Experimental Acidification Causes Soil Base-Cation Depletion at the Bear Brook Watershed in Maine

Ivan J. Fernandez,* Lindsey E. Rustad, Stephen A. Norton, Jeffrey S. Kahl, and Bernard J. Cosby

ABSTRACT

There is concern that changes in atmospheric deposition, climate, or land use have altered the biogeochemistry of forests causing soil base-cation depletion, particularly Ca. The Bear Brook Watershed in Maine (BBWM) is a paired watershed experiment with one watershed subjected to elevated N and S deposition through bimonthly additions of $(NH_4)_2SO_4$. Quantitative soil excavations in 1998 measured soil pools of exchangeable base cations 9 yr after treatments began. Stream sampling at the weirs on a weekly and event basis, and weekly precipitation sampling, were used for input-output estimates. The treated watershed had lower concentrations of exchangeable Ca and Mg in all horizons, with evidence for the greater depletion in the O horizon compared to underlying mineral soils, and in softwoods compared to hardwoods. This difference between watersheds is interpreted to be treatment-induced base-cation depletion, which was reinforced by model simulations. The difference between watersheds was 66 and 27 kg ha^{-1} of exchangeable Ca and Mg, respectively, after accounting for soil mass differences between watersheds. This was comparable with the total cumulative excess stream Ca and Mg export in West Bear after 9 yr of treatment of 55 and 11 kg ha^{-1}, respectively. Model simulations of watershed response to treatments predicted excess soil exchangeable Ca and Mg losses in the treated watershed of 47 and 9 kg ha^{-1}, respectively. These results indicate that the response to a step-increase in N and S deposition during the first decade of treatments in this experimental forested watershed was to invoke cation-exchange buffering, resulting in a net decline in soil exchangeable base cations.

ACCELERATED LEACHING of base cations from forest soils has been recognized as a possible consequence of acidic deposition for over 30 yr (Hutchinson and Havas, 1980; Fernandez, 1985; Gobran and Bosatta 1988; Johnson and Fernandez 1992; Driscoll et al., 2001; Bailey et al., 2003). Numerous field and laboratory studies in North America and Europe have demonstrated increases in base-cation concentrations and fluxes in soil solutions and surface waters in response to elevated strong acid anion loadings (Foster and Nicolson, 1988; Ulrich, 1989; Johnson and Fernandez, 1992; Matschullat et al., 1992; Abrahamsen et al., 1994; Rustad et al., 1993, 1996). These increases reflect the initial neutralization of acidic deposition by ion exchange reactions in the soil, whereby base cations are preferentially displaced from exchange sites by H or Al. Once mobilized, these cations move through the soil and into ground and surface waters accompanying SO_4^{2-} and NO_3^-, maintaining electrical charge neutrality. Reports of measured declines in soil base cation status, such as those by Falkengren-Grerup et al. (1987) and Hallbacken and Tamm (1986) for Swedish soils, or Johnson et al. (1994) in the Adirondacks of New York, had been dismissed as 'extreme' cases, the result of natural changes in stand dynamics as discussed by Krug and Frink (1983), or merely circumstantial.

More recently, however, studies have provided new evidence that long-term acidic deposition may be resulting in significant reductions in available base cations, particularly Ca and Mg, in forest soils. Ironically, these reductions may be exacerbated by decreased atmospheric deposition of base cations (Hedin et al., 1994), although evidence for declines in base-cation deposition is inconsistent and subject to further investigation (Lynch et al., 2000; Stoddard et al., 2003). Likens et al. (1996) focused attention on this issue by reporting declines in base-cation stream concentrations at the Hubbard Brook Experimental Forest (HBEF), and that they attributed primarily to declines in base-cation deposition and soil depletion. Reports of similar measured or inferred declines have recently been reported by Shortle and Bondietti (1992), Miller et al. (1993), Johnson et al. (1994), Lawrence et al. (1995, 1999), and Johnson et al. (2000) for other sites in New England. Yet Yanai et al. (1999) found that clear evidence for a regional decline in base-cation pools in the forest floor was difficult to detect, and concluded that no current base-cation depletion appears evident even though past conditions may have caused accelerated base-cation losses. Huntington et al. (2000) studied the potential for Ca depletion in the southeastern and mid-Atlantic regions of the USA and reported evidence of base-cation depletion in soils throughout the study area.

Tree ring analyses have provided additional circumstantial evidence of a decline in soil base-cation status. For example, Bondietti et al. (1990), Shortle and Bondietti (1992), Shortle et al. (1995), and Likens et al. (1996) reported that the Ca concentration of tree rings from dominant species at several sites in the eastern USA increased during the 1960s and then decreased thereafter, suggesting an initial increase in plant-available Ca followed by a decline, a pattern similar to the long-term stream record at the HBEF. This same pattern was reflected in short-term experimental work at the BBWM and reported by David et al. (1990) and Mitchell et al. (1994), where buried mineral soil bags installed under the O horizon first reflected a mobilization and translocation of base cations from acidifying treatments, ultimately followed by base-cation depletion.

I. J. Fernandez, Dep. of Plant, Soil, and Environmental Sciences, Univ. of Maine, Orono, ME 04469; L.E. Rustad, USDA Forest Service, Northeastern Experiment Station, Durham, NH 03824; S.A. Norton, Dep. of Geological Sciences, Univ. of Maine, Orono, ME 04469; J.S. Kahl, Senator George J. Mitchell Center for Env. & Watershed Research, Univ. of Maine, Orono, ME 04469; B.J. Cosby, Dep. of Environmental Sciences, University of Virginia, Charlottesville, VA 22904. Received 7 Nov. 2002. *Corresponding author (ivanjf@maine.edu).

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677 S. Segoe Rd., Madison, WI 53711 USA

The consequences of soil base-cation depletion include acidification of soil and surface water (van Breeman et al., 1983), and possible growth declines of forest vegetation (Shortle and Smith, 1988; McLaughlin et al., 1992; Likens et al., 1996). Growth declines may be due to insufficient Ca for forest growth (Shortle and Smith, 1988; Likens et al., 1996), or due to nutrient imbalances in trees, especially root and foliar Ca/Al and Mg/N ratios, as discussed by Shortle and Smith (1988), McNulty and Aber (1993), and Cronan and Grigal (1995). Increased stress on trees caused by these nutrient imbalances will also make forests more vulnerable to decline from secondary pathogens and insects (Shortle and Bauch, 1986) and more sensitive to cold and drought injury (Shortle and Smith, 1988; Schaberg et al., 2002).

