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IMPLICATIONS OF SODIUM MASS BALANCE FOR INTERPRETING THE CALCIUM CYCLE OF A FORESTED ECOSYSTEM

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Abstract. Disturbance of forest ecosystems, such as that caused by harvesting or acid deposition, is thought to alter the ability of the ecosystem to retain nutrients. Although many watershed studies have suggested depletion of available calcium (Ca) pools, interpretation of ecosystem Ca mass balance has been limited by the difficulty in obtaining mineral weathering flux estimates. While many studies have suggested that weathering flux is insufficient to maintain available soil pools, measurements of concomitant changes in available soil pools are rare. Here, we critically examined application of the Ca:Na ratio method in interpreting the long-term Ca budget of six northern hardwood watershed ecosystems at the Hubbard Brook Experimental Forest, Woodstock, New Hampshire, USA. Storage of sodium (Na) in biomass and secondary minerals and on cation exchange sites was low enough so that net ecosystem Na loss was essentially equivalent to mineral weathering flux. Mineral chemistry and mass balance considerations constrained the Ca:Na ratio of weathering products to a sufficiently narrow range that spatial and temporal changes in the ecosystem Ca:Na ratio could be interpreted as changes in contribution of available Ca pools to ecosystem loss. Depletion of available Ca pools was greater in the three experimentally manipulated watersheds with aggrading biomass compared to three reference watersheds with relatively mature forest conditions. Although accelerated loss of Ca in the first few years following disturbance has been documented by prior studies, this study suggests that excess Ca loss continues for at least three decades after treatment, with no evident trend toward the conditions shown in the reference watershed. It is not likely that changes in previously quantified Ca pools account for this sustained loss, suggesting that a previously unstudied Ca pool or release mechanism may be important in ecosystem response to disturbance. Possible sources include Ca oxalate, which is known to accumulate in forest soils, but has not been considered in the context of an ecosystem mass balance.

Key words: calcium cycle; Ca:Na ratio; disturbance; forest ecosystems; mineral weathering; nutrient cycling; sodium mass balance.

INTRODUCTION

Nutrient mass balance studies conducted at the watershed scale have commonly concluded that calcium losses exceed inputs, implying depletion of ecosystem pools (Federer et al. 1989, Likens and Bormann 1995, Bailey et al. 1996, Likens et al. 1996, 1998, Huntington et al. 2000). The extent of this phenomenon and its ecological consequences in terms of forest productivity and ecosystem function are topics of much current research (Binkley and Hogberg 1997, Markewitz et al. 1998, McLauglin and Wimmer 1999, Driscoll et al. 2001). In particular, Ca has been shown to affect cold tolerance of red spruce (DeHayes et al. 1997), to be a predisposing factor in sugar maple multiple stress syndrome (Horsley et al. 2002), and to be important in regulating ecosystem processes such as formation and stabilization of soil organic matter (Oyonarte et al. 1994), litter decomposition (Ulrich and Matzner 1986), and acid–base status of soils (van Breeman et al. 1983, Binkley and Richter 1987) and aquatic habitats (Baker and Christensen 1991). A general lack of coupled long-term soil and ecosystem studies contributes to scientific uncertainty about the nature and extent of soil dynamics (Richter and Markewitz 2001) and resulting impacts on ecosystem structure and function. In light of the controversy and potential implications of Ca depletion, there is a need to review and refine techniques used to quantify calcium mass balance and thoroughly examine the strength of existing data for inferring ecosystem dynamics.

In a review of watershed mass balance studies across the eastern United States, Federer et al. (1989) contended that Ca is the nutrient most likely to be depleted from available pools due to losses from acid deposition induced leaching and forest harvesting. They pointed out that uncertainty in weathering flux estimates limits accurate assessment of this phenomenon. As the Ca soil exchange pool is typically several orders of magnitude larger than estimates of weathering flux, small and perhaps undetectable changes in cation exchange storage could be much larger than the measured precision or even the magnitude of the weathering flux.

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Recent mass balance studies have used natural tracer techniques to constrain weathering flux estimates and thus refine estimates of inferred changes in available base cation pools. Strontium isotopes (Bailey et al. 1996) and Ca:Na ratio (Likens et al. 1996, 1998) have been used to refine the mass balance approach; both approaches confirmed earlier work suggesting that atmospheric inputs and mineral weathering flux were insufficient to explain hydrologic losses. In particular, the Ca:Na ratio approach has been used to constrain weathering flux estimates in geochemical studies on granitic terrain where the weathering of plagioclase feldspar is a dominant reactant releasing both Ca and Na (Garrels and McKenzie 1967, Clayton 1988, Hyman et al. 1998). The Ca:Na ratio of weathering reactants multiplied by the net ecosystem loss (streamwater output minus atmospheric deposition input) of Na can be used to estimate Ca weathering flux, and thus determine the relative contribution of weathering flux and net change in soil storage in hydrologic loss of Ca. For example, based on the average composition of bedrock (Ca:Na = 0.24) and long-term measurement of net ecosystem Na loss, Likens et al. (1996, 1998) calculated a mean weathering flux of 53 mol $Ca \cdot ha^{-1} \cdot yr^{-1}$ and a cumulative change in the available soil Ca pool of −21 100 mol Ca/ha from 1940 to 1995. The annual (1995) ecosystem depletion rate of −270 mol Ca/ha is five times the estimated weathering flux (Fig. 1a).

Despite the use of the Ca:Na ratio to estimate weathering, there has been no critical assessment of the uncertainty in the results from use of this method in ecosystem studies. Assumptions regarding the identification of weathering reactants and the conservative nature of Na are rarely stated or tested. We illustrate the potential implications in Fig. 2, a sensitivity analysis of the Ca depletion estimate of Likens et al. (1996). For a range of Ca:Na ratios of weathering reactants from 0.2 to 1.0, typical of sodic to intermediate plagioclase, which is the most common Ca-bearing soil mineral at Hubbard Brook Experimental Forest (HBEF), cumulative (1940–1998) ecosystem depletion estimates vary by a factor of two, from −20.7 to −10.1 kmol Ca/ha. This range corresponds to a reduction in exchangeable Ca in the solum (Oa to base of B horizon) from 76% to 60%, relative to recent levels measured in 1983 (Johnson et al. 1991*b*, Likens et al. 1998). For the same range in Ca:Na reactant ratios, the model yields estimates of annual (mean of the last 5 yr) soil-storage change ranging from a net depletion of -104 mol $Ca \cdot ha^{-1} \cdot yr^{-1}$ to net storage of 90 mol $Ca \cdot ha^{-1} \cdot yr^{-1}$. A Ca:Na ratio of 0.63 corresponds to a current net depletion rate of zero. A Ca:Na ratio <0.63 suggests that net depletion of ecosystem pools is continuing, while ratios greater than this value suggest that the depletion has ceased and recovery is underway with net storage of Ca. Similarly, a Ca:Na ratio of 0.72 corresponds to a cumulative depletion of 13.8 kmol Ca/ha, equivalent to net storage in biomass during the period. Ratios >0.72 imply that the loss of available Ca can be accounted for by net biomass storage, while ratios <0.72 suggest ecosystem losses in excess of that accounted for in net biomass uptake, raising the possibility that acid deposition-induced leaching may have affected ecosystem pools. Therefore, within this range of uncertainty is a wide range of scenarios critical to interpretation of long-term trends in ecosystem response to disturbances such as acid deposition and harvesting.

The objectives of our study were to examine the robustness of Ca mass balance by comparison with Na mass balance and to assess the implications of Ca:Na ratios as tools in interpreting ecosystem loss of Ca. Constraints in the use of an estimated Ca:Na ratio of weathering release were evaluated on the basis of geologic evidence and ecosystem mass balance considerations. Geologic origin of soils was investigated to determine the range of Ca:Na ratios of weathering reactants and address potential for differences, which might impact interwatershed comparisons. Temporal variation in ecosystem Ca:Na was examined as an indicator of processes contributing to Ca loss from six adjacent, gaged watersheds at the HBEF. In particular, this ratio contrasts patterns of Ca loss between relatively mature (biomass at steady state) and experimentally disturbed (aggrading biomass) forest ecosystems. We propose that dynamics of a previously ignored pool, such as soil Ca oxalate, best explain these patterns. Results of this analysis suggest a revision is needed in our understanding of the response of forest nutrient cycles to disturbance.

Methods

Setting

The Hubbard Brook Experimental Forest (HBEF) is within the southern White Mountains of central New Hampshire (43°56′ N, 71°45′ W). The climate is humid continental with a mean annual precipitation of 140 cm and 90 cm of runoff (Federer et al. 1990). The south-facing experimental watersheds are underlain by sillimanite-grade schist and calc-silicate granulite of the Silurian Rangeley Formation. The retreat of the Wisconsinan glacier ~14 000 years ago left a mantle of sandy loam glacial till from zero to 3.0 m thick. Soils are predominantly Haplorthods with minor inclusions of Inceptisols and Histosols. Mean solum thickness (to the base of the B horizon) is 0.5 m.

