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The biogeochemistry of calcium at Hubbard Brook

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Abstract. A synthesis of the biogeochemistry of Ca was done during 1963–1992 in reference and human-manipulated forest ecosystems of the Hubbard Brook Experimental Forest (HBEF), NH. Results showed that there has been a marked decline in concentration and input of Ca in bulk precipitation, an overall decline in concentration and output of Ca in stream water, and marked depletion of Ca in soils of the HBEF since 1963. The decline in streamwater Ca was related strongly to a decline in SO_4^{2-} + NO_3^- in stream water during the period. The soil depletion of Ca was the result of leaching due to inputs of acid rain during the past 50 yr or so, to decreasing atmospheric inputs of Ca, and to changing amounts of net storage of Ca in biomass. As a result of the depletion of Ca, forest ecosystems at HBEF are much more sensitive to continuing inputs of strong acids in atmospheric deposition than expected based on long-term patterns of sulfur biogeochemistry. The Ca concentration and input in bulk precipitation ranged from a low of 1.0 μmol/ℓ and 15 mol/ha-yr in 1986–87 to a high of 8.0 μmol/ℓ and 77 mol/ha-yr in 1964–65, with a long-term mean of 2.74 μmol/ℓ during 1963–92. Average total atmospheric deposition was 61 and 29 mol/ha-yr in 1964–69 and 1987–92, respectively. Dry deposition is difficult to measure, but was estimated to be about 20% of total input in atmospheric deposition. Streamwater concentration reached a low of 21 μmol/ℓ in 1991–92 and a high of 41 μmol/ℓ in 1969–70, but outputs of Ca were lowest in 1964–65 (121 mol/ha-yr) and peaked in 1973–74 (475 mol/ha-yr). Gross outputs of Ca in stream water were positively and significantly related to streamflow, but the slope of this relation changed with time as Ca was depleted from the soil, and as the inputs of sulfate declined in both atmospheric deposition and stream water. Gross outputs of Ca in stream water consistently exceeded inputs in bulk precipitation. No seasonal pattern was observed for either bulk precipitation or streamwater concentrations of Ca. Net soil release varied from 390 to 230 mol/ha-yr during 1964–69 and 1987–92, respectively. Of this amount, weathering release of Ca, based on plagioclase composition of the soil, was estimated at about 50 mol/ha-yr. Net biomass storage of Ca decreased from 202 to 54 mol/ha-yr, and throughfall plus stemflow decreased from 220 to 110 mol/ha-yr in 1964–69 and 1987–92, respectively. These ecosystem response patterns were related to acidification and to decreases in net biomass accretion during the study. Calcium return to soil by fine root turnover was about 270 mol/ha-yr, with 190 mol/ha-yr returning to the forest floor and 80 mol/ha-yr to the mineral soil. A lower content of Ca was observed with increasing elevation for most of the components of the watershed-ecosystems at HBEF. Possibly as a result, mortality of sugar maple increased significantly during 1982 to 1992 at high elevations of the HBEF. Interactions between biotic and abiotic control mechanisms were evident through elevational differences in soil cation exchange capacity (the exchangeable Ca concentration in soils was significantly and directly related to the organic matter content of the soils), in soil/till depth, and in soil water and in streamwater concentrations at the HBEF, all of which tended to decrease with elevation. The exchangeable pool of Ca in the soil is about 6500 mol/ha, and its turnover time is quite rapid, about 3 yr. Nevertheless, the exchangeable pools of Ca at HBEF have been depleted markedly during the past 50 years or so, $>$21,125 mol/ha during 1940–1995. The annual gross uptake of trees is about 26–30% of the exchangeable pool in the soil. Some 7 to 8 times more Ca is cycled through trees than is lost in stream water each year, and resorption of Ca by trees is negligible at HBEF. Of the current inputs to the available nutrient compartment of the forest ecosystem, some 50% was provided by net soil release, 24% by leaching from the canopy, 20% by root exudates and 6% by atmospheric deposition. Clear cutting released large amounts of Ca to stream water, primarily because increased nitrification in the soil generated increased acidity and NO_3^-, a mobile anion in drainage water; even larger amounts of Ca can be lost from the ecosystem in harvested timber products. The magnitude of Ca loss due to whole-tree harvest and acid rain leaching is comparable for forests similar to the HBEF, but losses from harvest must be superimposed on losses due to acid rain.