The BBWM is the site of a long-term, whole-watershed chemical manipulation using experimentally applied N and S (Norton and Fernandez, 1999). The objectives of the research reported here were to determine if: (i) there were differences between the treated and control watersheds in soil exchangeable base-cation pools after 9 yr of treatments; (ii) watershed mass balance calculations supported the hypothesis that these soil exchangeable base-cation pool differences were largely attributable to the treatments; and (iii) modeling predictions of response were consistent with observed ecosystem behavior.

MATERIALS AND METHODS

Site Description

The BBWM is located in eastern Maine (44°52′ N, 68°06′ W), ~50 km from the Gulf of Maine. The site lies on the southeast slope of Lead Mountain, with a maximum elevation of 475 m and a total relief of 210 m. The average slope of the watersheds from the summit to the weirs is 31%. Bear Brook Watershed in Maine is the location of a long-term paired watershed study (Norton et al., 1999a). The East Bear watershed (11.0 ha) serves as the reference watershed. The West Bear watershed (10.3 ha) has been treated bimonthly with ammonium sulfate [$(NH_4)_2SO_4$] starting in November 1989 as part of a whole-watershed manipulation experiment designed to investigate the effects of atmospheric deposition of N and S. Granular $(NH_4)_2SO_4$ has been aerially applied bimonthly at approximately 28.8 kg S ha^{-1} yr^{-1} and 25.2 kg N ha^{-1} yr^{-1}. Bedrock is mainly quartzite and gneiss with granitic intrusions. Soils are primarily coarse-loamy, mixed, frigid Typic Haplorthods formed from compact Wisconsinan age basal till (Rustad et al., 1993). Both the parent material and bedrock have a low to moderately low weathering potential (Lawrence et al., 1997). Soils are typically 0 to 1 m in thickness and are characterized as acidic with low effective cation-exchange capacity (CEC_e), low base saturation calculated using the CEC_e (BS_e), and low sulfate adsorption capacity (Norton et al., 1999a). Vegetation is predominately northern hardwood with stands of softwood on steeper slopes and higher elevations. Hardwoods are dominated by American beech (*Fagus grandifolia* Ehrb.), with interspersed yellow birch (*Betula alleghaniensis* Britt.), sugar maple (*Acer saccharum* Marsh.), and red maple (*Acer rubrum* L.). Softwoods are red spruce (*Picea rubens* Sarg.) with a minor component of balsam fir [*Abies balsamea* (L.) Mill.]. Average air temperature is 4.9°C and annual precipitation since 1988 ranged from 1.15 to 1.70 m. Additional site information is in Norton and Fernandez (1999).

Water Sampling

The BBWM site was chosen on the basis of contiguous watersheds with similar hydrology and stream waters with low total alkalinity (acid neutralizing capacity, or ANC). Each watershed is gauged with a standard 120° V-notch weir with redundant systems (stilling well float and pressure transducers) for recording discharge. Both weirs are anchored on bedrock. From 1987 to the present, we have monitored (i) precipitation volume and chemistry following NADP protocols Dossett and Bowersox (1999), (ii) discharge of both streams with 5 min resolution, and (ii) stream chemistry with weekly samples on Tuesdays (concurrent with precipitation samples) just above the weirs and bihourly samples during periods of high flow. Additional samples are collected less frequently on elevational transects and more frequently at the weirs with automated flow-activated (or preprogrammed) samplers (ISCO Inc., Columbus, OH, Model 3700) to investigate episodic hydrologic and chemical events. Field and laboratory methods are detailed in Hillman et al. (1986) and approved by the U.S. Environmental Protection Agency for its Long Term Monitoring Program. Additional details of the hydrochemical measurement program can be found in Norton et al. (1999a,b) and Kahl et al. (1999). Comparisons between stream export and soil pools include stream data only through 1998, when soils were sampled. Data for streams since 1998 are presented to provide additional insight on watershed processes.

Soil Sampling

Soil sampling at BBWM was performed in 1998 and focused on identifying potential contrasts between the East and West Bear watersheds within two dominant forest types after 9 yr of $(NH_4)_2SO_4$ additions. Eighty quantitative soil pedon excavations were performed during this study. Of these, 40 were full pedon excavations, and 40 were 'mini-pits' consisting of the upper three soil increments designed to increase our precision without requiring full excavations at all sites. Depth increments included the O horizon, the upper 5 cm of the B horizon, with full pedon excavations also including a 5- to 25-cm depth increment of the B horizon, and from 25 cm to the top of the C horizon. We did not sample or analyze the relatively thin, discontinuous E horizon where present because of its limited extent and relatively low reactivity. No A horizons were present. Bulk C horizon samples were also collected and properties were calculated to a 1-m depth on a mass per unit area basis. The original design included a 25- to 50-cm depth increment. However, only one of the sampling sites had a thick enough solum and therefore this increment was eliminated from the design. For the one site, with 25- to 50-cm depth increment, the material was incorporated into the C horizon estimate. Quantitative pedons were evenly distributed across two watersheds (East and West Bear), two forest types (hardwoods and softwoods), and the two most dominant soil series (Rawsonville [Coarse-loamy, isotic, frigid, Typic Haplohumods] and Tunbridge [Coarse-loamy, isotic, frigid Typic Haplorthods] soil series) so that in each sampling unit (e.g., West Bear-Softwood-Rawsonville) there would be five full pedon excavations and five 'mini-pits'. Soils were quantitatively sampled with a 0.71 by 0.71 m frame, as described in Fernandez et al. (1993), to 1 m or refusal.

Laboratory Analysis

Air-dried soil samples were sieved (6 mm for the organic horizon, 2 mm for the mineral horizons) and homogenized

Table 1. Volume-weighted grand means based on stream flow at the weirs for selected stream chemical properties. Means are for the 1997-1999 calendar years from East Bear (reference) and West Bear (treated) streams at the Bear Brook Watershed in Maine.