Forests are composed mostly of northern hardwoods dominated by *Acer saccharum* Marsh. (sugar maple), *Betula alleghanensis* Britt. (yellow birch), and *Fagus grandifolia* Ehrh. (American beech). At the highest elevations and in areas with shallow-to-bedrock soils there are conifer-dominated stands composed of *Picea rubens* Sarg. (red spruce), *Abies balsamea* (L.) Mill. (balsam fir), and *Betula papryifera* var. *cordifolia* (Regel) Fern. (mountain paper birch). Of the six south-facing experimental watersheds (Fig. 3), three (W1, W3, W6) are steady-state biomass second-growth for-

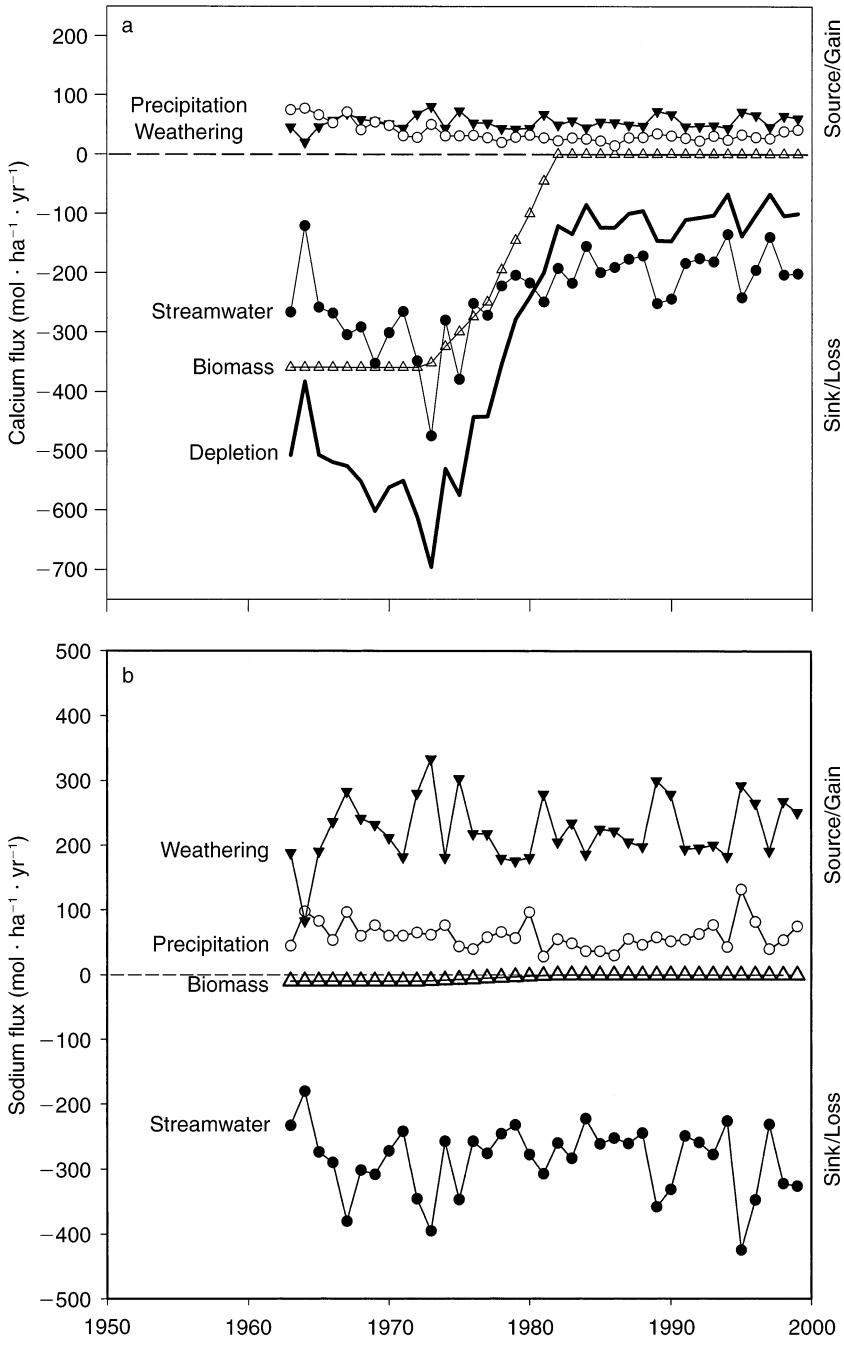

FIG. 1. Long-term mass balance of (a) calcium and (b) sodium for Hubbard Brook Experimental Forest Watershed 6 (after Likens et al. 1996). Precipitation, weathering, and streamwater flux estimates are based on weekly measurements. Net biomass storage is based on an inventory conducted every five years (open triangles), with interpolated values for the intervening years. Depletion is calculated by difference.

ests following logging from 1880 to 1920 and hurricane damage in 1938 (Bormann and Likens 1979). The other three have aggrading biomass third-growth forests following recent harvesting or deforestation experiments. Watershed 2 was clearfelled during the winter of 1965–1966 and then treated with herbicide to prevent regrowth during 1966–1968. Watershed 4 was strip harvested, with all stems removed in three operations; each harvesting removed every third 25-m wide strip along an elevational contour during fall/winter of 1970, 1972, and 1974. Watershed 5 was whole-tree harvested during the winter of 1983–1984 with all biomass (stems, limbs, branches) removed from stems >5cm dbh (93% aboveground biomass removal; Hornbeck et al. 1997).

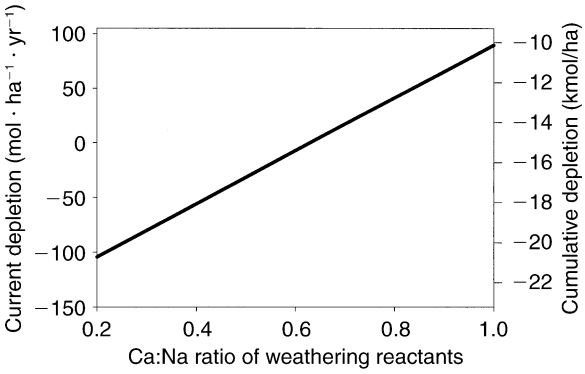

FIG. 2. Sensitivity of modeled current (mol·ha^{-1}·yr^{-1}) and cumulative (kmol/ha) depletion of soil calcium depending on Ca:Na ratio of weathering reactants.

Mass balance

The small watershed approach (Likens and Bormann 1995) was used to calculate nutrient budgets on an annual basis. The mass balance for a base cation x is determined by inputs of atmospheric deposition (P_x) and mineral weathering flux (W_x), stream output (S_x) and changes in ecosystem pools, including net biomass uptake (B_x), secondary mineral formation (M_x), and change in available soil pools (ΔA_x) as expressed by

$$P_x + W_x = S_x + B_x + M_x \pm \Delta A_x. \quad (1)$$

Operationally, available base cation pools are considered to be equivalent to, and are commonly referred to, as exchangeable soil pools (cf., Johnson et al. 1991*b*). However, for the purposes of this analysis, we have used the term available pool, keeping in mind the possibility that other forms of base cation storage, which may be at least partially available to ecosystem processes, may not be detected by salt extraction.

Ecosystem pools

The use of Na as an indicator of weathering is dependent on its conservative behavior in the ecosystem; that is, storage of Na in ecosystem pools including biomass, forest floor, secondary minerals, and soil exchange must be negligible so that potential changes in storage do not contribute significantly to ecosystem loss. When these conditions are met, Eq. 1 simplifies to stream output minus bulk precipitation input equals Na weathering flux. Likens and Bormann (1995) estimated standing stocks of Na at HBEF of aboveground biomass (70 mol/ha), belowground biomass (153 mol/

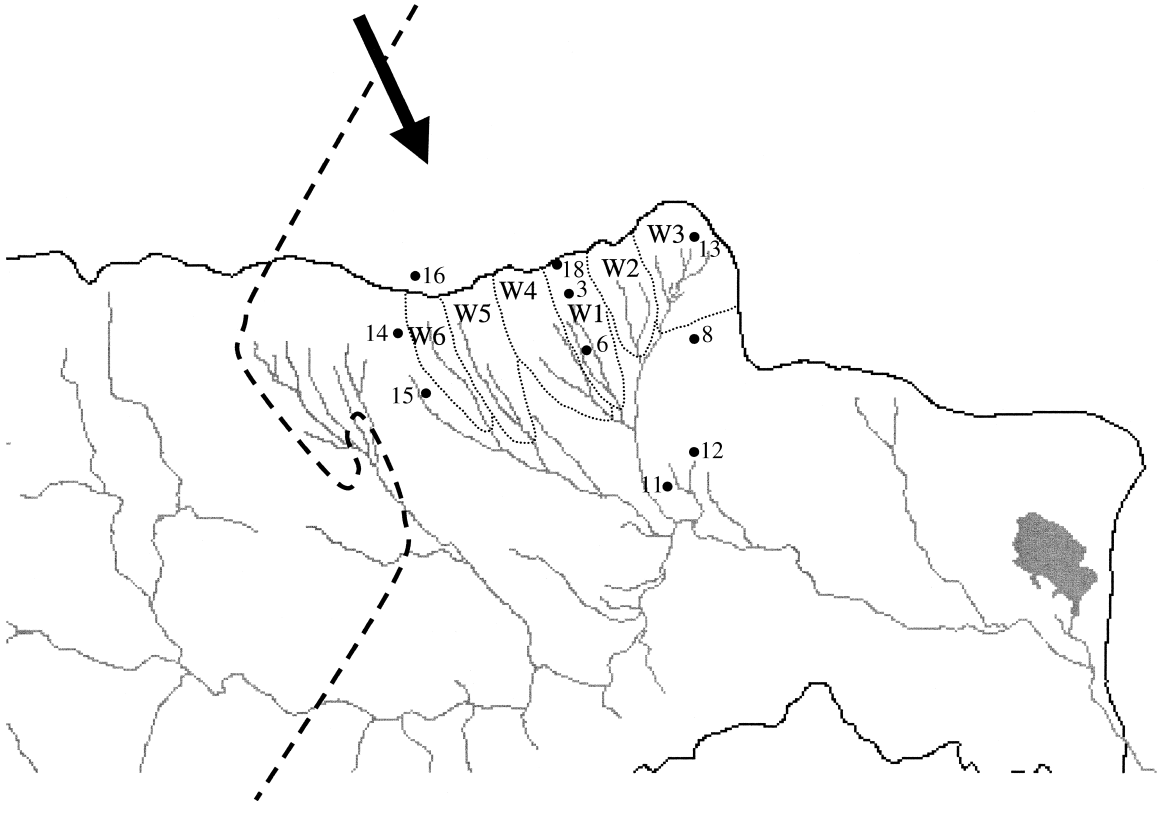

FIG. 3. Locus map of Hubbard Brook Experimental Forest Watersheds 1–6 (W1–W6). The heavy dashed line indicates the approximate location of the bedrock contact between the Rangeley Formation to the east and the Kinsman granodiorite to the west. The arrow indicates the direction of glacial movement and subsequent transport of materials in forming soil parent material. Numbered dots show the location of soil pits analyzed for lithologic composition.

