N increment reported for 1993–98 (Barker et al. 2002) and 1998–2003. The 1998–2003 N increment was obtained by dividing carbon (C) increments reported in Van Miegroet et al. (2007) by a C:N ratio of 200. To calculate the net N increment, we then subtracted N release calculated from coarse woody debris decomposition reported by Van Miegroet et al. (2007), again assuming a C:N ratio of 200. Finally, assuming the aggrading period might continue for approximately 50 years of the 100-year critical load modeling period, we divided the current net N increment by 2 to obtain an average annual net increment estimate over the entire 100-year period. We refer to this value as *N sequestration* (N_{se}). We used average N_{se} rates of 321 eq ha^{-1} y^{-1} (4.5 kg ha^{-1} y^{-1}) for the Upper Spruce-Fir site and 45 eq ha^{-1} y^{-1} (0.63 kg ha^{-1} y^{-1}) for the Lower Spruce-Fir site. This is consistent with greater growth responses at the highest elevation, where disturbance was most pronounced (Moore et al. 2008). We used the Bc:N ratio of 1.75 for nutrient content in overstory bole wood, based on IFS data (Johnson and Lindberg 1992), to estimate Bc_{se} (Ca + Mg + K sequestration) rates of 562 eq ha^{-1} y^{-1} for the Upper Spruce-Fir site and 79 eq ha^{-1} y^{-1} for the Lower Spruce-Fir site. There was no long-term nutrient sequestration for the mid- or low-elevation hardwood sites, which were not affected by the balsam woolly adelgid infestation.

Acid Neutralizing Capability Leaching. The acceptable ANC leaching rate quantifies the loss of ANC from the ecosystem. The acceptable ANC leaching rate is not a measured value; it is set based on a critical threshold that is intended to prevent adverse impacts on the forest ecosystem. The $ANC_{le,crit}$ can be calculated in multiple ways using different chemical criteria. For steady-state calculations of CL (S + N), we used four chemical criteria: Al:Bc (Al:(Ca + Mg + K); 0.1 and 1.0 mol mol^{-1}), base saturation of soil (no decrease), Al concentration (0.2 meq L^{-1}), and pH (4.2) in soil solution. Pardo and Duarte (2007) include the equations that use these criteria to calculate $ANC_{le,crit}$. These chemical criteria are the most widely used in critical loads assessment in Europe and North America (Cronan and Grigal 1995, Forsius et al. 2010, NEG/ECP 2003, Ouimet et al. 2001, Sverdrup and Warfvinge 1993). The Al:Bc ratio in soil solution is the most broadly used chemical criterion; the ratio of 1.0 mol^{-1} is most commonly used in Europe (Reinds et al. 2008). We set the lower threshold of 0.1 mol mol^{-1} to protect against decreases in base saturation. The criterion of base saturation, with a "no decrease" threshold, should have a similar effect. Aluminum and pH were included for comparison purposes. Aluminum may be used as a chemical criterion, especially if there is a drinking water standard that can be used as a critical threshold for Al concentration. The soil solution pH is typically selected as a criterion in systems with high organic matter, which interacts with Al to make it less available and thus less reliable as a chemical criterion.

Table 3.—Parameters used to calculate critical loads for nutrient N

Parameter	NO_3^-	Value	Comments
Acceptable nitrate concentration	$[N]_{le(acc)}$	0.2 mg N L^{-1}	From UBA (2004)
Acceptable soil N immobilization	N_i	0.5 kg N ha^{-1} y^{-1}	A range from 0 to 1 kg N ha^{-1} y^{-1} is typically used
Biomass N removal	N_u	0 kg N ha^{-1} y^{-1}	No harvesting is permitted in the park
Net N sequestration	N_{se}	0–5 kg N ha^{-1} y^{-1}	Varies with elevation
Denitrification	N_{de}	0 kg N ha^{-1} y^{-1}	Denitrification is assumed to be negligible in these upland forest soils

Critical Load of Nutrient Nitrogen

Both S and N deposition can acidify the ecosystem; atmospheric N deposition also represents a nutrient addition that is either stored in or lost from the ecosystem (via immobilization in the soil N pool, removal in biomass by harvesting, fire, or gaseous losses). The $CL_{nut}N$ is defined as the sum of the net N accumulation in the soil, net N removed via biomass removal, soil denitrification, and acceptable N leaching. The acceptable N leaching rate, $N_{le(acc)}$, is the maximum acceptable leaching rate for non-N-saturated ecosystems (Table 3) and is given in equation 3:

$$N_{le(acc)} = Q \times [N]_{crit} \quad [3]$$

where:

$[N]_{crit}$ = the N concentration in the soil solution above which would be considered detrimental to ecosystem or soil (see Table 3)

Q = hydrologic flux (m^3 ha^{-1} y^{-1})

Under steady-state ecosystem conditions, $CL_{nut}N$ is expressed as:

$$CL_{nut}N = N_i + N_u + N_{de} + N_{le(acc)} \quad [4]$$

We altered equation 4 to reflect the net N sequestration (N_{se}) until the stand reaches steady state for the Spruce-Fir sites, leading to the following modified expression of $CL_{nut}N$:

$$CL_{nut}N = N_i + N_u + N_{se} + N_{de} + N_{le} \quad [5]$$

We used an acceptable soil N immobilization of 0.5 kg ha^{-1} y^{-1} (UBA 2004). Because harvesting is not permitted in GSMNP, N_u is 0 kg ha^{-1} y^{-1}. Denitrification was negligible in these upland forest stands (Wells et al. 1988); N_{de} is 0 kg ha^{-1} y^{-1}. $[N]_{crit}$ was set to 0.2 mg N L^{-1}. N_{se} was determined as described above for CL (S + N).

Uncertainty in Critical Loads Calculations

Sources of uncertainty in these critical loads calculations come from measured and modeled parameters. The terms for deposition, soil mineral weathering, nutrient sequestration, and leaching—especially the acceptable ANC leaching—all introduce uncertainty into these calculations (Hall et al. 2001b). The mineral soil weathering rate has a particularly high uncertainty (Hodson and Langan 1999). Hall et al. (2001b), Hodson and Langan (1999), and Reinds et al. (2008) discuss in detail the sources of uncertainty in critical load calculations.

Methods for Dynamic Modeling Using the Very Simple Dynamic Model

We used the VSD model to compare the effects of multiple deposition scenarios on soil solution NO_3^-, ANC, Al, Al:Bc, pH, and soil base saturation between 1860 and 2150. The VSD model uses mass balance, equilibrium, and flux equations to simulate soil solution chemistry over time. Required input parameters include soil chemical and physical properties, cation weathering and uptake, and deposition and climate data. The model uses single time-steps, does not include sulfate adsorption, and assumes that initial concentrations are in equilibrium with inputs. We used modeled historical deposition data from the Southern Appalachian Mountain Initiative project (Sullivan et al. 2001 and B.J. Cosby, personal communication[3]) to estimate historical deposition at these sites (see Pardo and Duarte 2007). Observed soil C pool and C:N ratio values are required to calibrate initial C pool and C:N ratio values; observed base saturation is required to calibrate the exchange constants for Al:Bc exchange (log K Al:Bc)

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Table 4.—Deposition scenarios used for critical loads dynamic modeling in GSMNP

Scenario	Total S	NO_3^-	NH_4^+	Deposition reductions
1	No change	No change	No change	Current deposition (1999–2004 mean)
3	–48%	–56%	+5%	Deposition reductions evenly distributed from 2002 to 2015 (U.S. EPA-CAIR)
5	–80%	–80%	+9%	Deposition reductions evenly distributed from 2002 to 2015
11b	–90%	–90%	–80%	Scenario 3 reductions were used through 2015; the remainder of the deposition reductions are evenly distributed from 2015 to 2050

and H^+:Bc exchange (log K H^+:Bc). The VSD is a simple model, and these are the only calibrations made before the actual simulations were run. Posch et al. (2003) and Posch and Reinds (2009) describe the model fully.

In this analysis we focus on four deposition scenarios (Table 4) based on planned or hypothetical emissions control strategies; these span the range of responses of the 11 deposition scenarios we evaluated with the VSD model (Pardo and Duarte 2007). Scenario 1 holds 1999 deposition rates constant into the future. Scenario 3 uses the relative reduction factors for total S (SO_4^{2-}, SO_2) and total N (NO_3^-, NH_4^+) deposition from the U.S. Environmental Protection Agency (U.S. EPA)- Clean Air Interstate Rule (CAIR) based on 36-km Community Multiscale Air Quality modeled runs using 2001 as the base deposition year and 2015 as the target year. Scenario 5 has 80 percent reductions in total S and NO_3^- and a 9 percent increase in NH_4^+ spread evenly over 2002 to 2015. Scenario 11b uses scenario 3 reductions through 2015, followed by 90 percent reductions in total S and NO_3^- and 80 percent reduction in NH_4^+ to 2050. These scenarios allow us to model future trajectory of the ecosystems under current and reduced atmospheric inputs or evaluate rate of relative recovery.

Very Simple Dynamic Model Input Parameters

Posch and Reinds (2009) describe the required VSD input parameters; Table 2 summarizes these parameters for the GSMNP sites. Pardo and Duarte (2007) provide further information about applying the VSD model at GSMNP.

