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Johanna Szillery

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**SOIL SOLUTION DYNAMICS IN RESPONSE TO ELEVATED NITROGEN
AND SULFUR TREATMENTS AT THE BEAR BROOK
WATERSHED IN MAINE**

By

Johanna Szillery

B. A. Drew University, 1998

A THESIS

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Master of Science

(in Plant, Soil, and Environmental Sciences)

The Graduate School

The University of Maine

May, 2003

Advisory Committee:

Ivan J. Fernandez, Professor of Soil Science, Advisor

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By Johanna Szillery

Thesis Advisor: Dr. Ivan Fernandez

An Abstract of the Thesis Presented
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May, 2003

Base cation depletion in forest soils of northeastern North America is a continuing concern because of the ongoing elevated deposition of sulfur (S) and nitrogen (N), intensive management practices, and the often poorly understood implications of land-use history on modern ecosystem function. At the Bear Brook Watershed in Maine (BBWM), one of two paired, forested watersheds has been subjected to experimental additions of S and N for over a decade. Treatments consist of $28.8 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ and $25.2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in the form of granular $(\text{NH}_4)_2\text{SO}_4$ applied bimonthly by helicopter. Ceramic cup tension lysimeters were used to sample soil solutions in both the treated and

reference watersheds in 2001 and 2002. Soil solutions in the treated watershed had higher concentrations of most analytes compared with the reference watershed, with the largest relative increases in $\text{NO}_3\text{-N}$ (1650%), Al (480%) and $\text{SO}_4\text{-S}$ (300%). Acid neutralization mechanisms in the treated watershed have progressed through an initial stage of neutralization by base cation exchange, to an increasing role for Al hydrolysis. Treatments have also increased nitrification of both treatment and native N sources resulting in much higher concentrations of $\text{NO}_3\text{-N}$ in the treated watershed compared with the reference. Higher concentrations of most solutes under softwood stands compared with hardwoods were primarily the result of higher aerosol interception capacity and differences in litter quality. Long-term soil solution data showed steady increases in soil solution Al, H^+ , and $\text{SO}_4\text{-S}$ concentrations in response to treatments when soil solution data from this study were compared with previous soil solutions collected at BBWM. In contrast, Ca concentrations increased to a peak of $140 \mu\text{eq L}^{-1}$ after the first four years of treatment, and subsequently declined to near pre-treatment concentrations of $77 \mu\text{eq L}^{-1}$ in the treated watershed after 11 years of treatment. Soil solution $\text{SO}_4\text{-S}$ concentrations in the treated watershed were in excess of pre-treatment concentrations reflecting an equilibrium with $\text{SO}_4\text{-S}$ adsorption capacity at the lower ambient levels of deposition. Results from this study suggest net base cation depletion from the soil exchange complex may be occurring, which results in higher Al in soil solution and export to streams. Softwood forest types may be more vulnerable to acidification-induced Al mobilization than hardwoods due to initially lower base saturation and higher aerosol interaction capacity.

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INTRODUCTION

Atmospheric deposition of acidifying substances has been shown to have deleterious effects on terrestrial ecosystems. These effects include: changes in soil chemistry, decreases in water quality, increased production of greenhouse gases from microbial processes, and changes in forest productivity and composition (Aber et al., 1998; Fenn et al., 1998; Driscoll et al., 2001). Some of these impacts are the result of changes in nutrient cycling brought about by excess deposition of nitrogen (N) and sulfur (S). In the northeastern USA, a particular concern for forest health and sustainability is the potential for accelerated leaching of soil base cations. Chronic N and S deposition, intensive management practices, vegetative uptake, and decreases in atmospheric calcium (Ca) deposition are factors that may be contributing to net losses of exchangeable Ca pools (Adams et al., 2000; Federer et al., 1989; Bailey et al., 1996; Huntington et al., 2000). The combined impact of these phenomena has increased concerns over forest health and sustainability. Several studies in the northeastern and southeastern USA have suggested that, while Ca is not yet considered a limiting nutrient, current leaching losses and harvesting practices could lead to a Ca-limited ecosystem in five to seven decades (Adams et al., 2000; Federer et al., 1989; Bailey et al., 1996; Huntington et al., 2000).

The Bear Brook Watershed in Maine (BBWM) is a paired-watershed experiment that was established in 1987 with the goal of investigating the response of ecosystem processes to elevated N and S deposition. Research at BBWM has encompassed many ecosystem components and processes: stream chemistry (David et al., 1999; Norton et al., in press; Norton and Kahl, 2000; Norton et al., 1994; Roy et al., 1999), soil and soil

solution chemistry (Fernandez et al., in press; Fernandez et al., 1999; Rustad et al., 1993), foliar chemistry (White et al., 1999), soil N dynamics (Nadelhoffer et al., 1999; Shah, 2002; Wang and Fernandez, 1999), soil carbon (C) and N dynamics (Parker et al., 2001, 2002), and near-stream processes (Pellerin et al., 2002).

Because deposition of both N and S is still a concern, long-term studies are increasingly important for evaluating the evolution of ecosystem response to this stress. This thesis project was developed to observe the impact of elevated N and S deposition on soil solution chemistry. Specific objectives were to:

- 1) quantify changes in soil solution chemistry that result from long-term elevated N and S deposition,
- 2) assess the influence of hardwood- and softwood-dominated forest types on soil solutions, and how this alters ecosystem response to acidification, and
- 3) examine how response to acidification may change over the 12 years of treatment at BBWM

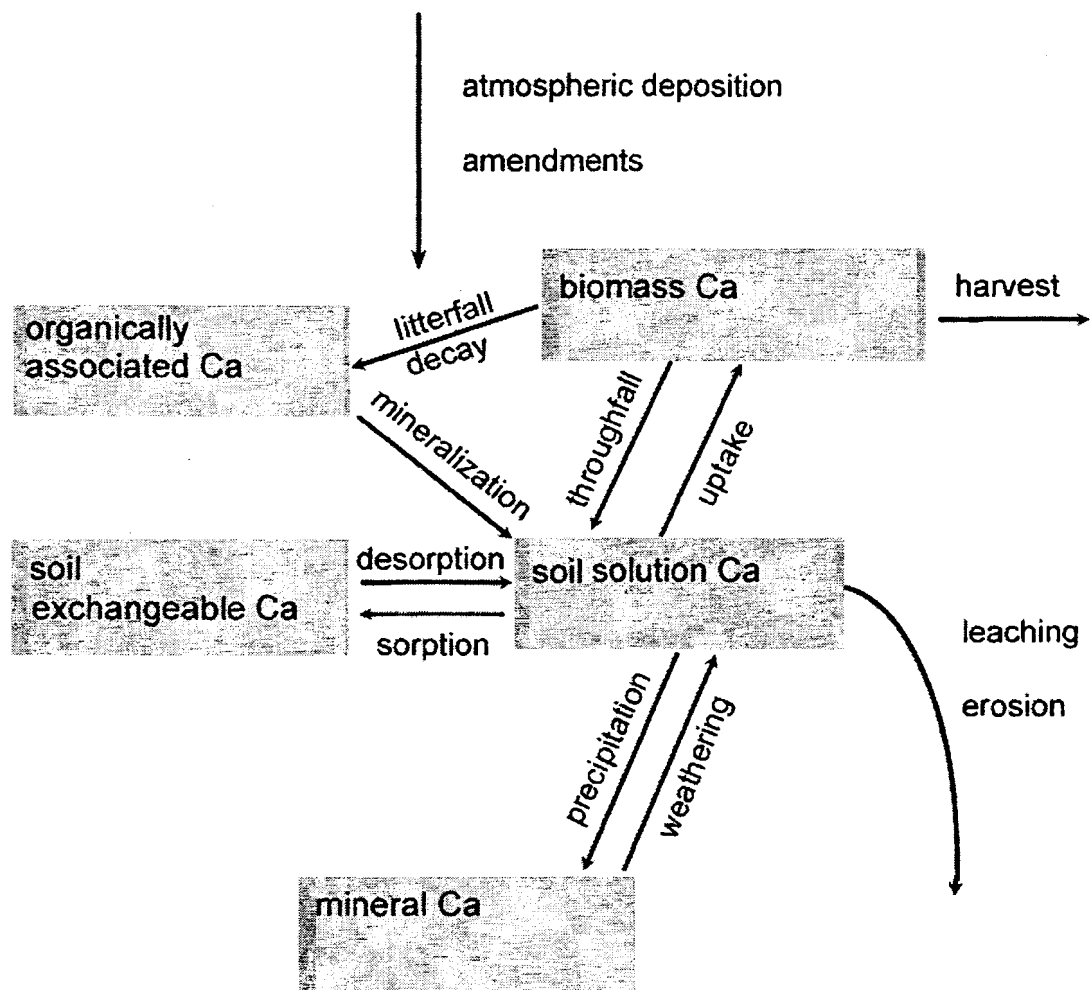
LITERATURE REVIEW

Calcium in Forested Ecosystems

Calcium Cycle

Calcium is an essential macronutrient for plant growth, and serves in both structural and signaling capacities. Calcium regulates many physiological processes including protein synthesis, cell division, membrane and stomatal function, and plant metabolism (McLaughlin and Wimmer 1999; DeHayes et al, 1999). McLaughlin and Wimmer (1999) suggested that Ca might play a limiting role in forest composition and function, as it is needed for both growth and response to stress, but is also the least mobile macronutrient in plants.

Figure 1 shows the major pools and fluxes of Ca in forested ecosystems. Stores of Ca in forested ecosystems are found in soil minerals, biomass (plant and microbial), organic matter and parent material; the readily available pools of Ca are primarily in soil exchangeable Ca. Fluxes of Ca internal to the ecosystem include: weathering or precipitation of mineral Ca, mineralization of organic matter or immobilization of Ca by microbes, desorption and sorption of Ca between soils and soil solution, litterfall and throughfall/stemflow or uptake of nutrients by vegetation. Inputs of Ca to forested ecosystems are through wet and dry atmospheric deposition and fertilization/amendments. Losses of Ca from the ecosystem are mainly due to leaching, harvesting, or erosion. The dynamic equilibrium among the various pools and fluxes of the Ca cycle govern biologically available Ca on time-scales from minutes to millennia.



modified after Fisher and Binkley, 2000

Figure 1. Fluxes and pools of the calcium cycle in forested ecosystems

Sizes of Pools and Fluxes

Tables 1 and 2 show sizes of both Ca and Mg pools and fluxes, respectively, in forested ecosystems. Cycling of Mg is similar to Ca and there is indication that depletion of Mg may be more of a concern than Ca depletion. The estimates of either pools or fluxes can vary widely based on location, geology, soil type, stand condition and age, land-use history, and methods of estimation, but these data provide valuable insight into the relative magnitude of components of the Ca and Mg cycles. Overall, the relative sizes of pools and fluxes shown in Tables 1 and 2 are surprisingly comparable, given the sources of variation noted above.

Mineral Pool. Comparisons among the pool sizes shown in Table 1 reveals that mineral Ca and Mg are the largest stores of these cations in forested ecosystems, and are 1-2 orders of magnitude larger than biomass and soil exchangeable pools. However, the flux of Ca from the weathering of this pool is comparable to the flux of Ca from atmospheric deposition (Table 2), and several authors have noted that the process of silicate weathering could not keep pace with the biological demand for Ca at current levels of Ca depletion (Federer et al., 1989; Bailey et al., 1996). However, because bedrock mineralogy can vary locally, some areas are not subject to concerns over base cation depletion. The Ca weathering fluxes found by Miller et al. (1993) were almost an order of magnitude larger when compared with other weathering fluxes in Table 2 due to the relatively Ca-rich bedrock found at their study site.

Soil Exchangeable Pool. Soil exchangeable cation pool size is determined largely by weathering rates of parent materials and mineralization rates of soil organic

Table 1. Pools of Ca and Mg in forested ecosystems

Compartment	Pool size	Location	Citation	Comments
Biomass				
Stemwood plus bark	838 kg Ca ha ⁻¹	Panola Mountain Research Watershed, Georgia, USA	Huntington et al., 2000	~ 70-90- year old mixed deciduous and coniferous stands; estimate based on field measurements, nutrient concentrations, and allometric equations
Aboveground	892 kg Ca ha ⁻¹	Newcomb, New York, USA	Johnson et al., 1994	~100-year old mixed deciduous and coniferous stands; estimate based on field measurements, nutrient concentrations, and allometric equations
Aboveground	170 kg Ca ha ⁻¹	Calhoun Experimental Forest, South Carolina, USA	Markewitz et al., 1998	34-year old loblolly pine plantation; estimate based on field measurements and nutrient concentrations
Aboveground	483 kg Ca ha ⁻¹	Cone Pond Watershed, New Hampshire, USA	Bailey et al., 1996	All-aged mixed-conifer forest; estimate based on field measurements and nutrient concentrations
Above- and belowground	630 kg Ca ha ⁻¹	Average of four northeastern USA sites	Federer et al., 1989	Spruce-fir, northern hardwood, and central hardwood; estimate based on field measurements, nutrient concentrations, and allometric equations

Table 1. (continued) Pools of Ca and Mg in forested ecosystems

Compartment	Pool size	Location	Citation	Comments
Biomass				
Aboveground	480 kg Ca ha ⁻¹	Average of temperate coniferous International Biological Programme sites	Cole and Rapp, 1981	34-440 year old temperate coniferous stands in USA, Sweden, Germany, and Japan; estimate based on field measurements, nutrient concentrations, and allometric equations
Aboveground	557 kg Ca ha ⁻¹	Average of temperate deciduous International Biological Programme sites	Cole and Rapp, 1981	30-200 year old temperate deciduous stands in USA, Belgium, Sweden, and Germany; estimate based on field measurements, nutrient concentrations, and allometric equations
Aboveground	1084 kg Ca ha ⁻¹	Walker Branch Watershed, Tennessee, USA	Johnson et al., 1988	Oak-hickory forest with some pine; estimate based on field measurements and nutrient concentrations
Aboveground	39 kg Mg ha ⁻¹	Calhoun Experimental Forest, South Carolina, USA	Markewitz et al., 1998	34- year old loblolly pine plantation; estimate based on field measurements and nutrient concentrations
Above- and belowground	62.5 kg Mg ha ⁻¹	Average of four northeastern USA sites	Federer et al., 1990	Spruce-fir, northern hardwood, and central hardwood; estimate based on field measurements, nutrient concentrations, and allometric equations

Table 1. (continued) Pools of Ca and Mg in forested ecosystems

Compartment	Pool size	Location	Citation	Comments
Biomass				
Above-ground	63 kg Mg ha ⁻¹	Walker Branch Watershed, Tennessee, USA	Johnson et al., 1988	Oak-hickory forest with some pine; estimate based on field measurements and nutrient concentrations
Soil				
Exchangeable	1800 kg Ca ha ⁻¹	Panola Mountain Research Watershed, Georgia, USA	Huntington et al., 2000	Exchangeable Ca to 1 m; Typic Kanhapludult soils
Exchangeable	195 kg Ca ha ⁻¹	Cone Pond Watershed, New Hampshire, USA	Bailey et al., 1996	Exchangeable Ca in whole soil profile to basal till; Typic, Lithic, and Aquic Haplorthod soils
Exchangeable	852 kg Ca ha ⁻¹	Walker Branch Watershed, Tennessee, USA	Johnson et al., 1988	Exchangeable Ca in forest floor and top 60 cm mineral soil; Typic Paleudult soils
Exchangeable	112 kg Mg ha ⁻¹	Walker Branch Watershed, Tennessee, USA	Johnson et al., 1988	Exchangeable Mg in forest floor and top 60 cm mineral soil; Typic Paleudult soils

Table 1. (continued) Pools of Ca and Mg in forested ecosystems

Compartment	Pool size	Location	Citation	Comments
Mineral				
	9500 kg Ca ha ⁻¹	Panola Mountain Research Watershed, Georgia, USA	Huntington et al., 2000	Weatherable minerals in soil to 1 m; biotite-oligoclase-quartz-microcline granite bedrock
	3066 kg Ca ha ⁻¹	Cone Pond Watershed, New Hampshire, USA	Bailey et al., 1996	Weatherable minerals in <2mm soil fraction in whole soil profile to basal till; quartz, muscovite, biotite, and almandine bedrock
	8040 kg Ca ha ⁻¹	Average of four northeastern USA sites	Federer et al., 1989	Total Ca in forest floor and mineral soil to 1 m.
	2113 kg Ca ha ⁻¹	Walker Branch Watershed, Tennessee, USA	Johnson et al., 1988	Total Ca in forest floor and top 60 cm mineral soil; dolomite bedrock
	16,347 kg Mg ha ⁻¹	Average of four northeastern USA sites	Federer et al., 1990	Total Mg in forest floor and mineral soil to 1 m.
	5970 kg Mg ha ⁻¹	Walker Branch Watershed, Tennessee, USA	Johnson et al., 1988	Total Mg in forest floor and top 60 cm mineral soil; dolomite bedrock

Table 2. Fluxes of Ca and Mg in forested ecosystems

Flux	Size	Location	Citation	Comments
Net depletion				
	2.1 kg Ca ha ⁻¹ yr ⁻¹	Cone Pond Watershed, New Hampshire, USA	Bailey et al., 1996	Mass-balance estimate based on Sr isotope work
	12.7 kg Ca ha ⁻¹ yr ⁻¹	Panola Mountain Research Watershed, Georgia, USA	Huntington et al., 2000	Mass-balance estimate
	0.5-1.5 kg Mg ha ⁻¹ yr ⁻¹	Synthesis of data from sites across northern and central Europe	Armbruster et al., 2002	Calculated as difference between throughfall and output
Gross loss				
	20.8 kg Ca ha ⁻¹ yr ⁻¹	Whiteface Mountain, New York, USA	Miller et al., 1993	Stream losses
	11.25 kg Ca ha ⁻¹ yr ⁻¹	Fernow Experimental Forest, West Virginia, USA	Adams et al., 1997	Stream losses
	4.1 kg Ca ha ⁻¹ yr ⁻¹	Cone Pond Watershed, New Hampshire, USA	Bailey et al., 1996	Stream losses
	13.3 kg Ca ha ⁻¹ yr ⁻¹	Average of four northeastern USA sites	Federer et al., 1989	Losses from below rooting zone for plot studies, and stream losses for watershed studies
	2.71 kg Ca ha ⁻¹ yr ⁻¹	Panola Mountain Research Watershed, Georgia, USA	Huntington et al., 2000	Losses from below rooting zone

Table 2. (continued) Fluxes of Ca and Mg in forested ecosystems

Flux	Size	Location	Citation	Comments
Gross Loss				
5.30 kg Mg ha ⁻¹ yr ⁻¹		Fernow Experimental Forest, West Virginia, USA	Adams et al., 1997	Stream losses
4.8 kg Mg ha ⁻¹ yr ⁻¹		Average of four northeastern USA sites	Federer et al., 1990	Losses from below rooting zone for plot studies, and stream losses for watershed studies
Weathering				
0.12 kg Ca ha ⁻¹ yr ⁻¹		Panola Mountain Research Watershed, Georgia, USA	Huntington et al., 2000	Weathering in surface 1 m; biotite-oligoclase- quartz-microcline granite bedrock
16.8 kg Ca ha ⁻¹ yr ⁻¹		Whiteface Mountain, New York, USA	Miller et al., 1993	Anorthosite bedrock and till weathering based on Sr isotopes
1.2 kg Ca ha ⁻¹ yr ⁻¹		Cone Pond Watershed, New Hampshire, USA	Bailey et al., 1996	Quartz, muscovite, biotite, and almandine bedrock and till weathering based on Sr isotopes
4.4 kg Mg ha ⁻¹ yr ⁻¹		Whiteface Mountain, New York, USA	Miller et al., 1993	Anorthosite bedrock and till weathering based on Sr isotopes
2.1-3.1kg Mg ha ⁻¹ yr ⁻¹		Synthesis of data from sites across northern and central Europe	Armbruster et al., 2002	Silicate weathering, calcareous sites excluded

Table 2. (continued) Fluxes of Ca and Mg in forested ecosystems

Flux	Size	Location	Citation	Comments
Throughfall				
	5.0 kg Ca ha ⁻¹ yr ⁻¹	Cone Pond Watershed, New Hampshire, USA	Bailey et al., 1996	Mixed conifer forest
	0.24-22.4 kg Mg ha ⁻¹ yr ⁻¹	Synthesis of data from sites across northern and central Europe	Armbruster et al., 2002	Larger throughfall fluxes at coastal sites
	1.5 kg Mg ha ⁻¹ yr ⁻¹	Calhoun Experimental Forest, South Carolina, USA	Markewitz et al., 1998	Loblolly pine plantation
Atmospheric deposition				
Bulk	2.24 kg Ca ha ⁻¹ yr ⁻¹	Panola Mountain Research Watershed, Georgia, USA	Huntington et al., 2000	
Wet	0.83 kg Ca ha ⁻¹ yr ⁻¹	Panola Mountain Research Watershed, Georgia, USA	Huntington et al., 2000	
Dry	1.41 kg Ca ha ⁻¹ yr ⁻¹	Panola Mountain Research Watershed, Georgia, USA	Huntington et al., 2000	
Bulk	6.2 kg Ca ha ⁻¹ yr ⁻¹	Netherlands	Hedin et al., 1994	Regression estimate
Bulk	1.7 kg Ca ha ⁻¹ yr ⁻¹	Sweden	Hedin et al., 1994	Regression estimate
Bulk	2.5 kg Ca ha ⁻¹ yr ⁻¹	Hubbard Brook Experimental Forest	Hedin et al., 1994	Regression estimate

Table 2. (continued) Fluxes of Ca and Mg in forested ecosystems

Flux	Size	Location	Citation	Comments
Atmospheric deposition				
Bulk	2.5 kg Ca ha ⁻¹ yr ⁻¹	Whiteface Mountain, New York, USA	Miller et al., 1993	Precipitation + clouldwater + dry deposition
Wet	3.9 kg Ca ha ⁻¹ yr ⁻¹	Fernow Experimental Forest, West Virginia, USA	Adams et al., 1997	
Wet	1.8 kg Ca ha ⁻¹ yr ⁻¹	Calhoun Experimental Forest, South Carolina, USA	Markewitz et al., 1998	
Bulk	0.80 kg Ca ha ⁻¹ yr ⁻¹	Cone Pond Watershed, New Hampshire, USA	Bailey et al., 1996	Bulk deposition plus modeled additional dry deposition
Bulk	1.5 kg Ca ha ⁻¹ yr ⁻¹	Average of four northeastern USA sites	Federer et al., 1989	
Bulk	0.51 kg Mg ha ⁻¹ yr ⁻¹	Whiteface Mountain, New York, USA	Miller et al., 1993	Precipitation + clouldwater + dry deposition
Wet	0.55 kg Mg ha ⁻¹ yr ⁻¹	Fernow Experimental Forest, West Virginia, USA	Adams et al., 1997	
Wet	0.36 kg Mg ha ⁻¹ yr ⁻¹	Calhoun Experimental Forest, South Carolina, USA	Markewitz et al., 1998	
Bulk	0.5 kg Mg ha ⁻¹ yr ⁻¹	average of four northeastern USA sites	Federer et al., 1990	

Table 2. (continued) Fluxes of Ca and Mg in forested ecosystems

Flux	Size	Location	Citation	Comments
Uptake				
	12.3 kg Ca ha ⁻¹ yr ⁻¹	Panola Mountain Research Watershed, Georgia, USA	Huntington et al., 2000	Based on uptake into stemwood and bark only; ~ 70-90- year old mixed deciduous and coniferous stands
	64.1 kg Ca ha ⁻¹ yr ⁻¹	Cone Pond Watershed, New Hampshire, USA	Bailey et al., 1996	All-aged mixed conifer forest; determined by multiplying ion content with annual mass production of tree components
	44.6 kg Ca ha ⁻¹	Average of temperate coniferous International Biological Programme sites	Cole and Rapp, 1981	34-440 year old temperate coniferous stands in USA, Sweden, Germany, and Japan; determined by multiplying ion content with annual mass production of tree components
	85.0 kg Ca ha ⁻¹	Average of temperate deciduous International Biological Programme sites	Cole and Rapp, 1981	30-200 year old temperate deciduous stands in USA, Belgium, Sweden, and Germany; determined by multiplying ion content with annual mass production of tree components
Litterfall				
	14.0 kg Ca ha ⁻¹ yr ⁻¹	Cone Pond Watershed, New Hampshire, USA	Bailey et al., 1996	Mixed conifer forest
	74 kg Ca ha ⁻¹ yr ⁻¹	Average of Copera and Morbio sites, Switzerland	Zimmermann et al., 2002	Chestnut stands

Table 2. (continued) Fluxes of Ca and Mg in forested ecosystems

Flux	Size	Location	Citation	Comments
Litterfall				
	22 kg Mg ha ⁻¹ yr ⁻¹	Average of Copera and Morbio sites, Switzerland	Zimmermann et al., 2002	Chestnut stands
	37.3 kg Ca ha ⁻¹	Average of temperate coniferous International Biological Programme sites	Cole and Rapp, 1981	34-440 year old temperate coniferous stands in USA, Sweden, Germany, and Japan
	67.7 kg Ca ha ⁻¹	Average of temperate deciduous International Biological Programme sites	Cole and Rapp, 1981	30-200 year old temperate deciduous stands in USA, Belgium, Sweden, and Germany

matter (McLaughlin and Wimmer, 1999; Fernandez, 1992). In a study to determine the relationship between soil Ca status and the condition of red spruce in the northeastern USA, Lawrence et al. (1997) sampled the forest floor and upper mineral soil (10 cm) and noted that the largest differences in soil Ca pools were due to differences in parent material mineralogy. Vejre and Hoppe (1998) found that about 50% of exchangeable Ca was in the O horizon in soils in western Denmark. Bailey et al. (1996) found that of the total exchangeable Ca pool ($195 \text{ kg Ca ha}^{-1}$), over half was in the O horizon ($108 \text{ kg Ca ha}^{-1}$) (Table 1).