Abbreviations: ANC = acid-neutralizing capacity; CEC = cation exchange capacity; dbh = diameter at breast height; DOC = dissolved organic carbon; HBEF = Hubbard Brook Experimental Forest; HBES = Hubbard Brook Ecosystem Study; HH = high elevation zone, dominated by deciduous vegetation; LAI = leaf area index; LH = low elevation zone, dominated by deciduous vegetation; LOI = loss-on-ignition; $\mathrm{mol_c}$ = moles of charge (equivalents); NTF = net throughfall flux; PC = pin cherry; PIR = Pre-industrial Revolution; SD = standard deviation; se = standard error; SF = stemflow; SFWB = zone at highest elevations dominated by red spruce, balsam fir and white birch; SKT = nonparametric seasonal Kendall-Tau trend analysis; $s_{\bar{x}}$ = standard error of the mean; TF = throughfall; W = watershed

Introduction

Biogeochemical properties of calcium

Calcium (AW = 40.08) is a member of the alkaline earth group (Be, Mg, Ca, Sr, Ba, Ra) of elements characterized by strong metallic properties. Because of their electronic configuration (ns^2, where n is the period) and very high third-stage ionization energies, elements in this group are predominantly divalent with a tendency toward covalency in the lighter elements (Be and Mg) (Greenwood & Earnshaw 1984). Calcium is the most common of the alkaline earth elements in Earth's crust (Wedepohl 1995). It comprises about 3.85% of crustal mass (2.94% of the upper continental crust; Wedepohl 1995), and is common in igneous rocks, such as granites, characteristic of the continental crust, but is considerably more abundant in mafic rocks such as basalts, which are more common in the oceanic crust (Bowen 1979). Because of the charge and ionic radius, Ca most often occurs in 8-fold coordination sites of aluminum-silicate minerals, such as pyroxenes, amphiboles and feldspars, especially plagioclase. Precipitate, evaporate and phosphoritic sedimentary rocks such as limestone, dolomite, gypsum and phosphorites contain abundant Ca, and underlie large areas of each continent (Bowen 1979). Calcium is relatively unimportant compared with potassium and magnesium as an interlayer metal in layered silicates such as clays and therefore is not highly abundant in hydrolysate sediments.

Calcium is relatively easily weathered as a soluble cation from both primary and secondary minerals, the rate largely depending on solution pH. When liberated, it moves readily into the soil solution where it may be adsorbed onto the cation exchange complex, taken up by plants or microbial organisms, or leached through the soil profile. Because of its divalent charge, relative abundance and modest extent of hydration, Ca is adsorbed strongly to clays and humates compared with other metallic cations. Thus, inorganic Ca exists in the rock-soil component of terrestrial ecosystems as a structural component of primary and secondary minerals, on the exchange complex, and as a cation in soil solution.

Because of its ionic charge, Ca is not readily lost from soils having significant cation exchange capacity, except in acidic soils with elevated concentrations of exchangeable aluminum. Thus, Ca is usually the most abundant of the alkali and alkaline earth elements on the soil exchange complex, and is important in the regulation of soil pH (Bowen 1979). Calcium is usually the dominant cation in freshwaters on an equivalence basis, varying with lithology in the source area (Hutchinson 1975).

Calcium is an essential element for prokaryotes, fungi, plants and animals. In the carbonate form, it is a structural component of certain algae, and many shelled invertebrates. It is present as apatite in vertebrate bones and teeth (Bowen 1979), and as pectates in higher plants (Mengel & Kirkby 1979). Calcium is very important as a growth regulator in plants, probably involving membrane permeability. It is a structural member of about 40 enzymes (Bowen 1979), but is relatively unimportant as an enzyme activator (Mengel & Kirkby 1979). Concentrations of Ca are relatively high (among the metals) in those biological groups in which it is a structural element. For example, the average concentration in woody angiosperms is 0.3 to 1.5%, approximately the same as for K (Bowen 1979; Likens et al. 1994).