Soil Input Parameters. Base cation weathering was determined as described above for CL (S + N). Additional soil input parameters for VSD include depth, bulk density, moisture, cation exchange capacity, base saturation, carbon pool, C:N, partial pressure of carbon dioxide (PCO_2) in soil solution, and organic acids concentration (cRCOO). All except PCO_2, cRCOO, and soil moisture are depth-weighted means calculated from measured values at each site. For the Upper and Lower Spruce-Fir and Beech Gap sites, soil data came from the IFS study (Johnson and Lindberg 1992). For the Mixed Hardwoods site, soil data came from pedon data used in creating the Natural Resources Conservation Service order 2 soil map for GSMNP (Khiel and Thomas 2007). We used the relationships from Brady (1990) to estimate soil moisture (field capacity) based on reported soil texture; we did not use the measured data, because these data indicate soil moisture at the time of sampling and do not necessarily represent typical field capacity. Because we did not have measured PCO_2 in soil solution (as a multiple of PCO_2 [atm] in air) for any of the sites, the VSD default value of 17 was used. We used B-horizon total organic carbon (TOC) values from Noland Divide (0.2636815 mol C m^{-3}; Van Miegroet, unpublished data[4]) in place of dissolved organic carbon values to determine the cRCOO and multiplied these values by the average carboxyl content (10 μeq mg^{-1} organic carbon) from Oliver et al. (1983). We selected the Oliver model to model the dissociation of organic acids.

Deposition and Climate Input Parameters for Very Simple Dynamic Model Calculations. Deposition and climate input parameters for VSD calculations include hydrologic flux (runoff) and atmospheric deposition (S, N, base cation, chloride) rates. The modeled hydrologic flux rate for the Upper and Lower Spruce-Fir and Beech Gap sites came from the IFS study (Vose and Swank 1992); the value for the Mixed Hardwood site came from a map of mean annual runoff for the Northeastern, Southeastern, and Mid-Atlantic United States (Krug et al. 1990). Deposition rates for the

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high-elevation sites are based on mean measured wet deposition data collected using an Aerochemetrics wet-only collector in an open clearing near the Lower Spruce-Fir site from 1999 to 2004 (Cai et al. 2010 and B. Robinson, personal communication[1]). The volume-weighted mean annual wet deposition values were then scaled, as described below, to estimate total (wet + dry + cloud) deposition (Table 1). Total deposition was measured during the IFS for the period 1986–89 (Johnson and Lindberg 1992).

For the Upper and Lower Spruce-Fir sites, we used the scaling factor of 4.4:1 for total: wet N deposition based on the ratios of total: wet N deposition from the IFS as reported by Van Miegroet et al. (2001) to estimate total (wet + dry + cloud) N deposition. For S deposition, we used a scaling factor of 3.7:1 based on the ratio of total: wet deposition reported in the IFS (Johnson and Lindberg 1992). Base cation deposition at the Upper and Lower Spruce-Fir sites was determined as described above for critical loads S + N calculations. For the Beech Gap site, we used the ratio from the year 2000 of total deposition at the Beech Gap site: total deposition at the Upper Spruce-Fir site, 0.50 as reported by Weathers et al. (2006, and K. Weathers, personal communication[2]), to estimate total deposition of N, S, and BC. For the Mixed Hardwood site, we used measurements of wet deposition data (S, N, BC, chloride) from the NADP site at Elkmont (NADP site # TN-11) and estimates of dry deposition (S and N only) from the CASTNET site at Look Rock. We estimated total BC_{dep} as described above for critical load S + N calculations.

Cation Exchange Input Parameters. We used the Gaines-Thomas relationship, which has been broadly used in critical loads calculations in the United States (Chen et al. 2004, Cosby et al. 2001, NEC/ECP 2001) to model the exchange between the solid phase and the soil solution for Al^{3+}, protons (H^+) and Bc (= Ca + Mg + K). Observed soil C pool and C:N ratio values are required to calibrate initial C pool and C:N ratio values; observed base saturation is required to calibrate the exchange constants for Al:Bc exchange (log K Al:Bc) and H^+:Bc exchange (log K H^+:Bc) (see Posch and Reinds 2009). The gibbsite equilibrium constant ($logKAlox\ (mol^2\ l^{-2})^{1-expAl}$) was set to 8.77 for all three sites, and the exponent [Al] term (gibbsite equilibrium) was 3, indicating a +3 charge on the Al ion in solution.

Nitrogen Input Parameters. Nitrogen cycling in VSD is also limited by minimum and maximum C:N ratios in soil. The VSD model uses measured C:N and the C pool in soil to calculate the N pool and determine the fraction of N that is immobilized (the balance is leached). Because the measured C:N ratios at these sites (Johnson and Lindberg 1992) were below the VSD minimum of 15, a default value of 15 was used, which underestimates the N pool but does not change the model function (all excess N is leached).

RESULTS

Critical Loads of Acidity and Nutrient Nitrogen and Exceedance

In the steady-state mass-balance calculations of critical loads, we compared four chemical criteria used to calculate ANC_{le}, a key part of the CL (S + N) calculation: Al concentration, Al:Bc ratio, pH in soil solution, and base saturation of soil. The critical threshold of Al:Bc = 0.1 resulted in the lowest critical load for acidity compared to other critical thresholds for most sites (Figure 2A), ranging from low of 1,252 eq $ha^{-1}\ y^{-1}$ for the Mixed Hardwood site to a high of 3,682 eq $ha^{-1}\ y^{-1}$ for the Lower Spruce-Fir site. The chemical criterion of no decrease in base saturation yielded similar results except for the Upper Spruce-Fir site where the critical load for no change in base saturation was higher. Using the solution Al concentration critical threshold (0.2 meq L^{-1}) yielded critical loads similar to those using the upper Al:Bc threshold (1.0), except at the Lower Spruce-Fir site, where it was lower. The critical threshold of pH = 4.2 consistently resulted in the highest critical loads values, from 4,965 eq $ha^{-1}\ y^{-1}$ for the Mixed Hardwood site to 8,785 eq $ha^{-1}\ y^{-1}$ for the Lower Spruce-Fir site.

Exceedance of the critical load can be used to evaluate the susceptibility of a site to S and N deposition (exceedance = actual deposition – critical load). Using the most conservative critical thresholds (Al:Bc = 0.1 and no decrease in base saturation), deposition exceeded CL (S + N) at all the sites except Mixed Hardwood (Figure 2B). Using the critical thresholds for Al concentration and Al:Bc = 1, the deposition was approximately equal to the critical load at the Upper Spruce-Fir site; the CL (S + N) was not exceeded for the remaining sites. At none of the sites was the CL (S + N) exceeded using the critical threshold of pH = 4.2.

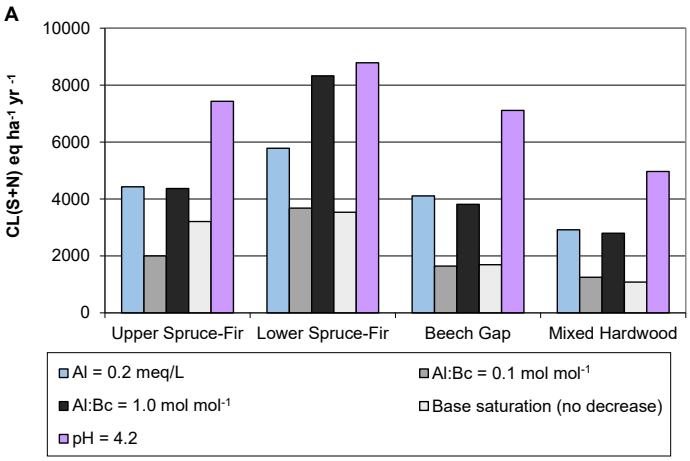

Figure 2A.—Critical load for (S+N) by site. Critical loads were calculated using four chemical criteria: Al concentration (0.2 meq L^{-1}), Al:Bc ratio (0.1 and 1.0 mol mol^{-1}), and pH (4.2) in soil solution, and base saturation of soil (no decrease). Using the critical thresholds of Al:Bc = 0.1 and no decrease in base saturation yielded the lowest critical load for acidity.

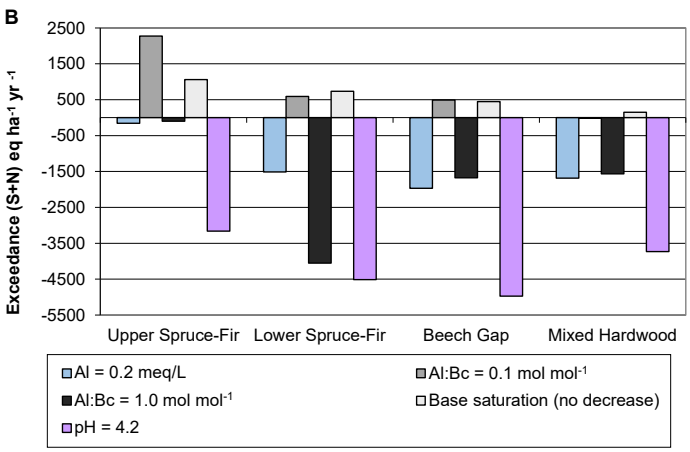

Figure 2B.—Exceedance by site. The exceedance is a useful tool for assessing the extent of risk to ecosystems under current and future deposition scenarios. Exceedance = actual deposition – critical load.

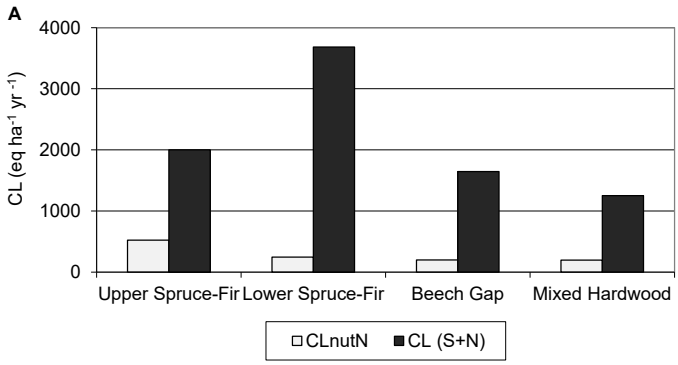

Figure 3A.—$CL_{nut}N$ and CL (S+N) using Al:Bc = 0.1.