Biomass Pool. Table 1 shows that the sizes of soil exchangeable Ca and biomass pools are within an order of magnitude. It is for this reason, along with the slow weathering supply of Ca in most areas, that several authors have expressed concern over the accelerated depletion of soil Ca pools in conjunction with harvesting (Adams et al., 2000; Adams et al., 1997; Federer et al., 1989; Huntington et al., 2000). Federer et al. (1989) calculated that intensive whole-tree harvesting on a 120-year rotation had the potential to reduce biomass and total soil pools of Ca by 20-60%, at the four northeastern and two southeastern USA sites they studied. At the Fernow Experimental Forest, West Virginia, USA, Adams et al. (1997) calculated that, on an 80-year rotation, a single whole-tree harvest would remove 16% of the total soil Ca pool, while clear-cutting removed an estimated 13%. Huntington et al. (2000) concluded that in ~ 80 years, soil Ca pools at the Panola Mountain Research Watershed, Georgia, could not support current growth of merchantable wood, and harvesting would accelerate this deficiency.

Atmospheric Deposition. Atmospheric deposition can be an important source of base cations that is comparable in magnitude to mineral weathering sources (Table 2).

Miller et al. (1993) used strontium (Sr) isotopes as a surrogate for Ca to determine sources of Ca in soils in the Adirondack Mountains, New York, USA. They found that deposition supplied as much as 60% of the Ca and Sr to biomass and to the forest floor. Bailey et al. (1996) used Sr isotopes in a similar manner at Cone Pond Watershed, New Hampshire, USA, but found contributions of atmospherically-deposited Ca to be ~30% of exchangeable forest floor and total biomass pools. On a regional scale, deposition of Ca and Mg can be strongly influenced by distance from marine influence or from areas generating soil dust. In a data synthesis of forested plots and watersheds around Europe, Armbruster et al. (2002) found that marine Mg deposition was highest ≤ 200 km from the ocean, with marine Mg contribution dropping to less than 50% of throughfall beyond this threshold.

Because atmospheric deposition can be a significant source of base cations, deposition trends over time are of interest. Hedin et al. (1994) reported decreases in base cation deposition across Europe and eastern North America from the 1970's to 1990, and noted that these declines were due to declines in fuel combustion and dust deposition. While the decline in base cation deposition from ~1970-1990 in northeastern North America and Europe is clear, current trends in base cation deposition are more contentious. Kelly et al. (2002) examined trends in precipitation, dry deposition and bulk deposition in southeastern New York, USA from 1988-1999. While there were decreases in particulate Ca, K, and Mg concentration over this time, there were no changes in base cation concentrations in wet precipitation. Stoddard et al. (2003) examined trends in wet deposition from 1990-2000 for the northern and eastern regions of the USA. There was a non-significant increase in the wet deposition of base cations in all regions examined.

Tessier et al. (2002) examined NADP data from 1985-1999 for base cation concentration and deposition trends in New York, Massachusetts, New Hampshire, and Vermont.

While the 15-year trend seemed to indicate declines in base cation concentrations and deposition, none of these declines were large enough to be statistically significant. As noted by Stoddard et al. (2003), there have been a variety of reports debating trends in base cation deposition for the time period of 1990-2000. Conflicting results are likely due to: 1) analysis of different time periods, 2) analysis of different geographic regions, 3) analysis at different geographic scales, and 4) analysis using different statistical measures.

Throughfall and Litterfall. Throughfall and stemflow are often more enriched in base cations than bulk deposition (Table 2). This is due to washing of dry deposition from foliage, leaching of foliar constituents, and active exchange (often of a H^+ ion from precipitation with Ca, Mg, or potassium [K] from foliage) between foliage and precipitation (Eaton et al., 1973; Friedland and Miller, 1999; Houle et al., 1999; Lawrence and Fernandez, 1991; McLaughlin et al., 1996). At some locations, the flux of nutrients through litterfall can be substantial. Zimmermann et al. (2002) studied the input of macronutrients by litterfall - including leaves, branches, twigs, flowers, and fruits - at two sites in Switzerland and found that the flux of nutrients through litterfall was 3.8-5.1 times greater than the flux from total (measured wet and throughfall + estimated dry) atmospheric deposition for N, Ca, Mg, and K. The flux of Ca in litterfall varies by forest type and region as well (Cole and Rapp, 1981) (Table 2).

Uptake. The rate of vegetative uptake is often estimated using nutrient concentrations in tree components (e.g., leaves, braches, leaves, roots) and the annual

biomass production of each of these components, with nutrient mass per unit area per year of uptake being estimated from allometric equations that relate tree size to biomass (Bailey et al., 1996; Cole and Rapp, 1981; Federer et al., 1989). Uptake varies by species, with higher uptake by deciduous species, and by age, with higher relative uptake in young trees. Uptake declines in stands after ~20-40 years (Cole and Rapp, 1981; Markewitz et al., 1998) (Table 2). Johnson et al. (1994) examined changes in soil chemistry and nutrient concentration from 1930 to 1984 in the Adirondacks of New York, USA, and their partial Ca budget suggested that most of the Ca lost from the forest floor could be attributed to net uptake over this time period.

Losses and Net Depletion. Losses of Ca and Mg are measured as stream losses at the watershed level or leaching losses in soil solutions below the rooting zone. In contrast, net depletion calculations take into consideration all other fluxes, and represent losses of Ca or Mg from biomass or soil exchangeable pools (Bailey et al., 1996). Armbruster et al. (2002) noted that losses of Mg were higher from watershed-level than from plot-level studies, and this is likely true for Ca as well. They explained that these differences were due possibly to weathering and exchange reactions in deep soil horizons and different sampling techniques. Net Ca depletion was greater than weathering at both sites for which these figures were available (Table 2), and it is this net depletion of available Ca that can have deleterious impacts on ecosystem health.

Sources and Trends of Acidic Deposition

Acidic Deposition

Acidic deposition occurs when nitrogen oxides (NO_x) and sulfur oxides (SO_x) react with water in the atmosphere to produce nitric (HNO_3) and sulfuric acid (H_2SO_4), which are deposited on the landscape (Dail et al., 1999; Nissinen, 1999; Stoddard et al., 2003). These compounds produce acidity, causing reactions that liberate hydrogen ions (H^+) and/or leach base cations from soils (Nissinen, 1999). While ammonia (NH_3) is basic, once in soils it is often oxidized by microbes to nitrate ($\text{NO}_3\text{-N}$), which produces two moles of H^+ for each mole of ammonium ($\text{NH}_4\text{-N}$) oxidized (Currie et al, 1999; Dail et al, 1999). Acidic deposition includes deposition of both wet precipitation (rain, snow), occult deposition (fog, marine aerosols), and dry deposition (dust, particulates, gases). In some areas, dry and occult deposition can make up 50-75% of total or bulk deposition for analytes such as sulfate ($\text{SO}_4\text{-S}$), chloride (Cl) and other locally variable constituents (Lovett et al., 1982; Miller and Friedland, 1999; Norton et al., 1988; Rustad et al., 1994). The proportion of total deposition that is attributable to dry deposition often depends on vegetation characteristics (Rustad et al., 1994), distance from marine influence (Armbruster et al., 2002; Norton and Kahl, 2000), and physiography (Miller and Friedland, 1999), as these factors influence the interception capacity of a watershed.

Sources of Natural Acidity

While the deposition of N and S has increased acidity in ecosystems, natural processes are also sources of H^+ , $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$ and $\text{SO}_4\text{-S}$. Rain, in equilibrium with

atmospheric carbon dioxide (CO_2), is expected to have a theoretical pH of ~ 5.6 (Drever, 1997) if other local and regional influences are not a factor (Stoddard et al., 2003).

Microbial activities are primary sources of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$, and marine aerosols can be a major natural source of sulfates (Schimel and Holland, 1998; Dail et al., 1999).

Internal sources of acidity in soils include: uptake of cations in excess of anions, soil respiration and CO_2 evolution, anion production or consumption, and oxidation of reduced N and S compounds (Johnson and Fernandez, 1992; Markewitz et al., 1998; Richter, 1986). Johnson and Fernandez (1992) concluded that northeastern USA spruce-fir forests were naturally acidic. In attempting to assess the contribution of anthropogenic versus natural causes of acidification at the Calhoun Experimental Forest, South Carolina, USA, Markewitz et al. (1998) estimated that $\sim 62\%$ of the observed acidification of soils was due to natural processes, such as respiration and organic matter decomposition, while 38% was due to acid deposition. Richter (1986) concluded that the natural processes produced more acidity than did atmospheric deposition at three forested sites in Tennessee, USA. It is important to note that naturally acidic environments have large amounts of relatively weak organic acidity in the form of dissolved organic carbon (DOC), whereas acidic deposition delivers a strong mineral acidity to ecosystems. A survey of Maine lakes, surface waters, and bogs found that acidic waters were dominated by natural sources of acidity (high DOC concentrations), anthropogenic sources (high $\text{SO}_4\text{-S}$ concentrations, presumed to be mostly of atmospheric origin), or a combination of these acidic influences (Kahl et al., 1989).

Sources and Levels of N and S Emissions in the United States

Anthropogenic activities in the last century have increased the levels of both N and S in the atmosphere. Excess S in the atmosphere is largely a result of industrial combustion of fossil fuels, while excess N is a result of fossil fuel combustion, but also non-point sources such as large-scale agriculture and motor vehicle exhaust (Dail et al., 1999; Stoddard et al., 2003). Emissions of S peaked in the mid-1970s in the northeastern USA at 29 million metric tons per year (Husar et al., 1991), with emissions in 1998 estimated at 18 million metric tons (Stoddard et al., 2003). In contrast, emissions of N reached 22 million tons in the late 1980's and have remained roughly constant.

In the mid- to late-1970's, as concern over "acid rain" was growing, research and regulatory emphasis was placed on S deposition because it was initially a larger source of precipitation acidity due to higher emission rates (Likens et al., 1979; Johnson, 1984). The declines in SO₂ emissions during the 1990s were primarily a result of the Clean Air Act of 1970, and Amendments to the Clean Air Act in 1990. The Amendments to the Clean Air Act in 1990 were specifically aimed at reductions in industrial emissions, which disproportionately lowered S deposition, as these sources have higher S emissions than N (Stoddard et al., 2003). Future phases of the Amendments target larger reduction in N emissions and further reductions in S emissions.

Trends in Acidic Deposition in the United States

The declines in S emissions produced large decreases in S deposition over the last three decades. Hedin et al. (1987) reported that at the Hubbard Brook Experimental Forest (HBEF), New Hampshire, USA, there was a decrease in both precipitation

concentration and total deposition of $\text{SO}_4\text{-S}$ from 1963-1983. There were similar trends for this period at National Atmospheric Deposition Program (NADP) sites in the mid-western and northeastern USA. At the time, however, Hedin et al. (1987) cautioned that S deposition was still 4 to 13 times greater at HBEF than deposition in remote “unpolluted” areas.

The Clean Air Act Amendments of 1990 resulted in similar additional improvements in precipitation chemistry. Kelly et al. (2002) examined trends in precipitation, dry deposition and bulk deposition in southeastern New York, USA from 1988-1999. There were decreases in gaseous and particulate forms of N and S over this period that resulted in decreases in the concentration of $\text{NH}_4\text{-N}$, $\text{SO}_4\text{-S}$, $\text{NO}_3\text{-N}$ and H^+ in precipitation and total N and S deposition. Stoddard et al. (2003) examined trends in wet deposition from 1990-2000 for the northern and eastern regions of the USA. Deposition of $\text{SO}_4\text{-S}$ declined in all areas but deposition of N declined only in the Northeast while remaining relatively constant elsewhere. The deposition trends over time reflected emissions trends in S and N. Fernandez and Wortman (1997) examined temporal trends in precipitation chemistry at a site in northern Maine, USA from 1980-1995. They found that while there were declines in both S concentration and deposition, N deposition remained constant or showed a slight increase.

Continuing Concerns Over Acidic Deposition

Despite large declines in emissions and deposition of S, acidic deposition remains a concern. While declines in S emissions and deposition have been accompanied by declines of $\text{SO}_4\text{-S}$ in surface waters (Stoddard et al., 2003; Clow and Mast, 1999;

Kirchner and Lydersen, 1995; Hedin et al., 1987), many long-term studies have failed to see the expected improvements in key indicators of water quality such as pH and acid neutralizing capacity (ANC) (Couture et al., 1995; Dillon and LaZerte, 1992; Kirchner and Lydersen, 1995; Likens et al., 1996; Neirynck et al., 2002; Stoddard et al., 2003; Watt et al., 2000). The fate of $\text{SO}_4\text{-S}$ in soils is strongly influenced by pH because of the pH-dependent charge of soil oxyhydroxide coatings, as well as uptake of S by biota and formation of Al-SO_4 complexes (David et al., 1991b; Meiwes et al., 1998; Meiwes and Khanna, 1981; Nodvin et al., 1986). High S deposition rates in the past may have decreased the ability of soils to adsorb additional $\text{SO}_4\text{-S}$. While the $\text{SO}_4\text{-S}$ adsorption capacity of soils serves as a buffer for nutrient leaching, the recovery of ecosystems following declines in S deposition can be delayed by desorption of $\text{SO}_4\text{-S}$ from the soil exchange complex (Galloway et al., 1983). In order to see improvements in water quality that result from reductions in deposition, further reductions in S deposition and time for soils to recover may be needed (Kirchner and Lydersen, 1995; Wesselink et al., 1995; Nierynck et al., 2002).

Because of the complexities of the N cycle and uncertainties over the impact of elevated N deposition, the lack of decline in N deposition is problematic. Nitrogen is commonly thought to be the most limiting nutrient in terrestrial ecosystems, as it is the only macronutrient that is not derived from primary minerals (Fernandez, 1992). As a result, N supply is controlled by biotic and abiotic fixation of N_2 , atmospheric deposition, and decomposition and mineralization of soil organic matter (Fernandez, 1992; Aber 1989; Dail et al., 1999). Increased N deposition changes the dynamics of an ecosystem through the disruption of nutrient cycling, resulting in N saturation- a state where N

inputs are in excess of biological demand (Nihlgård, 1985; Ågren and Bosatta, 1988; Aber et al., 1989). In a forested watershed, some of the implications of N saturation include: altered nutrient cycling creating nutrient imbalances, increased soil acidification, increased aluminum (Al) mobility, increased $\text{NO}_3\text{-N}$ leaching, increased base cation leaching, and increased production of nitric oxide (NO) and nitrous oxide (N_2O) gases. As a result of these changes, there can be declines in water quality and aquatic diversity, changes in vegetation composition and productivity, and possibly alterations to global climate (Aber, 1992; Fenn et al., 1992). As noted by Adams et al. (2000), N saturation “is an ecosystem state, largely driven by biological processes.”

Mechanisms and Models of Soil Response to Acidic Deposition

Acid-Consuming Processes in Soils

Just as there are soil processes that produce acidity, there are a variety of ways in which the acidity produced by deposition of HNO_3 , H_2SO_4 , and NH_3 can be neutralized in soils. The processes that operate in a given soil depend largely on initial soil chemistry.

Cation Exchange. An instantaneous acid neutralization mechanism in soils is base cation exchange. The HNO_3 and H_2SO_4 produced in the atmosphere dissociates in precipitation or in soil solution, with H^+ and a strong acid anion produced ($\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$). These anions are very mobile in soil solution (in comparison to DOC anions) and a counterbalancing cation is needed to maintain solution charge neutrality. In acidic

forest soils, Ca, Al, and H^+ are often the dominant organic (O) horizon exchangeable cations, but with increasing depth in the mineral soil, exchangeable Ca and H^+ concentrations decline and Al becomes the dominant exchangeable cation (Fernandez, 1992). However, due to the high affinity of Al for exchange sites, Ca or Mg are more likely to be leached with NO_3-N or SO_4-S anions. In contrast to organic acidity (DOC), which is decomposed or precipitates out of solution, strong mineral acidity is not readily immobilized in the mineral horizon (Lawrence et al., 1995). This can lead to a “moving front” of cation depletion, starting at the O horizon and progressing downward as base cations become depleted in upper horizons. The progressive response of Ca and other base cations downward in the soil profile has been observed in soil studies and inferred in soil solution studies (Adams et al., 1997; Fernandez et al., in press; Johnson et al., 1988; Knoepp and Swank, 1994; Markewitz et al., 1998; Meiwes et al., 1998; Stuanes and Kjønåas, 1998).

In addition, the H^+ that is produced in or deposited onto soils can have a high affinity for cation exchange sites (relative to other ions common in soil solution), and can displace di- and other monovalent cations from these sites.

Sulfate Adsorption. Sulfate adsorption is a process that consumes acidity (Johnson and Fernandez, 1992; Markewitz et al., 1998; Richter, 1986) because it occurs as the result of surface hydroxyl (OH^-) exchange (Nodvin et al., 1986). Markewitz et al. (1998) found that in soils at the Calhoun Experimental Forest in South Carolina, USA, SO_4-S adsorption was high in clay-rich soil horizons. In Spodosols, soils that are prevalent throughout much of the glaciated and forested northeastern USA, the Al and iron (Fe) sesquioxide rich coatings in the upper mineral horizons strongly adsorb SO_4-S

(Chao et al., 1964; David et al., 1991b; Nodvin et al., 1986). Sulfate adsorption capacity is also strongly governed by pH. Lower pH increases the positive charge on sesquioxide coatings, making them more effective at adsorption (Nodvin et al., 1986). Adsorption experiments on a B-horizon Spodosol by Nodvin et al. (1986) showed that the highest $\text{SO}_4\text{-S}$ adsorption occurred at $\sim\text{pH } 4$. Laboratory and field studies have shown that in addition to base cation exchange, $\text{SO}_4\text{-S}$ adsorption is one of the important initial acid neutralization responses (Dahlgren et al., 1990; David et al., 1991b; Markewitz et al., 1998; Meiwes et al., 1998; Skeffington and Brown, 1986)

Metal Mobilization. Aluminum is one of the most common elements in soils, constituting an average of 7% of the solid matter (Lindsay and Walthall, 1989; Wolt, 1990). Aluminum mobility in solution increases as solution pH declines below ~ 5.5 . The process of Al mobilization through Al oxyhydroxide dissolution consumes acidity, and produces water as a by-product. While Al mobilization consumes acidity, Al in solution can displace di- and monovalent cations from exchange sites because of the high affinity of Al for exchange sites. Lawrence et al. (1995) detailed a process by which mineral horizon Al can be cycled through vegetative uptake and litter fall and becomes enriched in the O horizon. A rising water table or capillary action can cycle Al to the O horizon as well. In the O horizon, which contains much of the total exchangeable Ca, Al can displace base cations from this large and bioavailable Ca pool. The depletion of Ca from the O horizon is problematic not only because it is a large part of the exchangeable Ca pool, but also because up to 50% of the fine root mass can be located in this horizon (Fahey et al., 1988). Thus, depletion from this horizon is likely to impact vegetation health and productivity. Mobilization of other metals, such as Fe and manganese (Mn)

(Meiwes et al., 1998; Norton et al., in press), also consumes acidity. In the case of Mn, because its average abundance is much lower than Al (0.085%; Wolt, 1990), it is not as important as Al overall as an acid-consuming mechanism. Laboratory and field studies have confirmed that mobilization of Al (Carnol et al., 1997; Emmett et al., 1998; Meiwes et al., 1998; Skeffington and Brown, 1986; Dahlgren et al., 1990) is a large sink for H^+ , while the importance of Fe and Mn (Meiwes et al., 1998; Norton et al., in press) are yet to be elucidated.