ha), and forest floor (157 mol/ha). These pools are relatively small, together totaling to an amount similar to annual streamwater loss. By contrast, the biomass and forest floor Ca pools are, respectively, 60 and 45 times greater than annual streamwater loss (Likens et al. 1998). Only a large and sudden change in the biomass or forest floor pools would contribute measurably to Na losses. Repeated measurements on the reference watershed, W6, document no measurable change in biomass since 1982 (Likens et al. 1998). Similarly, no change in forest floor mass has been detected over the last 20 yr (Yanai et al. 1999). Net Na uptake prior to reaching steady state (Fig. 1b) was estimated to be 6.5 $mol \cdot ha^{-1} \cdot yr^{-1}$ (Likens and Bormann 1995).

Hyman et al. (1998) found mica, mixed mica vermiculite, and hydroxy interlayered vermiculite to be the dominant minerals in the clay fraction at the nearby Cone Pond watershed. Calcium and Na are not structural components of these clay minerals (Hurlbut and Klein 1977) yet may be present in trace quantities. R. April (*personal communication*) reported Na content of 0.5% for clays in Adirondack Mountain region Spodosols. Based on a typical clay content of till soils in the White Mountains of 2% (Pilgrim and Harter 1971, Hoyle 1973) and a HBEF solum mass of 326 kg/m^2 (Johnson et al. 1991*a*), there are ~14 000 mol Na/ha in clay. Assuming that this clay is the secondary product of weathering that occurred in situ in the ~14 000 yr since till deposition, a mean of 1 mol Na/ha would be sequestered annually in secondary minerals. This amount is insignificant compared to streamwater losses >200 $mol \cdot ha^{-1} \cdot yr^{-1}$. Moreover, it likely is too high an estimate as some clay probably was derived from past aeolian deposition, inherited from parent material from preglacial weathering, or is simply clay-sized particles of primary minerals.

The amount of Na on soil cation exchange sites generally is considered insignificant to ecosystem pools, but is rarely quantified (Johnson et al. 1991*b*, Schad 1996). Previous workers have reported exchangeable Na $\leq$ 1 $cmol_c/kg$ (e.g., David and Lawrence 1995). In our own measurements (S. Bailey, *unpublished data*), Na extracted by 1M NH_4Cl (Blume et al. 1990) was generally <0.05 $cmol_c/kg$; problems with extract concentrations close to analytical detection limit and trace quantities of Na in reagents prevented precise determination at such low levels.

As Na is a poor competitor for cation exchange sites, it is probable that much of the Na measured in soil extracts is not attributable to cation exchange capacity, but was present as a dissolved ion in soil water before sample drying. For a mass balance conducted on a water-year basis, interannual variations in soil water content are minimized by beginning the water-year in June, after spring recharge. In this case, and because there are no long-term trends in Na in precipitation or streamwater (Fig. 1b), changes in available soil Na are negligible.

In summary, storage of Na in biomass, soil exchange pools, and secondary minerals is small compared to other terms in the mass balance. Thus the conditions are met at HBEF for net loss of Na to approximate Na weathering flux. We show in Fig. 1b the long-term model for Na mass balance at HBEF with Na weathering flux calculated by difference between streamwater output and bulk precipitation input.

Ecosystem mass balance

Inputs and outputs of water and major ions have been measured at the six south-facing watersheds at HBEF (Fig. 3) since 1963. Ecosystem inputs of base cations include wet and dry deposition, with nearly 80% falling as dissolved ions in bulk precipitation (Likens et al. 1998). Most dry deposition of base cations is particulate, which is mostly accounted for by open funnel-type precipitation collectors (Baker 1990, Bailey et al. 1996, Likens et al. 1998). Thus bulk precipitation collectors at HBEF approximate total atmospheric deposition of base cations (Likens et al. 1998). Watershed losses are measured by weekly streamwater samples collected for chemical analysis and continuous records of streamwater discharge measured at gaging stations. Due to essentially watertight bedrock, negligible flux occurs through deep seepage (<1% of atmospheric inputs). Instrumentation and analytical procedures are described fully in Likens and Bormann (1995) and Buso et al. (2000). Uncertainties incorporated in this approach include error in annual water flux measured by gages, estimated as 5% or less by Winter (1981) and determination of cation concentrations, estimated at 5% for precipitation and 1% for streamwater (Buso et al. 2000). Ecosystem Ca pools have been measured by various studies and compiled by Likens et al. (1998). Biomass storage is measured every five years by 100% inventory of the reference watershed. The best estimate of available soil pools is measurement of exchangeable Ca in W5 before treatment in 1983 (Johnson et al. 1991*a*, *b*).

To evaluate weathering flux of Ca by the Ca:Na ratio method, mineralogy and Ca and Na content of potential weathering reactants was compiled from regional geology studies reported in the literature. We supplemented these data with ion microprobe analyses of bedrock samples collected at HBEF. To evaluate potential spatial variability in mineralogy, which might affect watershed comparisons, lithologic composition of glacial till, the soil parent material, was determined by collecting and identifying 100–150 pebbles (1.9–7.6 cm) from the B and upper C horizons of each of 10 soil pits (Fig. 3). Pebbles were identified under a binocular microscope by comparison with a reference collection of White Mountain bedrock samples.

Results and Discussion

Variation in Ca:Na ratio of weathering reactants

In glaciated terrain where soil parent material is composed of transported sediments, minerals from several

TABLE 1. Chemistry of minerals possibly contributing to weathering flux of Ca and Na at Hubbard Brook Experimental Forest.

Mineral	Source	Volume (%)	Ca (%)	Ca:Na molar ratio	Reference
Plagioclase	W5 soil B horizon	20	2.9	0.24	Likens et al. (1998)
Plagioclase	Rangeley Formation mica schist	10	3.0	0.25	Williams and Billings (1938); Billings and Fowler-Billings (1975)
Plagioclase	Rangeley Formation calc-silicate	30	13.7	19.0	this study
Plagioclase	Kinsman Granodiorite	35	3.8	0.33	Englund (1976)
Plagioclase	Ammonoosuc Volcanics	40	6.0	0.67	Billings (1937)
Hornblende	Rangeley Formation calc-silicate	25	8.4	14.0	this study
Hornblende	Ammonoosuc Volcanics	45	8.8	3.9	Billings (1937); Billings and Fowler-Billings (1975)
Epidote	Rangeley Formation calc-silicate	3	17.1	650.0	this study

lithologic sources contribute to soil mineral content. As a result, the Ca:Na ratio of a range of minerals must be considered. Two alternative hypotheses for control of Ca and Na release by weathering reactions are: (1) a major mineral (15–20%), plagioclase, is the dominant reactant; or (2) minor minerals (e.g., apatite, hornblende, pyroxene, or epidote group minerals), although present in smaller amounts (0.1–2.0%), have a higher Ca content and faster dissolution rates and, therefore, control weathering release of Ca. A third hypothesis, that weathering of calcite (calcium carbonate) might be important, was rejected. No carbonate has been detected in soil or glacial till at HBEF (S. Bailey, *unpublished data*) based on samples measured by the pressure calcimeter method (Loeppert and Suarez 1996; detection limit 0.05% calcite). Furthermore, strontium isotopic composition of streamwater is more radiogenic (especially at base flow) than would be expected with a carbonate weathering source (Bailey et al. 1996; S. Bailey, *unpublished data*).

The watershed bedrock may contribute through weathering of the bedrock surface, and through its contribution to glacial till. As weathering flux is dependent on the mineral surface area exposed to drainage waters, bedrock weathering likely is limited by its small surface area compared to that of soil particles. The upper Rangeley Formation, the bedrock map unit underlying the study watersheds (Fig. 3), is composed of two contrasting lithologies (mica schist and calc-silicate granulite; Lyons et al. 1997). The lithology of all outcrops exposed in a representative area (W5) was determined by measuring the proportion of outcrop surface of each rock type. Measurement of 16 outcrops revealed that the Rangeley Formation in this watershed is 98.4% mica schist and 1.6% calc-silicate granulite. Both lithologies contain plagioclase feldspar (Table 1). Although the granulite makes up only a small portion of the formation, it has a greater plagioclase content and a more calcic plagioclase composition. These two compositions range in Ca:Na molar ratio from 0.25 to 19.0 (Table 1). Because calcic plagioclase (An_{90}) weathers at a rate two orders of magnitude faster than sodic plagioclase (An_{25}; Blum and Stillings 1995), a composite Ca:Na ratio for weathering of the Rangeley Formation is skewed toward the calcic composition (Ca:Na = 3.7). While plagioclase is the major Ca- and Na-bearing phase in the mica schist, the calc-silicate granulite also includes other Ca-rich phases such as hornblende and epidote, with Ca:Na ratios as high as 650 (Table 1).