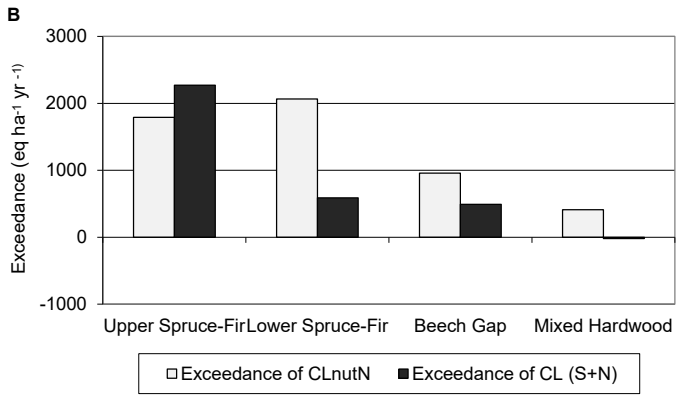

Figure 3B.—Exceedance $CL_{nut}N$ and CL (S+N) using Al:Bc = 0.1.

The $CL_{nut}N$ is typically very low at sites without significant timber harvesting. Indeed, for these four sites within GSMNP, $CL_{nut}N$ ranged from 200 to 500 eq ha^{-1} y^{-1} (2.8–7 kg N ha^{-1} y^{-1}) (Figure 3A), significantly lower than CL (S + N), irrespective of calculation method. The $CL_{nut}N$ was slightly higher for the Upper Spruce-Fir site than for the other sites, driven by the larger disturbance-induced regrowth and N_{se}. In all cases, the $CL_{nut}N$ was exceeded (Figure 3B).

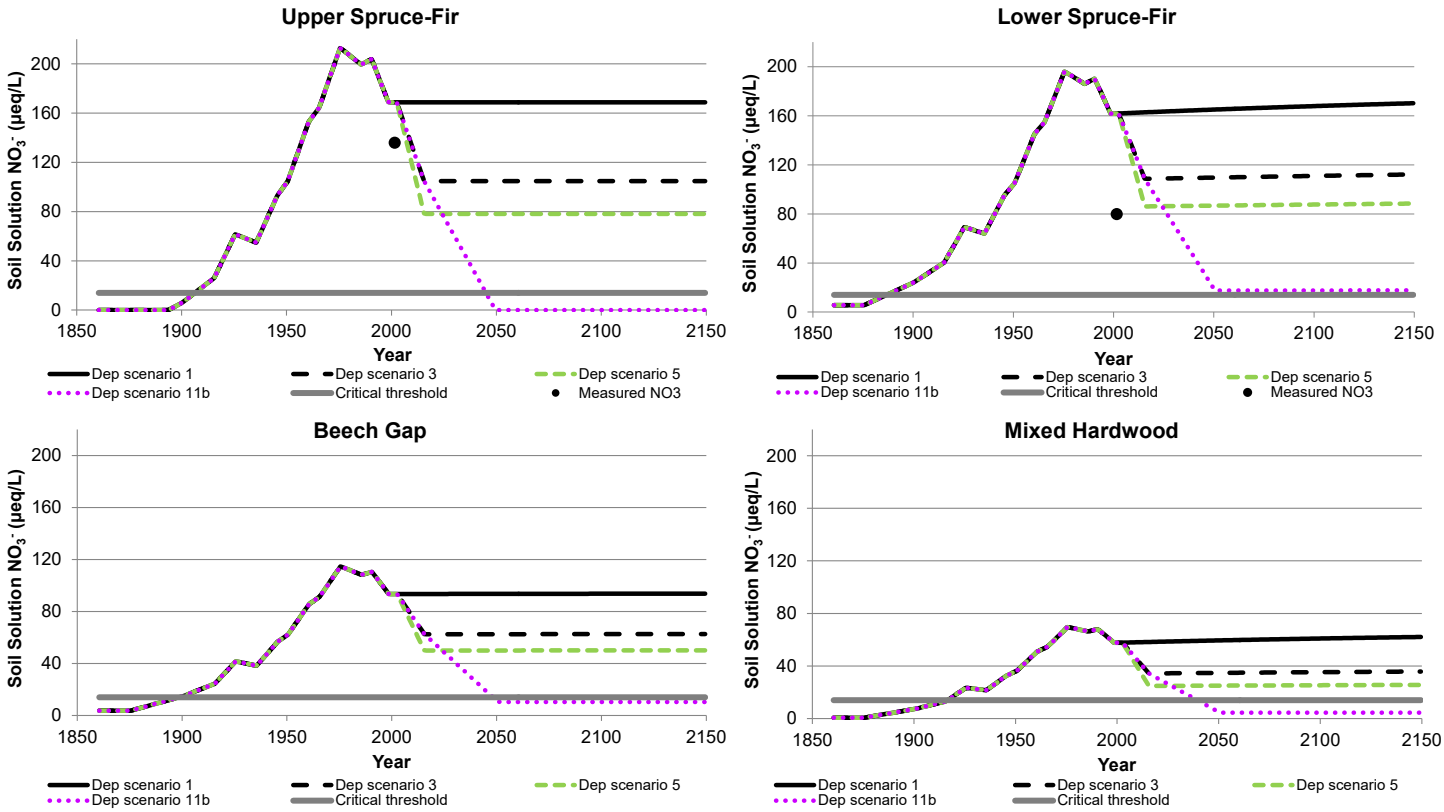

Figure 4.—VSD model results for soil solution NO_3^- for each of the four sites: Upper Spruce-Fir, Lower Spruce-Fir, Beech Gap, and Mixed Hardwood. Scenario 1 = no deposition change; scenario 3 = –48 percent S, –56 percent NO_3^-, +5 percent NH_4^+ deposition change; scenario 5 = –80 percent S, –80 percent NO_3^-, +9 percent NH_4^+ deposition change; scenario 11b = –90 percent S, –90 percent NO_3^-, –80 percent NH_4^+ deposition change.

Dynamic Modeling of Soil Solution Trends Over Time

The VSD model allows us to predict the response of various ecosystem parameters (soil solution ANC, NO_3^- concentration, etc.) over time to different deposition scenarios (Figures 4–9). The Upper Spruce-Fir site, with low base saturation and moderate weathering rate, had the lowest pH (Figure 8) and initial ANC (Figure 5). ANC, NO_3^-, and Al:Bc (Figures 4, 5, and 7) responded dramatically to increases in deposition and usually fell on the detrimental side of critical thresholds (lower for ANC; higher for NO_3^-, and Al:Bc) under scenarios 1, 3, and 5. At the Lower Spruce-Fir site, with moderately low base saturation and a high weathering rate, most soil solution parameters fell on the detrimental side of thresholds under scenario 1 but generally remained acceptable for scenarios 3, 5, and 11b, except for NO_3^- leaching and the upper ANC threshold of 100 µeq L^{-1}. Ecosystem parameters were generally within thresholds for the Beech Gap and Mixed Hardwood sites, which are characterized by moderate weathering and, respectively, high and moderate initial base saturation, except for NO_3^- leaching, the upper ANC threshold of 100 µeq L^{-1}, and base saturation for scenarios 1 and 3. Pardo and Duarte (2007) provide the results of all deposition scenarios for all sites and all parameters.

Nitrate Concentration and Flux

Modeled NO_3^- concentrations of soil solutions at all sites were at or near zero in 1860. Nitrate concentrations rose steadily in the 20th century, reaching a peak in the mid-1970s, with a high value of 210 µeq L^{-1} at the Upper Spruce-Fir site. Reported soil solution NO_3^- concentrations were about 80 µeq L^{-1} for the Lower Spruce-Fir site and 136 µeq L^{-1} for the Upper Spruce-Fir site (Van Miegroet et al. 1992). At all sites for scenarios 1, 3, and 5, the modeled NO_3^- concentration in soil solution exceeded the critical NO_3^- concentration threshold, $[N]_{crit}$, of 0.2 mg N L^{-1} (14 µeq L^{-1}). Deposition reductions of 90 percent for SO_4^{2-} and NO_3^- and reductions of 80 percent for NH_4^+ (scenario 11b) reduced modeled NO_3^- concentration below the critical NO_3^- concentration (Figure 4) for the Beech Gap, Mixed Hardwood, and Upper Spruce-Fir sites, but not for the Lower Spruce-Fir site.