Weathering. Weathering of parent material, either within or below the soil profile, consumes acidity, and releases base cations to restore exchangeable pools. Mazzarino et al. (1983) estimated that the H^+ consumption of weathering was 0.5-1.0 $kmol\ ha^{-1}\ yr^{-1}$, about 30-50% of the atmospheric H^+ inputs to the Solling, Germany site. However, it is uncertain whether acidic deposition increases weathering above “natural” levels. Some laboratory studies have found increases in weathering (Skeffington and Brown, 1986) while other laboratory studies (Dahlgren et al., 1990) and field studies (Likens et al., 1996; Norton et al., 1994, 1999) have not found evidence of accelerated weathering as a result of acidic deposition or treatments. Some of the difficulties with the determination of weathering rates are likely responsible for this disagreement: differences between conditions in laboratory studies, difficulty in mineralogy determination, and the complex fates of weathered constituents.

Other Acid-Consuming Processes. Other processes that consume H^+ include the release of base cations from biomass or organic matter mineralization and the reducing reactions with compounds in the soil (Markewitz et al., 1998; Richter, 1986).

However, most well drained soils do not support chemically reducing environments.

Uptake of $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ can also be considered a reducing reaction and thus produces alkalinity.

Integrated Model of Ecosystem Response to Acidic Deposition

Galloway et al. (1983) created a conceptual model of ecosystem response to acidic deposition that include $\text{SO}_4\text{-S}$ adsorption, base cation exchange, and metal mobilization as key processes regulating ecosystem response. The response of soils and streams to acidic deposition was divided into stages that represented conditions prior to, during, and recovery from elevated N and S deposition. Prior to increased emissions and deposition of N and S in this model, ecosystem processes are considered in relative equilibrium, with little change in stream or soil base cation concentrations over time. As N and S deposition increased, Galloway et al. (1983) predicted an initial increase in stream base cation along with $\text{SO}_4\text{-S}$ and $\text{NO}_3\text{-N}$ concentrations. The timing of increases in $\text{SO}_4\text{-S}$ and $\text{NO}_3\text{-N}$ concentrations is a function of the $\text{SO}_4\text{-S}$ adsorption capacity of the soil, and of the rate of microbial transformations of these elements in the soil. If exchangeable base cation pools become depleted, and soil pH drops, Al is mobilized. Because Al and H^+ preferentially displace base cations from soil exchange sites, soil exchangeable base cation pools become depleted. As a result, stream water concentrations of Al and H^+ increase, while stream base cation concentrations decline. Under constant S deposition, once the soil's $\text{SO}_4\text{-S}$ adsorption capacity is saturated, stream $\text{SO}_4\text{-S}$ concentrations will become about equal to concentrations of S deposition. Eventually, under constant elevated N and S deposition, a new equilibrium is reached,

with higher exchangeable Al and $\text{SO}_4\text{-S}$ concentrations in soils and lower exchangeable concentrations of base cations. In addition, soil base saturation approaches zero and exchangeable acidity (Al and H^+) is high. If N and S deposition decline, the watershed can begin recovery. Sulfate stream concentrations decline and pH increases. Base cation concentrations during recovery decline initially then rise, as they are being restored to soil exchange sites. As recovery is completed, the pH, ANC, and base saturation of the watershed reach an equilibrium similar to that prior to acidic deposition.

Amending this conceptual model, Norton et al. (in press) hypothesized that under elevated N and S deposition, as base cation buffering becomes depleted, Al buffering of decreasing pH results in Al mobilization, eventually followed by Fe buffering and mobilization in a sequence of acid-neutralization mechanisms. Within this model, episodic stream acidification takes place early in the process of ecosystem acidification, and chronic acidification takes place when base flow stream base cation concentrations decline (signaling depletion of soil exchangeable base cation pools), and forests are adversely affected when base saturation approaches zero (Norton et al., 1999).

Experimental Evidence for Altered Nutrient Cycling

Laboratory Studies

Laboratory soils studies have confirmed some of the important processes governing soil response to acidification. Dhalgren et al. (1990) leached a soil column of Spodosol Bs horizon with three levels of H_2SO_4 and then reduced loading to the lowest

concentration to observe recovery from acid inputs. They found that initial buffering responses were the release of base cations and adsorption of $\text{SO}_4\text{-S}$. As a new equilibrium was reached, Al dissolution became the primary mechanism of acid neutralization. Once levels of H_2SO_4 inputs were decreased, base cation concentrations in leachate solutions increased while Al concentrations decreased. Because of declines in $\text{SO}_4\text{-S}$ loading, $\text{SO}_4\text{-S}$ desorbed from soils so leachate $\text{SO}_4\text{-S}$ concentrations did not decline immediately. Dhalgren et al. (1990) concluded that changes in weathering did not contribute significantly to changes in leachate base cation concentrations because high silica (Si) release at the start of the experiment did not correspond well with high base cation release. Instead, high base cation release was coincident with high Al and H^+ release, indicating displacement of base cations from cation exchange sites. Skeffington and Brown (1986) found that the principal neutralization mechanisms to S additions were base cation exchange, $\text{SO}_4\text{-S}$ adsorption and Al dissolution when they leached a Spodosol profile with H_2SO_4 . Based on variations in base cation concentrations and mass balance, they inferred that acid leaching of the soil had increased weathering rates. David et al. (1991a) reported similar results for base cation mobilization in response to H_2SO_4 treatments of a Spodosol and an Alfisol. David et al. (1991b) also showed that $\text{SO}_4\text{-S}$ adsorption was higher in acidic S treatments (versus neutral salt) and sesquioxide-rich Spodosols (versus Alfisols).

Stream and Surface Water Studies

In addition to laboratory studies that have demonstrated the response of soils to acidic deposition, many more studies have reported on the effects of acidic deposition on

nutrient cycling in the field. Because stream chemistry integrates a variety of ecosystem processes, studies often monitor changes in stream chemistry through time.

Martin et al. (2000) monitored stream water chemistry in the White Mountains of New Hampshire, USA and found that between their two sampling periods (1973-1974 and 1994-1997) there were decreases in both base cation concentrations (especially Ca and Mg) and $\text{NO}_3\text{-N}$ concentrations in stream water. Martin et al. (2000) concluded that these changes in stream chemistry might be indicative of N saturation and base cation depletion. Mitchell et al. (1996) found increased stream $\text{SO}_4\text{-S}$ and base cation concentrations in a watershed in the Adirondack Mountains, New York, USA when data from 1983 to 1992 were analyzed. In a survey of deposition trends and stream chemistry at five headwater streams in the northeastern USA (Maine, New York, Virginia, Pennsylvania, and New Hampshire), Clow and Mast (1999) found decreases in Ca and Mg concentrations in three of the five streams between 1984-1996. The remaining streams had slightly increasing or constant Ca and Mg concentrations. Clow and Mast (1999) reported that while there were decreases in $\text{SO}_4\text{-S}$ concentrations in both precipitation and stream water at all sites, alkalinity only improved at one of the streams. The authors concluded that while stream $\text{SO}_4\text{-S}$ concentrations responded quickly to declines in deposition, decades of high N and S loading had depleted exchangeable base cation pools, which would need to be restored before alkalinity or ANC improvements would be seen. Likens et al. (1996) found that despite decreases in S deposition, which were accompanied by decreases in stream $\text{SO}_4\text{-S}$ concentrations, there were no improvements in ANC or pH at HBEF, New Hampshire, USA. Likens et al. (1996) concluded that it was likely that high S deposition from 1950-1970 depleted soil Ca

pools, which was evidenced by higher stream Ca concentrations during this time. They concluded that from 1970-1994, stream Ca concentrations declined as a result of depletion of soil Ca pools. Likens et al. (1996) have observed declines in forest biomass accumulation at HBEF, which they believe may be attributable to low soil base saturation. Other studies have shown evidence of base cation depletion in Norway (Kirchner and Lydersen, 1995), the Harvard Forest, Massachusetts (Currie et al, 1999), the Shenandoah National Park, Virginia, USA (Ryan et al., 1989), and in Toronto, Ontario, Canada (LaZerte and Scott, 1996).

Studies of the long-term impact of acidic deposition have also included treatment with N and/or S at different scales in an attempt to observe the resulting changes in ecosystem processes. These studies can be at the watershed scale or plot scale, and have the advantage of consistent loading of N and S for the period of the study. At the Bear Brook Watershed in Maine (BBWM), USA, Norton et al. (1994) found that in response to three years of $(\text{NH}_4)_2\text{SO}_4$ addition, the treated watershed had higher stream water concentrations of $\text{SO}_4\text{-S}$, $\text{NO}_3\text{-N}$, base cations, Al and H^+ than the reference watershed. Because mineral weathering had not increased (inferred from constant SiO_2 concentrations), base cation leaching was primarily from exchangeable soil pools. More recent data from BBWM showed that Ca and Mg stream concentrations peaked 4-5 years after treatments began, and have declined since (Fernandez et al., in press). At the Fernow Experimental Forest (FEF), West Virginia, USA, which is also treated with $(\text{NH}_4)_2\text{SO}_4$, increases in both the concentrations and total export of base cations in stream water have been observed (Adams et al., 1997). After five years of treatment with $(\text{NH}_4)_2\text{SO}_4$, exports of Ca were twice as large as atmospheric inputs, while exports of Mg

were six times as large as inputs. Further analyses after nine years of treatments at FEF by Edwards et al. (2002) showed differences in response to treatments based on land-use history. One of the two treated watersheds (WS3), which was logged in the early 1900's and salvage-logged in the 1940s, showed immediate changes in stream chemistry during peak flow and 1-2 years later in base flow. In contrast, the second watershed (WS9) was intensively farmed, eroded, and harvested, with the last disturbance occurring as recently as the 1980s. This watershed responded to treatments in both base and peak stream flow immediately, which Edwards et al. (2002) attributed to a land-use history that had degraded soil quality and soil base cation pools, and homogenized horizons. Similar to the reported results of Fernandez et al. (in press), and consistent with the conceptual model of Galloway et al. (1983), Edwards et al. (2002) showed increases followed by decreases in peak flow stream Ca and Mg concentrations in WS3. Moldan and Wright (1998) reported that both mean annual concentrations and peak concentrations of stream $\text{NO}_3\text{-N}$ were higher in the treated watershed after five years of treatment with NH_4NO_3 at the forested watershed in Gårdsjön, Sweden. They observed increases in stream $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, K, and Ca concentrations in the treated watershed when compared with the reference, but Al, H^+ , and $\text{SO}_4\text{-S}$ did not respond to the treatment. Nine years of HNO_3 additions to the watershed at Sogndal, Norway, resulted in only high peak $\text{NO}_3\text{-N}$ stream concentrations and a relative retention of $\text{NO}_3\text{-N}$ in the treated watershed that was equal to the reference (Wright and Tietema, 1995). Stream concentrations of $\text{SO}_4\text{-S}$ and base cations increased relative to the reference, and ANC decreased as a result.

Episodic stream acidification is also a concern as base cation pools become depleted and are less able to respond to acidification. Episodic stream acidification

occurs during high stream flow that results from high precipitation events (Lawrence et al., 2002), marine storms (Hindar et al., 1995; Norton and Kahl, 2000; Wright et al., 1988) and snowmelt (Galloway et al., 1987; Foster et al., 1989). High precipitation and snowmelt events primarily flow through organic-rich upper soil horizons and cause some combination of high DOC, Al, NO₃-N, SO₄-S and/or H⁺ levels in stream water (Lawrence et al., 2002; Wigington et al., 1996). In contrast, the influx of marine aerosols to acidic soils causes exchange of primarily Al and H⁺ for marine-derived Mg and Na on soil exchange sites, causing episodic acidification of streams that drains acidic soils (David et al., 1991a; Hindar et al., 1994; Hindar et al., 1995; Wright et al., 1988). This influx of marine aerosols can be the result of a marine episode, or the accumulation of dry marine deposition that is mobilized by precipitation. Episodic acidification has been shown to cause widespread fish mortality (Baker et al., 1996; Hindar et al., 1994; Hindar et al., 1995). Lawrence et al. (2002) concluded that episodic acidification of surface waters is becoming more problematic and widespread in the northeastern USA than chronic acidification because of depletion of exchangeable Ca in surface soil horizons coupled with storage of N and S in soils, which will delay recovery.

Soils and Soil Solutions

Soils are key in regulating ecosystem response to acidification, and soil solutions are the conduit between the solid phase of soils, plant or microbial uptake, or losses via stream flow. The soil reflects the history of soil forming processes at that site, while soil solutions are the best reflection of current soil dynamics (Marques et al., 1996). Field studies observing changes in soil and soil solution chemistry over time or as the result of

experimental enhancement of N and S deposition attempt to elucidate how acidification alters soils and the capacity of soils to respond to future perturbations.

Markewitz et al. (1998) compared soils sampled on 6 dates (between 1962-1990) and found that base saturation declined from 62% to 10% in the upper 15 cm of soil, and 70% to 44% in the 15-60 cm increment of soil, at Calhoun Experimental Forest, South Carolina, USA. Johnson et al. (1994) conducted similar comparisons of soil chemistry over time on soils collected in 1930 and 1984 from the Adirondack Mountains of New York, USA. The pH of the original mildly acidic (pH 4) samples decreased, while soils that were acidic originally (pH < 4) did not change. Organic horizons lost an average of 25% of the total exchangeable Ca pool over the time period sampled, with larger losses in the mildly acidic O horizons. Lawrence et al. (1997) surveyed soils throughout the northeastern USA to determine available Ca concentrations in red spruce forests. They found that while much of the variation in forest floor Ca was due to parent material mineralogy, acidic deposition had likely depleted exchangeable Ca pools in the mineral horizon. Falkengren-Grerup and Tyler (1992), Knoepp and Swank (1994), and Johnson et al. (1988) all noted similar declines in exchangeable or dilute-acid extractable Ca and Mg in various soil horizons over time. Falkengren-Grerup and Tyler (1992) and Johnson et al. (1988) also noted increases in extractable Al.

Extensive soil sampling at BBWM indicates depletion of Ca and Mg in response to experimental acidification (Fernandez et al., in press). Exchangeable Ca and Mg in all horizons were lower in the treated watershed, with the O horizon showing the largest declines. Over the 12-year study, the treated watershed lost approximately 66 kg Ca ha⁻¹ and 27 kg Mg ha⁻¹ from exchangeable pools.

In contrast to these soils studies, Nohrstedt et al. (2000) found no changes in base cation concentration or content in forest floor and upper mineral soil at a central Sweden site that received sporadic doses of N (four times during a 20-year period). While changes were noted in the N concentration and carbon to nitrogen (C/N) ratio of the O horizon, possible causes for a lack of response in base cation pools were attributed to increased weathering, changes in base cation deposition, or recovery of base cation pools from depletion. Yanai et al. (1999) compared soils sampled over time (1976-1996) at HBEF and found that there was no evidence for a statistically significant change in forest floor concentrations of Ca or Mg, largely due to the variability in concentrations of these analytes. There was also variability in O horizon response to acidic deposition in a survey conducted by Yanai et al. (1999) throughout the northeastern USA. Some sites showed base cation depletion between 1980-1990, while others showed accumulation. In attempting to explain these conflicting results, Yanai et al. (1999) noted that these studies did not rule out depletion of base cation pools prior to the study and that differences in land-use history had a large impact on Ca content of the forest floor.

When $(\text{NH}_4)_2\text{SO}_4$ was added at the plot level to a forest site in Solling, Germany, for 11 years, Meiwes et al. (1998) observed many changes in soil solutions. The added $\text{NH}_4\text{-N}$ was quickly oxidized in O horizons, while $\text{NO}_3\text{-N}$ leaching increased for the first three years, and remained constant thereafter. Concentrations of base cations, Al, DOC, $\text{SO}_4\text{-S}$, and Mn were all elevated in treated soil solutions relative to control plots. Most of these analytes initially increased in surface horizon soil solutions, and with the progression of acidification, lower soil horizons showed increased concentrations. This

as true especially of $\text{SO}_4\text{-S}$ and Al, and to a lesser extent Ca, Mg, and Mn. Potassium and Na showed only small differences between treated and control plots.

Plot level studies at the Aber Forest, Wales, United Kingdom showed a similar response of soil solution to additions of NH_4NO_3 during the five year monitoring period (Emmett et al., 1998). Ammonium was retained and oxidized, resulting in $\text{NO}_3\text{-N}$ leaching. In addition, Emmett et al. (1998) also treated plots with NaNO_3 . Both treatments had elevated concentrations of Al and H^+ in mineral soils, but in the NaNO_3 treatment, this was a short-term response and once a new equilibrium was established, soil solution Al and H^+ concentrations declined to near pre-treatment values. There were no changes in DOC or base cation concentrations in any treatment, but base cation to Al (BC/Al) ratios did decline due to Al mobilization. Currie et al. (1999) treated plots with three levels of NH_4NO_3 at the Harvard Forest, Massachusetts, USA, and evaluated soil solutions after six years of treatment. Currie et al. (1999) found that $\text{NO}_3\text{-N}$ leaching increased with increasing N treatment, and correlations between $\text{NO}_3\text{-N}$ and Ca, K, and Mg in soil solution varied by forest type. The headwater watershed at Gårdsjön, Sweden, was treated with NH_4NO_3 , and lysimeters monitored changes in soil solution chemistry. Stuanes et al. (1995) and Stuanes and Kjønaas (1998) reported on changes seen in solution chemistry after two and four years of treatment, respectively. The authors noted trends similar to those seen by Meiwes et al. (1998) with a progression of high $\text{NO}_3\text{-N}$ concentrations through soil horizons. The difference between $\text{NH}_4\text{-N}$ concentrations in ambient/control plots and treated plots was small, due to the rapid nitrification of $\text{NH}_4\text{-N}$ to $\text{NO}_3\text{-N}$. Base cation concentrations in the treated plots were positively correlated with $\text{NO}_3\text{-N}$, while $\text{NO}_3\text{-N}$ and base cation concentrations were negatively correlated in

control/ambient plots. The Fernow Experimental Forest, West Virginia, USA, is experimentally treated at the watershed scale with $(\text{NH}_4)_2\text{SO}_4$, and a nearby watershed serves as a reference. Adams et al. (1997) concluded that high variability in $\text{NO}_3\text{-N}$ concentrations obscured significant differences between the reference and treated watersheds; however, significant differences were detected for soil solution $\text{SO}_4\text{-S}$ concentrations in the A horizon between the treated and reference watersheds. Soil solution Ca concentrations increased over time in A and B horizons and relative to the reference, while Mg showed increases in the B and C-horizons. In a study that investigated both soil and soil solution chemistry at BBWM, Fernandez et al. (1999) found increased $\text{SO}_4\text{-S}$ adsorption in mineral soil bags in the acidified watershed, as well as increases in $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ in soil solution under hardwood stands, which accelerated base cation leaching.

Several studies (Adams et al., 1997; Fernandez et al., in press; Johnson et al., 1988; Knoepp and Swank, 1994; Markewitz et al., 1998; Meiwes et al., 1998; Stuanes and Kj  naas, 1998) have pointed out that acidification of soils occurs initially in surface horizons, followed by mineral horizons as acidification progresses deeper into the soil. Observations of stream chemistry differences during base flow and peak flow (Edwards et al., 2002; Moldan and Wright, 1998; Wright and Tietema, 1995) are consistent with progressive acidification through soil horizons, as the first soil layers to be acidified are only exposed to runoff solutions during events when soils are saturated and flow is dominantly through upper soil horizons. When conditions are drier, solutions percolate

through deeper soil layers that may not yet be influenced by the emerging acidification and therefore base flow conditions can show little evidence of acidification in early stages. These data also support the linkage between soil and stream chemistry.

Input-Output Budgets/ Mass Balance Analyses

Several authors have created ecosystem budgets for Ca that attempt to quantify and synthesize information on Ca pools and fluxes in the ecosystem. Data from some of these studies are shown in Tables 1 and 2. Quantification of these pools and fluxes is expensive and time intensive. In addition, Friedland and Miller (1999) also pointed out some of the difficulties in applying values: uncertainties in magnitude of vegetation cycling, possible changes in plant uptake over time, and uncertainties over how much of weathered material becomes “plant available.” Nonetheless, these studies provide valuable insights into Ca dynamics in forested ecosystems.

Several studies of Ca weathering have used Sr isotopes as an analogue for Ca. Bailey et al. (1996) used this technique at the Cone Pond Watershed, New Hampshire, USA, and found depletion of exchangeable Ca pools. They determined that where silicate minerals are the dominant parent material, weathering may not be able to replace base cation losses. Miller et al. (1993) found base cation pools to be stable using Sr isotopes at Whiteface Mountain, New York, USA, a site with relatively Ca-rich parent material.

Huntington et al. (2000) created an input-output budget using data from the Panola Mountain Research Watershed, Georgia, USA. They concluded that Ca depletion was occurring in this typical southern soil because of small exchangeable Ca pools, a

slow weathering rate, and the potential impact of harvesting practices. Using input-output budgets at Whiteface Mountain, Friedland and Miller (1999) showed that yearly losses of Ca were substantial compared to the exchangeable pool.

Impact on Vegetation

While altered nutrient cycling and base cation depletion have been seen in streams, soils, and soil solutions, investigators have examined changes in vegetation to consider whether this alteration is ecologically significant.

White et al. (1999) sampled the foliage of the dominant tree species at BBWM (red maple-*Acer rubrum* L., sugar maple- *Acer saccharum* Marsh., American beech- *Fagus grandifolia* Ehrh., and red spruce- *Picea rubens* Sarg.) and found all species had higher concentrations of N in the treated watershed compared with the reference, four years after the beginning of treatments. Sugar maple also had significantly lower foliar Ca concentrations in the treated watershed, while the other species did not show this response. Beech, red maple, and sugar maple all had increased foliar Al concentrations in the treated watershed. White et al. (1999) concluded that these differences in foliar chemistry were a reflection of changes in soil chemistry in response to acidification of the treated watershed. Foliar chemistry of trees at FEF revealed similar trends (Gilliam et al., 1996). Several tree species (sweet birch-*Betula lenta* L.; tuliptree- *Liriodendron tulipifera* L.; black cherry- *Prunus serotina* Ehrh.; red maple- *Acer rubrum* L.) on the experimentally acidified watershed had elevated foliar N concentrations and decreased foliar Ca concentrations compared with the reference watershed. The ground herb *Viola*

rotundifolia (Michx.) also exhibited these changes in plant tissue composition. Meiwes et al. (1998) found the same patterns as noted above in foliar N and Ca at the Solling site in Germany. Decreased Ca concentrations were contrary to the expected response, because over the study period, soil solution Ca increased. Meiwes et al. (1998) speculated declines in foliar Ca might have been the result of competition at root sites between $\text{NH}_4\text{-N}$ and Ca and leaching of Ca from soils. They also noted that high N uptake by trees may cause secondary deficiencies of other nutrients. At the Harvard Forest, Massachusetts, USA, plots were treated with low and high levels of N (Magill et al., 1997). Foliar analyses indicated that hardwood and softwood stands differed in their responses to treatments, with foliar N increasing 67% in softwoods stands, but only 20% in hardwoods. In response to treatment, wood production increased at the plot level in hardwoods, but decreased in softwood plots. The N content of fine roots also increased (Magill et al., 1997).