Calcium is not leached readily from living foliage due to its relative immobility in pectates and on membranes – a distinct contrast with K. Thus, in forest ecosystems Ca typically cycles between plants and soil through uptake-litterfall-mineralization processes. The biogeochemistry of Ca in a forest landscape is complex, its availability depends upon the interplay between supply from atmospheric deposition, cation exchange, mineral weathering, and mineralization of soil organic matter, and losses through leaching and sequestration in forest vegetation.

Calcium in northeastern forest ecosystems

Because Ca is a macronutrient for higher plants, spatial and temporal variations in its supply are important to the growth and vigor of vegetation within a forest ecosystem. There is some concern about long-term changes in pools of available Ca for forest ecosystems in the northeastern U.S. (Federer et al. 1989; Bailey et al. 1996; Likens et al. 1996; Lawrence et al. 1995). The concentrations and inputs of Ca via atmospheric deposition at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire, USA are among the lowest for any region of the United States (Figure 1), and are characteristic of much of the northern hardwood forest region. Glacially-derived soils at HBEF, like those underlying much of New England, are relatively young (ca. 13,000 BP; Likens & Davis 1975; Davis et al. 1985), with low clay content and high acidity. Parent materials are base poor (Johnson et al. 1968), and relatively little Ca is retained in labile soil pools (i.e. exchangeable and organically-bound). Natural or anthropogenic disturbances (e.g. forest harvest, acid rain), may result in significant losses of Ca from the ecosystem, adding to concerns about long-term forest productivity (e.g. Likens et al. 1970; Federer et al. 1989; Likens et al. 1996; Bailey et al. 1996; Lawrence & David 1996).

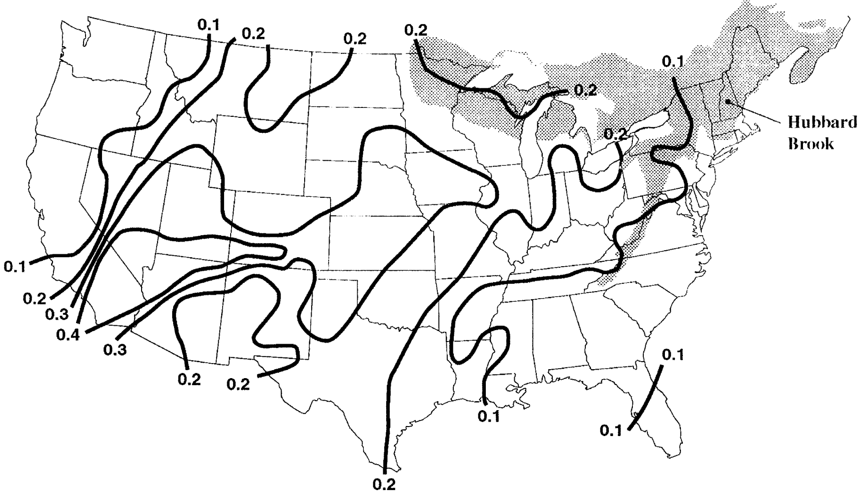
Long-term records and detailed biogeochemical studies at HBEF provide a unique opportunity to assess the biogeochemistry of Ca in the northern hardwood forest ecosystem. Calcium was a focus of one of the first studies (Likens et al. 1967) of the Hubbard Brook Ecosystem Study (HBES), and this paper provides an evaluation based on 29 years of intensive study (1963–1992). This period is sufficiently long to detect temporal changes in Ca fluxes. In this paper, we summarize these changes, and present ecosystem budgets for Ca for two 5-yr periods: 1964–69, early in the HBES, and a recent period, 1987–92.