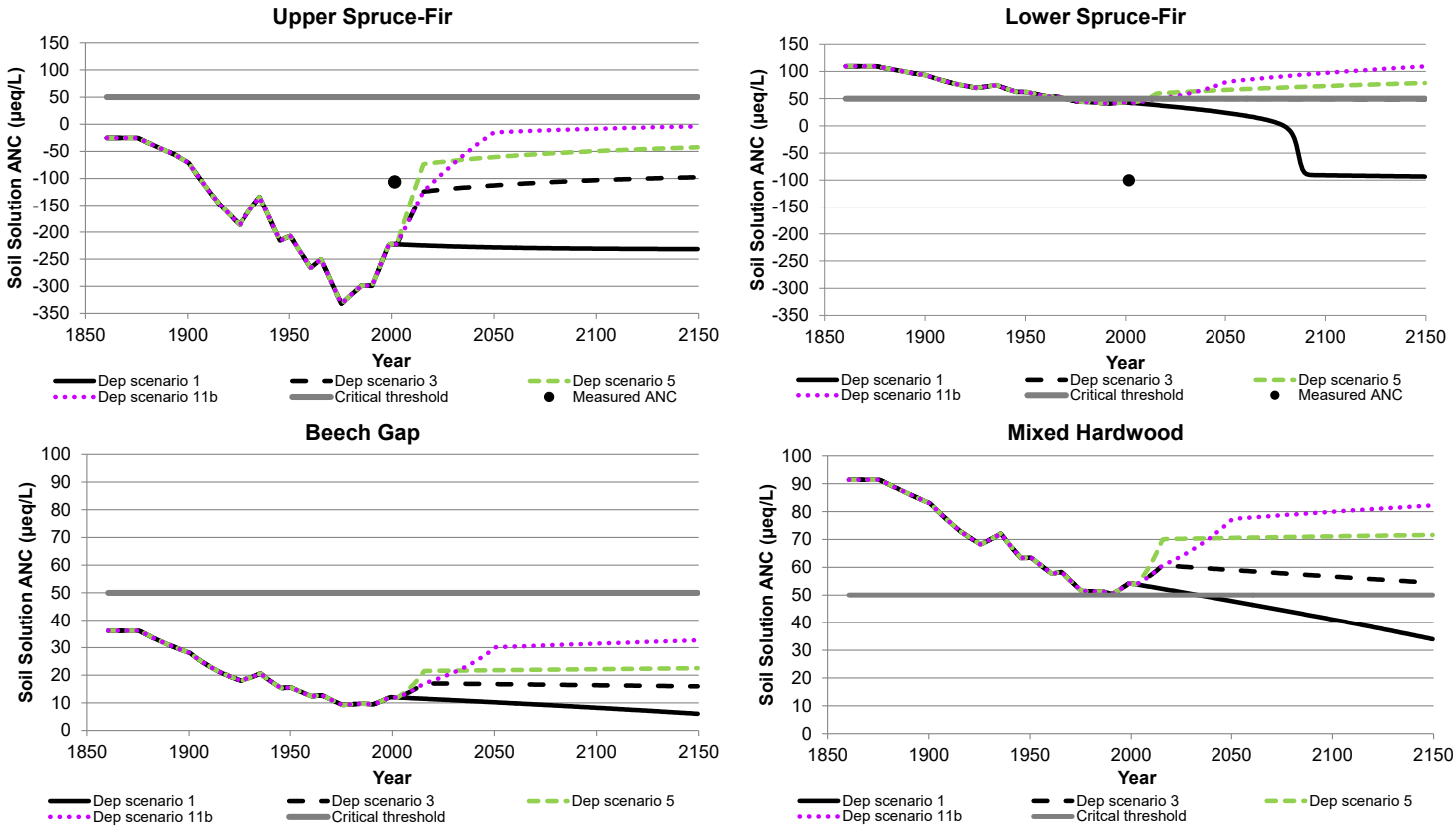

Figure 5.—VSD model results for ANC for each of the four sites: Upper Spruce-Fir, Lower Spruce-Fir, Beech Gap, and Mixed Hardwood. Scenario 1 = no deposition change; scenario 3 = –48 percent S, –56 percent NO_3^-, +5 percent NH_4^+ deposition change; scenario 5 = –80 percent S, –80 percent NO_3^-, +9 percent NH_4^+ deposition change; scenario 11b = –90 percent S, –90 percent NO_3^-, –80 percent NH_4^+ deposition change.

Acid Neutralizing Capability

There are several critical thresholds for ANC in soil solution. The most conservative is ANC = 100 µeq L^{-1}, which minimizes the risk of any soil solution acidification; the least conservative is ANC = 0 µeq L^{-1}, which is the minimum ANC value that would protect against chronic acidification. Because of concerns about episodic stream acidification, selecting a higher critical ANC value of 20 or 50 µeq L^{-1} is prudent (Driscoll et al. 2001). Initial modeled ANC values varied widely by site (Figure 5). The modeled soil solution ANC value at the Upper Spruce-Fir site was –25 µeq L^{-1} in 1860; Lower Spruce-Fir ANC was greater than 100 µeq L^{-1}. ANC values at all sites decreased in the 20th century, remaining below 0 µeq L^{-1} ANC at the Upper Spruce-Fir site under all scenarios, although ANC returned to preindustrial levels under scenario 11b. At the Lower Spruce-Fir site, scenarios 3, 5, and 11b resulted in modeled ANC of at least 50 µeq L^{-1} in 2150; scenario 1 (no change in deposition) resulted in a modeled ANC close to –100 µeq L^{-1}. At the Beech Gap and Mixed Hardwood sites, ANC values remained above 0 µeq L^{-1} for all scenarios. Scenarios 5 and 11b resulted in increasing ANC over time; scenarios 1 and 3 resulted in continued decreases in ANC over time.

Aluminum Concentration

Modeled soil solution Al values were below the critical threshold of 200 µeq L^{-1} (0.2 meq L^{-1}) at all sites in the year 2015 (Figure 6) and increased with time under scenario 1; however, these values approached the critical threshold only at the Upper Spruce-Fir site. At the Lower Spruce-Fir site, modeled Al concentrations increased dramatically but remained below critical thresholds with deposition scenario 1. All other deposition reduction scenarios resulted in decreases in modeled Al concentration across sites from a peak in the 1970s; modeled Al concentrations in beech and mixed hardwood sites all approach zero in 2150.

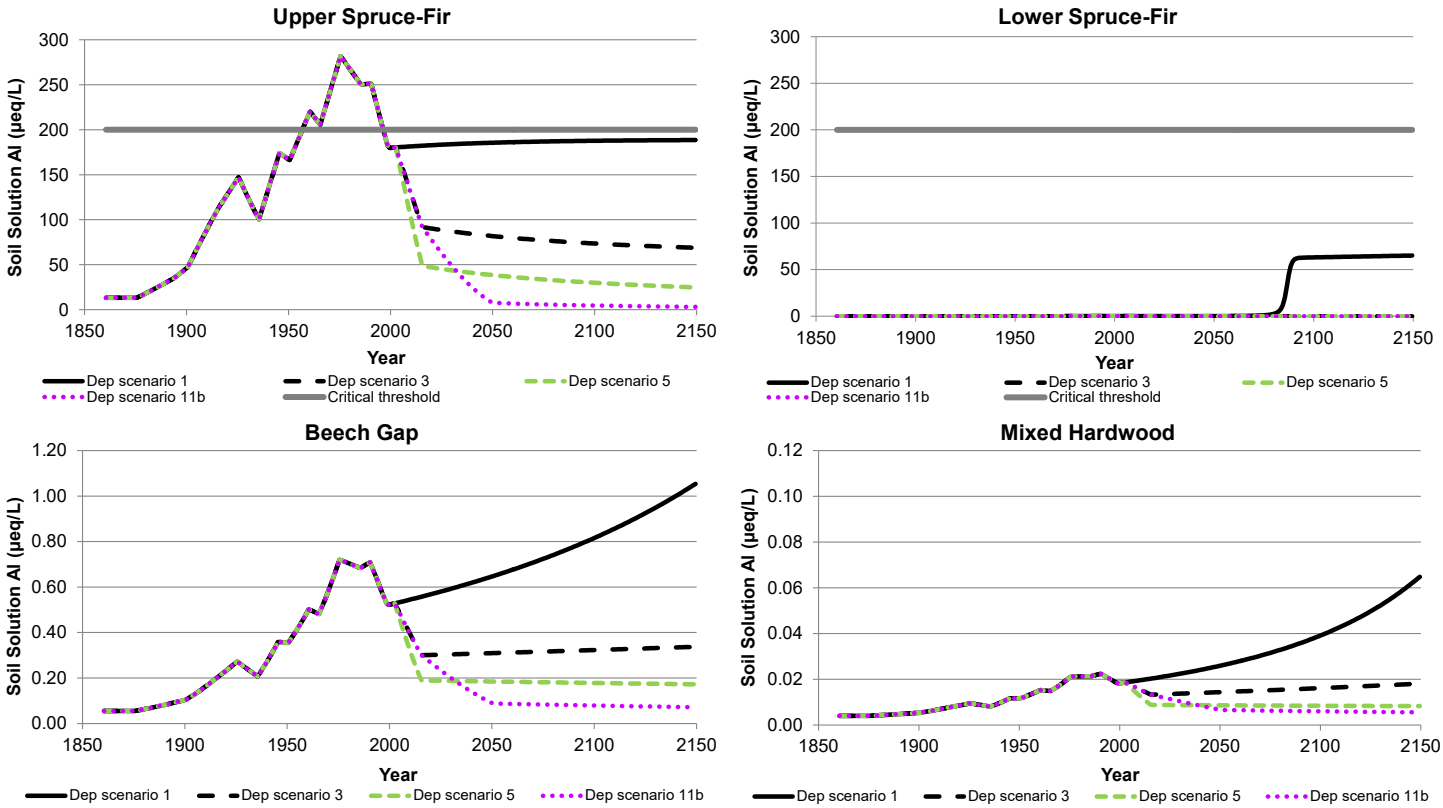

Figure 6.—VSD model results for soil solution Al for each of the four sites: Upper Spruce-Fir, Lower Spruce-Fir, Beech Gap, and Mixed Hardwood. Scenario 1 = no deposition change; scenario 3 = –48 percent S, –56 percent NO_3^-, +5 percent NH_4^+ deposition change; scenario 5 = –80 percent S, –80 percent NO_3^-, +9 percent NH_4^+ deposition change; scenario 11b = –90 percent S, –90 percent NO_3^-, –80 percent NH_4^+ deposition change. Soil solution Al for Lower Spruce-Fir scenario 1 reaches 0.065 µeq L^{-1} by 2150.