Joslin and Wolfe (1992) found that fine-root biomass and rooting depth were negatively impacted at high elevation red spruce sites, which also had higher soil solution $\text{NO}_3\text{-N}$ and Al concentrations and lower Ca/Al and Mg/Al ratios than did low elevation sites. Carnol et al. (1999) used in-growth cores to investigate changes in root mass and chemistry in response to treatment with $(\text{NH}_4)_2\text{SO}_4$. They found that treatment increased fine root N concentrations and fine root biomass was negatively correlated with fine root Al concentrations.

Minocha et al. (2000) surveyed foliar chemistry, soils, and soil solutions at red spruce sites throughout the northeastern USA. They found that foliar polyamines (compounds linked to stress response in plants) were higher in trees that were growing in

Ca-poor O horizons with high exchangeable Al concentrations, as compared with sites with the opposite characteristics. Many other studies of foliar chemistry and fine root response to acidic deposition also report similar findings as described above (e.g., Adams and Hutchinson, 1992; Gundersen, 1998; Joslin and Wolfe, 1994; McNulty and Aber, 1993; Schlegel et al., 1992).

Analyses of wood chemistry can reveal changes over time in the environment within which a tree developed. There are problems associated with this technique because species have varying accumulation patterns for certain nutrients, and some elements are mobile and can be radially translocated (DeWalle et al., 1999; Watmough, 1999). However, with the right species, supporting data, and control information, trends in element composition of wood can be another useful index of change. DeWalle et al. (1999) examined changes in wood chemistry at the experimentally acidified sites BBWM, FEF, and Clover Run, West Virginia, USA and found that treated watersheds all showed decreases in Ca and Mg in woody tissue, and increases in Mn relative to references. These trends were significant for the West Virginia sites, but not for BBWM. Regional analyses of wood chemistry in the northeastern USA by Shortle and Bondietti (1992) showed that wood Ca concentrations of overstory species declined since the 1950's or 1960's, apparently as the result of declines in exchangeable base cations in the O horizon. Further work by Shortle et al. (1997) on wood chemistry in the northeastern USA showed evidence that was interpreted as mobilization of Ca and Mg from exchange sites. These studies have lead to concerns that declines in base cation pools may impact the health and sustainability of forest ecosystems (Shortle and Smith, 1988). Literature reviews by Joslin et al. (1992) and Cronan and Grigal (1995) concluded that high Al

concentrations and declines in Ca concentrations in soil solutions were reflected in wood chemistry, root length and chemistry, and foliar chemistry. Joslin et al. (1992) concluded that both Al toxicity and deficiencies in Ca and Mg play a role in the decline of red spruce in eastern North America.

These changes in foliar, wood, and root chemistry have implications for tree health. In a literature review on the impact of N deposition on vegetation, Fangmeier et al. (1994) concluded that high plant N concentrations could disrupt metabolic processes, leading to lower resistance against environmental stress factors. McLaughlin and Wimmer (1999) noted that Ca is important in both metabolic processes, such as membrane synthesis and function and carbohydrate metabolism, as well as response to environmental stresses, such as disease resistance and cold tolerance. DeHayes et al. (1999) and Schaberg et al. (2002) showed that acidic deposition decreased the cold tolerance and increased freezing injury of red spruce. This was likely due to leaching of cell membrane-associated Ca from red spruce needles, which decreased their cold resistance. Igawa et al. (2002) showed a similar phenomenon in a laboratory study with fir trees (*Abies firma* Siebold & Zucc.).

Connections to Global Carbon Cycling

Because acidic deposition alters nutrient cycling, changes in ecosystem processes that are a result of acidic deposition may affect global climate and the C cycle. Rastetter et al. (1991) used modeling to show that forest response to long-term changes in the

environment would be dominated by changes in soil processes. Mäkipää (1995) found that experimental N enrichment at a long-term site in Finland increased C storage of the O and mineral horizons, possibly as the result of increased litterfall and decreased microbial activity. Though the C storage in aboveground biomass was slightly decreased, its overall C storage was small in comparison to that of soils. In contrast, other studies have shown a fertilizing effect on forests as a result of N deposition (Magill et al., 1997) and therefore possibly increased C storage in trees. Magill and Aber (1998) studied the impact of elevated N deposition on litter decomposition and found that treated plots had greater litter mass remaining and this litter had higher lignin content than in control plots. This suggests that elevated N deposition may increase global C sequestration.

Ammonification and nitrification of organic N can be followed by denitrification, which produces the greenhouse gases NO and N₂O. Magill et al. (1997) found that the production of N₂O in softwood N treated plots was twice as great as in softwood control plots. Venterea et al. (2003) found that softwood stands at the Harvard Forest responded to all levels of elevated N deposition with elevated NO production. In contrast, only the highest level of elevated N deposition elicited the elevated production of NO in hardwood stands. Venterea et al. (2003) concluded that soil temperature has a positive effect on NO emissions, while soil moisture could have either a positive or negative effect.

Because global climate change can increase average temperatures, this can alter the rate of microbial transformations. Murdoch et al. (1998) found stream NO₃-N concentrations correlated better with mean annual temperature than with N deposition. The authors concluded that in areas that receive excess N inputs, the export of NO₃-N

might be controlled by climate rather than deposition, as the microbial process of N mineralization and nitrification are temperature dependent. Thus, increases in mean annual temperature may result in high $\text{NO}_3\text{-N}$ leaching in sensitive watersheds.

Conclusions

Calcium is an essential macronutrient that is central in a variety of plant processes. Because of its importance in growth and stress responses, Ca availability in forested ecosystems can determine forest structure and dynamics (McLaughlin and Wimmer, 1999). Though emissions and deposition of S have declined substantially in the past decades, continuing N and S deposition remains a concern in the northeastern USA as expected improvements in stream chemistry such as ANC and pH have not been seen. There is a great deal of evidence from temporal, spatial, and experimental studies on forested ecosystems that indicate that base cation depletion is occurring in soils as a result of long-term acidic deposition. Episodic acidification of surface waters may also become more prevalent as a result of base cation depletion. Several studies have suggested that while Ca is not currently considered a limiting nutrient in most forests, variations in base cation deposition combined with harvesting practices may change this in the future (Federer et al., 1989; Huntington et al., 2000). Depletion of Ca and other base cations influences many aspects of forest ecosystem form and function, ranging from water quality and forest health to fisheries productivity and global climate.

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CHAPTER 1. NITROGEN AND SULFUR EFFECTS ON FOREST SOIL SOLUTIONS AT THE BEAR BROOK WATERSHED IN MAINE

Introduction

The Clean Air Act of 1970 and Clean Air Act Amendments of 1990 have contributed to the reduction of sulfur (S) emissions in the northeastern USA from 29 million metric tons per year in the mid-1970s (Husar et al., 1991), to an estimated at 18 million metric tons in 1998 (Stoddard et al., 2003). As a result of the large declines in S emissions, trends in precipitation chemistry throughout the northeastern USA have shown declines in sulfate ($\text{SO}_4\text{-S}$) concentrations and deposition (Fernandez and Wortmann, 1997; Hedin et al., 1987, Kelly et al., 2002; Stoddard et al., 2003). In contrast, emissions of nitrogen (N) reached 22 million metric tons in the late 1980s and have remained roughly constant (Husar et al., 1991; Stoddard et al., 2003). Nitrogen deposition has remained relatively constant in the Northeast (Fernandez and Wortman, 1997, Lynch et al., 2000; Stoddard et al., 2003), although there are some reports of declining N deposition trends in the literature (Kelly et al., 2002).

While declines in S deposition have been accompanied by declines of $\text{SO}_4\text{-S}$ in surface waters (Stoddard et al., 2003; Clow and Mast, 1999; Kirchner and Lydersen, 1995; Hedin et al., 1987), many long-term studies have failed to observe the expected improvements in water quality indicators of such as pH and alkalinity (Couture et al., 1995; Dillon and LaZerte, 1992; Kirchner and Lydersen, 1995; Likens et al., 1996;

Neiryneck et al., 2002; Stoddard et al., 2003; Watt et al., 2000). Because of the complexities of the N cycle and uncertainties over the impact of elevated N deposition, the lack of decline in N deposition is problematic.

Long-term experimental acidification studies have been key in elucidating mechanisms of ecosystem response to elevated N and S deposition. Soil solutions and streams respond to increased N and S inputs with increased export of $\text{SO}_4\text{-S}$ and $\text{NO}_3\text{-N}$ (Adams et al., 1997; Edwards et al., 2002; Meiwes et al., 1998; Moldan and Wright, 1998; Norton et al., 1994; Wright and Tietema, 1995), the timing of which is a function of a number of factors, particularly $\text{SO}_4\text{-S}$ adsorption capacity, and of the rate of microbial N transformations in the soil. The rates of accelerated N leaching can change over time as a direct reflection of soil properties such as N pool sizes and organic matter quality (Aber et al., 2003; Emmett et al., 1998; Fernandez et al., 2000; Shah, 2002), or as an indirect reflection of climatic variations (Murdoch et al., 1998). Mobilization of base cations and aluminum (Al) also has been commonly observed in soil solutions and streams in response to acidification (Currie et al., 1999; Edwards et al., 2002; Emmett et al., 1998; Meiwes et al., 1998; Moldan and Wright, 1998; Norton et al., 1994; Stuanes and Kj  naas, 1998; Wright and Tietema, 1995). Long-term studies have found that after an initial period of mobilization in response to acidification, concentrations of base cations in soil solutions and streams decline, particularly calcium (Ca) and magnesium (Mg), (Edwards et al., 2002; Fernandez et al., in press; Norton et al., in press), and can represent a net depletion of exchangeable base cation pools (Fernandez et al., in press). Aluminum, manganese (Mn) and iron (Fe) hydrolysis can become increasingly important

acid-neutralizing mechanisms as base cation exchange mechanisms become exhausted (Meiwes et al., 1998; Norton et al, in press).

The Bear Brook Watershed in Maine (BBWM) is a paired-watershed experiment that was established in 1987 with the goal of investigating the long-term response of a northeastern USA forested ecosystem to elevated N and S deposition. The objectives of this study were to (a) evaluate evidence of forest type and watershed N and S treatment effects on soil solution chemistry after 12 years of chemical manipulations, and (b) compare these findings with historical soil solution data from earlier in the BBWM program to define possible long-term patterns of ecosystem function.

Methods

Study Site

The Bear Brook Watershed in Maine (BBWM) is located in eastern Maine, USA, on the upper southeastern slope of Lead Mountain, approximately 60 km from the Atlantic Ocean. Adjacent East and West Bear Brooks form the paired watershed experiment at BBWM, and drain 11.0 and 10.3 ha of land, respectively. Elevation within the watersheds ranges from 210 m to 475 m, with an average slope of 31% (Norton et al., 1999). Mean annual temperature is ~5°C, and typically ranges from 25°C in the summer to -20°C in winter. Annual precipitation is ~1.3 to 1.4 m, with ~25% of this precipitation as snow.

The dominant soils at BBWM are loamy, mixed, frigid Typic Haplorthods formed on till (Norton et al., 1999). Soils associated with softwoods are generally thin mineral soils or organic (Folists) soils on steeper slopes; in contrast, soils associated with hardwood-dominated areas are thicker, well-drained mineral soils. Soils are generally acidic, and have low base saturation, sulfate adsorption capacity, and cation exchange capacity. Based on these characteristics, BBWM is considered vulnerable to acidification (Norton et al., 1999).

Bedrock consists of non-calcareous, non-sulfidic meta-pelites and quartzites at higher elevations, while lower in the watersheds calc-silicate gneiss predominates. Granite dikes and sills are common in the bedrock, and bedrock outcrops are prevalent in the upper portion of the watershed (Norton et al., 1999). Till covering the bedrock ranges in thickness from 0 to 5 m, with an average thickness of 1 m.

Vegetation consists of hardwoods at lower elevations, a zone of mixedwoods, and softwoods at higher elevations. The lower boundary for the softwoods is not natural, but resulted from logging in the 1950's (Norton et al., 1999). The hardwoods are ~55 years old, and the softwoods are >100 years old, with individuals >150 years old (Elvir., 2001). Major hardwood species at BBWM are American beech (*Fagus grandifolia* Ehrh.), sugar maple (*Acer saccharum* Marsh.), and red maple (*Acer rubrum* L.) with smaller amounts of yellow birch (*Betula alleghaniensis* Britton) and paper birch (*Betula papyrifera* Marsh.). Red spruce (*Picea rubens* Sarg.) accounts for the majority of the softwood stand, with minor amounts of balsam fir (*Abies balsamea* (L.) Mill) and hemlock (*Tsuga canadensis* (L.) Carrière). Both species composition and cover of each of the forest types are comparable between East and West Bear (Elvir, 2001).

Treatment

East and West Bear streams were hydrologically and chemically similar before the treatments began in November 1989, based on observations from 1987-1989 (Norton et al., 1999). West Bear watershed has been treated by helicopter since 1989 with bi-monthly additions of 300 eq $(\text{NH}_4)_2\text{SO}_4 \text{ ha}^{-1}$, for a total yearly loading of 1800 eq ha^{-1} (25.2 kg N $\text{ha}^{-1} \text{ yr}^{-1}$ and 28.8 kg S $\text{ha}^{-1} \text{ yr}^{-1}$). During this study, treatments were applied on: 6/25/2001, 8/22/2001, 10/11/2001, 12/4/2001, 2/7/2002, 4/5/2002, and 6/25/2002. East Bear serves as the untreated reference watershed. Ambient wet deposition to BBWM averaged 118 eq $\text{ha}^{-1} \text{ yr}^{-1}$ for $\text{NH}_4\text{-N}$, 192 eq $\text{ha}^{-1} \text{ yr}^{-1}$ for $\text{NO}_3\text{-N}$ and 350 eq $\text{ha}^{-1} \text{ yr}^{-1}$ for $\text{SO}_4\text{-S}$ (4.3 kg N $\text{ha}^{-1} \text{ yr}^{-1}$ and 5.6 kg S $\text{ha}^{-1} \text{ yr}^{-1}$) for calendar years 1998-2000 (Nelson, unpublished data).

Lysimeter Design

Tension lysimeters were constructed in March and April of 2001. Both right-angled and straight lysimeters consisted of a PVC body (40 mm i.d.) with a porous ceramic cup (Soil Moisture Corporation, Santa Barbara, CA) at one end, and a rubber stopper and sampling access tubes at the other. Right-angled lysimeters minimize soil disturbance above the collection surface of the ceramic cup by allowing installation horizontally from an adjacent soil pit. Straight lysimeters can result in solutions being channeled down the sides of the lysimeter but they avoid the degree of site disturbance during installation that results with right-angled lysimeters. In preparation for sampling, lysimeters were washed in 10% hydrochloric acid (HCl) once, and thoroughly rinsed with deionized water a minimum of five times.

Experimental Design and Lysimeter Installation

Five 5 by 5 m plots were established in June of 2001 in each combination of forest type and watershed: (1) East Bear hardwood, (2) East Bear softwood, (3) West Bear hardwood, (4) West Bear softwood. There were a total of 20 plots. Within each of these plots, one right-angled tension lysimeter was installed 25 cm below the surface of the mineral soil. As Spodosols dominate the watershed, this depth was typically in the Bs horizon, below the Bhs, a zone of illuvation of soil organic matter (SOM), aluminum (Al), and iron (Fe). In 12 of these plots, a strait tension lysimeter was installed to a 50-60 cm depth below the surface of the mineral soil, depending on depth to basal till. Taxonomically, this was typically in the BC horizon. In total, 32 tension lysimeters were installed at BBWM (20 right-angled and 12 straight), evenly distributed among the four compartments. All lysimeter data were pooled in this study to evaluate the influences of forest type and watershed.

Solution Collection and Analyses

There were 11 soil solution collection dates between July 2001 and June 2002: 7/25/2001, 8/29/2001, 9/27/2001, 10/9/2001, 11/8/2001, 11/15/2001, 5/3/2002, 6/4/2002, 6/7/2002, 6/10/2002, and 6/13/2002. Between -300 and -500 kPa tension was applied to lysimeters prior to collection, and solutions were collected by evacuation 24 to 48 hours later. Soil solutions were refrigerated at 4°C until analysis. Within 10 days of collection, solutions were filtered through a 0.45 µm membrane filter before analysis for major cations and anions. Calcium, Mg, potassium (K), sodium (Na), Al, Fe, and manganese (Mn) were determined by inductively coupled plasma atomic emission spectroscopy

(ICP-AES); $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ were determined colorimetrically by flow injection analysis (FIA); $\text{SO}_4\text{-S}$ and chloride (Cl) were determined by ion chromatography (IC). Dissolved organic carbon (DOC) and pH were also measured for collection dates November 8 and 15, 2002. Dissolved organic carbon was determined by oxidation with phosphoric acid and infrared detection (IR) and pH was measured potentiometrically by glass electrode. The molar ratios Ca/Al and Ca/Mg were calculated as the ratio of the means of soil solution Ca, Al, and Mg concentrations. Quality assurance measures included field blanks and triplicate splits.

Data Analyses

Data were evaluated for normality using skewness, kurtosis, the Shapiro-Wilk W statistic, and histogram plots. Data were transformed when necessary to meet the assumptions for normality. Chloride and DOC data required no transformation; Ca, K, Mg, Al, Mn, Na, and $\text{NH}_4\text{-N}$ were log transformed; Fe, $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ data were rank transformed. Mixed-model analysis of variance was used to model the variance structure of the data. This technique also models the fixed and random effects associated with an experimental design. This ANOVA was used to detect significant differences between watershed and forest type. When the interaction between watershed and forest type was significant, a protected Tukey's HSD means separation was used to detect differences between these means. Statistical analyses were performed on Statistical Analysis System (SAS, 1999) at an *a priori* determined significance level of 0.10, unless otherwise stated.

Due to missing data, sampling dates were divided into two periods (period 1 = July 2001 to October 2001; period 2 = November 2001 to June 2002). Data from the four collections in period 1 were not included in the ANOVA of main effects and interactions

due to poor collection efficiencies. All data were used in the evaluation of short- and long-term temporal trends. Results were similar when data from both lysimeter types were analyzed separately or pooled and thus only pooled results are reported for simplicity.

Data from the present study were compared with soil solution data from Fernandez et al. (1999). Fernandez et al. (1999) investigated changes in soil solution chemistry at BBWM using a similar compartmentalized design (watershed and forest type). For the long-term time series presented here we used data from their ceramic cup tension lysimeters located at 25 cm below the mineral soil surface. Data from Fernandez et al. (1999) covered years 1989-1995, with sampling in 1989 immediately prior to the beginning of treatments to West Bear.

Results and Discussion

Treatment and Forest Type Effects

Table 3 shows mean concentrations of selected analytes in soil solution by watershed (East Bear, the reference watershed; West Bear, the treated watershed), and by forest type (softwood, hardwood). Soil solutions appeared to respond to N and S treatments in West Bear with higher concentrations for most analytes, with the exception of Fe and DOC. The largest relative increases in West Bear compared to the reference East Bear soil solution analyte concentrations were for $\text{NO}_3\text{-N}$ (1650%), Al (480%), and $\text{SO}_4\text{-S}$ (300%). Softwood forest types typically had higher mean soil solution

concentrations for most analytes compared with hardwood forest types. The consistent exception to this pattern was significantly higher Ca soil solution concentrations under hardwoods resulting in higher hardwood Ca/Mg and Ca/Al ratios.

Table 4 shows mean soil solution concentrations for the interaction of forest types within watersheds. These data show that the pattern of higher concentrations for most analytes in West Bear was consistent for both forest types, and that the relative differences attributable to forest types were preserved but with higher concentrations in West Bear. However, for some analytes, such as Mn, Table 4 shows that the differences between forest types were not consistent for each watershed. For Mn, soil solution concentrations were significantly higher in softwoods compared to hardwoods in East Bear. The opposite was true in West Bear, although forest types were not significantly different from each other and both were significantly greater than either forest type in East Bear. Some analytes, most notably Na, Cl, and Fe, showed greater differences as a result of forest type than treatment.

Base Cation Mobilization

The soil solution concentration of Ca was higher than Mg by a factor of ~1.5, and both analytes were 150% higher in West Bear soil solutions compared to East Bear (Table 3). Although the concentrations of K and Na were not significantly different between watersheds, they were numerically higher in West Bear compared with East Bear. When soil base saturation is sufficient, one of the initial responses to excess acid anion loading is the mobilization of base cations from exchange sites and accelerated leaching losses with the mobile anions. Evidence for this mobilization takes the form of higher base

cation concentrations in soil solution, and an increased risk of net base cation depletion from the soil exchange complex. Given that the increased concentrations (West Bear compared to East Bear) of both Ca and Mg are comparable, and the soil Mg pool is much smaller, it is likely that the relative depletion of soil Mg is greater than the relative depletion of Ca, even though more acid neutralization may be attributable to Ca.

Fernandez et al. (in press) found that total exchangeable pools of Ca and Mg were 66 kg ha⁻¹ and 27 kg ha⁻¹ lower in West Bear compared to East Bear, respectively, which suggests a potential loss of 25% and 47%, respectively, of total pedon pools after eight years of treatment. Because BBWM is ~ 60 km from the Atlantic Ocean, the site exhibits enhanced marine aerosol deposition (Norton and Kahl, 2000; Norton et al., 1999). East Bear. Some analytes, most notably Na, Cl, and Fe, showed greater differences as a result of forest type than treatment.

The soil solution concentration of Ca was higher than Mg by a factor of ~1.5, and both analytes were 150% higher in West Bear soil solutions compared to East Bear (Table 3). Although the concentrations of K and Na were not significantly different between watersheds, they were numerically higher in West Bear than in East Bear. When soil base saturation is sufficient, one of the initial responses to excess acid anion loading is the mobilization of base cations from exchange sites and accelerated leaching losses with the mobile anions. Evidence for this mobilization takes the form of higher base cation concentrations in soil solution, and an increased risk of net base cation depletion from the soil exchange complex. Given that the increased concentrations (West Bear compared to East Bear) of both Ca and Mg are comparable, and the soil Mg pool is much

Table 3. Means for selected soil solution chemical parameters (standard errors in parentheses) by watershed or forest type for November 2001 to June 2002. Means followed by * are statistically different between watersheds or forest types at $\alpha=0.10$.