	Ca	Mg	K	Na	NH_4	SO_4	NO_3	Cl	ANC	Al	DOC	pH_{eq}
	$\mu mol_c\ L^{-1}$									$\mu mol\ L^{-1}$		
East Bear	51	20	7	66	0	84	2	60	0	7	230	5.38
West Bear	102	38	10	85	2	178	48	74	−8	19	145	4.96
Difference	52	18	3	19	1	95	46	14	−8	12	−86	−0.42

before being subsampled for analysis. Percentage of air-dry moisture was calculated for fine-earth soils to allow for the expression of all data on an oven-dried basis. Soil pH was measured on fine-earth soils using $CaCl_2$ (0.01 *M*) and deionized water (Hendershot et al., 1993). Exchangeable base cations and Al were extracted with 1 *M* NH_4Cl (Blume et al., 1990) at a ratio of 2 g of organic soil or 5 g of mineral soil to 100 mL extraction solution. Samples were shaken for 1 h. All extracts were vacuum filtered through Whatman 42 filter paper(Whatman Inc., Clifton, NJ) and analyzed by flame emission (K and Na) or plasma emission spectroscopy (Ca, Mg, and exchangeable Al). Exchangeable acidity was determined by extraction with 1 *M* KCl (Blume et al., 1990) with titration to the phenolphthalein endpoint. Percentage soil organic matter was determined on oven-dried samples by loss-on-ignition (LOI) over 12 h at 450°C using a muffle furnace. Cation-exchange capacity was calculated as the sum of the exchangeable base cations (Ca, Mg, K, and Na) plus exchangeable acidity. Base saturation was calculated as the percentage of the CEC_e occupied by exchangeable bases, whereas Ca or Mg saturation was the percentage of the CEC_e occupied by these individual exchangeable cations.

Soil Pool Calculations

Total soil pools of exchangeable cations were calculated from the soil mass and exchangeable cation concentration data for each sampling depth increment or horizon as defined above. Individual depth increment or horizon exchangeable cation pools were then summed to determine total pedon exchangeable cation pools expressed as kilograms per hectare for each watershed. Base-cation concentrations were presumably the same in both watersheds before treatments, as suggested by pretreatment stream chemistry. East Bear would have started the experiment with a slightly greater exchangeable cation pool than West Bear because East Bear has a slightly greater soil mass per hectare than West Bear. To determine the cation loss in West Bear attributable to treatments, we subtracted the differences in soil cation pools between watersheds that would have existed before treatments from the differences in cation pools measured in the 1998 samples.

Statistical Analysis

All analyses were performed using the Statistical Analysis System (SAS Institute, Inc., 1988), with an α level of 0.05. An analysis of variance (ANOVA) was performed using 'Proc Mixed', with soil and forest type as nested factors within the watersheds (Littell et. al., 1996). 'Proc Mixed' was used because of its ability to accommodate an experimental design that had both fixed (e.g., forest type) and random (e.g., block) factors. It appropriately calculates error sums of squares (e.g., variance/covariance structure) for complex designs. All data were log transformed to meet the assumptions of normality and equality of variance.

RESULTS AND DISCUSSION

Comparing Stream Chemistry Between Watersheds

Both streams were monitored for 2 yr before the onset of treatments to the West Bear watershed in November of 1989. This pretreatment comparison demonstrated highly comparable stream chemistries between the two watersheds (Norton et al., 1999b) making one a reasonably good reference watershed for the other during the whole-watershed manipulation. Table 1 shows volume-weighted means for the major inorganic solutes in both East Bear (the reference watershed) and West Bear (the treated watershed) for 1997 to 1999. Both streams are relatively dilute, low ANC systems. West Bear stream chemistry had higher concentrations of Ca, Mg, Na, K, Al, SO_4^{2-}, and NO_3^-, and lower ANC, pH, and DOC than East Bear. Sulfate and NO_3 dominate the excess anion export in West Bear reflecting treatment with S and N. Higher Ca and Al are primarily responsible for the excess cation export most likely reflecting desorption from exchange sites and dissolution of secondary Al phases in the soil. The sum of the base cations and strong acid anions is approximately the same in East Bear, while strong acid anions exceed base cations in West Bear reducing ANC as acidification progresses.

Figure 1 shows the time series of Ca and Mg concentrations in both streams since the beginning of the experiment. Both East and West Bear Ca and Mg concentrations were similar in both concentration and temporal variation before the beginning of treatments to West Bear. Shortly after the onset of treatments, West Bear showed an increase in both Ca and Mg concentrations reflecting desorption from soil exchange sites in response to excess SO_4 and NO_3 in soil solution. Increases in Ca concentrations were several times the increases in Mg

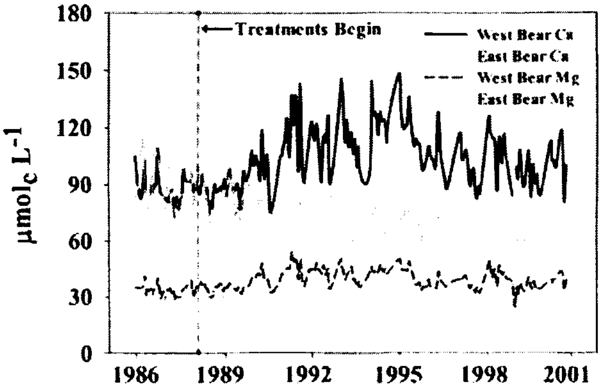

Fig. 1. Stream Ca and Mg concentrations in East and West Bear streams from weekly collections at the weirs over the study period.

concentrations, and concentrations of Ca and Mg in West Bear increased to approximately twice those in East Bear. Stoichiometrically, Ca plays the largest role in balancing excess anion export, followed by Al if predominantly trivalent, Mg, and Na. Figure 1 also shows a decline in Ca concentrations in East Bear, the reference watershed, that is likely attributable to the decline in SO_4^{2-} deposition in this region (Fernandez and Wortman, 1997; Lynch et al., 2000; Stoddard et al., 2003). Precipitation base-cation concentrations were essentially unchanged during the study period at BBWM, and throughout Maine (Fernandez and Wortman, 1997). Therefore, it is not likely that declining stream base-cation export in the reference East Bear watershed was due to declining base-cation deposition as has been discussed in the literature (Likens et al., 1998; Hedin et al., 1994).