Aluminum:Base Cation Values

At all sites except the Upper Spruce-Fir Site, Al:Bc ratios throughout the modeling run were below the critical thresholds of both 0.1 mol mol^{-1} and 1.0 mol mol^{-1} for deposition reduction scenarios; the Al:Bc ratio increased dramatically at the Lower Spruce-Fir site under scenario 1 and exceeded the critical threshold of 0.1 mol mol^{-1} (Figure 7). At the Upper Spruce-Fir site, modeled Al:Bc values in 1860 exceeded the critical threshold of 1.0 mol mol^{-1}. At the Upper Spruce-Fir site, Al:Bc values decreased over time with all deposition reduction scenarios and resulted in an Al:Bc ratio below the critical threshold of 0.1 mol mol^{-1} under scenario 11b reductions.

pH

The modeled soil solution pH values were higher than the critical pH threshold of 4.2 at all sites for all deposition scenarios (Figure 8), and modeled soil solution pH increased with deposition reductions. Modeled pH values at the Lower Spruce-Fir site decreased significantly under scenario 1.

Base Saturation

Soil base saturation decreased over time under scenario 1 at all sites (Figure 9). At the Upper Spruce-Fir site, base saturation increased with all deposition reduction scenarios. At the Lower Spruce-Fir, Beech Gap, and Mixed Hardwood sites, base saturation decreased slightly under scenario 3 and increased slightly under scenarios 5 and 11b.

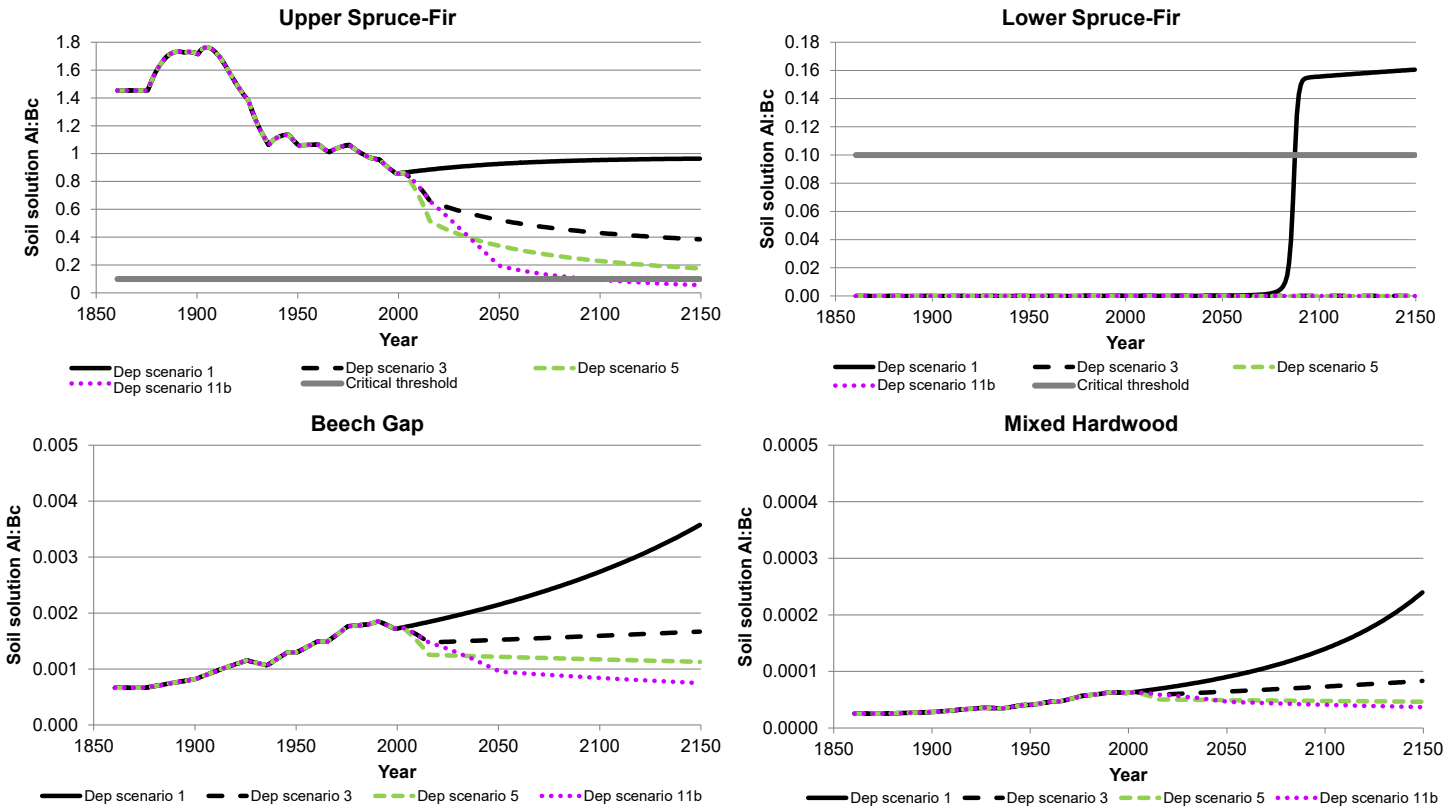

Figure 7.—VSD model results for Al:Bc for each of the four sites: Upper Spruce-Fir, Lower Spruce-Fir, Beech Gap, and Mixed Hardwood. Scenario 1 = no deposition change; scenario 3 = -48 percent S, –56 percent NO_3^-, +5 percent NH_4^+ deposition change; scenario 5 = –80 percent S, –80 percent NO_3^-, +9 percent NH_4^+ deposition change; scenario 11b = –90 percent S, –90 percent NO_3^-, –80 percent NH_4^+ deposition change.

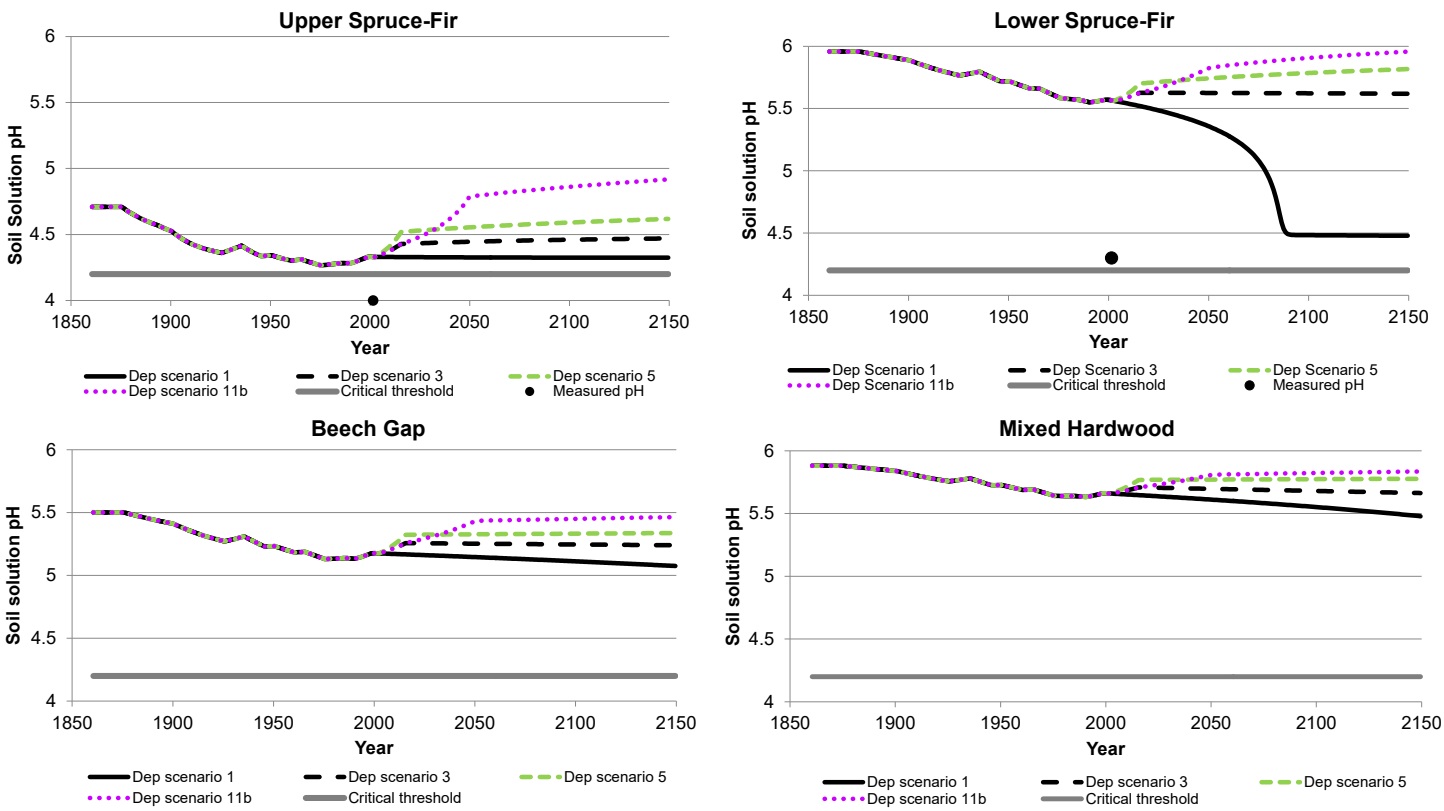

Figure 8.—VSD model results for pH for each of the four sites: Upper Spruce-Fir, Lower Spruce-Fir, Beech Gap, and Mixed Hardwood. Scenario 1 = no deposition change; scenario 3 = –48 percent S, –56 percent NO_3^-, +5 percent NH_4^+ deposition change; scenario 5 = –80 percent S, –80 percent NO_3^-, +9 percent NH_4^+ deposition change; scenario 11b = –90 percent S, –90 percent NO_3^-, –80 percent NH_4^+ deposition change.