Solute	Watershed		Forest Type	
	East Bear	West Bear	Hardwood	Softwood
Ca	53 (4.3)	79 (5.4) *	87 (6.0)	48 (3.1) *
Mg	35 (1.3)	53 (3.1) *	36 (2.1)	51 (2.7) *
K	9.0 (1.4)	10.8 (1.5)	7.6 (1.0)	12 (1.7)
Na	103 (4.6)	114 (5.4)	77 (2.9)	136 (4.5) *
NH ₄ -N	2.7 (0.22)	5.7 (1.4) *	3.4 (0.35)	4.8 (1.3)
NO ₃ -N	5.4 (2.1)	89 (9.8) *	15 (3.1)	75 (9.8) *
SO ₄ -S	95 (3.8)	280 (13) *	131 (9.5)	235 (14) *
Cl	118 (7.6)	143 (9.8)	93 (5.9)	163 (9.2) *
Al	15 (1.4)	72 (5.9) *	9.9 (1.2)	73 (5.2) *
Fe	0.78 (0.17)	0.02 (0.04)	0.05 (0.01)	0.90 (0.16) *
Mn	0.42 (0.08)	1.4 (0.22) *	0.80 (0.20)	0.98 (0.15)
DOC	587 (114)	382 (36) *	186 (13)	620 (73) *
pH	4.6 (0.10)	4.3 (0.05) *	4.7 (0.10)	4.3 (0.04) *
Ca/Mg	1.5	1.5	2.4	0.94
Ca/Al †	1.8	0.55	4.4	0.33

Units are $\mu\text{eq L}^{-1}$ for all analytes, except $\mu\text{mol L}^{-1}$ for Al, Fe, and Mn, and $\mu\text{mol C L}^{-1}$ for DOC

† molar (mol/mol) ratio

Table 4. Means for selected soil solution chemical parameters (standard error in parentheses) for the interaction between watersheds and forest types. Means within rows followed by the same letter, or without letters, are not significantly different from each other at $\alpha=0.10$.

Solute	East Bear		West Bear	
	Hardwood	Softwood	Hardwood	Softwood
Ca	68 (6.5)	36 (3.8)	113 (9.7)	57 (4.2)
Mg	32 (1.7)	38 (1.8)	42 (4.3)	60 (4.1)
K	5.0 (0.62) a	14 (2.8) b	11 (2.2) b	10 (2.1) ab
Na	86 (4.3) a	123 (7.6) b	64 (2.3) a	146 (5.1) b
NH ₄ -N	2.4 (0.17) a	3.2 (0.43) ac	4.9 (0.74) b	6.1 (2.3) c
NO ₃ -N	4.4 (3.6)	6.6 (1.7)	29 (4.3)	127 (13)
SO ₄ -S	77 (3.4)	117 (5.6)	208 (14)	326 (16)
Cl	96 (8.7)	144 (12)	89 (7.3)	177 (13)
Al	4.6 (0.53)	28 (1.5)	17 (2.1)	107 (5.6)
Fe	0.04 (0.01) a	1.7 (0.32) b	0.06 (0.01) a	0.31 (0.06) b
Mn	0.18 (0.02) a	0.70 (0.17) b	1.7 (0.45) c	1.2 (0.23) c
DOC	200 (16) a	889 (130) b	156 (16) a	434 (28) a
pH	4.8 (0.14)	4.5 (0.03)	4.5 (0.05)	4.2 (0.04)
Ca/Mg	2.1	0.95	2.7	0.95
Ca/Al†	7.4	0.64	3.3	0.27

Units are $\mu\text{eq L}^{-1}$ for all analytes, except $\mu\text{mol L}^{-1}$ for Al, Fe, and Mn, and $\mu\text{mol C L}^{-1}$ for DOC

† molar (mol/mol) ratio

smaller, it is likely that the relative depletion of soil Mg is greater than the relative depletion of Ca, even though more acid neutralization may be attributable to Ca.

Fernandez et al. (in press) found that total exchangeable pools of Ca and Mg were 66 kg ha⁻¹ and 27 kg ha⁻¹ lower in West Bear compared to East Bear, respectively, which suggests a potential loss of 25% and 47%, respectively, of total pedon pools after eight years of treatment.

Because BBWM is ~ 60 km from the Atlantic Ocean, the site exhibits enhanced marine aerosol deposition (Norton and Kahl, 2000; Norton et al., 1999). Table 5 shows the marine-influence corrected East Bear soil solution data for Ca, Mg, K, Na, SO₄-S, and Cl, and the percent marine contribution for each analyte. These are calculated to remove marine-derived ion concentrations based on the assumption that all Cl is from marine aerosols and other ions are proportional to Cl as found in seawater (Bucher et al. 1992). Enhancements to soil solution Na and Mg suggest over 99% and 68%, respectively, of these analytes are of marine origin. Calcium, K, and SO₄-S had more modest marine deposition enhancements. This suggests that for BBWM, marine Mg deposition may offset accelerated leaching losses and the net depletion of exchangeable Ca may be of greater concern.

Metal Mobilization

Aluminum and Mn soil solution concentrations also show evidence of mobilization by treatments (Table 3) in West Bear soil solutions compared to East Bear. Along with the mobilization of these metals, pH was 0.3 units lower in West Bear than East Bear, which corresponds to a two-fold difference in H⁺ concentration (50 and 25 µeq L⁻¹ in West and

East Bear, respectively). As base cations are depleted from soils, acid neutralization mechanisms shift from base cation exchange to the hydrolysis and mobilization of Al from oxyhydroxide minerals in soils making Al significantly more prevalent in soil solutions below pH ~5.5. Reuss (1983) showed through modeling that when the soil solution Ca concentrations decline to less than 5-15% of total soil solution ionic charge, Al is rapidly mobilized and becomes dominant. Thus, a seemingly small decline in base saturation, especially in base-poor or “sensitive” soils, can lead to Al dominance in soil solutions. This inverse relationship between base cations and Al in soil solutions reflects the same relationship between base saturation and Al on soil cation exchange sites. While Mn mobilization also occurs with declining soil pH, reflecting Mn contributions to acid neutralization, the low content of soil Mn makes it a relatively small sink for H^+ (Norton et al., in press). This results in much lower Mn compared to Al concentrations in soil solutions.

Iron mobilization, which did not show a significant response to treatments in this study, could also contribute to acid neutralization but this usually occurs at lower pHs or as a result of more advanced acidification of soils compared to the conditions that activate Al mobilization (Norton et al., in press). If acidification of soils in West Bear progresses over time, Fe could be an important contributor to acid neutralization. Neutral salt extractions of soil Fe at BBWM were 10 times the concentrations found for Mn (Fernandez, unpublished data), highlighting the potential for Fe mobilization with chronic acidification. It is noteworthy that Norton et al. (in press) recently pointed out that sample collection and filtering procedures for solutions can artificially omit particulate

Table 5. Marine influence corrected soil solution chemistry means for the reference watershed. Corrections based on Cl and seawater composition in Butcher et al. (1992).

Solute	East Bear		
	Measured values	Corrected values	% Marine contribution
Ca	53	48	10
Mg	35	11	68
K	9.0	6.6	27
Na	103	1.5	99
SO ₄ -S	95	83	13
Cl	118	-	-

Units are $\mu\text{eq L}^{-1}$ for all analytes.

phases of Fe from solution analyses and thereby dramatically underestimate Fe mobilization in soil solution. If this were occurring in the BBWM soil solutions, then it is possible that Fe mobilization is occurring although it is not evident in our data. To date, it seems clear that Al mobilization has become the most important acid neutralization mechanism in these forest soils and that this process is reflected in West Bear soil solution Al data.

Base cation and metal mobilization, particularly Al, has been noted in numerous field (e.g., Emmett et al., 1998; Fernandez et al., 1999; Rustad et al., 1993; Stuanes et al., 1995, 1998; Meiwes et al., 1998) and laboratory (e.g., Dahlgren et al., 1990; David et al., 1991a; Skeffington and Brown, 1986) studies of forest soil response to elevated N and S treatments. Meiwes et al. (1998) found mobilization of base cations, Al, and Mn in soil solution in response to $(\text{NH}_4)_2\text{SO}_4$ treatments in Solling, Germany, while Fe concentrations remained below detection limit. As with results from BBWM, they found that Al mobilization became an increasingly important acid-neutralization mechanism as base saturation declined. The laboratory study of Dahlgren et al. (1990) and field soil core lysimeter study of Carnol et al. (1997) showed evidence of initial neutralization dominated by base cations followed by a switch to Al over time.

Changes in soil solution composition in response to treatments in West Bear influenced the relationships between cations, including a decrease in the Ca/Al ratio. Soil solution Ca/Al molar ratios were lower in West Bear compared to East Bear, largely as the result of greater soil solution concentrations of Al compared to Ca. Molar Ca/Al ratios have been used as indices of potential Al stress, with wide variation in the literature, including: average 0.7 in red spruce stands on Whitetop Mountain, Virginia,

USA (Joslin and Wolfe, 1992); highs of 13.6, average >2 at the Gårdsjön watershed, Germany (Stuanes et al., 1995); average ~ 0.3 in Sitka spruce stands at the Aber Forest, Wales (Emmett et al., 1998); average ~ 3.3 in spruce fir stands in Howland, Maine, USA (Lawrence and Fernandez, 1991); average ~ 1.6 at Huntington Forest, New York, USA (Cronan et al., 1989); averages between 0.25 and 1.5 in beech and spruce stands at Solling and Harz sites, Germany (Schulze, 1989). When comparing Ca/Al ratios between studies, it is important to consider the method of calculation. As an example, the ratio of mean molar Ca and Al concentrations for West Bear (shown in Table 3) was 0.55, but the mean of individual sample Ca/Al ratios would be 7.4. Because it is not uncommon to find a few samples in a study that have their highest Ca concentrations coincident with their lowest Al concentrations, this results in either atypically high or low Ca/Al ratios. When this occurs, soil solution Ca/Al molar could be quite different depending on whether they are calculated as the ratio of the means, or the mean of the ratios. This pragmatic consideration is important when comparing literature values, and when considering how biologically meaningful thresholds might be defined. Molar Ca/Al ratios of 1.0 have been suggested as the threshold where there is a 50% risk of negative impacts on tree health (Cronan and Grigal, 1995), with significant declines in tree health and growth seen below this threshold (e.g., Schulze, 1989; Shortle and Smith, 1988; Shortle and Bondietti, 1992). Growth of sugar maple in West Bear, measured as basal area increment (BAI), has shown declines in response to treatment, after an initial growth increase (Elvir et al., in press). No significant differences were seen in red spruce BAI between watersheds.

Forest Type and Canopy Effects

Soil solution Na concentrations were twice as high in softwoods as in hardwoods, and the effect of forest type was much greater than the effect of treatments (Table 3). Potassium soil solution concentrations were numerically but not statistically higher under softwoods compared to hardwoods, but these differences were not statistically significant. The ionic strength of soil solutions under softwoods is expected to be greater than under hardwoods due to the higher aerosol interception capacity of softwood canopies as a result of canopy architecture and their evergreen character (Currie et al., 1999; Houle et al., 1999; Hultberg and Grenfeldt, 1992; Norton et al., 1988; Rustad et al., 1994; Waring et al., 1981). The higher interception capacity of softwood canopies, combined with the proximity of BBWM to the Atlantic Ocean, resulted in especially enhanced forest type effects on soil solution concentrations of Mg, Na and Cl. Chloride is a relatively conservative ion in throughfall and stemflow, and as a result was a good indicator of the degree to which softwood interception enhanced soil solution solute concentrations. Similarly, Na concentrations at the interaction level (Table 4) were much higher under softwoods than under hardwoods, with no statistically significant differences between watersheds. The large external input of Na by marine aerosols, coupled with the low Na saturation of cation exchange sites, likely precludes a detectable response of Na to treatments. Higher soil solution $\text{SO}_4\text{-S}$ concentrations, and to a lesser extent $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ concentrations, were attributable to a greater interception of dry and occult deposition by softwood canopies and the treatment.

Despite some enhancement of soil solution Ca concentrations by marine aerosol capture in softwood canopies (Tables 4 and 5), hardwood soil solution Ca concentrations

were nearly twice softwood soil solution Ca concentrations (Table 3). These differences in soil solution Ca concentrations were a reflection of litter quality, biomass nutrient content, and elemental cycling rates. Forest type effects on soil solution composition can dominate on a time scale of decades to centuries whereas characteristics of the geologic substrate likely dominate over millennia. Typically biomass Ca, Mg, and K concentrations are greater, and cycling rates of these elements are faster, in hardwoods than in softwoods (Cole and Rapp, 1981). Hart et al. (2003) reported that the relative amounts of nutrients in soils reflected the relative amounts in biomass. Similar results from Northup et al. (1995a, b) showed that foliar chemistry was related to soil chemistry, and softwood litter had higher phenolic content, making decomposition more difficult. White et al. (1999) also inferred that changes in soil chemistry at BBWM were responsible for the changes in foliar chemistry they observed. On longer time-scales, vegetation changes have also been shown to alter soil chemistry and morphology (Willis et al., 1997). Thus, there are intimate cyclical links between vegetation and soil chemistry (Clarholm, 2002).

Nitrogen Responses

While soil solution concentrations of both forms of inorganic N increased in response to treatments, the relative increases in $\text{NO}_3\text{-N}$ were much greater than for $\text{NH}_4\text{-N}$ (Table 3). Ambient wet deposition of inorganic N ($\text{NH}_4\text{-N} + \text{NO}_3\text{-N}$) to BBWM averaged 310 eq ha⁻¹ yr⁻¹ (4.3 kg ha⁻¹ yr⁻¹) for 1998-2000, and treatment amendments to West Bear increased the annual deposition by 1800 eq ha⁻¹ yr⁻¹ (25.2 kg ha⁻¹ yr⁻¹) as $\text{NH}_4\text{-N}$. Estimates of dry deposition for 1988- 1992 indicate that for some ions, such as

SO₄-S and Cl, this contribution can be 0.7-2.2 and 1.1-2.4 times greater, respectively, than wet-only precipitation (Rustad et al., 1994). When considered in this context, there is a significant additional input of N from dry deposition. Despite treatments to West Bear, the difference between the watersheds in soil solution NH₄-N concentrations was small, while the difference in NO₃-N was large. The small increases in soil solution NH₄-N concentrations in West Bear despite the treatments were likely attributable to some combination of microbial immobilization and transformation, vegetative uptake, and cation exchange.

In contrast to NH₄-N, soil solution NO₃-N concentrations in West Bear were much greater than East Bear. This reflects an accelerated rate of nitrification in West Bear soils in response to treatments as a result of accelerated nitrification of both treatment NH₄-N and ambient soil N pools. Nadelhoffer et al. (1999) demonstrated that the rapid response in stream NO₃-N concentrations when West Bear treatments began was primarily from nitrification of ambient soil N and not the direct nitrification of treatment NH₄-N. Over time, both treatment-derived N and ambient soil N became the substrate for nitrification and continued increases in NO₃-N in soil solutions and streams. Research on soil N dynamics at BBWM has shown increased rates of nitrification in West Bear attributed to treatments (Wang and Fernandez 1999, Shah 2002). Shah (2002) showed that while net N mineralization in mineral soils was not significantly different between watersheds, significantly more of net N mineralization was attributable to nitrification in West Bear as a result of treatments. Biotic and abiotic controls on ecosystem response to elevated N deposition can result in NH₄-N being tightly cycled and retained, even when ecosystems seem “leaky” or saturated with respect to NO₃-N

(Fernandez et al., 1999). Despite accelerated inorganic N export in West Bear compared to East Bear, nearly 80% of total (wet + estimated dry deposition) plus treatment N inputs to West Bear watershed were still retained in 2001, while N retention was ~97% in the reference East Bear (Shah, 2002).

Both softwoods and hardwoods showed similar significant increases in $\text{NH}_4\text{-N}$ concentrations in West Bear soil solutions (Table 4). Soil solution $\text{NO}_3\text{-N}$ concentrations were numerically higher in West Bear compared to East Bear, but much of that increase was attributable to softwood soil solutions rather than hardwoods. Wang and Fernandez (1999) reported that in 1992 West Bear hardwood O horizons had significantly higher rates of potential net nitrification, but no apparent effect of treatments was evident in West Bear softwood O horizons at that time. More recently (2000-2001), Shah (2002) found that West Bear softwood O horizons had significantly higher rates of net N mineralization than West Bear hardwood O horizons, and West Bear softwood mineral soils had numerically higher net N mineralization rates than West Bear hardwood mineral soils. The high mean $\text{NO}_3\text{-N}$ concentrations for softwood soil solutions presumably reflect this higher rate of soil N mineralization and nitrification in West Bear softwoods.

It appears that N pools were accumulating over the first decade of treatments in West Bear softwood soils before a threshold was reached where higher N mineralization rates were realized (Shah, 2002). In contrast, litter quality and nutrient cycling differences in hardwood stands resulted in initially rapid increases in potential net nitrification in West Bear hardwood stands in response to treatments (Wang and Fernandez, 1999). In studies of the impact of N deposition on N dynamics and leaching, several authors surmised that nitrification rates are more related to the size of N pools and

changes in these pools rather than the amount of N deposition (Aber et al., 2003; Emmett et al., 1998; Fernandez et al., 2000). These and other authors have concluded that nitrification would begin, with the associated $\text{NO}_3\text{-N}$ leaching, only when the carbon to nitrogen (C/N) ratios were below a certain threshold. The onset of net nitrification and $\text{NO}_3\text{-N}$ leaching in O horizons occurs at threshold C/N ratios of ~20-25 (Aber et al., 2003; Gundersen et al., 1998; Ollinger et al., 2002). This threshold can vary by dominant tree species, due to litter quality differences not reflected in the C/N ratio (Aber et al., 2003; Lovett and Rueth, 1999; McNulty et al., 1991). This was likely the case in softwood stands at BBWM, where C/N ratios averaged 33 in the O horizon in 1992 (Wang and Fernandez, 1999), and 29 at the time of Shah's (2002) study. In contrast, hardwood O horizon C/N ratios have been relatively unchanged (23 in 1992 and 22 in 2001) after 9 years of treatment, but the changes in N cycling rates suggest that labile C pools might have been reduced over time, leaving more recalcitrant substrates, which have limited response to N treatments. This resulted in lower net N mineralization rates in West Bear hardwood soils compared with West Bear softwood soils (Shah, 2002), which was manifest in this study as lower $\text{NO}_3\text{-N}$ concentrations in West Bear hardwood than softwood stands.

Other studies in the literature using experimental amendments of $(\text{NH}_4)_2\text{SO}_4$ or NH_4NO_3 to forest soils have also reported relatively low concentrations of soil solution $\text{NH}_4\text{-N}$ despite $\text{NH}_4\text{-N}$ inputs, which is usually attributed to rapid microbial immobilization and nitrification (Adams et al., 1997; Currie et al., 1999; Emmett et al., 1998; Fernandez et al., 1999; Magill et al., 1997; Meiwes et al., 1998; Stuanes and

Kjønaas, 1998). Currie et al. (1999) noted that any $\text{NH}_4\text{-N}$ in excess of plant and soil microbial demand is not expected to have a long residence time in soil solutions due to rapid nitrification by nitrifying bacteria.

Sulfur Responses

West Bear soil solution $\text{SO}_4\text{-S}$ concentrations were almost three times the concentrations in East Bear, a direct result of treatments. Ambient wet deposition of $\text{SO}_4\text{-S}$ to BBWM averaged $350 \text{ eq ha}^{-1} \text{ yr}^{-1}$ ($5.6 \text{ kg ha}^{-1} \text{ yr}^{-1}$) for 1998-2000, and treatments to West Bear increased this by $1800 \text{ eq ha}^{-1} \text{ yr}^{-1}$ ($28.8 \text{ kg ha}^{-1} \text{ yr}^{-1}$). Dry deposition of $\text{SO}_4\text{-S}$ is estimated to be 0.7 to 2.2 times larger than wet for both East and West Bear watersheds, and is strongly influenced by forest type (Rustad et al., 1994). West Bear soils are retaining perhaps a quarter of the total wet plus estimated dry plus treatment $\text{SO}_4\text{-S}$ based on stream export, but this ability to retain $\text{SO}_4\text{-S}$ is diminishing over time (Kahl et al., 1999). While organic S is the largest pool in most soils, laboratory studies have shown little response in this pool to elevated S deposition (David et al., 1991b), and $\text{SO}_4\text{-S}$ retention is primarily controlled by adsorption to soil surfaces, which is strongly influenced by pH (David et al., 1991b; Meiwes and Khanna, 1981; Nodvin et al., 1986). The Al and Fe oxyhydroxide coatings in the upper mineral horizons of Spodosols strongly adsorb $\text{SO}_4\text{-S}$ in these soils (Chao et al., 1964; David et al., 1991b; Nodvin et al., 1986). Acidification increases $\text{SO}_4\text{-S}$ retention by increasing the positive charge on soil oxyhydroxide coatings, which increases anion exchange capacity (David et al., 1991b; Nodvin et al., 1986).

Organic Acidity and Forest Type

While most solute concentrations were higher in West Bear, DOC was ~35% lower (Table 3). Although these results may be due to other factors or antecedent conditions, we believe it is plausible that these differences reflect treatments effects. It is possible that microbial activity in response to treatments, and increased decomposition of organic matter in West Bear, reduced labile DOC and soil O horizon mass. Parker et al. (2001) hypothesized that treatments to West Bear increased decomposition rates and created differences in forest floor mass, which resulted in lower forest floor C pools in West Bear than in East Bear. Table 4 shows that softwood soil solution DOC was significantly lower in West Bear compared to East Bear, although numerical trends were parallel for hardwoods. Figure 2 shows the relationship between soil solution DOC concentrations from this study, aggregated to the plot level, with coarse (>6 mm) and fine (<6 mm) O horizon soil C/N from an extensive quantitative soil pit study by Fernandez (unpublished data). Figure 2 shows that even within the limited scope of this study, it appears that soil solution DOC was well correlated with both coarse and fine O horizon C/N. Meiwes et al. (1998) also concluded that in response to $(\text{NH}_4)_2\text{SO}_4$ additions there was an increase in mineralization rates manifested as increased DOC in soil solutions 40 cm below the mineral horizon. In contrast, after 5 years of treatments with various levels of NaNO_3 and NH_4NO_3 , Emmett et al. (1998) saw no changes in DOC concentrations in any treatment.

Both Al and Fe concentrations were significantly higher in softwood stands than in hardwoods (Table 3). Higher DOC and lower pH in soil solutions under softwood stands would contribute to the mobilization and transport of these metals. Huang and

Kiang (1972) showed that organic acid solutions dissolved equal or greater amounts of Al compared with silica (Si) in experiments on the weathering of feldspar, but in deionized water, Si was dissolved more readily than Al. Similar mechanisms were likely responsible for higher Mn in East Bear softwood compared to hardwood soil solutions; however, in West Bear Mn concentrations were significantly higher under both forest types, likely attributable to treatments, which masked any possible forest type effect on Mn in this watershed (Table 4).

The lower pH, Ca/Mg ratio, and Ca/Al ratio of softwood stands (Table 3) is an integrated reflection of many processes in softwoods: higher interception capacity, lower Ca saturation, slower nutrient cycling, higher organic acidity, higher metal content and concentration, and currently at BBWM, higher nitrification in these stands. The Ca/Al ratio of 0.5 in softwoods is at the threshold where Cronan and Grigal (1995) estimated there was a 75% chance of detrimental impacts on tree health. Some of the intrinsic characteristics associated with softwood stands, such as higher acidity, lower litter quality, and higher interception capacity, may make softwood stands more sensitive to atmospheric deposition-induced effects.