Conceptual Model of Watershed Base-Cation Depletion

Increased leaching of strong acid anions in the soil is expected to accelerate leaching of cations. When base-cation supplies are sufficient, base-cation buffering dominates the biogeochemical response to elevated N and S deposition. As exchangeable base-cation supplies decline, we expect an increasing contribution from the mobilization of Al. The evolution of this stream response to N and S deposition was conceptualized by Galloway et al. (1983) and is further refined in Fig. 2 with a soils component. This figure portrays the change in stream base-cation concentrations, which are dominated by Ca in both absolute concentrations and in response to treatments, during a hypothetical experiment of increased loading of N and S. State I in this figure represents equilibrium stream Ca concentrations and soil BS_c before the onset of increased N and S deposition. The initial response to increased deposition of N and S is increasing stream Ca concentrations as base cations are released to runoff through cation exchange to be leached with excess strong acid anions (II). During this stage soil exchangeable base cations are sufficient to support increasing Ca export despite declining soil BS_c. This pattern of increasing Ca loss continues until soil exchangeable Ca is depleted to a point that can no longer support increasing Ca export, at which time stream Ca concentration begins to decline and the ecosystem enters Stage III. Eventually exchangeable Ca desorption is no longer the dominant soil pH buffering mechanism and is replaced by Al, at which time Ca export in the stream is in equilibrium with mineral weathering rates for Ca in soils (IV). Storage of Ca in biomass and the forest soil is then at steady state. Recovery occurs as excess N and S deposition ceases or decreases, and stream Ca concentration declines as soil exchangeable Ca pools recover through adsorption under lower strong acid anion concentrations in soil solution (V). This is not a period of equilibrium but represents a period where the soil-solution system is evolving to a new equilibrium at the lower levels of deposition. As the rate of soil exchangeable Ca recovery begins to slow, stream Ca concentrations increase (VI) back to equilibrium once again equal to mineral weathering rates (VII).

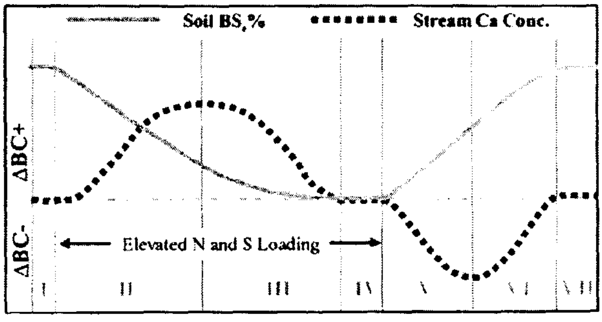

Fig. 2. Conceptual model for the evolution of stream Ca concentrations and soil base saturation (BS_e%) through both response and recovery when exposed to elevated atmospheric deposition of nitrogen and sulfur. ΔBC+ and ΔBC− indicate a relative increase or decrease in base cations from the starting equilibrium for either stream concentrations or soil exchangeable concentrations. See text for explanation of Roman numerals.

The experiment at BBWM illustrates several of the characteristics defined in this conceptual model of Ca response to N and S loading. Figure 3 shows the temporal pattern of Ca and Mg concentrations in East and West Bear streams from 1989 through 2001. In East Bear, the reference watershed, there is a relatively continuous decline in the concentrations of both Ca and Mg in streams, consistent with regional patterns of declining SO_4 deposition and subsequent decreased leaching losses of cations (Stoddard et al., 1999). In addition, long-term declines in East Bear stream Ca and Mg concentrations could represent phase V of the conceptual model during which exchangeable Ca and Mg pools in soils are replenished under a lower N and S deposition scenario. Declines in base-cation concentrations in streams are in excess of declines in strong acid anions, which suggests another mechanism of base-cation retention or the release of strong acid anions is contributing to these results. East Bear shows the greatest change from starting conditions over the first decade of treatment in response to declining ambient SO_4^{2-} deposition.

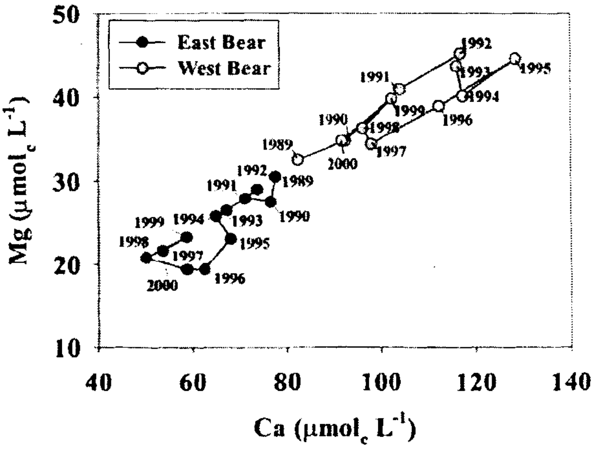

Fig. 3. Progression of stream Ca and Mg concentrations relative to each other over the study period for East and West Bear streams.

Only by comparing West Bear to East Bear can the relative effects of treatments be determined. West Bear treatments represented approximately 54 yr of wet deposition through 1998 when the soil studies reported here were performed, estimated by dividing total cumulative treatment for the study period by annual average wet-only deposition of S. While this calculation does not include dry deposition and extrapolations through time oversimplify complex systems, the calculation puts the treatment regime into perspective relative to possible response timeframes.

West Bear stream Ca and Mg concentrations followed a very different trajectory beginning in 1989 with increasing concentrations that reflect Stage II of increased base-cation export as a result of increased N and S inputs. Concentrations of Ca and Mg in West Bear continued to increase until 1995, then reversed and decreased. This change in trajectory in 1995 likely reflects a shift from Stage II to Stage III as soil exchangeable base-cation pools become depleted. The general decrease in Ca and Mg in both watersheds stops and reverses in 1998, and then resumes the decline in 2000. We hypothesize that this interruption in the long-term pattern is attributable at least in part to a 2-yr pulse of base-cation release from increased litterfall and decomposition as a result of the January 1998 ice storm that struck northern New England (Norton et al., 2003). Additional litterfall and increased soil temperatures from decreases in canopy closure would result in a transient increase in Ca and Mg release from the forest floor through organic mineralization. This effect could have been magnified if the decrease in photosynthetic leaf area during this event also reduced base cation uptake by trees.