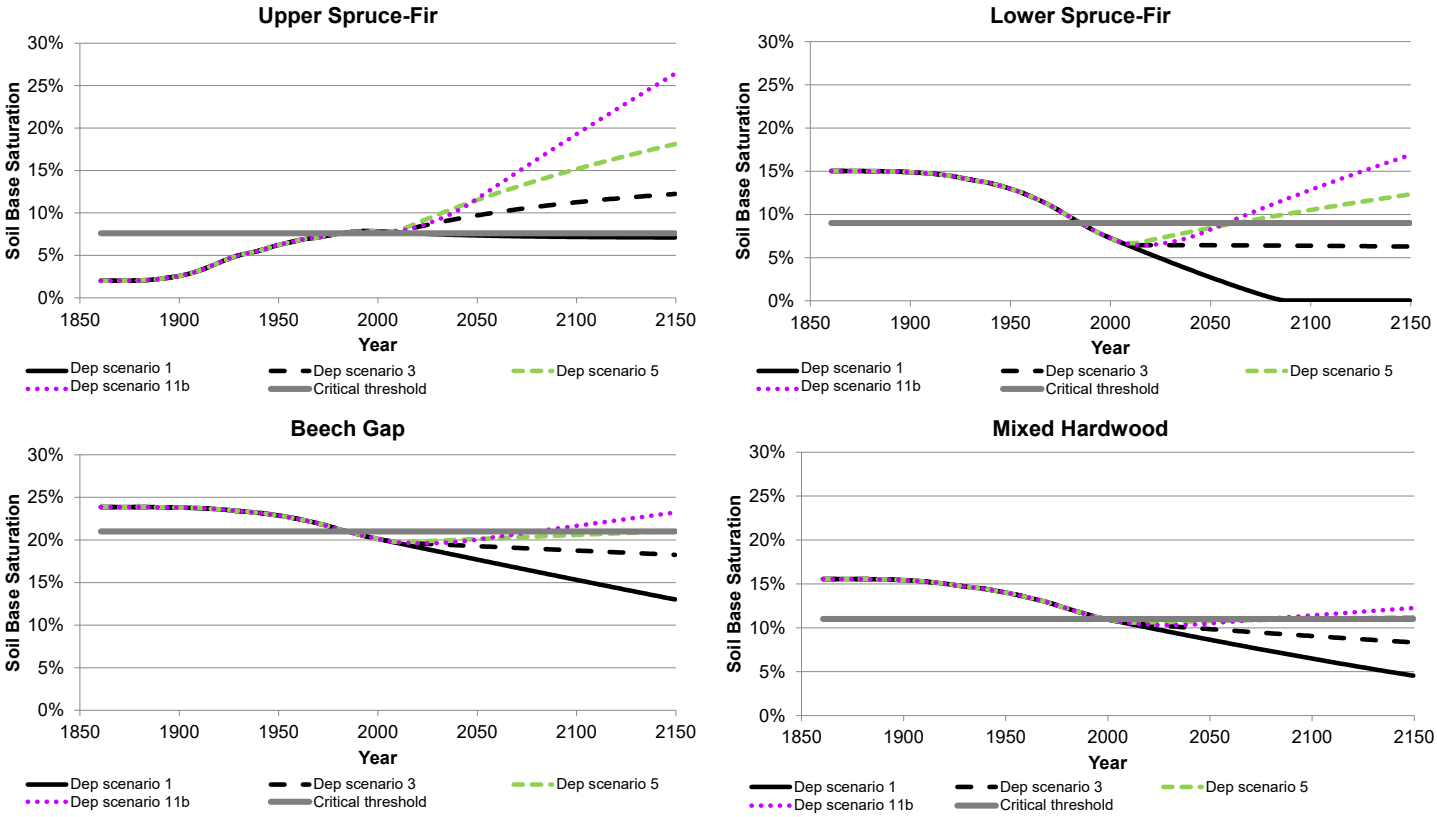

Figure 9.—VSD model results for base saturation for each of the four sites: Upper Spruce-Fir, Lower Spruce-Fir, Beech Gap, and Mixed Hardwood. Scenario 1 = no deposition change; scenario 3 = –48 percent S, –56 percent NO_3^-, +5 percent NH_4^+ deposition change; scenario 5 = –80 percent S, –80 percent NO_3^-, +9 percent NH_4^+ deposition change; scenario 11b = –90 percent S, –90 percent NO_3^-, -80 percent NH_4^+ deposition change.

DISCUSSION

The critical loads calculated for these sites fall within the range reported for mountainous areas in the Northeastern United States. (Duarte et al. 2004, 2011, 2013; NEG/ECP 2003). Miller (2005) reported that critical loads of acidity in New Hampshire and Vermont ranged from <250 eq ha^{-1} y^{-1} to >2500 eq ha^{-1} y^{-1}; exceedances in New Hampshire and Vermont were 250–2000 eq ha^{-1} y^{-1}. In a study in Eastern Canada (Environment Canada 2004), Ouimet et al. (2006) reported mean critical loads of 519–2063 eq ha^{-1} y^{-1} by province. Mean exceedance by province was 0–700 eq ha^{-1} y^{-1} based on protecting 95 percent of forest area. Earlier assessments in this region suggest that the critical load for acidity has been exceeded for terrestrial and aquatic ecosystems (Fox et al. 1989; Sullivan and Cosby 2002, 2004; Sullivan et al. 2003). In an assessment of 66 streams in the Southern Blue Ridge province adjacent to GSMNP, most would not achieve an ANC >50–100 µeq L^{-1} over the long term (2100) (Sullivan et al. 2011a). Most streams could tolerate acid inputs equivalent to only 0–10 kg S ha^{-1} y^{-1} (0–624 eq ha^{-1} y^{-1}) over the long term. Similarly, in their dynamic modeling assessments for streams of GSMNP using the PnET-BGC model, Zhou et al. (2015) found that the high-elevation Noland Divide Watershed, located in the Spruce-Fir site, could not attain ANC >0 under any future deposition scenario. Their target load for S + N of 400–1300 eq ha^{-1} y^{-1} (Zhou et al. 2015) falls within the range of critical load values we obtained for the Upper Spruce-Fir and Lower Spruce-Fir sites (Figure 3), consistent with the Noland Divide Watershed straddling these two elevation bands. McDonnell et al. (2014) report extensive exceedance of the critical load for S deposition in GSMNP using a critical threshold of ANC = 50 µeq L^{-1}; they report critical loads of 0–750 eq ha^{-1} y^{-1}. Oja and Arp (1998) reported CL (S + N) of 593–922 eq ha^{-1} y^{-1} for the Beech Gap and the Upper and Lower Spruce-Fir sites (based on IFS data). They report $CL_{nut}N$ of 178–614 eq ha^{-1} y^{-1} for the Beech Gap and Upper and Lower Spruce-Fir sites. These estimates are somewhat lower than the values we report for CL (S + N) and very similar to the range that we report

for $CL_{nut}N$. Empirical critical loads for nutrient N for forest ecosystems in the Eastern Forest ecoregion, which includes GSMNP, are > 3–8 kg ha^{-1} y^{-1} (200–600 eq ha^{-1} y^{-1}) N (Gilliam et al. 2011, Pardo et al. 2011a), which are similar to the range we calculated in this study. The consequences of this acidification of soil and surface water include documented adverse effects on fish and macroinvertebrate assemblages (Baldigo et al. 2018).

Critical Loads and Exceedances for Acidity (S + N)

The net input of base cations ($BC_{dep} + BC_w - Bc_u$) is a measure of base cation availability within the ecosystem. Because Bc_u is zero when no biomass is removed by harvesting, as is the case in GSMNP, the biggest drivers of the CL (S + N) were the BC_w and the BC_{dep}, and their relative importance differed by site. (The base cation sequestration [Bc_{se}] term, used to account for the non-steady-state aggrading period in the Lower and Upper Spruce-Fir sites, is considerably smaller than BC_{dep}). In some cases, the soil mineral weathering was significantly greater than the BC_{dep} inputs (Lower Spruce-Fir and Mixed Hardwood). At the Upper Spruce-Fir site, the BC_{dep} was greater than the mineral soil weathering; at the Beech Gap site, they were of similar magnitude. The site with the lowest net base cation inputs had the lowest critical load (Mixed Hardwoods; using the chemical criteria Al:Bc = 0.1). As the net base cation input increased across sites so did the critical load.

Critical load and exceedance values varied greatly with chemical criteria. None of the critical loads using the criteria of Al = 0.2 meq L^{-1}, pH = 4.2, and Al:Bc = 1.0 were exceeded at any site in GSMNP, whereas the critical load was exceeded for most sites with Al:Bc = 0.1—except Mixed Hardwoods—and for all sites with criteria of no change in base saturation. These results demonstrate the importance of selecting chemical criteria in modeling critical loads. Hall et al. (2001a) used various chemical criteria and critical thresholds to evaluate critical loads in the United Kingdom; their work and others (see Reinds et al. 2008, Watmough and Dillon 2003) highlight the need to choose the appropriate criteria and threshold to protect sensitive elements of a given ecosystem.