Short-Term Temporal Patterns

Figure 3 shows the time series of soil solution concentrations by watershed for Ca, Al, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, $\text{SO}_4\text{-S}$ and precipitation depths for July 2001- June 2002, the study period. Precipitation depth at BBWM were measured by a Belfort® rain gage at the East Bear wier (Norton et al., 1999).

Aluminum, $\text{NO}_3\text{-N}$, and $\text{SO}_4\text{-S}$ in West Bear soil solutions were consistently

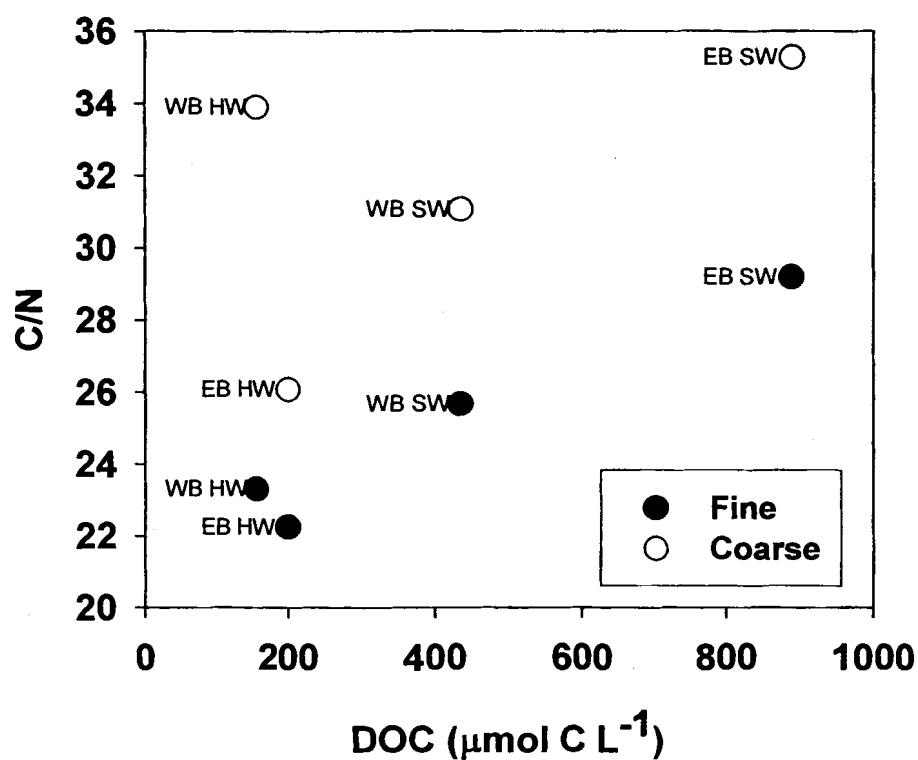


Figure 2. The relationship between soil solution dissolved organic carbon concentrations and the carbon to nitrogen ratio of O horizon coarse (>6 mm) and fine (<6 mm) material in West Bear hardwood (WBHW), West Bear softwood (WBSW), East Bear hardwood (EBHW) and East Bear softwood (EBSW) compartments.

higher than East Bear throughout the study period (Figure 3b, 3d, 3e), despite the high overall variability in concentration for these analytes. Over the period of this study, stream chemistry showed similar responses to treatment. West Bear stream $\text{SO}_4\text{-S}$ concentrations were consistently higher than East Bear, while differences between East Bear and West Bear $\text{NO}_3\text{-N}$ concentrations were largest during the growing season (Norton et al., in press).

During the growing season of 2001, a drought resulted in fewer soil solution collections and lower collection volumes. Collection efficiencies were especially low in the West Bear hardwood compartment, likely skewing West Bear data for this period. Precipitation depth data for this period showed that events were smaller and less frequent from July 2001 to January 2002 compared with the remainder of the study period (Figure 3f). While mean annual precipitation depth for 1990-2000 was 1.3 m at BBWM, precipitation depth for 2001 was 760 mm. Moisture availability in 2002 was in the normal range.

Soil solution Ca concentrations were more variable during the period of low precipitation, and no clear differences were evident between watersheds (Figure 3a). This variability in data could be treatment induced, and may be enhanced by the growing season or by drought. During a more normal period of precipitation in 2002, West Bear soil solution Ca concentrations were consistently higher than East Bear. Temporal variation in soil solution Mg concentrations (not shown) was similar to Ca throughout the study.

Soil solution $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ concentrations are partly a result of the rates of N mineralization and nitrification, which are expected to be greatest when temperatures are

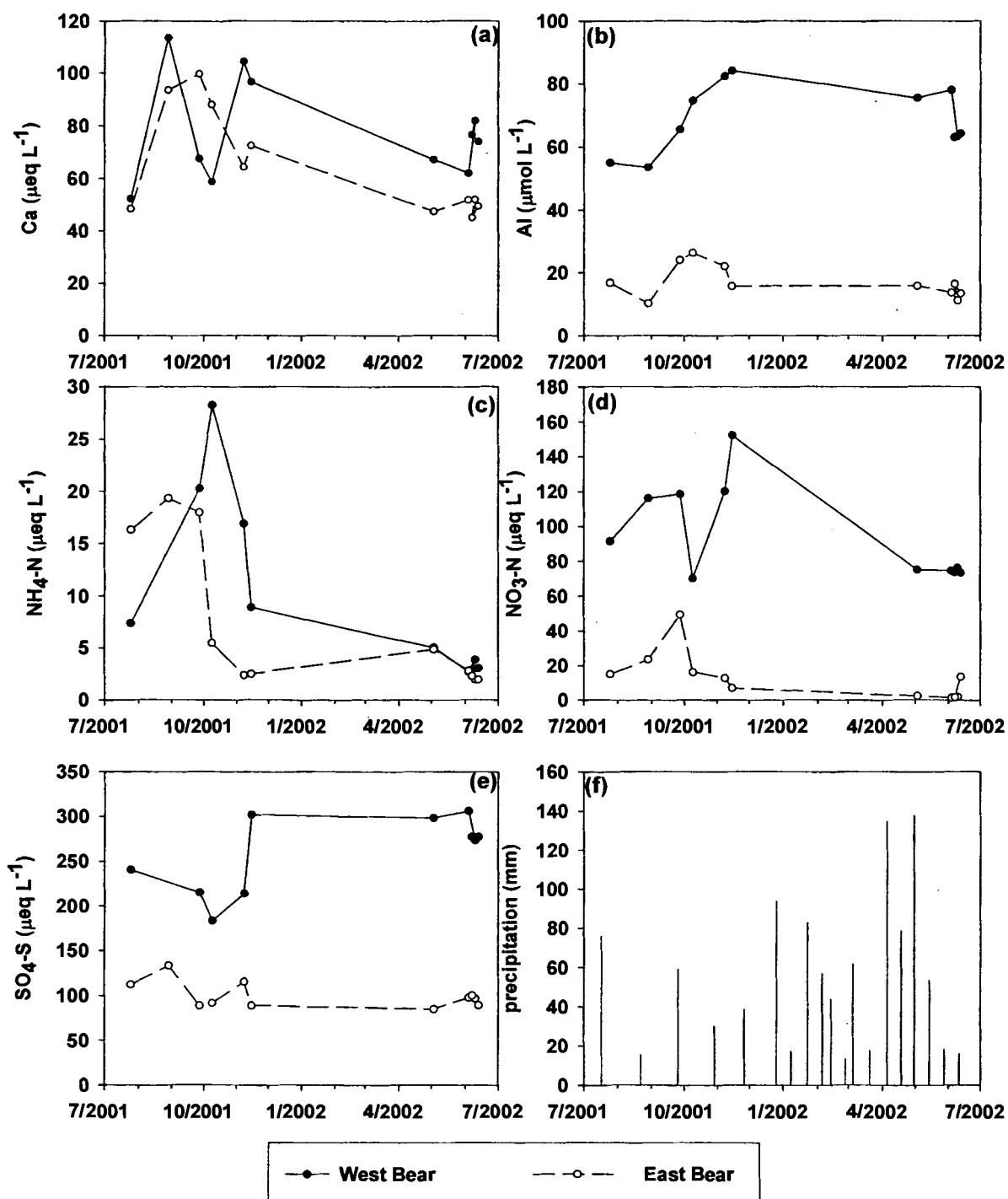


Figure 3. Short-term soil solution temporal trends in concentrations of (a) calcium (b) aluminum (c) ammonium (d) nitrate (e) sulfate and (f) precipitation depth in the experimental (West Bear) and reference (East Bear) watersheds.

highest as long as moisture is not limiting (Foster, 1989; Gilliam et al., 1996; Holmes and Zak, 1994; Myrold, 1998). The results of Foster et al. (1989) and Holmes and Zak (1994) suggested the highest rates of N mineralization occurred in early to mid-fall, coinciding with optimum temperature, moisture, and substrate availability. La Zerte and Scott (1996) thought that drought increased $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ soil solution concentrations in summer by reducing plant uptake and/or enhancing microbial mortality. Our data are consistent with these studies, as highest concentrations of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ occurred during early fall, when temperature and moisture availability were most favorable (Figure 3c, 3d). While consistent differences were present throughout most of the study period for $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$ did not show such distinct differences between East and West Bear, which is consistent with rapid microbial immobilization and transformation.

Long-Term Temporal Patterns

Figure 4 compares soil solution data from this study with previous soil solution data at BBWM that used a similar experimental design and lysimeter type (Fernandez et al., 1999). Earlier soil solution studies at BBWM were from 1989 to 1995, with sampling in 1989 occurring immediately prior to the onset of treatments to West Bear. Figure 4 shows annual means for East Bear and West Bear, with the exception of Figure 4d, which shows the soil solution Al means for both forest types within each watershed. Concentrations of all analytes were higher in West Bear compared to East Bear in response to 12 years of treatment with $(\text{NH}_4)_2\text{SO}_4$, and there were steadily increasing concentration differences between watersheds over this time period for H^+ , Al, and $\text{SO}_4\text{-S}$. In contrast, West Bear soil solution Ca concentrations reached a maximum in 1993

(mean = 140 $\mu\text{eq L}^{-1}$), more than double the 1993 East Bear soil solution Ca concentration (Figure 4a). By 2001, West Bear soil solution Ca concentrations had declined to approximately pre-treatment values. Long-term temporal patterns for Mg (not shown) were similar to those of Ca but concentrations were lower, with West Bear concentration maxima in 1993, and current West Bear Mg concentrations approaching pre-treatment values. Long-term Mg concentrations were more variable than Ca in both East and West Bear due to the influence of marine aerosol Mg deposition. Concentrations of Ca and Mg in East Bear were relatively constant over this period.

An initial increase in base cations in soil solutions followed by a decline in the treated West Bear watershed is consistent with mechanisms (Johnson and Fernandez, 1992; Markewitz et al., 1998; Richter, 1986) and models (Galloway et al. 1983) of ecosystem response to acidification. Acid neutralization through base cation exchange is the initial response to increased N and S deposition, with base cations accompanying the increased strong acid anion concentrations in soil solutions to maintain charge balance. The concentration maxima in 1993 and subsequent declines for Ca and Mg suggest depletion of exchangeable pools after the initial period of increased export. West Bear streams showed a similar response over the first decade of treatments, with stream Ca and Mg concentration maxima in ~1994 to 1995 (Fernandez et al., in press). They also showed evidence of depletion of exchangeable Ca and Mg in West Bear, with the greatest losses from the surface O horizons. As base cation acid neutralization mechanisms were depleted in West Bear, Al hydrolysis and mobilization became an increasingly important mechanism for acid neutralization, consistent with the soil solution concentrations shown here and stream data from BBWM (Norton et al., in press).

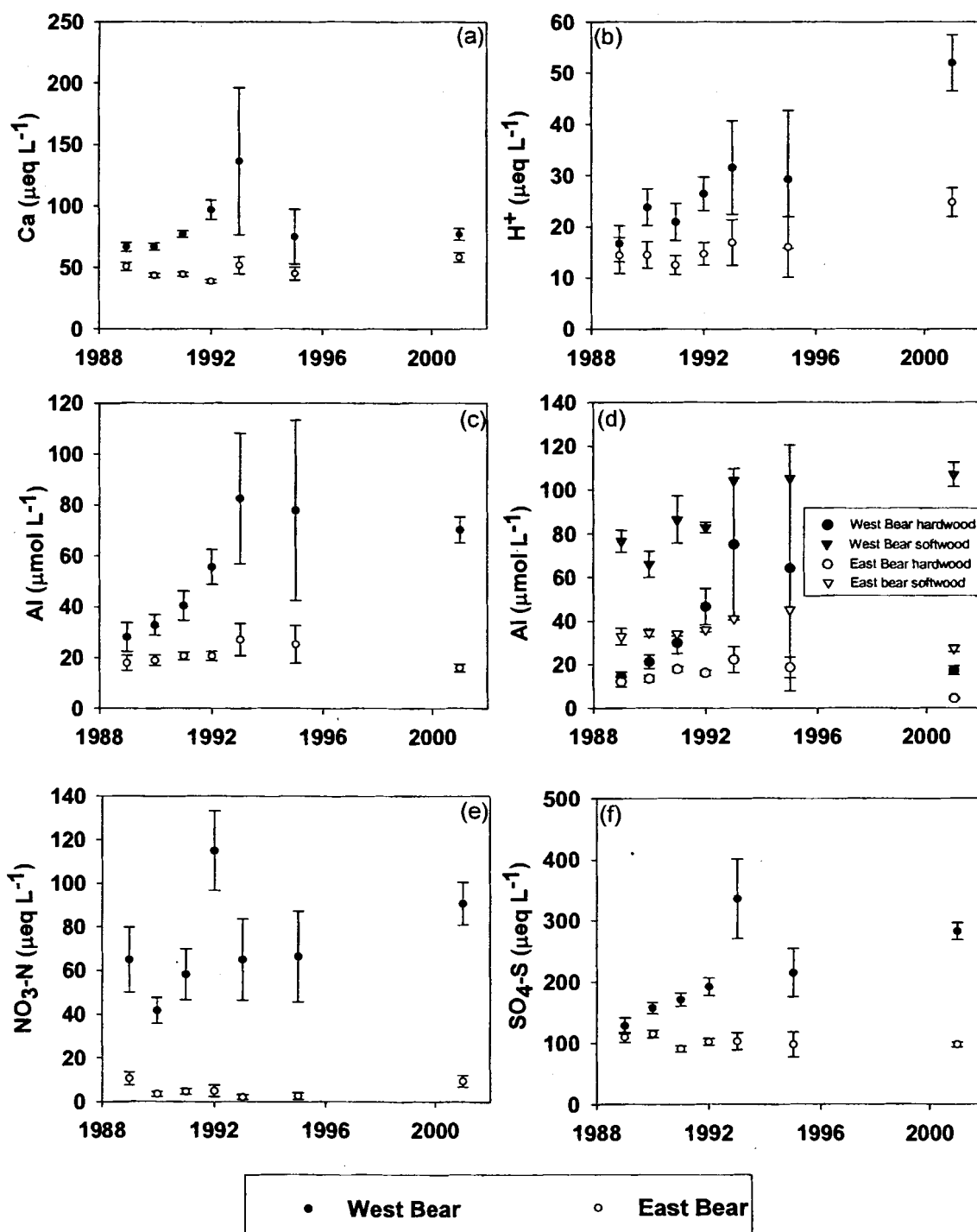


Figure 4. Long-term soil solution temporal trends in concentrations of (a) calcium (b) hydrogen (c) aluminum (d) aluminum by watershed and forest type (e) nitrate and (f) sulfate in the experimental (West Bear) and reference (East Bear) watersheds. Bars represent the standard error associated with each mean.

Figures 4a, 4c and 4d show that the long-term decline in soil solution Ca was coincident with increases in Al concentrations. Figure 4c shows soil solution Al concentrations by watershed and Figure 4d by forest type within watershed. For all other analytes, temporal patterns were relatively consistent between forest types and are represented by the overall watershed means. In the case of Al, there were notable differences in soil solution Al concentrations by forest type within watersheds, particularly in the treated West Bear soils. Interannual variability in soil solution Al concentrations in East Bear was small in both forest types and there were no clear patterns over time. Aluminum concentrations in West Bear soil solutions consistently increased until 1993, but there was no evidence for a continuation of this trend when we added the data for 2001-2002 (Figure 4c). Closer examination of these trends by forest type within West Bear (Figure 4d) shows that Al concentrations were much higher in West Bear softwoods from the beginning of the treatments, and have subsequently increased over time. For West Bear hardwoods, concentrations increased until 1993, but declined to pre-treatment values in this study. The early mobilization of Al with treatments in both watersheds is consistent with the increasing role of Al in acid neutralization as acidification due to treatments progresses. Softwoods and hardwoods appeared to start out with much different labile Al soil pools resulting in higher West Bear soil solution Al concentrations from the outset. Over time, labile Al may be depleted in West Bear hardwoods resulting in declining soil solution Al concentrations, while softwoods appear to maintain high concentrations of soil solution Al reflecting progressive soil acidification. Skeffington and Brown (1986) showed experimental evidence of soil labile Al depletion with acidification when they reported declines in

amorphous Al in forest soils from the United Kingdom in response to laboratory treatment with H_2SO_4 . In laboratory treatments of B horizon soils from BBWM with H_2SO_4 , Dahlgren et al. (1990) found decreases in total Al concentrations in leachate while the relative proportion of Al species remained constant. Emmett et al. (1998) showed evidence to suggest that total Al in soil solutions initially increased, then declined slightly, after approximately three years of NH_4NO_3 treatment at the Aber Forest, North Wales, United Kingdom.

Soil solution $\text{NO}_3\text{-N}$ concentrations were much higher in West Bear than East Bear. Both watersheds show considerable interannual variability in $\text{NO}_3\text{-N}$ concentrations. Interannual variability in $\text{NO}_3\text{-N}$ concentrations is larger in West Bear because mean concentrations of $\text{NO}_3\text{-N}$ are larger (Adams et al., 1997; David and Gertner, 1987; David et al., 1990; Foster et al., 1989; LaZerte and Scott, 1996; Laverman et al., 2002), and treatments may increase these sources of variability. Despite high interannual variability in West Bear, soil solution $\text{NO}_3\text{-N}$ concentrations increased over time. West Bear stream $\text{NO}_3\text{-N}$ concentrations increased almost immediately when treatments began in 1989 (Norton et al., 1999). Since that time, there have been increasing maxima in West Bear $\text{NO}_3\text{-N}$ stream concentrations in spring and fall, but high biological demand during the summer continues to result in much smaller differences between East and West Bear stream $\text{NO}_3\text{-N}$ concentrations (Norton et al., in press).

Although there have been large declines in S emissions and deposition in the northeastern US over the last decade (Kelly et al., 2002; Stoddard et al., 2003), with up to 50% less wet-only S deposition in Maine since 1980 (Fernandez and Wortman, 1997), Figure 4f shows only a slight decline in soil solution $\text{SO}_4\text{-S}$ concentrations in East Bear

over 1988-2001. Concentrations of $\text{SO}_4\text{-S}$ in East Bear soil solutions in 1989 were $110 \mu\text{eq L}^{-1}$ and had declined to $95 \mu\text{eq L}^{-1}$ by 2001 (Figure 4f). Smaller relative declines in East Bear soil solution $\text{SO}_4\text{-S}$ compared with declines in S deposition could be due to some combination of (1) desorption of accumulated $\text{SO}_4\text{-S}$ from soils (Dahlgren et al., 1990; Galloway et al., 1983), (2) the largest declines in S deposition occurring prior to soil solution chemistry monitoring at BBWM, and (3) variation in the dry deposition of marine $\text{SO}_4\text{-S}$.

West Bear had increasing concentrations of $\text{SO}_4\text{-S}$ in soil solution over the study period in response to treatments (Figure 4f). Kahl et al. (1999) found that annual S retention in West Bear had declined from 86% in 1990 to 34% in 1997 based on the total wet plus estimated dry plus treatment inputs and stream export. Thus, the ability of soils to retain excess $\text{SO}_4\text{-S}$ is diminishing over time, as reflected in declines in additional S retention. This indicates the decreasing ability of West Bear soils to adsorb $\text{SO}_4\text{-S}$, resulting in higher soil solution concentrations.

The similarities between long-term trends in soil solution chemistry and stream chemistry (Fernandez et al., in press; Norton et al., 1999; Norton et al., in press) are indicative of the close relationship between soil processes and stream chemistry and that the same acid-neutralization mechanisms are operating throughout the watershed. Concentrations of some analytes, such as Mg, Cl, $\text{NO}_3\text{-N}$, $\text{SO}_4\text{-S}$ and DOC, were higher in soil solutions than streams, while solutes such as Ca had higher concentrations in streams than in soil solutions. This indicates that there may be cation exchange in deeper soils or biotic uptake operating that alters solution chemistry along flow paths to the stream than were sampled in this study. Conversely, for Ca, additional neutralization

of soil solutions may increase concentrations in deeper flow en route to the stream. Other solutes, such as Na, show little difference in concentration between soil solution and streams, possibly due to minimal influence of soil exchange processes in the lower solum.

Conclusions

Most solute concentrations increased in response to $(\text{NH}_4)_2\text{SO}_4$ treatments to West Bear compared with East Bear, with the greatest increases in $\text{NO}_3\text{-N}$, Al, and $\text{SO}_4\text{-S}$. Evidence of base cation and Al acid neutralization mechanisms reported from stream chemistry was also evident in soil solution chemistry, demonstrating the linkage between soil processes and stream chemistry. Forest type influenced soil solution chemistry as a result of differences in aerosol interception capacity and litter quality. Higher soil solution Mg, Na, Cl, $\text{NH}_4\text{-N}$, and $\text{SO}_4\text{-S}$ concentrations in softwood stands reflected enhanced canopy capture of marine aerosols and dry deposition. Higher litter quality under hardwoods led to higher soil solution Ca concentrations, while softwood stands had higher soil solution Al and Fe concentrations. Higher soil solution $\text{NO}_3\text{-N}$ concentrations in West Bear were consistent with concurrent studies of N cycling that showed higher rates of nitrification in West Bear compared to East Bear.

These results provide evidence for changes in the integrated watershed response to acidification over time, in spite of the high variability of soil solution data. Soil solution studies over the initial decade of treatments showed a progressive increase, then decrease, of base cations in streams and consistent with evidence of soil base cation

depletion. Increasing concentrations of Al point to the consistently increasing importance of Al mobilization in the progressive acidification of West Bear watershed. Higher NO_3^- -N in soil solutions in West Bear appear to have existed since the outset of the experiment, but concentrations have increased over time. In contrast, soil solution concentrations of SO_4 -S were nearly identical in both watersheds at the outset of the experiment, but West Bear has shown consistent and dramatic increases over time compared to East Bear. What is unknown is how much different forest types and areas within each watershed contribute to the integrated stream response, and how these components of each watershed will change over time in response to trends in climate, ambient deposition, and long-term experimental acidification.