The dominant lithology of pebbles (1.9–7.6 cm mean diameter) was a porphyritic granodiorite (Table 2), probably derived from the Kinsman granodiorite, the bedrock unit immediately northwest of the experimen-

TABLE 2. Lithology of pebbles from soil B and C horizons in the vicinity of Watersheds 1–6.

Lithology	Pit										Mean
	3	6	8	11	12	13	14	15	16	18	
Porphyritic granodiorite	26†	71	59	83	81	58	65	86	78	71	68
Schist	63	13	2	7	8	19	19	1	2	3	14
Granoblastic granite		1	18	1	4	3	2	3	13	1	4
Pegmatite	0	1	3	2	2	0	10	4	2	8	3
Diabase	1		4	2	3	11		1	0	6	3
Miscellaneous		1	4	1	1	6	4	1	3	2	2
Amphibolite	2	5	5	2	0	1	1	1	1	2	2
Biotite granite	5	1	0	2	0	1		3	1	3	2
Calc-silicate	1	8	1	1	1	0				2	1
Quartzite	2	0	3	0	1	1		1		1	1

† All numbers are percentages by mass from samples of 100–150 pebbles.

tal watersheds (Fig. 3). On average, this lithology contributed 68% by mass of the pebbles in the till. Plagioclase feldspar is the major Ca-bearing phase in the Kinsman, and is slightly more calcic than the plagioclase in the Rangeley Formation schist (Table 1). The second most common lithology was mica schist, the dominant lithology of the local bedrock. Other granitic rocks, calc-silicates, amphibolite, and miscellaneous rocks contributed the remainder (Table 2). Most of the calc-silicates probably were derived from the local Rangeley Formation. Amphibolite, a minor but consistent component of the till, may be important as a source of weathering reactants due to its high content of relatively calcic plagioclase and hornblende (Table 1).

Although a decrease in the contribution of porphyritic granodiorite with increasing distance from the bedrock contact (toward the southeast) might be expected, no regular trends in content of this or any of the other lithologies present in glacial till were apparent. One site, pit 3, had substantially higher schist content than the other nine sites (Table 2). This pit was in a boulder field near the base of a bedrock cliff. Pebbles in pit 3 were more angular than those in other pits, suggesting that the higher schist content was due to local inputs rather than glacial transport. It is expected that other locations in the watersheds downslope of bedrock cliffs would show a similar disproportionate influence of the underlying bedrock. Other than local variation due to the influence of such cliffs, neither the pebble counts nor the bedrock map pattern suggest differences among watersheds in the composition of weathering reactants.

Likens et al. (1998) reported that limited ($n = 12$) analysis of Bs_2 horizon samples yielded a mean plagioclase composition of An_{19} (Ca:Na ratio = 0.24; Table 1). However, given the geologic complexity of bedrock and till, including nearly the entire compositional range of plagioclase (Ca:Na ratio from 0.25 to 19.0; Table 1), much more analysis would be required to portray accurately the distribution of plagioclase composition present in the watersheds. Other Ca minerals, present both in the bedrock and till, include hornblende and epidote. These minerals range in Ca:Na ratio from ~4 to 650. As there is no evidence for differences among watersheds in the lithologic composition of bedrock or till, little spatial variability in the Ca:Na ratio of ions released from weathering is likely across this portion of HBEF. To date, analyses suggest a large range in Ca:Na ratio of minerals in both the bedrock and the glacial till.

Evaluation of ecosystem Ca:Na ratio as a process indicator

Despite the utility of net ecosystem Na loss in estimating Na weathering flux, the great range in Ca:Na ratio of potential weathering reactants would seem to preclude the use of this ratio to translate the Na weathering flux estimate to Ca. However, through mass balance considerations, the ecosystem Ca:Na ratio can also constrain the Ca:Na ratio of weathering release to a sufficiently narrow range to suggest important implications for ecosystem Ca dynamics. By simple algebra, Eq. 1 can be rewritten as

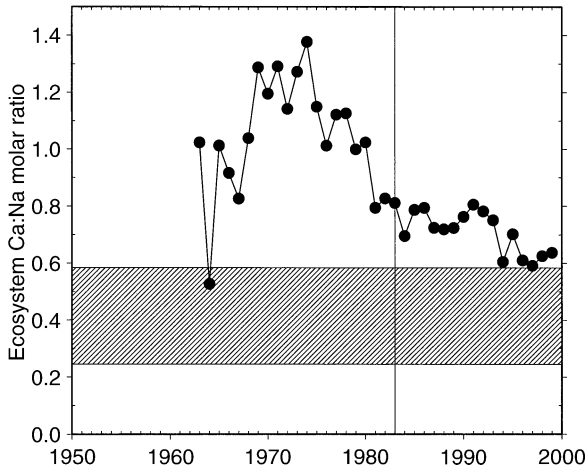

FIG. 4. Temporal trends in ecosystem Ca:Na ratio determined by measurements of streamwater loss and bulk precipitation input, for Hubbard Brook Experimental Forest Watershed 6. The shaded box shows the range of Ca:Na ratio of weathering release constrained by mineral composition at the low end, and by mass balance of Na at the high end. The vertical line separates periods of net biomass accumulation from steady-state biomass storage since 1983.

$$S_x - P_x = W_x - B_x - M_x \pm \Delta A_x. \quad (2)$$

As discussed previously (see *Methods*: *Ecosystem pools*), the secondary mineral formation term is negligible for Ca while secondary mineral formation, biomass uptake, and available soil terms are negligible for Na. Therefore, the following ratio, which we define here as the ecosystem Ca:Na ratio, can be derived from Eq. 2 as

$$\text{ecosystem Ca:Na} \equiv (S_{Ca} - P_{Ca})/(S_{Na} - P_{Na}) = (W_{Ca} - B_{Ca} \pm \Delta A_{Ca})/W_{Na}. \quad (3)$$

Temporal change in the ecosystem Ca:Na ratio, as calculated by measurements of atmospheric deposition and stream output for a small watershed, can be interpreted as changes in ecosystem processing of Ca, as described by the right side of Eq. 3. Changes in weathering flux can be estimated by monitoring net Na flux. If this is done in conjunction with monitoring variation in the ecosystem Ca:Na, changes due to variation in the storage of available soil Ca (ΔA_{Ca}) and accumulation of biomass (B_{Ca}) can also be inferred. Where available soil and biomass Ca pools are at steady state (i.e., no change between measurement periods), the ecosystem Ca:Na equals the Ca:Na ratio of weathering release. Also, when biomass storage is constant (i.e., for a steady-state biomass forest), changes in the ecosys-

tem Ca:Na ratio can be interpreted to represent varying contributions of available soil Ca pools to Ca export.

We show in Fig. 4 the variation in the ecosystem Ca:Na ratio over the period of record for W6, indicating a decreasing trend in the ecosystem Ca:Na ratio, even since 1983 when the forest reached steady state (net biomass uptake = 0; Likens et al. 1994). This pattern suggests that the contribution of Ca lost from available ecosystem pools has decreased over time, consistent with the model of Likens et al. (1996), which showed a decrease in Ca depletion rate since 1974 (Fig. 1a). In other words, the ecosystem Ca:Na ratio was most influenced by Ca depletion from available pools in 1974 when it peaked at 1.38. The ecosystem Ca:Na ratio was closest to the ratio of weathering reactants in 1997 when the lowest ratio (0.59) was observed. While 0.24 is the lowest Ca:Na ratio determined for any possible weathering reactants, the minimum observed ecosystem Ca:Na ratio of 0.59 provides an upper bound on the Ca:Na ratio of weathering release. When net biomass uptake is zero, the Ca:Na ratio of weathering release could be higher than the ecosystem Ca:Na ratio only if the ecosystem had a mechanism for storing Na. Since Na storage is minimal in biomass, the available soil pool, and secondary minerals, there is no known mechanism to accomplish this storage.

A range of Ca:Na ratio of weathering release from 0.24 to 0.59 could be achieved by combinations of weathering of plagioclase from the various possible sources, or by combinations of plagioclase weathering and weathering of Ca-rich minerals such as hornblende, epidote, or apatite. Blum et al. (2002) suggest that plagioclase and apatite are the main weathering sources of Ca in W1. Within this range of Ca:Na ratio of weathering reactants, the sensitivity analysis presented in Fig. 2 yields cumulative (1940–1998) ecosystem depletion estimates of from −20 200 mol/ha to −15 600 mol/ha, respectively. Current (mean of 1994–1998) soil depletion estimates range from −95 to −10 $mol \cdot ha^{-1} \cdot yr^{-1}$. While this range is slightly lower than the Ca depletion estimate calculated by Likens et al. (1996), the magnitude and implications for long-term ecosystem mass balance are similar.

Comparison of steady-state biomass and aggrading biomass watersheds

Comparison of net Na loss and ecosystem Ca:Na ratio among watersheds reveals differences in weathering flux and dynamics of available soil pools as well as response to experimental disturbance. In Figs. 5–7, each of the south-facing watersheds at HBEF is compared to W6, the biogeochemical reference. There is no trend in Na loss over time for any watershed. This pattern suggests that Na weathering flux is relatively stable over the period of record. Most of the annual variability in net Na ecosystem loss can be explained by variation in streamflow (r = 0.89 for W6), suggesting strong hydrologic control of weathering flux.