Because this study evaluates effects over a long period, we are in the unusual position of being able to comment on which critical load is best correlated with the forest condition. When the critical load is exceeded, detrimental effects may not yet be observable, because critical loads represent the long-term response of the ecosystem, and there may be a time lag before detrimental ecological effects are observable. In contrast, if the acid deposition is the cause of forest damage, then if one observes forest damage, there should be exceedance of the critical load. Hence, when measured values fall on the detrimental side of a critical threshold (higher for NO_3^-, Al, Al:Bc, and lower for pH, ANC, and base saturation), this indicates that the ecosystem is experiencing a harmful ecological effect and the critical load is exceeded. For the Upper Spruce-Fir and Lower Spruce-Fir sites, measured values fell on the detrimental side of critical thresholds of soil solution NO_3^-, ANC, and pH. These detrimental conditions indicate that the critical load is exceeded. The chemical criteria of Al = 0.2 meq L^{-1}, pH = 4.2, and Al:Bc = 1.0 did not lead to exceedance of the critical load. However, the GSMNP ecosystem was damaged during the modeled period; therefore, these chemical criteria may not adequately protect the ecosystem from excess acidic deposition. The chemical criteria of no decrease in base saturation and Al:Bc = 0.1 may better protect sensitive elements of the ecosystem at the Upper Spruce-Fir and Lower Spruce-Fir sites.

Critical Loads and Exceedances for Nitrogen

As is often observed (Duarte al. 2011, 2013), the $CL_{nut}N$ is a small fraction of the CL (S + N), even when we use the most conservative critical threshold for CL (S + N) (Al:Bc = 0.1). The critical load function including the $CL_{nut}N$ (Figure 10) indicates which combinations of N and S deposition will protect an ecosystem from detrimental effects of both acidification and N saturation. The N deposition should not be greater than the $CL_{nut}N$ (Figure 10, dashed vertical lines), and the S deposition should be lower than the critical load function line at the point where the $CL_{nut}N$ line intersects it (Figure 10).

The standard critical loads protocol (UBA 2004) suggests a range of 0–1 kg ha^{-1} y^{-1} (0–71 eq ha^{-1} y^{-1}) N for the acceptable soil N accumulation term (N_i); however, no consensus has yet been reached on long-term sustainable rates of soil N immobilization. We used the value of 0.5 kg ha^{-1} y^{-1} (36 eq ha^{-1} y^{-1}), which is widely used for temperate forests (UBA 2004). Given the low values typically reported for $CL_{nut}N$ (in this

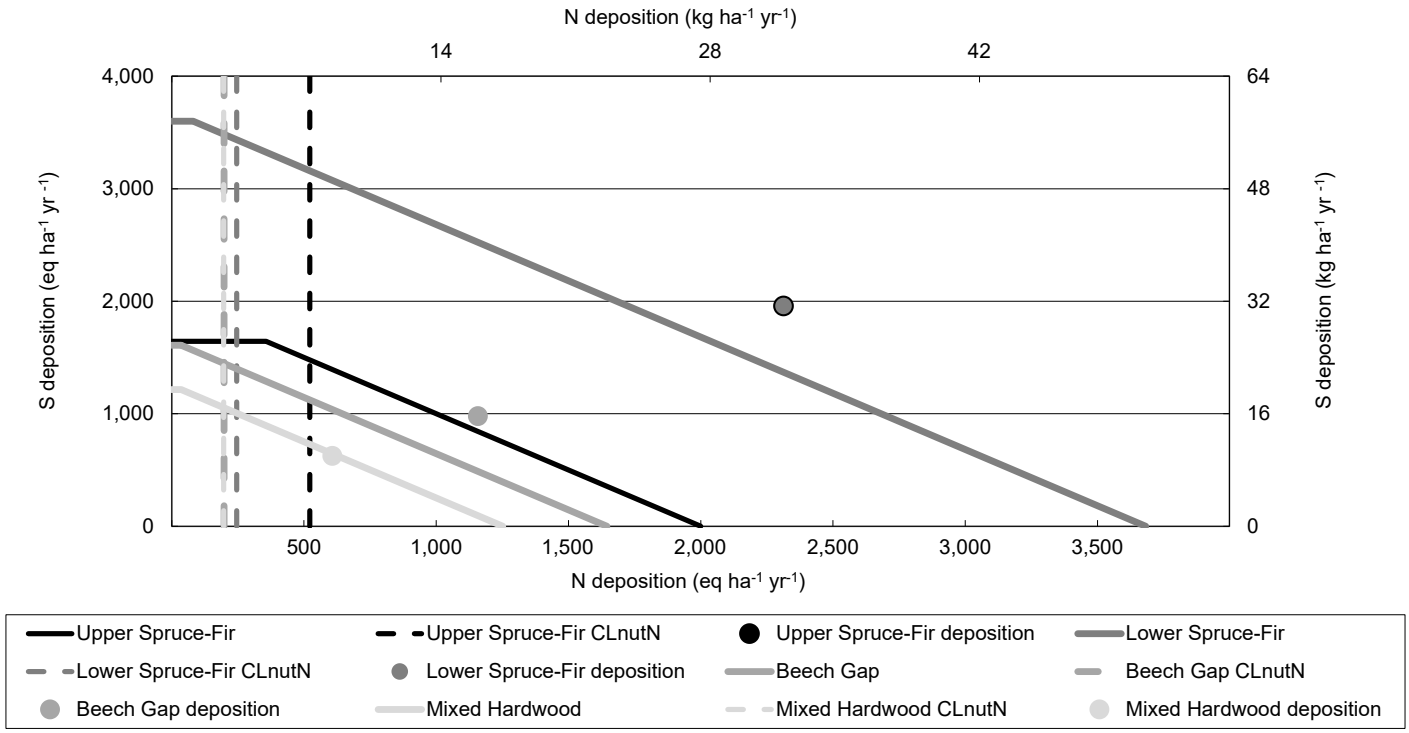

Figure 10.—Critical load functions using the chemical criteria Al:Bc = 0.1 mol mol^{-1} with $CL_{nut}N$ marked. The critical load function is shown as a solid line for each site. The $CL_{nut}N$ is shown for each site with a dotted line. Deposition is shown with a filled circle; deposition for the Upper and Lower Spruce-Fir sites is the same. The N deposition should not exceed the $CL_{nut}N$, and the S deposition should be lower than the critical load function line.

study 2.8–7 kg ha^{-1} y^{-1}, or 200–500 eq ha^{-1} y^{-1}), there is some concern that the critical thresholds used in calculating the $CL_{nut}N$ are too low. Gundersen (1992) suggested a range for acceptable N leaching loss ($N_{le(acc)}$) for old growth stands of 4–5 kg ha^{-1} y^{-1} (290–360 eq ha^{-1} y^{-1}); the method we used gave us a value of about 3 kg ha^{-1} y^{-1} (210 eq ha^{-1} y^{-1}). If we were to add 0.5 kg ha^{-1} y^{-1} for additional N_i and 2 kg ha^{-1} y^{-1} (140 eq ha^{-1} y^{-1}) for additional $N_{le(acc)}$ (to reach the maximum acceptable leaching loss of 5 kg ha^{-1} y^{-1}), we would calculate the highest possible $CL_{nut}N$. Adding a total of about 2.5 kg ha^{-1} y^{-1} (180 eq ha^{-1} y^{-1}) of allowable inputs would increase the $CL_{nut}N$ to 5.6–10 kg ha^{-1} y^{-1} (400–700 eq ha^{-1} y^{-1}). In all cases, the $CL_{nut}N$ would still be exceeded and would be significantly lower than the CL (S + N), even if the $CL_{nut}N$ were increased by 200 eq ha^{-1} y^{-1}.

The critical nitrate concentration, $[N]_{crit}$, is also a term that could be refined for the Eastern United States once data linking NO_3^- concentration with ecosystem responses are available. De Vries et al. (2007) used such data in Europe to refine $[N]_{crit}$, based on observed detrimental responses by specific species.

Trends in Modeled Soil Solution Over Time

At all sites, deposition reductions improved the quality of soil solution: pH increased, and Al:Bc ratio, Al, and NO_3^- concentrations decreased (Table 5). In some cases, these improvements included crossing a critical threshold (e.g., a defined Al:Bc ratio). In other cases, for example, Al concentration and pH, the values were already on the "healthy" side of the threshold (above for pH, below for Al concentration), so further deposition reductions would provide additional protection against detrimental effects of acid deposition including those associated with episodic acidification. Similarly, any increase in base saturation protects against any future acidification associated with the removal of base cations. VSD does not model responses to episodic acidification, because critical loads are calculated over the long term and the VSD operates on an annual time step.

Reductions required to lower total (N + S) deposition below the critical load for Al:Bc = 0.1 mol mol^{-1} are 14 percent at the Lower Spruce-Fir site, 23 percent at the

Table 5.—Summary of soil solution responses to deposition scenario modeling to 2150[a]

Site	Deposition scenario	NO_3^- (μeq L^{-1})	ANC (μeq L^{-1})	Al (μeq L^{-1})	Al:Bc (mol mol^{-1})	pH	BS %
Upper Spruce-Fir	1	+/-	-	+	+	+/-	-
	3	+/-	+	-	-	+	+
	5	+/-	+	-	-	+	+
	11b	+/-	+	-	-	+	+
Lower Spruce-Fir	1	+	-	+	+	-	-
	3	+	+/-	-	+/-	+/-	+/-
	5	+	+	-	-	+	+
	11b	+/-	+	-	-	+	+
Beech Gap	1	+/-	-	+	+	-	-
	3	+/-	-	-	+	-	-
	5	+/-	+	-	-	+	+/-
	11b	+/-	+	-	-	+	+
Mixed Hardwood	1	+	-	+	+	-	-
	3	+	-	-	+	-	-
	5	+	+	-	+/-	+/-	+/-
	11b	+/-	+	-	-	+	+/-

[a] Response symbols indicate increasing (+), decreasing (-), and stable (+/–) values. Shaded cells exceed critical thresholds. Critical thresholds: 14 μeq L^{-1} NO_3^-, 50 μeq L^{-1} ANC, 200 μeq L^{-1} Al (0.2 meq L^{-1}), 0.1 Al:Bc mol mol^{-1}, pH 4.2, no decrease in base saturation.