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CHAPTER 2. USING ION-EXCHANGE RESINS TO STUDY SOIL RESPONSE TO A WHOLE-WATERSHED ACIDIFICATION EXPERIMENT

Introduction

Studies of soil and soil solution chemical responses to elevated atmospheric nitrogen (N) and sulfur (S) deposition have shown that depletion of base cations, nitrate ($\text{NO}_3\text{-N}$) leaching, and sulfate ($\text{SO}_4\text{-S}$) adsorption occur initially in surface horizons, followed by subsoil mineral horizons as acidification progresses deeper into the soil profile over time (Adams et al., 1997; Fernandez et al., in press; Johnson et al., 1988; Knoepp and Swank, 1994; Markewitz et al., 1998; Meiwes et al., 1998; Rustad et al., 1993; Stuanes and Kj  naas, 1998). Stream chemistry differences between peak and base flow (Edwards et al., 2002; Moldan and Wright, 1998; Wright and Tietema, 1995) can reveal the progressive acidification through soil horizons, as these differences reflect soil chemical differences during deep and shallow flow through soils.

Organic horizons (or upper mineral [A] horizons) have important roles in nutrient cycling and storage in forested ecosystems. Vejre and Hoppe (1998) found that ~50% of exchangeable calcium (Ca) was in the organic (O) horizon in soils in western Denmark. Bailey et al. (1996) found that at the Cone Pond Watershed, New Hampshire, USA over half ($108 \text{ kg Ca ha}^{-1}$) of the total exchangeable Ca pool ($195 \text{ kg Ca ha}^{-1}$) was in the O horizon. Knoepp and Swank (1994) reported that the upper 25-30 cm of soil at the Coweeta Hydrological Laboratory, North Carolina, USA, contained 31-46%, 31-43% and 12-25% of the total exchangeable Ca, potassium (K), and magnesium (Mg), respectively,

with variation by soil type. However, depletion of base cations from surface horizons, both organic and mineral, is problematic not only because it is a large part of the exchangeable pool, but also because a large proportion of the fine root mass is located in these horizons (Fahey et al., 1988), making nutrient depletion likely to impact vegetation health and productivity. In addition, as soil acidification progresses into lower mineral horizons and mobilizes aluminum (Al), Al can be cycled by vegetative uptake and litter fall, enriching the O horizon and displacing base cations from the large bioavailable pool typical in surface forest soils (Lawrence et al., 1995).

Soil solution flux data provide the best information on current soil dynamics (Marques et al., 1996; Ranger et al., 2001), but are difficult to measure in O horizons. Tension lysimeters, which sample both freely draining soil water and that held under tension, give information on solutions that have had more time to interact with soils than solutions sampled by zero-tension lysimeters. However, tension lysimeters are impractical to install in porous and commonly thin O horizons. For this reason, some researchers have experimented with ion-exchange resins (IER) to sample soil and soil solution chemistry.

The behavior of IER is analogous to soil particles (Skogley and Dobermann, 1996) and IER provide several advantages over traditional soil solution sampling: holding times prior to analysis are less stringent (Giblin et al., 1994), installation and sampling are less time consuming (Johnson et al., 2001; Giblin et al., 1994), and the sampled area is less disturbed by resin installation (Gibson, 1986). However, some researchers (Binkley and Matson, 1983; Binkley et al., 1992; Giblin et al., 1994; Hart and Binkley, 1985; Lundell, 1989) have found poor correlations between amount or

accumulation rate of ions on IER compared with more traditional measures of nutrient availability, such as extractable nutrients and *in situ* incubations. These researchers concluded that IER may provide better relative measures of nutrient availability and are more sensitive to site conditions compared to traditional methods. The majority of research that has found good correlations between ions extracted from resins and traditional measures of nutrient availability occurred in laboratory or controlled greenhouse environments (Binkley and Matson, 1983; McLaughlin et al., 1993; Saggar et al., 1990; Subler et al., 1995; van Raij et al., 1986), but some field studies have drawn similar conclusions (Kj  naas, 1999; Lajtha, 1988). In either laboratory or field work, researchers point out that measurements of nutrient availability by IER may incorporate site factors not assessed by other measures, such as moisture and temperature, and may be more valuable (Binkley and Matson, 1983; Hart and Binkley, 1985; Lajtha, 1988; Lundell, 1989).

Previous investigators have used IER primarily for the quantification of N and P dynamics, and typically under ambient conditions not subjected to chemical manipulations. This study utilized IER techniques to evaluate soil solutions at the Bear Brook Watershed in Maine (BBWM), which is the site of a long-term, whole-watershed chemical manipulation using N and S. Building on the existing framework, the objectives of this study were to (a) compare IER data with tension lysimeter soil solution data at BBWM for effects of treatments and forest types, and (b) compare the response of IER to other measures of chemical change in the watershed (e.g. soil chemistry, foliar chemistry).

Methods

Study Site

The Bear Brook Watershed in Maine (BBWM) is located in eastern Maine, USA, on the upper southeastern slope of Lead Mountain, approximately 60 km from the Atlantic Ocean. Adjacent East and West Bear Brooks form the paired watershed experiment at BBWM, and drain 11.0 and 10.3 ha of land, respectively. Elevation within the watersheds ranges from 210 m to 475 m, with an average slope of 31% (Norton et al., 1999). Mean annual temperature is $\sim 5^{\circ}\text{C}$, and typically ranges from 25°C in the summer to -20°C in winter. Annual precipitation is ~ 1.3 to 1.4 m, with $\sim 25\%$ of this precipitation as snow.

The dominant soils at BBWM are loamy, mixed, frigid Typic Haplorthods formed on till. Soils associated with softwoods tend to be thin mineral soils, or organic soils (Folists) on steeper slopes; in contrast, soils in hardwood-dominated areas are thicker, well-drained mineral soils. Soils are generally acidic, and have low base saturation, sulfate adsorption capacity, and cation exchange capacity. Based on these characteristics, BBWM is considered vulnerable to acidification (Norton et al., 1999).

Bedrock consists of non-calcareous, non-sulfidic meta-pelites and quartzites at higher elevations, while lower in the watersheds calc-silicate gneiss predominates. Granite dikes and sills are common in the bedrock, and bedrock outcrops are common in the upper portion of the watershed (Norton et al., 1999). Till covering the bedrock ranges in thickness from 0 to 5 m, with an average thickness of 1 m.

Vegetation consists of hardwoods at lower elevations, a zone of mixedwoods, and softwoods at higher elevations. The lower boundary for the softwoods is not natural, but

resulted from logging in the 1950's (Norton et al., 1999). The hardwoods are ~55 years old, and the softwoods are >100 years old, with individuals >150 years old (Elvir., 2001). Major hardwood species at BBWM are American beech (*Fagus grandifolia*), sugar maple (*Acer saccharum*), and red maple (*Acer rubrum*) with smaller amounts of yellow birch (*Betula alleghaniensis*) and paper birch (*Betula papyrifera*). Red spruce (*Picea rubens*) accounts for the majority of the softwood stand, with minor amounts of balsam fir (*Abies balsamea*) and hemlock (*Tsuga canadensis*). Both species composition and cover of each of the forest types are comparable between East and West Bear (Elvir, 2001).

Treatment

East and West Bear streams were hydrologically and chemically similar before the treatments began in November 1989, based on observations from 1987-1989 (Norton et al., 1999). West Bear watershed has been treated by helicopter since 1989 with bi-monthly additions of 300 eq (NH₄)₂SO₄ ha⁻¹, for a total yearly loading of 1800 eq ha⁻¹ (25.2 kg N ha⁻¹ yr⁻¹ and 28.8 kg S ha⁻¹ yr⁻¹). During this study, treatments were applied on: 6/25/2001, 8/22/2001, 10/11/2001, 12/4/2001, 2/7/2002, 4/5/2002, and 6/25/2002. East Bear serves as the untreated reference watershed. Ambient wet deposition to BBWM averaged 118 eq ha⁻¹ yr⁻¹ for NH₄-N, 192 eq ha⁻¹ yr⁻¹ for NO₃-N and 350 eq ha⁻¹ yr⁻¹ for SO₄-S (4.3 kg N ha⁻¹ yr⁻¹ and 5.6 kg S ha⁻¹ yr⁻¹) for calendar years 1998-2000 (Nelson, unpublished data).

Resin Preparation and Unit Assembly

Bio-Rad® AG50W-X8 (BioRad® Laboratories, California, USA) is a strong cation resin and was used in the H^+ form, 20-50 mesh. Bio-Rad® AG1-X8 (BioRad® Laboratories, California, USA) is a strong anion resin and was used in the Cl^- form, 20-50 mesh. The resin was enclosed in circular (45 mm diameter) Nitex® nylon bags with 3.0 g of either anion or cation exchange resin. Once resin bags were assembled, they were soaked separately in 0.5 M hydrochloric acid (HCl) for one hour. After soaking, the bags were rinsed six times in deionized water.

Resin bags were placed in a PVC assembly unit that consisted of a coupler into which two rings were inserted (Figure 5). This unit held the Nitex® resin-filled bag firmly in place. All PVC components were washed in 10% HCl and rinsed six times in deionized water.

Experimental Design and Resin Installation

Five 5 by 5m plots were established in June of 2001 in each combination of forest type and watershed - (1) East Bear hardwood, (2) East Bear softwood, (3) West Bear hardwood, (4) West Bear softwood. There were a total of 20 plots. Within each of these plots, ion exchange resins and lysimeters were used to monitor soil solution chemistry.

Resin units were deployed on 6/28/2001, 10/26/2001, and 5/18/2002 for a period of 116, 192, and 142 days, respectively. At each lysimeter plot, one anion and two cation resin units were installed at the bottom of the organic horizon. The organic horizon was gently lifted, and the resin assembly was pressed into the top of the mineral soil surface. The organic horizon was replaced in its original position with a minimum of disturbance.

This placement at the interface of the abrupt boundary between the organic and underlying mineral soil was intended to capture soil solution leaching from the bottom of the organic horizon prior to mineral soil interaction. Field resin blanks were made by placing resin units into plastic bags, then installing blanks under the organic horizon. These field blanks were treated similarly to other resin units prior to and following placement in plots.

In order to determine the minimum amount of time resins needed to be in the field, we conducted a study of resin adsorption after varying lengths of deployment of 32, 53, 95 and 116 days. Based on the limited data from this one study, it appeared that a minimum of 95 days was needed before IER adsorbed enough ions to provide a clear concentration signal readily detectable above background concentrations resident in the resin. When field blanks and new, unused resins were extracted, concentrations of ions in field blanks were an average of 4.5 times the new resin, and ranged from 1-15X. When length of resin deployment was 95 days or greater, the concentrations of ions on field blanks were at least an order of magnitude smaller than sample values.

Resin Collection, Extraction, and Analyses

Resins installed in June 2001 were collected in August, September and October 2001; resins installed in October 2001 were collected in May 2002 and resins installed in May 2002 were collected October 2002. New resin units were installed at each collection. Soil and other debris were removed from the unit, and it was placed in a plastic bag. Resin units were stored at 4°C after collection. Within a week of collection,

resin units were disassembled, and resin bags were rinsed in deionized water to remove remaining soil particles and stored at 4°C until extraction.

For extraction, resins were placed in a 150 ml Erlenmeyer flask with 100 ml of the extracting solution and covered with parafilm. The flasks were placed on a mechanical shaker and shaken for 30 minutes, then filtered through a 0.45µm membrane filter and stored at 4°C until analysis. One set of cation resins were extracted with 0.5 M hydrochloric acid (HCl) and analyzed for Ca, Mg, Al, manganese (Mn), potassium (K), sodium (Na), iron (Fe) and lead (Pb) by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The second set of cation resins were extracted with 1 M KCl and analyzed colorimetrically for NH₄-N by flow injection analysis (FIA). The anion resin was extracted with 1 M NH₄Cl and analyzed for total S by ICP-AES and for NO₃-N by cadmium reduction with flow injection analysis (FIA).

Quality assurance measures included field blanks, laboratory blanks, reagent blanks, and triplicate splits. Concentrations of solutes extracted from the resins were normalized to an aerial per day basis, and all means were weighted by days of deployment to account for different deployment periods. The molar ratios Ca/Al and Ca/Mg were calculated from means of extracted Ca, Al, and Mg

Lysimeters

Ceramic-cup tension lysimeters were installed in the same plots as ion exchange resin units. In all plots, a tension lysimeter was installed 25 cm below the mineral soil surface. These lysimeters were right-angled, so that they could be installed horizontally

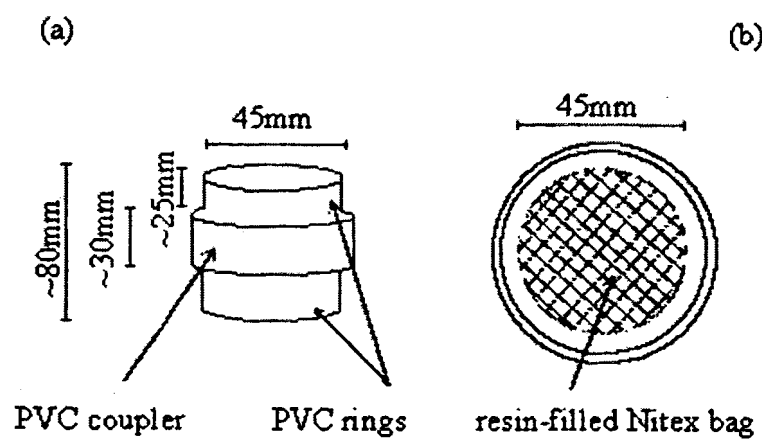


Figure 5. Side (a) and top (b) view of the ion exchange resin unit.

from an adjacent soil pit, thereby minimizing disturbance of the area that the ceramic cup sampled. Twenty tension lysimeters were evenly distributed among the 20 plots within the four compartments.

There were 11 soil solution collection dates between July 2001 and June 2002: 7/25/2001, 8/29/2001, 9/27/2001, 10/9/2001, 11/8/2001, 11/15/2001, 5/3/2002, 6/4/2002, 6/7/2002, 6/10/2002, and 6/13/2002. Prior to collection, -300 to -500 kPa tension was applied to each lysimeter, and lysimeters were sampled one or two days later. Soil solutions were refrigerated at 4°C until analysis. Within 10 days of collection, solutions were filtered through a 0.45 µm membrane filter before analysis for major cations and anions. Calcium, Mg, K, Na, Al, Fe, and Mn were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES); NO₃-N and NH₄-N were determined colorimetrically by flow injection analysis (FIA); SO₄-S and chloride (Cl) were determined by ion chromatography (IC). Solutions extracted from IER were analyzed for total S by ICP, which measures all forms of S present. This would undoubtedly contribute to differences in the conclusions regarding S when IER is compared with lysimeter S data, which was determined by ion chromatography and thus only measured ionic SO₄-S.

Data Analyses

All data were evaluated for normality using skewness, kurtosis, the Shapiro-Wilk W statistic, and histogram plots. All data were log transformed to meet the assumptions of normality, with the of exception lead (Pb), which required no transformation, and NO₃-N, which required a rank transformation. Mixed-model analysis of variance was

used to model the variance structure of the data. Mixed-model analysis also models the fixed and random effects associated with an experimental design. This ANOVA was used to detect significant differences between watershed and forest type. When the interaction between watershed and forest type was significant, a protected Tukey's HSD means separation was used to detect differences between these means. Using overall means for the study period, resin data and lysimeter data were aggregated to the plot level and linear regression was performed to determine the relationship of solutes extracted from resin to that in soil solution. For linear regression, all data were log transformed, with the exception of S, K and lead (Pb) data, which required no transformation. Statistical analyses were performed using the Statistical Analysis System (SAS, 1999) at an *a priori* determined significance level of 0.10, unless otherwise stated. Soils were quantitatively sampled in 1998 at BBWM (Fernandez, unpublished data) and foliar and litter samples were collected from the dominant tree species in 2000 and 1999, respectively (Rustad, unpublished data). Shah (2002) measured *in situ* net N mineralization and net nitrification in BBWM O and mineral soils from 2000-2001. The relative trends in their data, in addition to soil solutions collected by tension lysimeters, were compared with trends in IER data.

Results and Discussion

Treatment and Forest Type Effects

Mean concentrations of selected solutes extracted from IER, expressed on a per day basis, are shown in Table 6 by watershed (East Bear, the reference watershed and West

Bear, the treated watershed) and by forest type (softwood and hardwood). With the exception of Fe, all solutes responded to treatments in West Bear with higher accumulation rates on IER when compared with East Bear. The only statistically significant increases in resin-extracted concentrations in West Bear relative to East Bear were for Mn, $\text{NO}_3\text{-N}$, and $\text{NH}_4\text{-N}$, which were 450%, 230%, and 440% higher, respectively. Accumulations of Na, Al, Fe, and Pb onto IER were significantly greater in softwood stands than in hardwoods, and most numerical differences that were not significant followed this pattern. Calcium and Mn were the exception to this at the forest type level, and had higher accumulation rates in hardwoods. Higher Ca to Mg ratios (Ca/Mg) and Ca to Al ratios (Ca/Al) in hardwood stands were primarily a result of higher resin Ca concentrations in hardwoods. Table 7 shows mean IER accumulation rates for the interaction between forest type and watershed. Within each watershed, the relationship between forest types was consistent, with most solutes having higher concentrations in softwoods compared to hardwoods and treatment of West Bear increased these differences. These data show that in some cases, the main effect differences in Table 6 were primarily driven by a particular compartment, such as watershed differences largely due to West Bear hardwood for Mn, and West Bear softwood for Al and $\text{NO}_3\text{-N}$. In contrast, the significant response of $\text{NH}_4\text{-N}$ to treatment (Table 6) is more consistent across forest types in West Bear (Table 7). Higher rates of Ca and Mg accumulation onto IER in West Bear (Table 6) are consistent with the hypothesis that base cation exchange is initially the most important mechanism of acid neutralization. The mobilization of base cations from exchange sites is one of the primary responses to elevated acid anion loading, as long as soil base saturation is

sufficient. As a result of this exchange process, soil solution concentrations of base cations initially increase, which can result in a net base cation depletion from the soil exchange complex if rates of base cation supply from mineral weathering, atmospheric deposition, or management can not keep pace. As base cations are depleted from soils, acid neutralization mechanisms shift from base cation exchange to the hydrolysis and mobilization of Al and other metals. Aluminum is mobilized from soils below pH ~5.5 from oxyhydroxide minerals, and becomes increasingly prevalent in soil solutions with acidification (Reuss, 1983). Aluminum accumulation rates by IER were not significantly different between East Bear and West Bear (Table 6), but the numerical differences suggested a greater difference in Al accumulation between watersheds (500%) than between forest types (220%). Manganese mobilization was four times greater in West Bear than East Bear, which was statistically significant. However, numerical differences in the means suggest that high variability in the Al data prevented statistically significant differences in this analysis although quantitatively Al appeared to be most likely the responsible metal compared to Mn as an acid neutralization mechanism. Recent work at BBWM has suggested that Fe mobilization could also be a significant acid neutralization mechanism after over a decade of treatments (Norton et al., in press). Soil solution Fe concentrations from this study did not show evidence of Fe mobilization in response to acidification. This lack of response for Fe in soil solutions could indicate that stream Fe changes due to acidification are originating from watershed positions or soil depths beyond the soil zone sampled by our resins, or artifacts of sample processing are excluding a particulate Fe phase and with it the signal of response to treatments (Norton et al., in press). Soil solution data (Szillery, 2003) showed that Al mobilization had

Table 6. Weighted means of selected solutes extracted from ion-exchange resins (and standard errors in parentheses) in the reference and experimental watersheds and hardwood and softwood forest types. Means followed by * are statistically different by watershed or forest type at $\alpha=0.10$.

Solute	Watershed		Forest Type	
	East Bear	West Bear	Hardwood	Softwood
Ca	0.0059 (0.0015)	0.0061 (0.0011)	0.0076 (0.0016)	0.0044 (0.0009)
Mg	0.0061 (0.0011)	0.0078 (0.0019)	0.0049 (0.0010)	0.0089 (0.0019)
K	0.0062 (0.0015)	0.0089 (0.0027)	0.0046 (0.0009)	0.0105 (0.0029)
Na	0.0160 (0.0040)	0.0190 (0.0062)	0.0072 (0.0034)	0.0277 (0.0061) *
Al	0.00039 (0.00011)	0.00259 (0.00123)	0.00009 (0.00003)	0.00289 (0.0012) *
Fe	0.00012 (0.00004)	0.00006 (0.00001)	0.00002 (0.000005)	0.00015 (0.00003) *
Mn	0.00010 (0.00002)	0.00042 (0.00009) *	0.00034 (0.00009)	0.00018 (0.00004)
Pb	0.0000018 (0.0000003)	0.0000030 (0.0000007)	0.0000016 (0.0000003)	0.0000033 (0.0000007) *
NO ₃ -N	0.0117 (0.0034)	0.0259 (0.0090) *	0.0065 (0.0023)	0.0312 (0.0090)
NH ₄ -N	0.0055 (0.0013)	0.0256 (0.0064) *	0.0133 (0.0040)	0.0178 (0.0058)
S	0.0304 (0.0066)	0.0859 (0.0677)	0.0141 (0.0043)	0.1022 (0.0653)
Ca/Mg	0.97	0.78	1.55	0.49
Ca/Al †	7.6	1.17	42.2	0.76

Units are $\mu\text{eq cm}^{-2} \text{ day}^{-1}$ for all analytes, except $\mu\text{mol cm}^{-2} \text{ day}^{-1}$ for Al, Fe, Mn and Pb

† molar (mol/mol) ratio

Table 7. Weighted means of selected solutes extracted from ion-exchange resins (and standard errors in parentheses) for the interaction between watershed and forest type. Means within rows followed by the same letter, or without letters, are not significantly different from each other at $\alpha=0.10$.