Dahlgren et al. (1990) acidified columns of reconstructed Bs horizon soil from BBWM with 100 and 160 μM H_2SO_4, and compared these with a 40 μM H_2SO_4 reference treatment that was based on mean soil solution chemistry from field studies at the BBWM site. They found a pattern of release of Ca and Mg that generally mimics that of Fig. 2 and 3. Initial responses to higher levels of acid inputs were for increased leachate concentrations of base cations followed by a decline. After cessation of the acid treatments, Ca and Mg in the effluent from the acidified columns were sharply reduced to below the 40 μM reference treatment, as BS_e was restored in the soil. They found no evidence of increased chemical weathering. Neutralization of the acid was through base-cation desorption, mobilization of Al, and adsorption of SO_4. A parallel whole watershed chemical manipulation using aerial applications of $(NH_4)_2SO_4$ has been conducted at the Fernow Experimental Forest in north central West Virginia for approximately the same length of time as the study at BBWM. These watersheds are dominated by central Appalachian hardwoods. Edwards et al. (2002a,b) reported on the long-term response to treatments at the Fernow and also found a period of increasing Ca and Mg export followed by a decline that they interpreted to be evidence of soil base-cation depletion. They reported evidence that stream base-cation declines were expressed in peakflow discharge and not baseflow, suggesting the source of the base-cation depletion was upper soil layers. This is consistent with the findings report at BBWM, and as shown in the soils data discussed below.

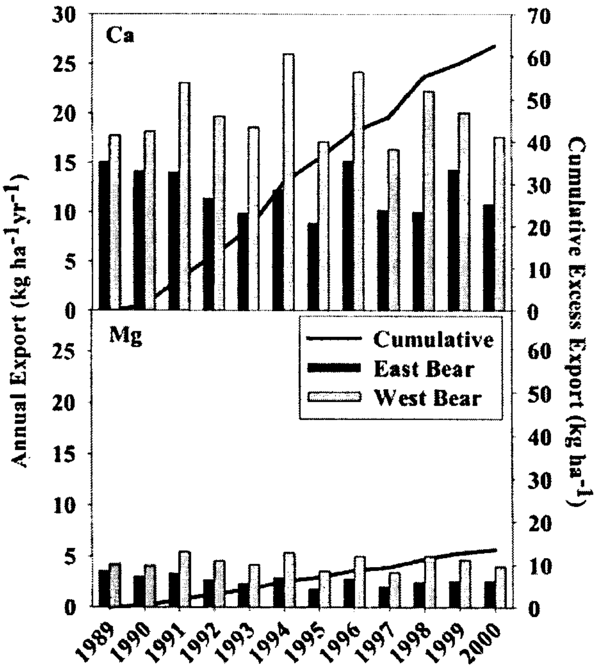

Fig. 4. Annual stream Ca and Mg export (paired bars), and cumulative excess export in West Bear compared to East Bear (line), over the study period.

Stream export integrates many processes within the ecosystem that result in the chemistry measured at the weir. In the BBWM experiment the chemical manipulation has resulted in a clear but variable increase in annual Ca and Mg export from West Bear shown in Fig. 1 and 3. The solid lines in Fig. 4 represent the cumulative excess export of Ca and Mg in West Bear, compared with East Bear, which we attribute to the treatment. Annual differences vary but West Bear base-cation export is clearly and consistently greater than East Bear. The total cumulative excess export in West Bear compared with East Bear over the period 1989 to 1998, in excess of pretreatment differences between watersheds, is approximately 55 and 11 kg ha^{-1} yr^{-1}, for Ca and Mg respectively.

Characteristics of Soil Base-Cation Concentrations

Table 2 shows concentration data for Ca and Mg from the quantitative pedons with selected relevant characteristics of these soils. The LOI and pH data show that these are classic New England forest soils with a surface mor-like O horizon with from 60 to 80% organic matter, and a low pH controlled by organic acidity. Soil pH in 0.01 M $CaCl_2$ ranges from a low of 2.88 in the softwoods of East Bear to a high of 4.38 in the C horizon of hardwoods in West Bear. Despite the low pH of the O horizon, BS_e is higher in the O horizon than any of the mineral soil horizons and largely dominated by Ca, with

Table 2. Means for selected soil concentration parameters in 1998 by watershed and forest type at BBWM.

	East Bear		West Bear	
	Hardwood	Softwood	Hardwood	Softwood
		O Horizon		
LOI	67†	79†	65†	75†
pHs	3.30†	2.88†‡	3.33†	3.08†‡
Ca, $cmol_c\ kg^{-1}$	8.9	5.8‡	10.1†	3.4†‡
Mg, $cmol_c\ kg^{-1}$	2.2	2.9‡	1.6†	1.3†‡
CEC_e, $cmol_c\ kg^{-1}$	24†	29†	23†	26†
BS_e, %	48†	33†‡	52†	21†‡
Ca/Al, mol/mol	5.7	1.5‡	20.6†	0.7†‡
Ca Sat, %	35†	20†‡	41†	13†‡
Mg Sat, %	8.8	8.9‡	7.0†	4.8†‡
		B Horizon, 5-cm increment		
LOI	18	20	18	19
pHs	3.78†	3.59†	3.72	3.69
Ca, $cmol_c\ kg^{-1}$	0.51†	0.28†	0.65†	0.19†
Mg, $cmol_c\ kg^{-1}$	0.20†‡	0.15†	0.15†	0.12†
CEC_e, $cmol_c\ kg^{-1}$	9†	12†	10	10
BS_e, %	10†‡	5†	9†	5†
Ca/Al, mol/mol	0.07†	0.03†	0.11†‡	0.02†
Ca Sat, %	5.4†	2.2†	6.1†	1.8†
Mg Sat, %	2.2†‡	1.2†	1.5†	1.1†
		B Horizon, 5–25 cm increment		
LOI	13	17	15	14
pHs	4.16†	3.92†	4.17†	3.99†
Ca, $cmol_c\ kg^{-1}$	0.21	0.15	0.21†	0.12†
Mg, $cmol_c\ kg^{-1}$	0.07	0.10	0.07	0.05
CEC_e, $cmol_c\ kg^{-1}$	5†	8†	5	6
BS_e, %	9†‡	5†	7†‡	5†
Ca/Al, mol/mol	0.05†	0.02†	0.05†	0.02†
Ca Sat, %	4.5†	1.9†	4.0†	2.0†
Mg Sat, %	1.3†	1.1†	1.2†	0.9†
		BC Horizon, 25–C increment		
LOI	10	12	11	11
pHs	4.30	4.20	4.33	4.23
Ca, $cmol_c\ kg^{-1}$	0.13	0.14	0.11	0.09
Mg, $cmol_c\ kg^{-1}$	0.03	0.05‡	0.03	0.02‡
CEC_e, $cmol_c\ kg^{-1}$	4	5	3	4
BS_e, %	8	7	7	5
Ca/Al, mol/mol	0.05	0.03	0.03	0.02
Ca Sat, %	3.8	2.9	3.1	2.1
Mg Sat, %	0.8	1.0	0.7	0.6
		C Horizon		
LOI	7	14	7	8
pHs	4.33	4.19	4.38	4.30
Ca, $cmol_c\ kg^{-1}$	0.08	0.08	0.06	0.05
Mg, $cmol_c\ kg^{-1}$	0.02	0.03	0.01†	0.01†
CEC_e, $cmol_c\ kg^{-1}$	3	5	2	3
BS_e, %	6†	4†	5	5
Ca/Al, mol/mol	0.03†	0.01†	0.03†	0.01†
Ca Sat, %	3.1†	1.2†	2.5	1.4
Mg Sat, %	0.5	0.6	0.3	0.4