Except for the first five years following treatment of W2 and the first two years following treatment of W5, net Na losses from W1, W2, and W5 were on average within 5% of net Na loss from W6, suggesting that weathering flux of Na-bearing minerals is similar among these watersheds. The excess Na flux due to treatment of W2 and W5 was calculated by subtracting the W6 Na flux from the observed flux. This calculation yields an estimate of excess Na flux from W2 of 1745 mol/ha. By contrast, the sum of Na in biomass and in the forest floor was 380 mol/ha. Complete mineralization of these pools over five years could account for only 22% of the excess loss. The most likely explanation of this minor Na response to treatment is a short-term increase in weathering rates. A smaller excess Na loss of 226 mol/ha was calculated for the two years following treatment of W5. No obvious change in Na flux was observed following the progressive strip-cut treatment of W4 (Fig. 6b).

In contrast to the long-term similarity in net Na flux among W1, W2, W5, and W6, net Na flux from W3 and W4 was on average 29%, and 49% greater, respectively, than net Na flux from W6, suggesting a consistently greater weathering flux in these watersheds (Fig. 6a, b). Greater soil depth, finer soil texture, or differences in hydrologic flowpaths or mineralogy could account for greater weathering flux in W3 and W4. The lithologic similarity of bedrock and glacial till suggests that differences in mineralogy are not a likely explanation. Existing soil surveys are not sufficiently detailed to evaluate quantitatively any of the other possibilities.

Untreated W3 shows nearly identical ecosystem Ca:Na ratios as W6 (Fig. 6a), suggesting that both have had a similar history in terms of the relative contributions of weathering and depletion of available pools to Ca export. The other untreated watershed, W1, shows a mean of 23% greater net Ca loss, with a concomitant influence on the net ecosystem Ca:Na ratio (Fig. 5a) suggesting that depletion of ecosystem Ca pools has had a relatively larger contribution to Ca loss in W1. Calcium loss for W1 and W6 was correlated to the sum of acid anions (streamwater nitrate plus sulfate; r = 0.99 and 0.97, respectively). The greater Ca loss for W1 is probably related to lesser S retention of W1 relative to the reference.

Both W2 and W5 showed elevated ecosystem Ca:Na loss in response to treatment. Increased ecosystem Ca:Na ratios were observed for five years in W2 and two years in W5 (Figs. 5b and 7). Unlike net Na loss, which returned to pretreatment conditions after the initial spike, both W2 and W5 showed elevated ecosystem Ca:Na loss continuing to the present. Watershed 4, which showed no clear response in net Na loss to treatment, showed the same long-term trend in the ecosystem Ca:Na (Fig. 6b) as W2 and W5, suggesting that despite the less pronounced disturbance in W4 (Martin et al. 2000), treatment was sufficient to trigger similar

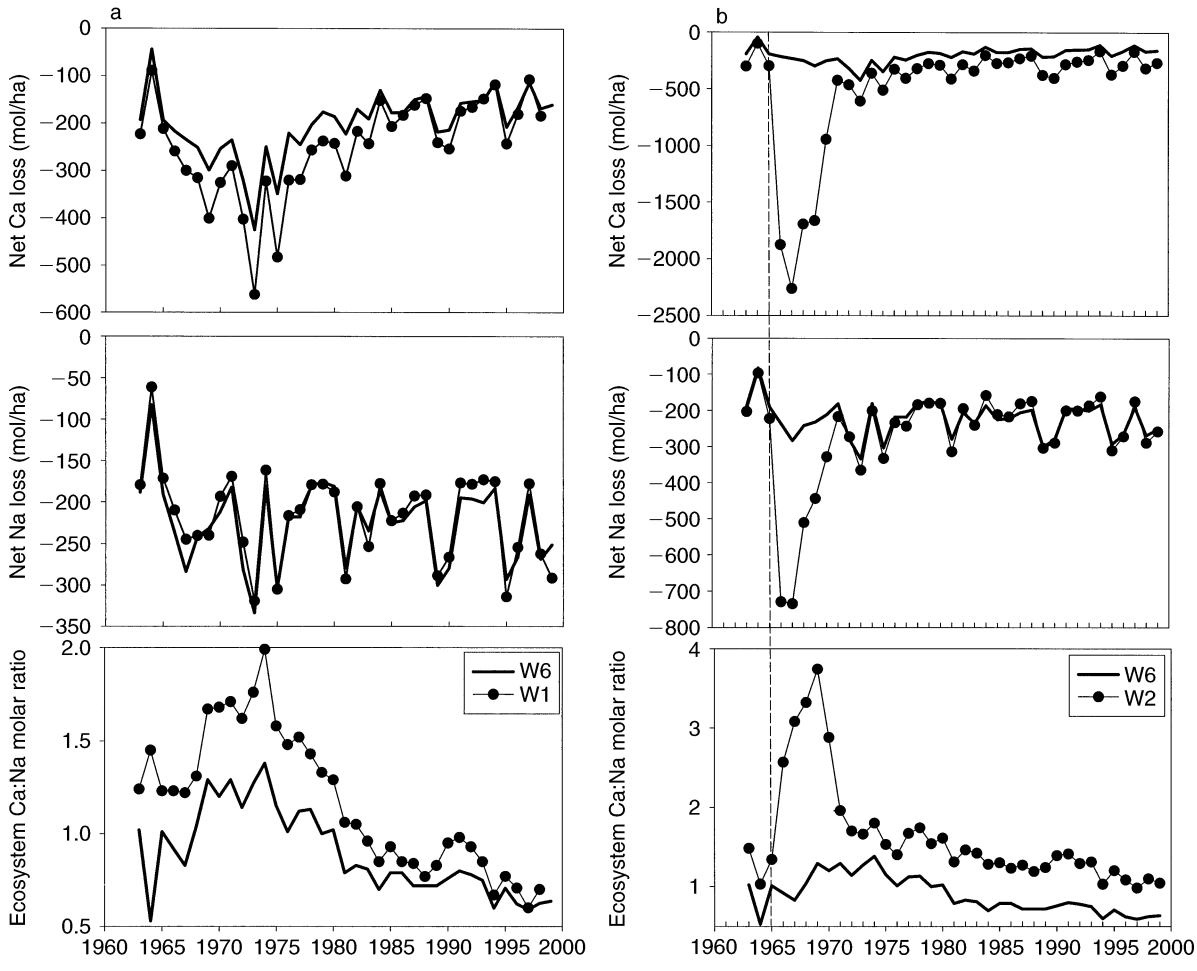

FIG. 5. Temporal trends in net Ca and Na loss (streamwater minus bulk precipitation) and the ecosystem Ca:Na ratio in south-facing watersheds (a) W1 and (b) W2, compared to the reference watershed, W6. Ecosystem Ca:Na ratio was calculated from streamwater and bulk precipitation fluxes by Eq. 3. Vertical dashed lines indicate dates of experimental manipulations for W2.

enhanced depletion of Ca pools. Conversely, ecosystem Ca:Na ratio in the untreated watersheds has decreased during this period. Thus the difference in the ecosystem Ca:Na ratio between steady-state biomass and aggrading biomass watersheds is increasing, with no overlap in this ratio between treated and untreated watersheds since 1983 (Fig. 8).

Enhanced leaching of available Ca pools from W5 is suggested by the 2-yr spike in the ecosystem Ca:Na ratio in W5 immediately after harvest and continuing offset in the ecosystem Ca:Na ratio between W5 and W6 from treatment to the present. An estimate of the minimum excess export of ecosystem Ca over the first eight years since treatment can be estimated by (1) multiplying the net Na flux by the upper possible weathering ratio (Ca:Na = 0.59) to estimate a maximum possible Ca weathering flux, and (2) subtracting the Ca weathering estimate from net ecosystem loss of Ca to determine Ca depletion from available pools. This yields an estimate of additional Ca loss due to treatment of 1300 mol/ha over eight years. The difference between measured biomass growth during the same period (4700 mol/ha; Likens et al. 1998), measured root decay (2600 mol/ha; Likens et al. 1998), and assuming complete decomposition of aboveground biomass debris remaining after whole-tree logging (1290 mol/ha), suggests an additional loss of 810 mol/ha. Johnson et al. (1997) found that exchangeable soil pools were unchanged eight years after whole-tree harvesting of W5. Some Ca source other than exchangeable soil pools, mineral weathering, or atmospheric deposition must have provided the Ca needed to close this mass balance.