Solute	East Bear				West Bear			
	Hardwood		Softwood		Hardwood		Softwood	
Ca	0.0084	(0.0030)	0.0033	(0.0006)	0.0068	(0.0013)	0.0055	(0.0018)
Mg	0.0058	(0.0018)	0.0063	(0.0014)	0.0040	(0.0009)	0.0116	(0.0036)
K	0.0042	(0.0011)	0.0081	(0.0026)	0.0049	(0.0014)	0.0128	(0.0052)
Na	0.0133	(0.0068)	0.0186	(0.0045)	0.0010	(0.0004)	0.0367	(0.0111)
Al	0.00014	(0.00005)	0.00063	(0.00019)	0.00004	(0.00002)	0.00514	(0.0024)
Fe	0.00003	(0.00001)	0.00021	(0.00006)	0.00002	(0.000007)	0.00010	(0.00002)
Mn	0.00006	(0.00001)	0.0001400	(0.00004)	0.0006100	(0.0001)	0.00023	(0.00007)
Pb	0.0000137	(0.0000003) a	0.0000022	(0.0000005) ab	0.0000017	(0.0000005) a	0.0000043	(0.0000001) b
NO ₃ -N	0.0017	(0.00005)	0.0218	(0.0064)	0.0113	(0.0043)	0.0405	(0.0168)
NH ₄ -N	0.0045	(0.0015)	0.0065	(0.0020)	0.0221	(0.0072)	0.0291	(0.0108)
S	0.0131	(0.0046)	0.0476	(0.0116)	0.0150	(0.0075)	0.1568	(0.1352)
Ca/Mg	1.45		0.52		1.70		0.47	
Ca/Al †	30.0		2.62		85.0		0.54	

Units are $\mu\text{eq cm}^{-2} \text{ day}^{-1}$ for all analytes, except $\mu\text{mol cm}^{-2} \text{ day}^{-1}$ for Al, Fe, Mn and Pb

† molar (mol/mol) ratio

become the most important acid neutralization mechanism in these forest soils after a decade of treatments, and IER data support that interpretation.

Sodium and Pb had larger responses to forest type than treatment, based on IER accumulation rates. Higher concentrations of solutes under softwood stands compared to hardwoods were interpreted to be the result of a higher aerosol interception capacity of softwood canopies (Currie et al., 1999; Houle et al., 1999; Hultberg and Grenfeldt, 1992; Norton et al., 1988; Rustad et al., 1994; Waring et al., 1981). Because of the proximity of BBWM to the Atlantic Ocean, evidence of a greater aerosol interception capacity in the canopy for softwoods compared to hardwoods was best expressed as higher accumulations of Na and Mg on IER in softwood stands due to marine aerosol interception. Higher IER N, S, and Pb accumulation rates were attributable to a greater interception of dry and occult deposition by softwood canopies.

In contrast, Ca accumulation rates on IER were higher in hardwoods than softwoods. The Ca results reflect higher Ca content in hardwood vegetation and the cyclical connection between litter, soil, and biomass chemistry (Clarholm, 2002; Cole and Rapp, 1981; Hart et al., 2003). Another impact of forest type was manifest as higher accumulation rates of Al, Fe, and Pb on IER in softwood stands. Higher DOC and lower pH in soil solutions under softwood stands (Szillery, 2003) contributed to the enhanced mobilization of these metals (Huang and Kiang, 1972). The exception to this phenomenon was higher Mn accumulation rates on IER in hardwood stands (Table 6), which was largely a product of West Bear hardwood accumulation rates (Table 7). Szillery (2003) surmised that because of historically elevated net N mineralization and nitrification rates in West Bear hardwoods (Wang and Fernandez, 1999; Shah, 2002),

labile Al oxide coatings may have declined, while Mn may have been mobilized. This would result in elevated concentrations of Mn in West Bear hardwoods as compared with other compartments.

Higher accumulation rates of $\text{NH}_4\text{-N}$ and total S on IER in West Bear was expected as a direct result of treatments to West Bear with $(\text{NH}_4)_2\text{SO}_4$ (Table 6). The significantly higher accumulation rates of $\text{NO}_3\text{-N}$ in West Bear reflect higher rates of nitrification, consistent with previous studies of soil N transformations at BBWM (Nadelhoffer et al., 1999; Shah, 2002). The highest rates of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ accumulation on IER were in West Bear softwood stands (Table 7). Although softwood organic horizons are thought to have lower rates of N turnover than hardwoods, Shah (2002) found that in West Bear, O horizons under softwoods had significantly higher rates of net N mineralization than under hardwoods. Shah (2002) suggested that this unexpected contrast in forest type N mineralization at BBWM may reflect changes in the response of West Bear softwoods as a result of the build-up of soil N pools over the first decade of treatment where threshold carbon to nitrogen (C/N) ratios may have been attained, resulting in increased N mineralization.

Comparison of Resin and Lysimeter Data

Linear regressions were determined using data aggregated to the plot level to assess the correlation between solute accumulations on IER and soil solution concentrations (Table 8). Graphical representations of the data for Ca, Al, Na, and $\text{NO}_3\text{-N}$ are shown in Figure 6. Only 17 of the possible 20 plot-level lysimeter means were

used in these regressions due to low collection efficiencies for three plots, which were the result of drought conditions during the summer of 2001.

The correlations between IER-extracted and soil solution Na and Al concentrations were the strongest of the solutes in this study, with r^2 of 0.55 and 0.42, respectively (Table 8). It is also evident from Figure 6 that individual plot data within compartments (e.g. West Bear watershed, softwood forest type) were somewhat clustered showing the watershed and forest type effects on the results. Other solutes such as Ca and $\text{NO}_3\text{-N}$ showed greater variability among plots within compartments and between IER and soil solution data. As soil solution $\text{NO}_3\text{-N}$ concentrations increased, the variability of $\text{NO}_3\text{-N}$ extracted from IER increased (Figure 6b). Ion exchange resins may be better suited to estimates of $\text{NO}_3\text{-N}$ than $\text{NH}_4\text{-N}$ when used as surrogates for soil solutions because soil solution $\text{NO}_3\text{-N}$ concentrations had a significant relationship with IER $\text{NO}_3\text{-N}$, while the regression of resin and soil solution $\text{NH}_4\text{-N}$ concentrations was not significant (Table 8). However, Hart and Binkley (1985) reported that IER underestimated $\text{NH}_4\text{-N}$ but overestimated $\text{NO}_3\text{-N}$, compared with traditional measures of N availability.

Comparison with Other Measures of Ionic Availability

Figures 7 and 8 compare Ca, Al, Mg, $\text{NH}_4\text{-N}$, and $\text{NO}_3\text{-N}$ IER data with other measures of treatment response at BBWM. These comparisons are achieved by normalizing all data against East Bear means for each measurement. Therefore, West Bear means are expressed as a percent difference from East Bear means.

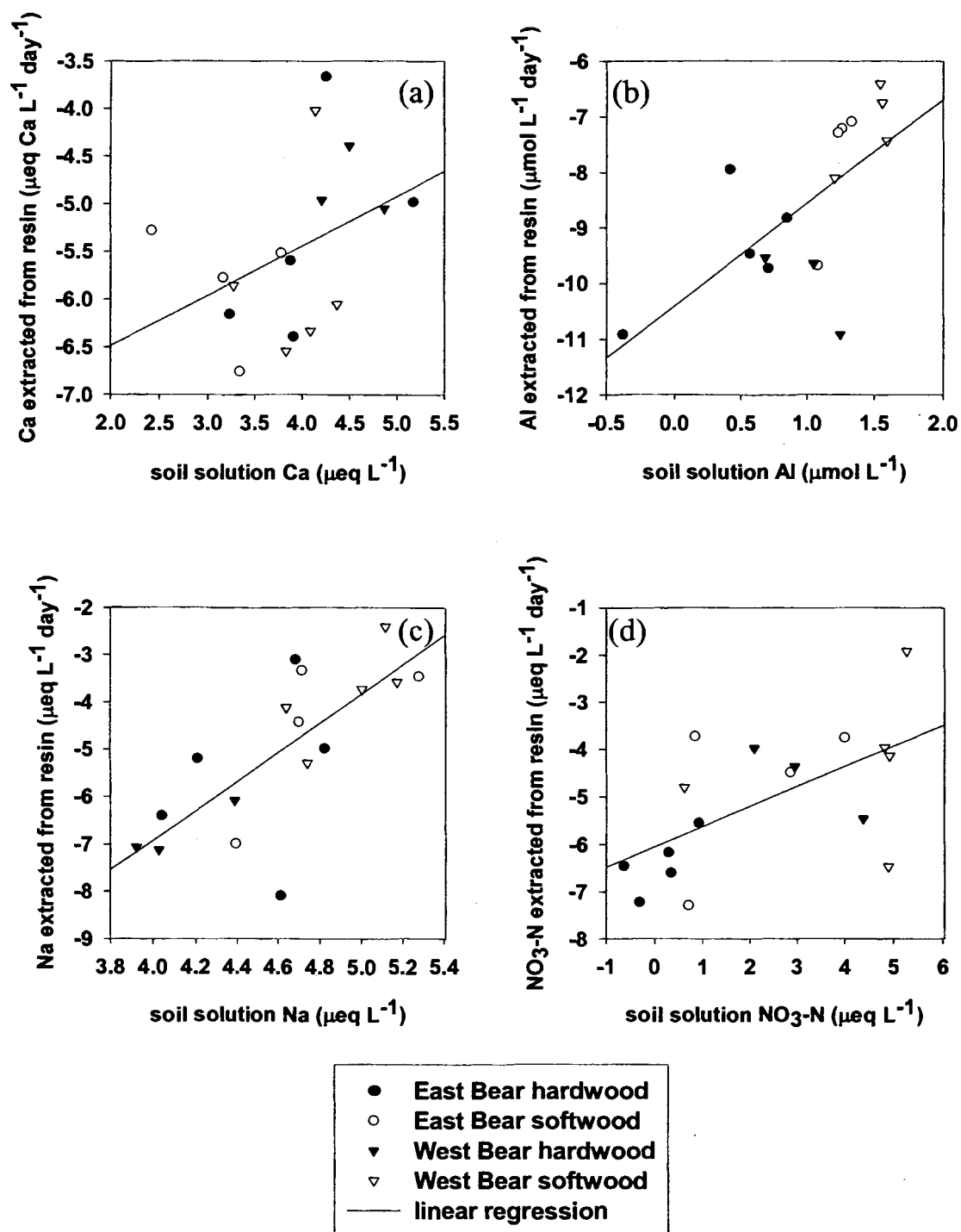


Figure 6. Linear regression of solutes extracted from ion-exchange resins against solutes in soil solutions for: (a) calcium, (b) aluminum, (c) sodium, and (d) nitrate. All values were log transformed.

Table 8. Linear regression equations, coefficients of determination (r^2) and p-values for the linear regression of solutes extracted from ion-exchange resins (y) against soil solution solute concentrations (x).

Solute†	Regression equation	r^2	P-value
Ca	$y=0.52x-7.53$	0.16	0.11
Mg	$y=0.91x-8.68$	0.19	0.08
K	$y=0.0005x+0.004$	0.18	0.09
Na	$y=3.10x-19.31$	0.55	0.0006
Al	$y=1.86x-10.41$	0.42	0.006
Fe	$y=0.57x-8.73$	0.31	0.02
Mn	$y=0.76x-8.27$	0.19	0.08
Pb	$y=-0.0002x+0.000003$	0.007	0.74
NO ₃ -N	$y=0.43x-6.05$	0.36	0.011
NH ₄ -N	$y=0.26x-5.19$	0.02	0.57
S/SO ₄ -S	$y=-0.000008x+0.024$	0.002	0.86

† All values were log transformed, with the exception of S, K, and Pb.

Figure 7 shows that for Ca, Al, and Mg, IER data were most similar to soil solutions in their response to treatments and both methods of studying soil solutions reflect the mobilization of base cations and metals. Organic soil horizons exhibited lower concentrations of Ca and Mg in West Bear compared to East Bear reflecting a depletion of soil exchangeable Ca and Mg from surface horizons, while Al concentrations increased. Fernandez et al. (in press) found evidence of Ca and Mg depletion in soils at West Bear after eight years of treatment, with significantly less Ca and Mg in West Bear O horizons compared to East Bear. Thus, IER results appeared to be consistent with soil solution response to acidification. Whether other measures of chemical response were directly or inversely proportional to IER results depended on the mechanisms of response involved and the stage ecosystem response to experimental acidification (e.g. soil solution and IER concentrations can increase for base cations while soil exchangeable pools decrease). Sugar maple foliar and litter chemistries were most similar to IER results of the additional indicators considered with increased base cation concentrations relative to the reference, while beech and red spruce results suggested declining concentrations such as was reported for soils. Cronan and Grigal (1995) suggested that foliar Al concentrations were not good indicators of soil solution Al, consistent with the IER and soil solution results reported here compared with foliar data. They found that Al was retained in root tissue, and foliar Al concentrations were only a small fraction of root concentrations.

Figure 8 compares normalized $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ IER data with other measures of N availability at BBWM. Most measures of N availability indicated higher availability

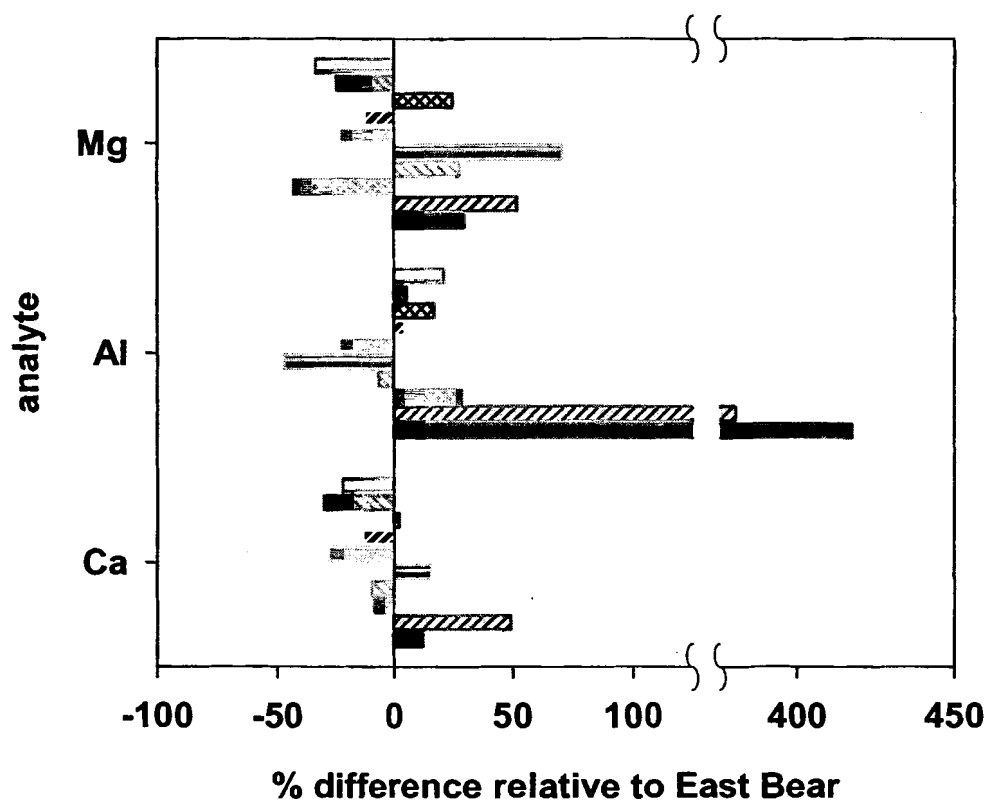


Figure 7. Comparison of Ca, Al, and Mg measures by various methods. Each measure has been normalized to East Bear values, and represents the percent difference between West Bear and East Bear. Data for comparisons are from (1) Fernandez, unpublished data and (2) Rustad, unpublished data.

in West Bear, when compared with East Bear. The relative magnitude of this availability was most comparable in soil solutions, resins, and O horizon net nitrification. More modest increases in N availability were evident in foliar and litter N concentrations in all tree species. Laboratory soil incubations that have compared N mineralization and nitrification rates with IER $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ concentrations have often shown good agreement (e.g., Binkley and Matson, 1983; DiStefano and Gholz, 1986). Field comparisons of these methods have not always agreed as well. Hart and Binkley (1985) reported that in laboratory incubations they found high ammonification but only minimal net nitrification, but IER accumulations for $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ were of the same magnitude in their study. Giblin et al. (1994) did not find good correlations between IER and traditional measures of N and P availability, but found that landscape differences in N and P availability indicated by resins corresponded well with soil and soil solution N/P (nitrogen to phosphorous ratios). Lajtha (1988) also reached this conclusion in a study of N and P availability in a New Mexico chronosequence that utilized IER and traditional measures of N and P availability. The IER results reported here suggest that accumulations of inorganic N reflect relative changes in N dynamics between watersheds. This can be taken to support the use of IER for qualitative evaluations of ecosystem change, but more study is required to determine if the approach used here is a surrogate approach for measuring quantitative fluxes of solutes *in situ*.

All forest species showed increases of comparable magnitude in foliar and litter N in West Bear relative to East Bear (Figure 8). Meiwes et al. (1998) and Gilliam et al. (1996) also reported elevated N concentrations in the foliage and litter of dominant tree

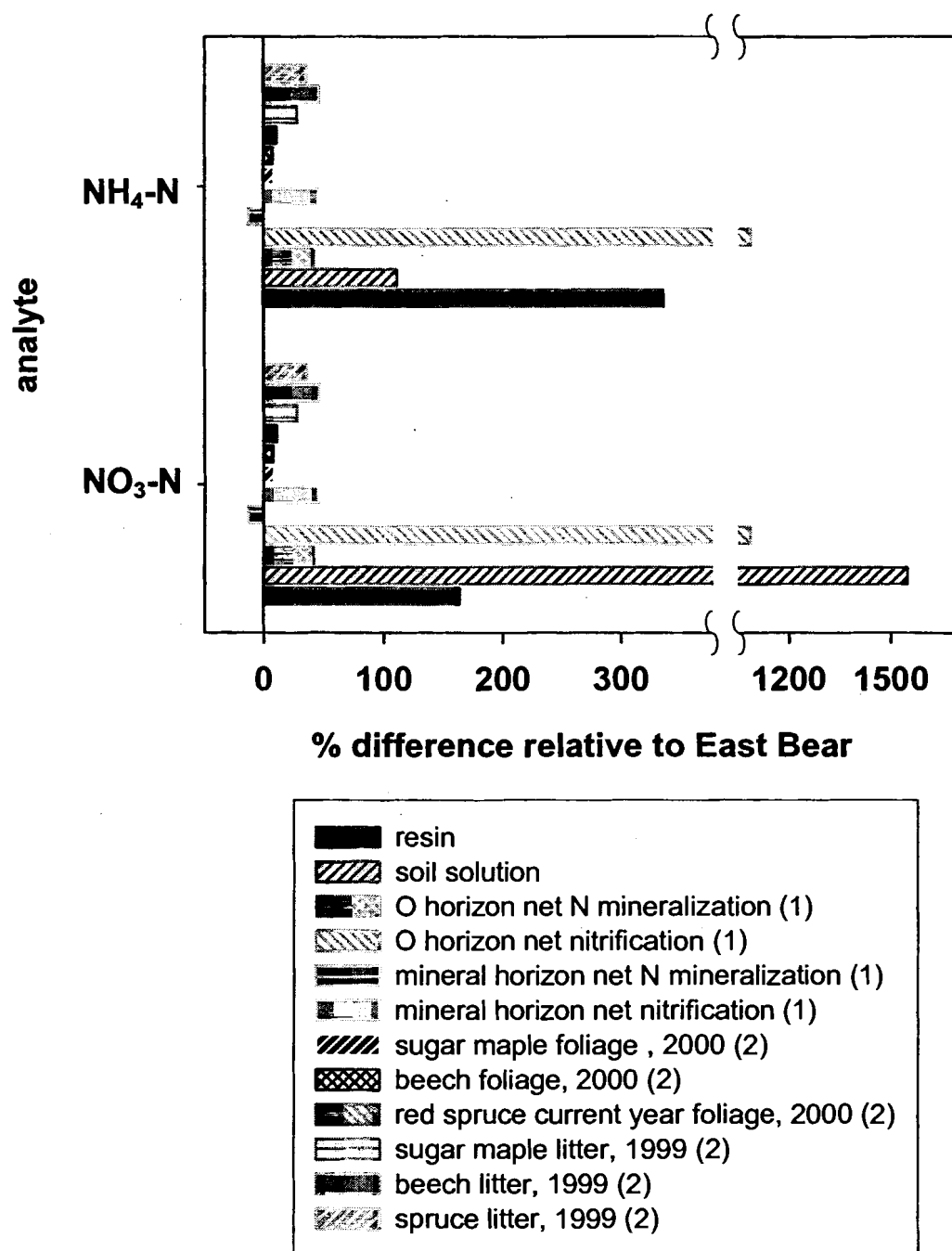


Figure 8. Comparison of NO₃-N and NH₄-N measures by various methods. Each measure has been normalized to East Bear values, and represents the percent difference between West Bear and East Bear. Data for comparisons are from (1) Shah, 2002 and (2) Rustad, unpublished data.

species in response to experimentally elevated N and S studying acidic deposition effects on forests. Schulze (1989) suggested that this excess N uptake by trees might stimulate growth and result in secondary nutrient deficiencies.

Conclusions

Ion-exchange resin and tension lysimeter measurements of solutes in soil solutions indicated that similar processes were important in the response of a forested watershed to N and S additions. The IER system used in this study did not provide direct contact between IER and solid soil materials, but channeled soil solutions through IER by using a small PVC chamber. The intent was to capture a cumulative sample of solutes moving in soil solutions under the O horizons as a surrogate to other measures of determining the biogeochemical changes in ecosystems. In this instance, IER results compared well with lysimetry as an index of change in soil solutions, and the relative responses to forest types and watershed N and S treatments were consistent with changes in soil chemistry. IER techniques that aim to capture soil solution chemical losses may be suitable for this type of field research. They have the advantage of providing an integration of leaching losses over time without multiple field trips and the hydrological uncertainties typical of traditional lysimeter techniques. However, lysimeter studies that were conducted parallel to this IER research were not intensive enough to determine chemical fluxes in solutions so direct quantitative comparisons of lysimeter and IER flux were not possible. Further research should be carried out on a wider range of soil and forest community conditions, with more intensive lysimetry using simultaneous IER

measurements as employed here, to provide quantitative comparisons between these techniques. These studies will be valuable in defining the scope of potential uses for this type of IER approach in ecosystem research.

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BIOGRAPHY OF THE AUTHOR

Johanna Szillery was born in Budapest, Hungary in 1974. She and her mother immigrated to the United States in 1981 and lived in Illinois for a few years. Most of her childhood, Johanna spent growing up in Montgomery County, Pennsylvania. She enjoyed attending Gwynedd-Mercy Academy, where she had great friends and her love of running and sports grew. She graduated from Gwynedd in 1993. Johanna attended Drew University for her undergraduate degree. While working for Dr. Sara Webb, her adviser, Johanna got her first experience in field ecology and botany in Minnesota. During her undergraduate work, Johanna was fortunate enough to gain field experience in both Minnesota and Virginia. Johanna graduated from Drew University in 1998 with a Bachelor of Arts, with an emphasis in Biology. Through several jobs and continuing education classes, Johanna learned about soils and was fascinated by the wonderful balance it presented between chemistry, biology and geology. She also met Dr. Ivan Fernandez, who would be her adviser. In the fall of 2001, she enrolled in the Plant, Soil, and Environmental Sciences program as a Master of Science candidate.

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