Flux and cycling of calcium in a forest ecosystem

The Hubbard Brook Experimental Forest – procedures of study

The HBEF is located within the Hubbard Brook Valley of the White Mountain National Forest of central New Hampshire. Details about the forest ecosystem, and general procedures and analytical methods used in the HBES are summarized in Likens et al. (1967, 1994). Only the procedures unique to this paper are given here. Unless specified otherwise, data presented are for Watershed 6 (W6), the biogeochemical reference watershed of the HBEF (Figure 2).

1991 Annual
Weighted Mean Calcium Ion Concentrations (mg/L)



Estimated Calcium Ion Deposition (kg/ha)

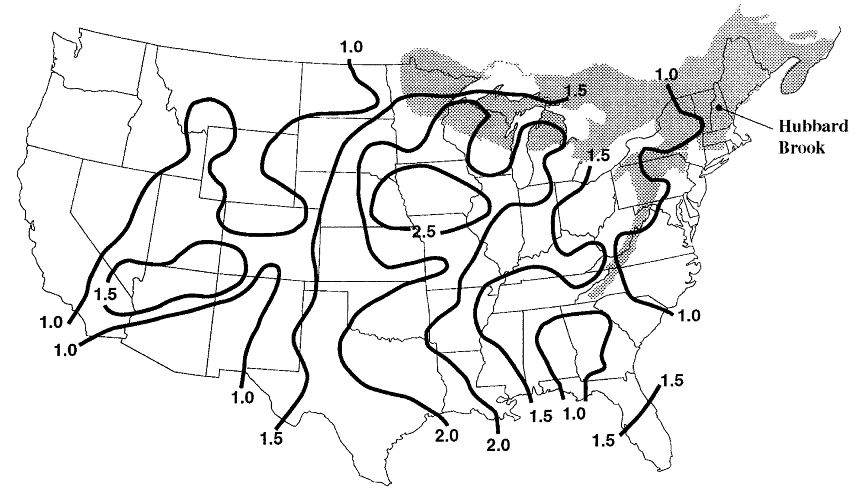


Figure 1. Annual volume-weighted concentration and deposition of Ca throughout the U.S. during 1991. The shaded area indicates the approximate range of the northern hardwood forest (precipitation chemistry data from the National Atmospheric Deposition Program).

Mean annual precipitation is approximately 1395 mm (SD = 189), with 25–33% of the total occurring as snow (Federer et al. 1990). Mean annual precipitation has varied from 975 mm in 1964–65 to 1888 mm in 1973–74. Mean annual streamflow is 869 mm (SD = 175), and has varied from 496 mm

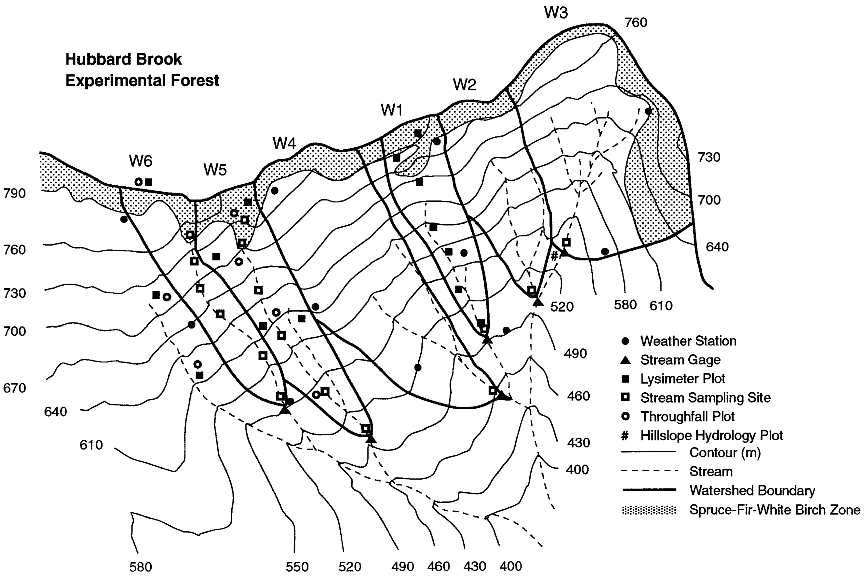


Figure 2. Map of the south-facing, experimental watersheds within the HBEF (modified from Likens et al. 1994).

in 1964–65 to 1401 mm in 1973–74. Some 50% of annual streamflow occurs during March, April and May of each year (see Federer et al. 1990).