Furthermore, the long-term offset in the ecosystem Ca:Na ratios between the reference watershed and all three treated (aggrading biomass) watersheds suggests continuing enhanced depletion of Ca pools long after these early treatment responses, into a period when net biomass accumulation in the regrowing forest is still high while losses from decomposing logging debris and

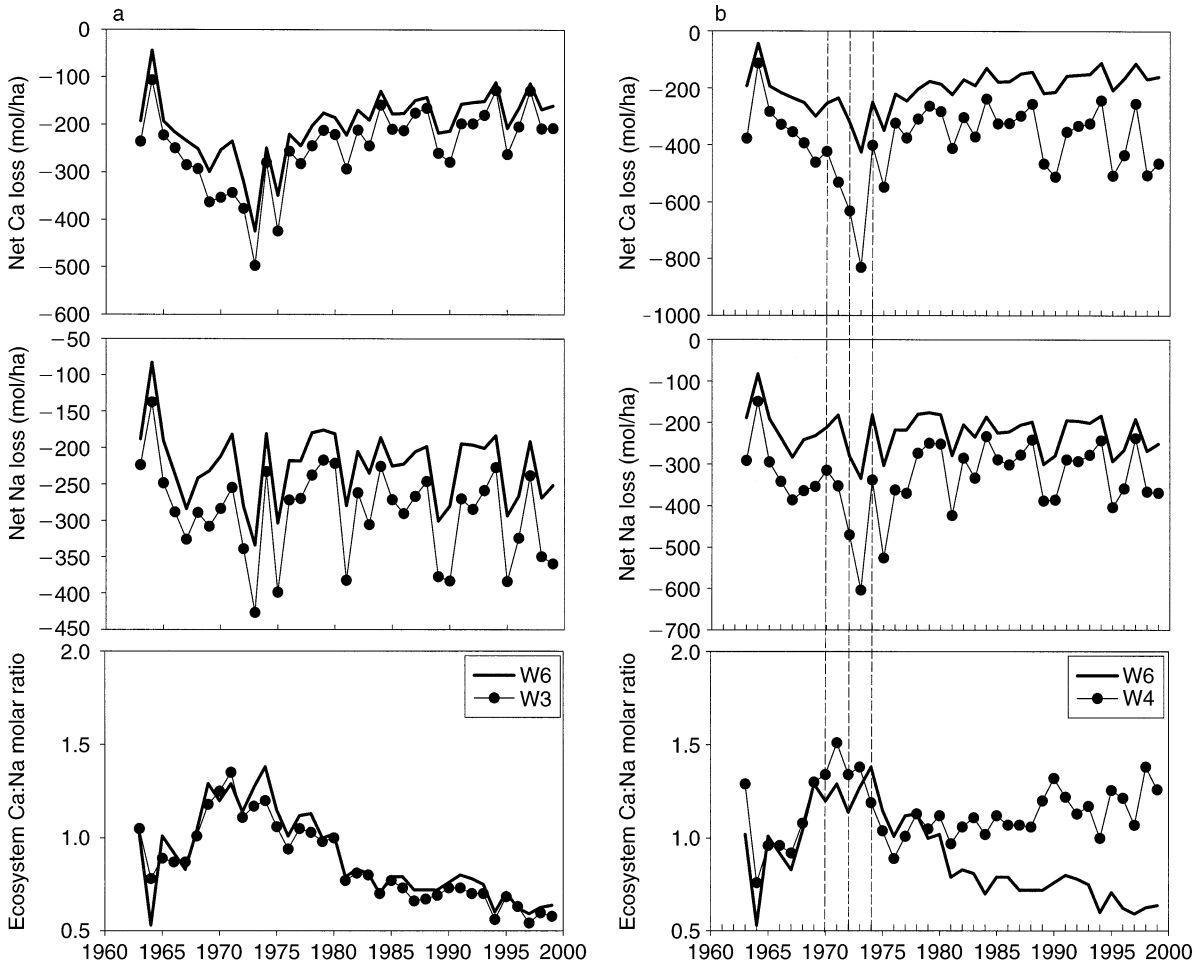

FIG. 6. Temporal trends in net Ca and Na loss (streamwater minus bulk precipitation) and the ecosystem Ca:Na ratio in south-facing watersheds (a) W3 and (b) W4, compared to the reference watershed, W6. Ecosystem Ca:Na ratio was calculated from streamwater and bulk precipitation fluxes by Eq. 3. Vertical dashed lines indicate dates of experimental manipulations for W4.

roots have subsided. This result seems counterintuitive as heavy demand for nutrients by regrowing vegetation might be expected to minimize leaching of Ca. Further, although net export of Ca is highly correlated with net export of acid anions (Likens et al. 1998), the watershed treatments, excepting the nitrate pulse during the first three years after treatment, have not resulted in enhanced export of acid anions relative to the reference watershed (Fig. 9). Besides Ca, the only other parameters in W5 streamwater that show a long-term response to the treatment are pH, which has increased from 5.0 to 5.6 (Fig. 9), acid neutralizing capacity (ANC) which has increased from -11 $\mu mol_c/L$ to $+12$ $\mu mol_c/L$, and an increase in dissolved silica export from 33 to 202 $mol \cdot ha^{-1} \cdot yr^{-1}$. These data indicate that HCO_3^- is currently the anion that is balancing enhanced export of Ca in W5 streamwater. While dissolved silica is primarily a result of mineral weathering, we do not think the silica response can be taken as an indication of a mineral weathering response because, unlike Na, silica is cycled by vegetation, with substantial concentrations seen in biomass and throughfall of certain species, and silica is a primary component of solid weathering products, especially amorphous coatings, whose stability might be altered by soil dynamics.

Hydrogen ion budget considerations suggest that streamwater pH might be expected to decrease during a period of net biomass accumulation following biomass removals by harvesting. In a steady-state biomass ecosystem, uptake of base cations by vegetation is neutral with respect to the H^+ cycle as H^+ production associated with root uptake is balanced by H^+ consumption as base cations are released through decomposition (Binkley and Richter 1987). However, in aggrading biomass watersheds, where most of the aboveground biomass has been removed by harvesting, uptake exceeds decomposition, leading to net production of H^+.

Enhanced H^+ production would be expected to lower stream and soilwater pH, and remove base cations from the soil exchange complex, none of which has been

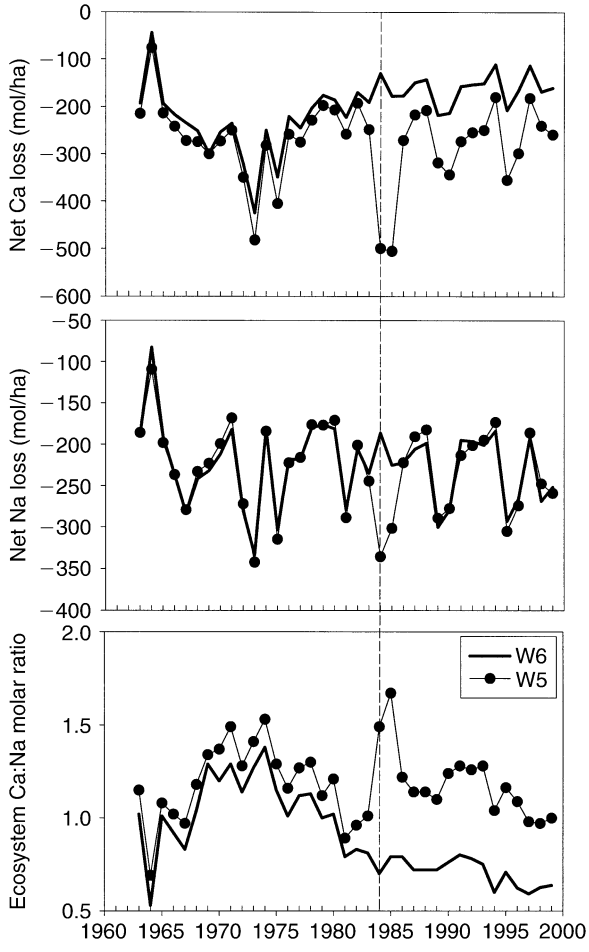

FIG. 7. Temporal trends in net Ca and Na loss (streamwater minus bulk precipitation) and the ecosystem Ca:Na ratio in the south-facing watershed, W5, compared to the reference watershed, W6. Ecosystem Ca:Na ratio was calculated from streamwater and bulk precipitation fluxes by Eq. 3. Vertical dashed lines indicate dates of experimental manipulations for W5.

observed in the long-term response to the watershed treatments, suggesting that some other process is consuming H^+ and releasing Ca.

We hypothesize that the observed enhanced export of Ca coupled with an increase in streamwater pH and ANC suggest the contribution of a potentially unrecognized process controlling Ca export from these forest ecosystems. A scenario that fits the observations is that production of H^+ by vegetative uptake accelerates dissolution of a portion of the available Ca pool that is not measured by standard salt extraction. One possible Ca source is dissolution of Ca oxalate. Oxalate crystals would not be dissolved and thus accounted for in a salt extraction process used to estimate soil exchangeable pools. However, increased H^+ production could enhance dissolution of oxalate as its solubility increases with decreasing pH, especially below pH 5 (Gadd 1999). Dissolution of Ca oxalate coupled with oxidation of the oxalate ion would release Ca and carbonic acid, resulting in an increase in ANC and Ca, as observed in W5.

Calcium oxalate crystals are common in forest soils (Graustein et al. 1977, Certini et al. 2000), formed as a metabolic byproduct of fungal activity, and in roots (April and Keller 1990). An additional, largely unstudied, source of Ca oxalate is the decomposition of tree litter as much of the Ca in foliage is stored as intracellular oxalate crystals (Franceschi and Horner 1980, DeHayes et al. 1997). Although it has been suggested that Ca oxalate may provide an important reservoir for Ca in the ecosystem (Dutton and Evans 1996), the size and availability of this pool has not been determined in the context of an ecosystem nutrient budget. The most complete study in forest soils found oxalate to a depth >2 m in an Inceptisol under silver fir (*Abies alba* Mill.) in Tuscany (Certini et al. 2000). Based on their data, with concentrations of oxalate of 150 mg/kg in the upper 50 cm, and a mean bulk density of 1.2 Mg/m^3, a Ca pool of >10 000 mol/ha is implied, almost twice as large as the exchangeable Ca pool at HBEF. While we have no way of assessing the applicability of these oxalate data to northern hardwood soils, they suggest the potential for a pool that is large enough to contribute to the dynamics observed at the HBEF treatments. We suggest that buffering of ecosystem Ca losses by dissolution of Ca oxalate crystals may reconcile watershed mass balance studies and soil retrospective studies where changes in soil base cation storage have not been detected and where available soil pools have been estimated only by salt extraction methods.

CONCLUSIONS

Storage of Na in ecosystem pools was minimal at Hubbard Brook Experimental Forest, allowing use of net Na loss as an estimate of Na weathering flux. Differences in net Na loss indicate subtle differences in weathering flux between similar watersheds, and that weathering processes can be affected temporarily by severe forest disturbance. Other than short-term response of Na weathering flux to treatment (two years for W5; five years for W2) there were no long-term trends in Na weathering flux and most of the interannual variability was due to variability in streamflow.