† Indicates significant differences between forest types within watersheds.
‡ Indicates significant differences between watersheds within forest types.

Mg a distant second. Cation-exchange capacity and BS_e decline precipitously from the O to mineral soil horizons. Statistical contrasts shown in Table 2 include differences between both forest types within individual watersheds, and differences between watersheds within forest types.

Most of the significant differences between forest types and watersheds were in the O horizon, followed by the upper 5-cm increment of the B horizon. We did not sample or analyze the relatively thin, discontinuous E horizon where present. The 5-cm increment represents the uppermost 5 cm of the morphological B horizon (a spodic horizon) and a zone most likely to reflect mineral soil responses to perturbations from above (Fernandez and Rustad, 1990). The sensitivity of this uppermost initial increment of the B horizon in these Spodosols is a function of both their location in the profile and the abrupt morphological horizon transitions evident in these soils. For most of the data reported in Table 2, means for hardwood forest types were significantly higher than means for softwood forest types in both watersheds. Higher soil exchangeable Ca and Mg, and higher pH are consistent with the higher foliar Ca and Mg concentrations found in hardwoods at BBWM (White et al., 1999), as well as with other evidence that demonstrates the importance of tree species in influencing soil Ca and Mg concentrations (Ovington 1958; Alban 1982). Forest type effects on soil Ca and Mg were best expressed in the upper increments of the B horizon and almost no differences were evident below 25 cm. The upper 0- to 5-cm and 5- to 25-cm increments correspond to morphologically expressed spodic horizons in most pedons, and therefore represent the depth of active soil formation for these Spodosols. The 25 to C increment represents a transitional zone (i.e., the BC horizon) between the B horizon and the underlying parent material (C horizon). These data suggest that the contribution of forest type to soil properties is low in these lower solum materials.

The concentration data show an overall pattern of significantly lower Ca and Mg in the treated West Bear compared with the reference East Bear watershed, but only in softwood stands. Similar differences are evident if the data are expressed on a percentage of saturation basis, which eliminates the possibility of the differences being due to changes in CEC_e. The pH is significantly higher in West Bear softwood O horizons, opposite of what would be expected in light of the significantly lower BS_e in the O horizon based on conventional wisdom for agronomic mineral soils. However, recent studies of forest soils in the northeastern USA have demonstrated that Al behaves more like a base in the O horizon because of the low pH attributable to weak organic acidity (Ross et al., 1996; Johnson et al., 2000; Johnson, 2002). Therefore, O horizon pH is typically well correlated with the percent of the CEC_e occupied by H^+, but not BS_e unless Al is included as a base in the calculation. This would explain the higher pH in West Bear softwood O horizons even though exchangeable Ca and Mg concentrations were lower. Soil pH is numerically lower in West Bear mineral soils for all mineral soil increments beneath the O horizon, as is mineral soil BS_e.

Exchangeable Al represents the other half of the story in soil exchange phase phenomena. Forest soil exchangeable acidity increases as BS_e declines. Exchangeable acidity is composed of both exchangeable Al and H in the O horizon, and almost solely exchangeable Al in the mineral soil horizons (Fernandez et al., 1993). The balance between Ca and Al has been widely studied as an indicator of the degree of soil acidification and potential for negative effects on plant communities (Ulrich 1983; Lawrence et al., 1995; Cronan and Grigal 1995; Shortle et al., 1997), with soil solution Ca/Al molar ratios <1 often considered a threshold for potential Al toxicity. Identifying threshold ratios of soil exchangeable Ca/Al for biological effects has not been easy or widely reported (De Wit et al., 2001). Reuss (1983) reported that soil solutions would be dominated by Ca above a BS_e of 20%, and a Ca saturation of 15%. He predicted that between 5 and 15% Ca saturation in soils there should be an abrupt change with Al mobilization resulting in Al domination in soil solutions. These model concepts were developed for, and apply to, our understanding of exchange in mineral soils, not O horizons. Nevertheless, taking these ranges into consideration, all of the mineral soils in both the reference and treated watersheds at BBWM are <15% BS_e. Most fall between 5 and 10% BS_e despite a declining CEC_e with depth. Softwood mineral soils generally have lower BS_e than hardwoods, and these differences are significant in the upper increments of the B horizon. The BS_e data suggest these soils are in, or are moving into, a chemical state where Al replaces Ca as most prevalent in soil solutions. These soils generally do not fall below the 5% BS_e threshold for potential cation toxicity for sensitive species reported by Ulrich (1983). Interestingly, the higher BS_e hardwood mineral soils showed a significantly lower BS_e in the treated West Bear compared with the reference East Bear watersheds, even though exchangeable Ca did not show a similar effect. It seems that softwood O horizons were potentially more responsive to Ca losses with treatments while hardwood mineral soils showed a similar, but less pronounced, response.