The northern hardwood forest at HBEF is dominated by American beech (*Fagus grandifolia* Ehrh.), sugar maple (*Acer saccharum* Marsh.) and yellow birch (*Betula alleghaniensis* Britt). At higher elevations, white birch (*B. papyrifera* Marsh.), red spruce (*Picea rubens* Sarg.) and balsam fir (*Abies balsamea* L.) increase in abundance. The experimental watersheds have been divided into three elevation zones for sampling and analysis. The highest elevation zone, SFWB, is dominated by red spruce, balsam fir and white birch (Figure 2). The next highest zone, HH, is dominated by deciduous species, as is the lowest zone, LH, of this northern hardwood forest.

Biomass of this northern hardwood forest was calculated from measurements in 1965, 1977 and at 5-yr intervals thereafter (Likens et al. 1994). In the 1960's and 1970's, the forest showed significant rates of biomass accumulation (above- plus belowground) (4.85 Mg/ha-yr, 1965–1977; Likens et al. 1977; Bormann & Likens 1979; Whittaker et al. 1974). However, after 1982 total biomass accumulation has declined to a small rate (0.89 Mg/ha-yr during 1987–1992; Likens et al. 1994).

Soil chemical data are reported for the fine-earth fraction (<2 mm for mineral soils and <5 mm for O horizons). Soil analyses were performed on air-dry soils, but chemical data are reported on an oven, dry-mass basis

(105 °C). Exchangeable Ca was determined by extracting soils with 1 M NH_4Cl in a mechanical-vacuum extractor (Johnson et al. 1991b). Extract Ca concentrations were determined by inductively-coupled, plasma-emission spectrophotometry.

Long-term monitoring efforts pertinent to this study include: collection of forest floor samples at 5-yr intervals (since 1977); monthly collection of stream water from several elevations (since 1982); monthly collection of soil solution from three soil horizons at three sites adjacent to W6 (since 1984); annual collection of overstory canopy foliage of the dominant species (1992–95); and collection of throughfall in 1969, and 1989 to present (Likens et al. 1994; Lovett et al. 1996).

Much care has been taken since the beginning of the HBES to maintain the integrity of the long-term chemical and hydrologic databases. Continuous and rigorous quality control of procedures for data collection and chemical analyses have been done since 1963, including interlaboratory comparisons, use of chemical reference materials such as those from the National Bureau of Standards, and overlap of analytical procedures before new procedures were adopted (Buso et al. 1997).

Sources of calcium for the watershed-ecosystem

Atmospheric inputs in bulk deposition – concentrations, fluxes and trends

Rain and snow are important sources of Ca for forest and associated aquatic ecosystems of HBEF (e.g. Likens et al. 1967, 1977, 1985; Bormann & Likens 1979; Likens & Bormann 1995). Annual concentrations of Ca in bulk precipitation decreased sharply from 1963–64 to the mid-1970s, then were relatively constant thereafter (Figures 3A, 4; Table 1). Long-term trends showed statistically significant decreases ($p < 0.0001$; seasonal Kendall-Tau test) in Ca concentrations in precipitation during this period (median slope: -0.07 μmol/ℓ-yr). Significant declines were also reported for The Netherlands and Sweden during this period (Hedin et al. 1994). The long-term (1963–1992), volume-weighted mean concentration of Ca at HBEF was 2.74 μmol/ℓ (0.11 mg/ℓ) in bulk deposition during 1963–1992. Annual volume-weighted mean concentrations ranged from a low of 1.00 μmol/ℓ (0.04 mg Ca/ℓ) in 1986–87, to a high of 7.98 μmol/ℓ (0.32 mg Ca/ℓ) in 1964–65 (Figure 3A; Table 1).