Beech Gap site, and 53 percent at the Upper Spruce-Fir site (Pardo and Duarte 2007). The U.S. EPA-CAIR deposition reduction level (scenario 3) represents reductions of approximately 40 percent of total N + S deposition, inadequate to reduce deposition below the critical load at the Upper Spruce-Fir site. This scenario would reduce the deposition below the critical load at the other three sites. Historical modeling shows that ANC values (Figure 5) and Al:Bc (Figure 7) at the Upper Spruce-Fir site fell on the detrimental side of the critical thresholds before anthropogenic deposition increased. Zhou et al. (2015) support this low ANC value at the Upper Spruce-Fir site. They report a modeled initial stream water ANC value of 1860 for the Nolan Divide Watershed of 28 μeq L^{-1}, which falls between the values we report here of –25 μeq L^{-1} for Upper Spruce-Fir site and 100 μeq L^{-1} for the Lower Spruce-Fir site and is consistent with Nolan Divide Watershed draining both forest types. Historical site conditions should, if available, be considered when determining critical thresholds in critical loads modeling.

The VSD model does not include SO_4^{2-} adsorption, which introduces uncertainty about the timing of SO_4^{2-} losses: there is a time lag during periods of SO_4^{2-} adsorption and accelerated losses during periods of desorption. The net SO_4^{2-} retention observed at Noland Divide Watershed in GSMNP (Cai et al. 2010, 2011a, 2011b; Nodvin et al. 1995) suggests that soil SO_4^{2-} capacity at this site was relatively low in the 1980s (Harrison et al. 1989). Rapid movement of SO_4^{2-} through the soil profile also suggests limited SO_4^{2-} adsorption in the upper part of the soil profile (Cai et al. 2010). Recent soil column and field lysimeters studies (Cai et al. 2011a) suggest that although SO_4^{2-} adsorption is considerable under current deposition (scenario 1), deposition reductions would trigger desorption of SO_4^{2-}. For streams in the Southern Blue Ridge province adjacent to GSMNP, Sullivan et al. (2011b) assumed reduced SO_4^{2-} adsorption and increased mobilization of SO_4^{2-} from soils to streams. We do not include the dynamics of SO_4^{2-} adsorption and desorption in our steady-state critical load calculations, considering that over the long term, under steady-state conditions there should be no net storage of SO_4^{2-} on the soil exchanger. However, if adsorbed sulfate remains on the soil exchange complex over the long term, the acceptable amount of acid deposition would increase. In that case, the critical load that we report may be too low.

Trends in Modeled Soil Solution Nitrate Over Time

Elevated NO_3^- concentration in soil solution is an indication of both N saturation and acidification. High NO_3^- leaching suggests a disruption of the internal N cycle, which is an early step in the progression toward N saturation (Aber et al. 1989, Stoddard 1994). The $CL_{nut}N$ is exceeded in all cases (Figure 3B), so it is not surprising that modeled NO_3^- concentrations in soil solution were greater than the critical threshold even when the CL (S + N) was not exceeded (Figure 3B).

Both the observed mean annual volume-weighted soil solution NO_3^- for the period 1985–88 (Van Miegroet et al. 1992) and for 1991–2006 at the Upper Spruce-Fir site (97–124 μeq L^{-1}) (Cai et al. 2010) are well above the critical threshold but lower than the modeled value. Because the model is a simplified one, especially with respect to N cycling and includes certain assumptions of equilibrium, there may be a time lag before modeled conditions occur in the ecosystem. Nonetheless, a considerable body of evidence suggests that the upper sites are indeed N saturated, in spite of the increased post-disturbance N uptake in the Upper Spruce-Fir site and the high N uptake in understory vegetation including regeneration (Barker et al. 2002; Moore et al. 2007, 2008). Evidence of N saturation at the upper sites includes low soil C:N ratio, high nitrification rates, and long-term elevated stream water NO_3^- concentrations (Cai et al. 2012, Garten 2000, Johnson and Lindberg 1992, Nodvin et al. 1995, Van Miegroet et al. 2001).

Deposition reductions of 90 percent for NO_3^- and 60 percent for NH_4^+ at the Upper Spruce-Fir site, 80 percent for NH_4^+ at the Beech Gap site, and 40 percent for NH_4^+ at the Mixed Hardwood site are necessary to lower the total N deposition below the $CL_{nut}N$ (Pardo and Duarte 2007). None of the deposition reduction scenarios used in our model simulation lower the total N deposition below the $CL_{nut}N$ at the Lower Spruce-Fir site. The most stringent reduction scenario (11b) results in a reduction of total N deposition (NO_3^- + NH_4^+) of ~86 percent, short of the 89 percent total N deposition (NO_3^- + NH_4^+) necessary. The Upper Spruce-Fir site can tolerate a higher level of N deposition because this site has been aggrading more rapidly, since the woolly adelgid infestation, than the Lower Spruce-Fir site (Barker et al. 2002, Van Miegroet et al. 2007).

CONCLUSIONS

By calculating critical loads and exceedances for four sites within the GSMNP and using different critical thresholds, we were able to evaluate which threshold is most likely to provide accurate results. The Al:Bc = 0.1 mol mol^{-1} and no decrease in base saturation gave the most accurate assessment of the critical load based on long-term observation of site conditions. In spite of decreases in S emissions and deposition over the last few decades, recovery of these ecosystems would require very stringent reductions in deposition. The N deposition reductions necessary to lower deposition below the critical load for nutrient N range from 68 percent to 90 percent of total N deposition; reductions required to lower total (N + S) deposition below the critical load range from 14 percent to 53 percent. These reductions would not, however, lower soil solution concentrations to below the critical thresholds before 2150. The CAIR (U.S. EPA, n.d.) deposition reduction scenario represents reductions of only approximately 40 percent of N + S and would therefore not be adequate to reduce deposition below the critical load at the most sensitive site. Continued emissions reductions associated with attaining National Ambient Air Quality Standards or visibility improvements in federally mandated class 1 areas may eliminate exceedance of critical loads at GSMNP.

Effects of elevated S and N deposition do not occur in isolation from other environmental stressors. Climate change is the primary environmental stressor, in many cases, and when coupled with disturbance (including pests) and elevated S and N deposition, may significantly aggravate detrimental effects on ecosystems (McDonnell et al. 2018; Porter et al. 2012, Wu and Driscoll 2010). We are not able to evaluate the extent to which susceptibility of the high-elevation Spruce-Fir sites to the balsam woolly adelgid may have increased because of the historical elevated N deposition. Certainly, numerous studies have reported linkages between increased foliar N and increased infestation of various pests (Pontius et al. 2006), including the balsam woolly adelgid (Carrow and Betts 1972). Similarly, a recent assessment by Porter et al. (2012) indicated that interactions between climate change and N deposition can have significant deleterious effects on biodiversity. Wu and Driscoll (2010) report that incorporating climate change—increasing temperature, precipitation, carbon dioxide, and water use efficiency—into a dynamic model,

PnEt-BGC, lowered the CL (S + N). These preliminary studies clearly illustrate the need for further investigation into the interaction of S and N deposition and other stressors to protect ecosystems in the future.

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Great Smoky Mountains National Park (GSMNP) is subject to high levels of sulfur (S) and nitrogen (N) deposition, which can adversely affect forest vegetation and aquatic biota. We used multiple chemical criteria to calculate critical loads for S and N deposition (CL (S+N)) and nutrient N ($CL_{nut}N$) and used the Very Simple Dynamic (VSD) model to predict the effects of deposition reduction scenarios on critical thresholds for four forested sites in GSMNP. Critical loads were exceeded for current deposition at three of four sites using critical thresholds of aluminum to base cations (Al:Bc) = 0.1 or no decrease in base saturation but were not exceeded using the chemical criteria of Al = 0.2 meq L^{-1}, Al:Bc = 1.0, and pH = 4.2. With deposition reductions of 48 percent S and 56 percent nitrate (NO_3^-), neither the critical thresholds of acid neutralizing capacity (ANC) = 20 µeq L^{-1} nor a decrease in base saturation was achieved. With deposition reductions of 90 percent S and 90 percent NO_3^-, ANC = 100 µeq L^{-1} was achieved at a single site. Historical ANC values affected a site's ability to achieve ANC critical thresholds. The critical threshold for soil solution NO_3^- was exceeded for all but the most stringent deposition scenarios (–90 percent S and –90 percent NO_3^-). Deposition reductions of 90 percent for NO_3^- and 80 percent for ammonium (NH_4^+) were not sufficient to lower deposition below the $CL_{nut}N$ at all sites. Data indicate that upper sites at GSMNP are N saturated; to protect these sites from acidification, the more protective chemical criteria of no decrease in base saturation and Al:Bc = 0.1 should be used when determining critical loads. When choosing chemical criteria in deposition reduction modeling, care should be taken to ensure that the criteria chosen will protect sensitive ecosystem elements.

KEY WORDS: critical load, acidic deposition, exceedance, nitrate leaching, nitrogen saturation

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