While bedrock maps and soil pebble counts suggest no difference in mineralogy between the experimental watersheds at HBEF, several minerals, from a variety of geologic sources and with a range of stoichiometries, are potential reactants in the weathering process. Thus a wide range of Ca:Na ratios of weathering release are possible. Sodic plagioclase (Ca:Na = 0.24) provides a lower bound to Ca:Na weathering release while the minimum ecosystem Ca:Na ratio observed (0.59) provides an upper bound on weathering release. This range constrains estimates of mean Ca weathering flux from 54 to 132 $mol \cdot ha^{-1} \cdot yr^{-1}$. Similarly, estimates of net soil

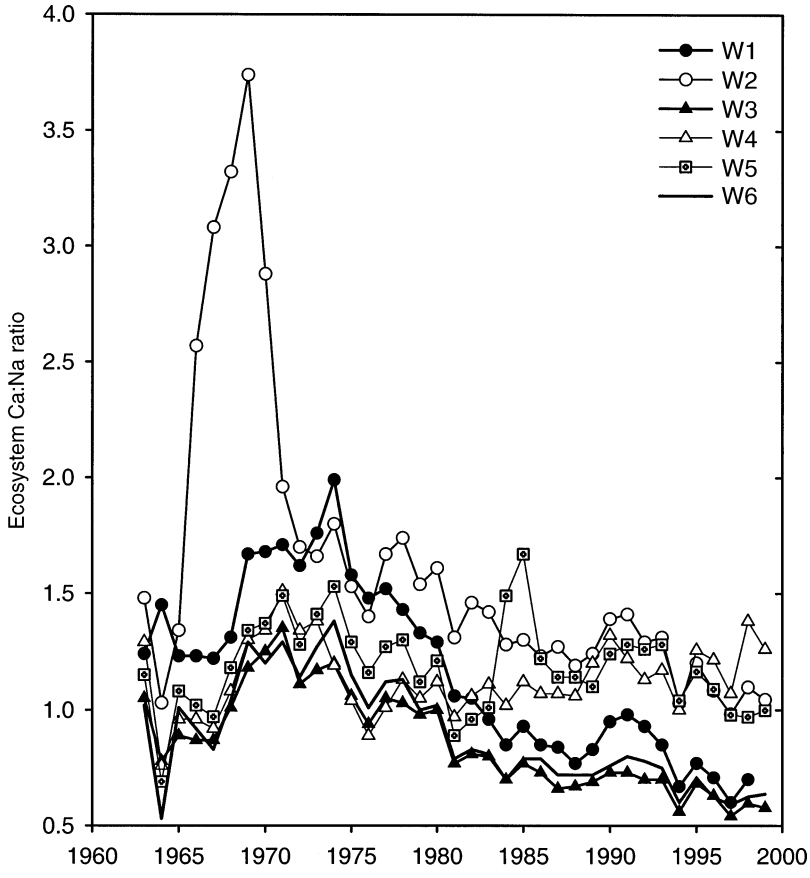

FIG. 8. Comparison of the ecosystem Ca:Na ratio for Hubbard Brook Experimental Forest Watershed 1–6. Watershed 2 was clearfelled and regrowth was sequestered during 1966–1968; W5 was strip cut in 1970–1974; W5 was whole-tree harvested in 1983–1984.

depletion are constrained to a range where net loss over the past 50 yr exceeds the amount of Ca sequestered by aggrading biomass during the same period, demonstrating additional loss due to acid anion leaching. Although the long-term mass balance model suggests that Ca depletion rates peaked in the early 1970s (Likens et al. 1996, 1998), net depletion continues to the present at a reduced rate, suggesting that further reductions in acid anions will be necessary to prevent continued net loss of base cation pools.

The net Ca:Na ecosystem ratio is a useful tool for evaluating ecosystem Ca dynamics. This approach demonstrates that excess leaching of Ca continues to the present from all three experimentally treated watersheds, the oldest of which has 32 yr of regrowth since the end of the treatment. This finding implies a much longer impact of forest disturbance on nutrient cycling than previously recognized. Further, none of the treated watersheds show signs of recovery toward conditions of Ca retention indicated by the untreated watersheds (Fig. 8). Although it might be expected that strongly aggrading forest stands sequester nutrients efficiently due to high uptake demands, our findings suggest that enhanced leaching, possibly accelerated by H^+ release by root uptake processes, is a consistent feature of anthropogenically disturbed forest ecosystems, compounding the long-term impacts of acid deposition.

Depletion of exchangeable Ca pools does not appear to be an important source of enhanced Ca export following disturbance; no change in the exchangeable pool size has been detected following whole-tree harvest (Johnson et al. 1997). If reduction of exchangeable Ca pools were responsible for long-term Ca depletion calculated by Likens et al. (1996), and affirmed by the findings of the present study, then this implies a 76% reduction in exchangeable Ca (from 26 500 to 6500 $mol \cdot ha^{-1} \cdot yr^{-1}$). Assuming no change in cation exchange capacity, this implies that base saturation 50 yr ago was 30%, an unlikely value in a region dominated by very acidic Spodosols. Decomposition of the forest floor, roots, and litter is also not a likely source as no changes in forest floor Ca have been detected (Yanai et al. 1999) and decomposition has been less than storage in the regrowing forest (Likens et al. 1998). Net Na loss patterns suggest that changes in mineral weathering also cannot account for increased Ca losses. Dissolution of Ca oxalate crystals in the soil is an unex-

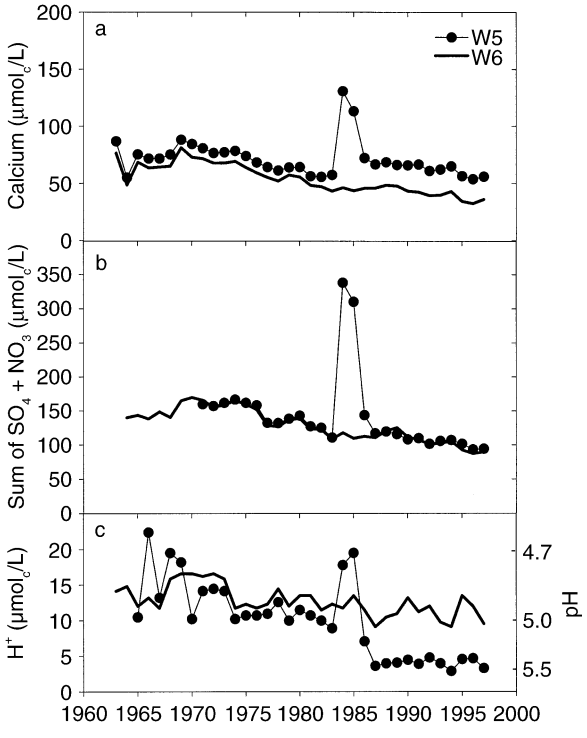

FIG. 9. Comparison of Watersheds 5 and 6 streamwater output for (a) Ca, (b) sum of SO_4 and NO_3, and (c) H^+.

plored, potential mechanism to explain the sustained loss of Ca. However, the extent of this pool and its ability to buffer long-term losses is unknown. The size of this pool and its dynamics should be determined in future attempts to understand forest ecosystem Ca cycling and response to disturbance.

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LITERATURE CITED

April, R., and D. Keller. 1990. Mineralogy of the rhizosphere in forest soils of the eastern United States. Biogeochemistry **9**:1–18.

Bailey, S. W., J. W. Hornbeck, C. T. Driscoll, and H. E. Gaudette. 1996. Calcium inputs and transport in a base-poor forest ecosystem as interpreted by Sr isotopes. Water Resources Research **32**:707–719.

Baker, L. A. 1990. Regional estimates of atmospheric dry deposition. Pages 645–653 *in* D. F. Charles, editor. Acidic deposition and aquatic ecosystems: regional case studies. Springer Verlag, New York, New York, USA.

Baker, J. P., and S. W. Christensen. 1991. Effects of acidification on biological communities in aquatic ecosystems. Pages 83–106 *in* D. F. Charles, editor. Acidic deposition and aquatic ecosystems: regional case studies. Springer-Verlag, New York, New York, USA.

Billings, M. P. 1937. Regional metamorphism of the Littleton–Moosilauke area, New Hampshire. Geological Society of America Bulletin **48**:463–566.

Billings, M. P., and K. Fowler-Billings. 1975. Geology of the Gorham Quadrangle New Hampshire–Maine. State of New Hampshire Department of Resources and Economic Development, Concord, New Hampshire, USA.

Binkley, D., and P. Hogberg. 1997. Does atmospheric deposition of nitrogen threaten Swedish forests? Forest Ecology and Management **92**:119–152.

Binkley, D., and D. Richter. 1987. Nutrient cycles and H^+ budgets of forest ecosystems. Advances in Ecological Research **16**:1–51.

Blum, A. E., and L. L. Stillings. 1995. Feldspar dissolution kinetics. Pages 291–352 *in* A. F. White and S. L. Brantley, editors. Chemical weathering rates of silicate minerals. Reviews in Mineralogy. Volume 31. Mineralogical Society of America, Washington, D.C., USA.

Blum, J. D., A. Klaue, C. A. Nezat, C. T. Driscoll, C. E. Johnson, T. G. Siccama, C. Eagar, T. J. Fahey, and G. E. Likens. 2002. Mycorrhizal weathering of apatite as an important calcium source in base-poor forest ecosystems. Nature **417**:729–731.