Soil Mass Balance Comparisons

The differences between watersheds in stream Ca and Mg export since the onset of treatments in 1989 in West Bear appear to reflect treatment effects. These differences could be caused by several mechanisms, but would require that these mechanisms operate selectively only on the West Bear watershed. These include treatment-induced: (a) increased base-cation release from litter decomposition and soil mineralization processes, (b) increased mineral weathering, (c) increased base-cation deposition due to changes in canopy structure, (d) decreased base-cation uptake and retention by vegetation, or (e) desorption of soil exchangeable base cations. Litter decomposition and foliar chemistry studies are in progress at present to better define these processes at BBWM. Studies of foliar and wood chemistry in the first 5 yr of treatment by White et al. (1999) and DeWalle et al. (1999) indicated changes in the availability and uptake of Ca and Mg, generally with lower tissue base-cation concentrations on the treated West Bear watershed. They speculated that increased base-cation leaching from the soil caused these differences and therefore increased Ca and Mg uptake in West Bear would not be the cause of decreasing stream export. However, without accurate biomass estimates and longer-term measurements of biomass uptake and accretion, it is not possible to quantitatively define the role of biomass in watershed response to treatments at this time. The difference in stream Si concentrations between East and West Bear has remained unchanged over the period of study, which we interpret as evidence of relatively small or no significant effects of treatments on mineral weathering (Norton et al., 2003). There is no evidence of changes in long-term wet deposition of base cations at the BBWM or throughout Maine during the past two decades (Fernandez and Wortman 1997) that could be contributing to stream base-cation export trends. Precipitation Ca concentrations at BBWM have been ≤2 $\mu mol_c\ L^{-1}$ (or $\mu eq\ L^{-1}$) throughout the study period, preventing this mechanism from being a contributor to stream export trends described here.

This research was designed to evaluate soil exchangeable base cations as a possible source of increased stream Ca and Mg export between watersheds. Table 2 indicates differences between watersheds exist in exchangeable base-cation concentrations, but differences in soil mass on a mass per unit area basis determines how these concentrations are translated into soil base-cation pools. Both watersheds have similar soil masses with small differences in soil thickness and density resulting in the West Bear watershed having ~6% less fine-earth soil mass compared with East Bear, as determined from quantitative pedon excavations in 1998. Mass per unit area of exchangeable Ca and Mg were calculated using soil fine-earth mass and concentration data, and are represented in Fig. 5. West Bear had a significantly lower exchangeable Ca and Mg pool compared with East Bear, with both O and mineral soil horizons contributing to these differences. The differences in soil pools between watersheds were 80 and 31 kg ha^{-1} of exchangeable Ca and Mg, respectively. Adjusting these Ca and Mg pool differences for the lower total fine-earth soil mass in West Bear compared with East Bear resulted in 66 and 27 kg ha^{-1} less exchangeable Ca and Mg, respectively, that was not due to differences in soil mass. If these differences represent treatment-induced depletions of exchangeable Ca and Mg in West Bear, they are remarkably similar to the total cumulative excess Ca and Mg export from West Bear of 55 and 11 kg ha^{-1}, respectively, by 1998 when we sampled soils. These depletions represent approximately one-third of the pools of exchangeable Ca and Mg compared with East Bear.

The majority of the calculated depletion in West Bear compared with East Bear was attributable to differences in the O horizons, which explained 84 and 77% of the

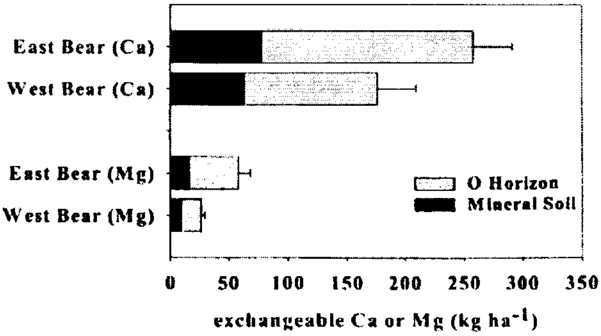

Fig. 5. Soil exchangeable Ca and Mg pools (kg ha^{-1}) in East and West Bear watersheds showing the contributions of O and underlying mineral soil horizons. Differences between watersheds are significant for total exchangeable Ca and Mg.

total soil exchangeable Ca and Mg differences, respectively. Other factors contributing to the retention and release of Ca and Mg in these watersheds are undoubtedly critical to defining base-cation cycling, but possibly had little net influence on changing Ca and Mg export due to treatments during the first 9 yr of whole-watershed chemical manipulation. Because the treatments are introduced from the surface, it is logical that the O horizon was most responsive with respect to accelerated base-cation leaching losses in West Bear. Some of the base cations lost from the O horizon could be readsorbed in subsurface mineral soils, minimizing the differences we saw after 9 yr of treatment in mineral soil exchangeable Ca and Mg. A unique buried mineral bag study was conducted at BBWM on experimentally acidified plots adjacent to the watersheds in the early stages of the BBWM program. In that study, mineral soil bags were installed under the O horizon with subsamples of a single homogenized B horizon material in each bag. Soil exchangeable base-cation concentrations initially increased in these bags which was reported to be a result of base cations being desorbed from the overlying O horizon and subsequently adsorbed in the underlying mineral soil bags (David et al., 1990). Mitchell et al. (1994) later reported that after several years of treatment, base-cation concentrations declined in the soil bags as the result of the progressive acidification from the surface O horizon to the underlying mineral soil bag, with base-cation displacement by Al through cation exchange. It is also probable that lateral and channelized flow in these soils helps define the linkages between O horizon base-cation depletion and stream export, and explains how the stream could reflect changes most evident only in surface soils. These soil analyses suggest that the net export of Ca during the first decade can be largely attributable to simple cation exchange reactions in the soil and reflect evidence of experimentally induced forest soil base-cation depletion on a whole watershed scale. This mechanism of acid neutralization is expected to decrease as the watersheds at BBWM, particularly the treated West Bear, become depleted of base cations. Acid neutralization would then become dominated by Al and eventually Fe (Norton et al., 2003).