Blume, L. J., B. A. Schumacher, P. W. Schaffer, K. A. Cappo, M. Papp, R. D. Van Remortel, D. S. Coffey, M. G. Johnson, and D. J. Chaloud. 1990. Handbook of methods for acid deposition studies: laboratory analyses for soil chemistry. EPA/600/4–90/023. U.S. Environmental Protection Agency. Environmental Monitoring Systems Laboratory, Las Vegas, Nevada, USA.

Bormann, F. H., and G. E. Likens. 1979. Pattern and processes in a forested ecosystem. Springer-Verlag, New York, New York, USA.

Buso, D. C., G. E. Likens, and J. S. Eaton. 2000. Chemistry of precipitation, streamwater, and lakewater from the Hubbard Brook Ecosystem Study: a record of sampling protocols and analytical procedures. General Technical Report NE-275. USDA Forest Service, Northeastern Research Station, Newtown Square, Pennsylvania, USA.

Certini, G., G. Corti, and F. C. Ugolini. 2000. Vertical trends of oxalate concentration in two soils under *Abies alba* from Tuscany (Italy). Journal of Plant Nutrition and Soil Science **163**:173–177.

Clayton, J. L. 1988. Some observations on the stoichiometry of feldspar hydrolysis in granitic soil. Journal of Environmental Quality **17**:153–157.

David, M. L., and G. B. Lawrence. 1995. Soil and soil solution chemistry under red spruce stands across the northeastern United States. Soil Science **161**:314–328.

DeHayes, D. H., P. G. Schaberg, G. J. Hawley, C. H. Borer, J. R. Cumming, and G. R. Strimbeck. 1997. Physiological implications of seasonal variation in membrane associated calcium in red spruce mesophyll cells. Tree Physiology **17**: 687–695.

Driscoll, C. T., G. B. Lawrence, A. J. Bulger, T. J. Butler, C. S. Cronan, C. Eagar, K. F. Lambert, G. E. Likens, J. L. Stoddard, and K. C. Weathers. 2001. Acidic deposition in the northeastern United States: sources and inputs, ecosystem effects, and management strategies. BioScience **51**: 180–198.

Dutton, M. V., and C. S. Evans. 1996. Oxalate production by fungi: its role in pathogenicity and ecology in the soil environment. Canadian Journal of Microbiology **42**:881–895.

Englund, E. J. 1976. The bedrock of the Holderness Quadrangle, New Hampshire. New Hampshire Department of Resources and Economic Development, Concord, New Hampshire, USA.

Federer, C. A., L. D. Flynn, C. W. Martin, J. W. Hornbeck, and R. S. Pierce. 1990. Thirty years of hydrometeorologic data at the Hubbard Brook Experimental Forest, New Hampshire. General Technical Report NE-141. USDA Forest Service, Northeastern Forest Experiment Station, Radnor, Pennsylvania, USA.

Federer, C. A., J. W. Hornbeck, L. M. Tritton, C. W. Martin, R. S. Pierce, and C. T. Smith. 1989. Long-term depletion of calcium and other nutrients in eastern US forests. Environmental Management **13**:593–601.

Franceschi, V. R., and H. T. Horner. 1980. Calcium oxalate crystals in plants. Botanical Review **46**:361–427.

Gadd, G. M. 1999. Fungal production of citric and oxalic acid: importance in metal speciation, physiology and biogeochemical processes. Advances in Microbial Physiology **41**:47–92.

Garrels, R. M., and F. T. McKenzie. 1967. Origin of the chemical compositions of some springs and lakes. Pages 222–242 *in* R. F. Gould, editor. Equilibrium concepts in natural water systems. American Chemical Society Advances in Chemistry Series 67.

Graustein, W. C., K. Cromack, and P. Sollins. 1977. Calcium oxalate: occurrence in soils and defect on nutrient and geochemical cycles. Science **198**:1252–1254.

Hornbeck, J. W., C. W. Martin, and C. Eagar. 1997. Summary of water yield experiments at Hubbard Brook Experimental Forest, New Hampshire. Canadian Journal of Forest Research **27**:2043–2052.

Horsley, S. B., R. P. Long, S. W. Bailey, R. A. Hallett, and P. M. Wargo. 2002. Health of eastern North American sugar maple forests and factors affecting decline. Northern Journal of Applied Forestry **19**:34–44.

Hoyle, M. C. 1973. Nature and properties of some forest soils in the White Mountains of New Hampshire. Research Paper NE-260. USDA Forest Service, Northeastern Forest Experiment Station, Upper Darby, Pennsylvania, USA.

Huntington, T. G., R. P. Hooper, C. E. Johnson, B. T. Aulenbach, R. Cappellato, and A. E. Blum. 2000. Calcium depletion in a southeastern United States forest ecosystem. Soil Science Society of America Journal **64**:1845–1858.

Hurlbut, C. S., and C. Klein. 1977. Manual of mineralogy. 19th edition. John Wiley and Sons, New York, New York, USA.

Hyman, M. E., C. E. Johnson, S. W. Bailey, R. H. April, and J. W. Hornbeck. 1998. Chemical weathering and cation loss in a base poor watershed. Geological Society of America Bulletin **110**:85–95.

Johnson, C. E., A. H. Johnson, T. G. Huntington, and T. G. Siccama. 1991*a*. Whole-tree clear-cutting effects on soil horizons and organic-matter pools. Soil Science Society of America Journal **55**:497–502.

Johnson, C. E., A. H. Johnson, and T. G. Siccama. 1991*b*. Whole-tree clear-cutting effects on exchangeable cations and soil acidity. Soil Science Society of America Journal **55**:502–508.

Johnson, C. E., R. B. Romanowicz, and T. G. Siccama. 1997. Conservation of exchangeable cations after clear-cutting of a northern hardwood forest. Canadian Journal of Forest Research **27**:859–868.

Likens, G. E., and F. H. Bormann. 1995. Biogeochemistry of a forested ecosystem. Second edition. Springer-Verlag, New York, New York, USA.

Likens, G. E., C. T. Driscoll, and D. C. Buso. 1996. Long-term effects of acid rain: response and recovery of a forest ecosystem. Science **272**:244–246.

Likens, G. E., C. T. Driscoll, D. C. Buso, T. G. Siccama, C. E. Johnson, G. M. Lovett, T. J. Fahey, W. A. Reiners, D. F. Ryan, C. W. Martin, and S. W. Bailey. 1998. The biogeochemistry of calcium at Hubbard Brook. Biogeochemistry **41**:89–173.

Likens, G. E., C. T. Driscoll, D. C. Buso, T. G. Siccama, C. E. Johnson, D. F. Ryan, G. M. Lovett, T. J. Fahey, and W. A. Reiners. 1994. The biogeochemistry of potassium in the Hubbard Brook Experimental Forest, New Hampshire. Biogeochemistry **25**:91–125.

Loeppert, R. H., and D. L. Suarez. 1996. Carbonate and gypsum. Pages 437–474 *in* D. L. Sparks, editor. Methods of soil analysis. Part 3. Chemical methods. SSSA book series number 5. Soil Science Society of America, Madison, Wisconsin, USA.

Lyons, J. B., W. A. Bothner, R. H. Moench, and J. B. Thompson. 1997. Bedrock geologic map of New Hampshire. 1: 250,000. U.S. Geological Survey, Denver, Colorado, USA.

Markewitz, D., D. D. Richter, H. L. Allen, and J. B. Urrego. 1998. Three decades of observed soil acidification in the Calhoun Experimental Forest: has acid rain made a difference? Soil Science Society of America Journal **62**:1428–1439.

Martin, C. W., J. W. Hornbeck, G. E. Likens, and D. C. Buso. 2000. Impacts of intensive harvesting on hydrology and nutrient dynamics of northern hardwood forests. Canadian Journal of Fisheries and Aquatic Sciences **57**:19–29.

McLaughlin, S. B., and R. Wimmer. 1999. Calcium physiology and terrestrial ecosystem processes. New Phytologist **142**:373–417.

Oyonarte, C., A. Perez-Pujalte, G. Delgado, R. Delgado, and G. Alendros. 1994. Factors affecting soil organic matter turnover in a Mediterranean ecosystem from Sierra de Gador (Spain): an analytical approach. Communications in Soil Science and Analysis **25**:1929–1945.

Pilgrim, S. A. L., and R. D. Harter. 1971. Spodic horizon characteristics of some forest soils in the White Mountains, New Hampshire. New Hampshire Agricultural Experiment Station, Bulletin 507. Durham, New Hampshire, USA.

Richter, D. D., and D. Markewitz. 2001. Understanding soil change. Cambridge University Press, Cambridge, UK.

Schad, D. E. 1996. The biogeochemistry of silicon and sodium at the Hubbard Brook Experimental Forest. Thesis. Syracuse University, Syracuse, New York, USA.

Ulrich, B., and E. Matzner. 1986. Anthropogenic and natural acidification in terrestrial ecosystems. Experientia **42**:344–350.

van Breeman, N., J. Mulder, and C. T. Driscoll. 1983. Acidification and alkalinization of soils. Plant Soil **75**:283–308.

Williams, C. R., and M. P. Billings. 1938. Petrology and structure of the Franconia Quadrangle, New Hampshire. Geologic Society of America Bulletin **49**:1011–1044.

Winter, T. C. 1981. Uncertainties in estimating the water balance of lakes. Water Resources Bulletin **17**:82–115.

Yanai, R. D., T. G. Siccama, M. A. Arthur, C. A. Federer, and A. J. Friedland. 1999. Accumulation and depletion of base cations in forest floors in the northeastern U.S. Ecology **80**:2774–2787.