Comparing Observed Results with MAGIC

The data from the BBWM project have been used to calibrate and test models of biogeochemical processes in watersheds that control the accumulation and release of base cations in soils. The MAGIC model, for instance, has been applied to both the treatment and control watersheds (Norton et al., 1992; Cosby et al., 1996) and has been updated throughout the years of the experiment. MAGIC is a long-term, mass-balance model designed primarily to simulate changes in soil pools and stream fluxes in response to changing atmospheric deposition. It is instructive in the present case to examine the simulated stream fluxes of base cations and the simulated changes in base cations in soils derived from the most recent model update, and to compare these simulated data with the measured soil and stream data presented above.

The model was calibrated for both watersheds using the 1989 pretreatment data from each watershed. The current model was used to simulate the responses of each watershed from 1989 to 1999 using the observed trends in atmospheric deposition of S, N, and base cations, and the treatment input data for West Bear over that time period. The model simulations give explicit values for all base-cation fluxes in the watershed, including deposition, weathering, cation exchange, and net leaching. The simulations also provide a mass-balance accounting of the change in exchangeable base cations in the soil pool. Unlike the measured data, however, the soil pool in the model is a single compartment with no separate simulation of O and B mineral horizons, and with no differentiation of soils under softwoods or hardwoods. The simulated values can only be compared, therefore, with aggregated changes and fluxes observed in the experiment.

The measured soils data indicate that in 1998 West Bear soils had 66 and 27 kg ha^{-1} less exchangeable Ca and Mg, respectively, than East Bear soils. These differences may be attributable to the effects of the treatments on West Bear soils or may reflect conditions before the treatments. Soils studies were not conducted before the beginning of treatments and therefore antecedent conditions are not known. It is likely that the observed 1998 differences in soil exchangeable Ca and Mg pools result from both factors. As a first approximation, we can use the model results to partition the observed differences in sources of Ca and Mg. Model simulations suggest that exchangeable Ca and Mg in West Bear Brook soils declined by 50 and 10 kg ha^{-1}, respectively, over the treatment period (1990–1998) to produce the stream chemistries that have been observed. The simulated declines in exchangeable Ca and Mg in East Bear soils over the same period were only 3 and 1 kg ha^{-1}, respectively. According to the model, therefore, the treatment should, by 1998, result in declines in exchangeable Ca and Mg that are 47 and 9 kg ha^{-1} greater in West Bear than in East Bear soils. Based on the MAGIC simulation we could conclude that the observed differences in the soils in 1998 (66 and 27 kg ha^{-1} for Ca and Mg, respectively) might have resulted from an initial difference of approximately 19 kg ha^{-1} for both exchangeable Ca and Mg before treatment, with subsequent higher losses of exchangeable cations in West Bear Brook increasing the differences to the 1998 values.

The measured stream flux data indicate that, over the period 1989 to 1998, the cumulative Ca and Mg export from West Bear was in excess of the cumulative Ca and Mg export from East Bear by 55 and 11 kg ha^{-1}, respectively (corrected for differences that existed before treatment began). The model simulations produced a similar result, with West Bear fluxes of Ca and Mg exceeding East Bear fluxes by 70 and 20 kg ha^{-1}, respectively. Using the model simulations, it is possible to partition these simulated excess fluxes between increased losses of exchangeable base-cations due to the treatment, and differences in mineral weathering between the two watersheds. This correction to the simulated results is conceptually similar to the correction applied to the observed data for pre-treatment differences in stream fluxes. Subtracting the cumulative weathering differences in the model provides a corrected excess base cation flux that is derived only from the cation exchange processes that are accelerated by the treatment. Applying this correction to the simulation values results in West Bear fluxes of Ca and Mg exceeding East Bear fluxes by 45 and 9 kg ha^{-1}, respectively.

Under the assumption that atmospheric inputs of base cations to each watershed were approximately the same and that the treatment did not significantly increase mineral weathering, the excess stream cation flux observed in West Bear must have as its source the pool of exchangeable base cations in the watershed soils and/or pre-existing differences in weathering in the watershed soils. This leads to the expectation that the excess fluxes of Ca and Mg from West Bear compared with East Bear over the treatment period must equal the excess declines in exchangeable Ca and Mg that occurred in West Bear soils as a result of the treatment. In other words, the excess Ca and Mg fluxes that were observed and corrected for pretreatment differences (55 and 11 kg ha^{-1}) and that were simulated by the model as being derived from cation exchange reactions alone (45 and 9 kg ha^{-1}) should be the same as the differences in the soil pools that were observed in 1998 (66 and 27 kg ha^{-1}) or that were corrected by the model for differences that existed before treatment began (47 and 9 kg ha^{-1}). However these observed and simulated data are compared, the agreement is remarkably good.

CONCLUSIONS

Nine years of amendment of the West Bear watershed with N and S produced a response in stream and soil chemistry that is consistent with our modern understanding of cation-exchange phenomena in soils, and particularly the initial predicted response of a forested watershed to increased N and S deposition. Stream chemistry integrates a wide range of whole watershed processes that result in the response to the treatment at BBWM. West Bear stream chemistry showed an accelerated loss of base cations, particularly Ca, in response to treatments compared with the reference East Bear stream. Intensive soil investigations revealed differences between watersheds in exchangeable Ca and Mg that are strikingly consistent with the cumulative excess export of Ca and Mg from the West Bear watershed after the initial 8 yr of treatment. Changes in Ca and Mg storage and fluxes within the watersheds, such as foliar composition changes, biomass accumulation, organic matter mineralization, atmospheric deposition of base cations, and mineral weathering rates may occur but are judged to be insignificant relative to soil exchange phenomena in the BBWM experiment to date. The good agreement between excess stream export and watershed differences in soil exchangeable Ca and Mg suggests that the exchangeable base-cation pools were the primary source of increased stream Ca and Mg export and dominated initial watershed buffering to acidification during the first decade of treatment. MAGIC model simulations of changes in soil BS_e, driven by the long-term record of stream chemistry in both East and West Bear, agreed well with measured soil exchangeable cation differences and further supported the conclusion that much of the initial buffering was simple base-cation exchange that resulted in the loss of approximately one third of the soil exchangeable base-cation pools adjusted for initial differences between watersheds. We conclude that we have induced, under the experimental conditions at the Bear Brook Watershed in Maine, documented soil exchangeable base-cation depletion and stream acidification of a forested New England watershed.

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