The earliest measurements known to us of annual Ca concentrations in precipitation for the eastern U.S. were made in 1955–56 by Junge & Werby (1958). They reported Ca concentrations in precipitation for the HBEF area of 12.5 μmol/ℓ (0.5 mg Ca/ℓ). This value is approximately 2 times greater than the highest concentrations measured during the initial years (1963–66) of our study (Figures 3, 4; Table 1). Precipitation amount during 1955–56 was about 8% greater than the long-term average for the HBEF (Federer et

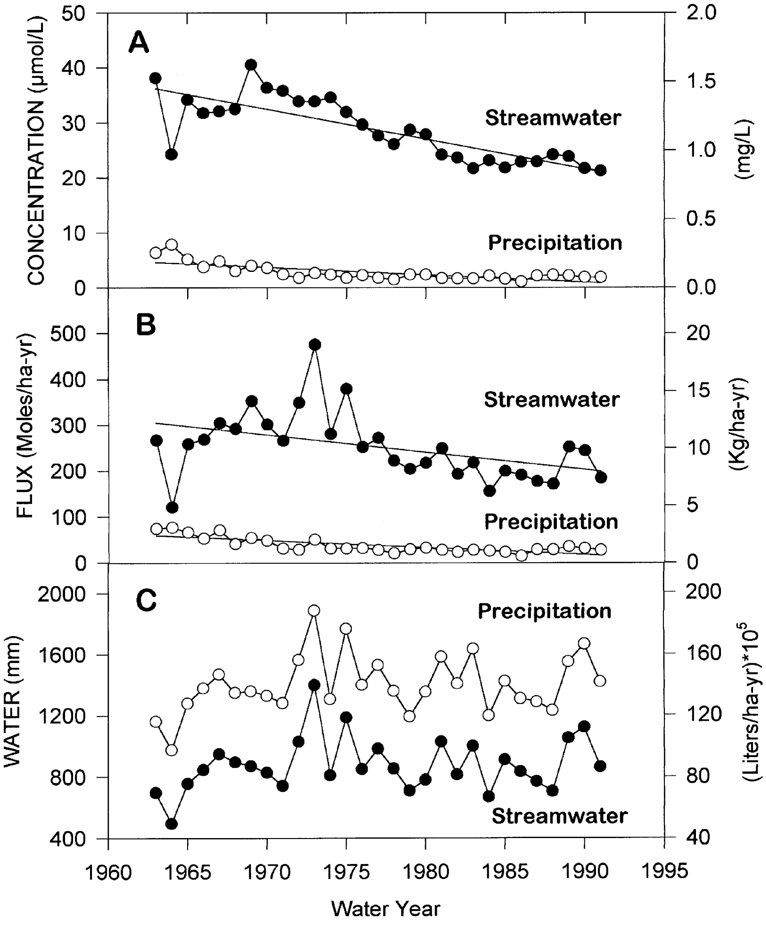


Figure 3. **A**. Annual volume-weighted concentrations of Ca in bulk precipitation (—○—) and stream water (—●—) for W6 of HBEF during 1963–1992. The probability for a larger F-ratio for both regression lines is <0.0001; the r^2 for stream water is 0.70, and for bulk precipitation is 0.52.

B. Annual inputs of Ca in bulk precipitation (—○—) and outputs in stream water (—●—) for W6 during 1963–1992. The probability of a larger F-ratio for the regression line for stream water is 0.006, $r^2 = 0.24$; and for bulk precipitation, is <0.0001, $r^2 = 0.58$.

C. Annual amount of precipitation (—○—) and streamflow (—●—) for W6 of HBEF during 1963–1992.

al. 1990). Note that by the time national precipitation chemistry monitoring networks were established, such as the National Atmospheric Deposition Program (NADP) in 1978 and MAP3S/AirMon in 1976, the sharp decrease in Ca concentration at HBEF had already occurred (Figure 4). The decline in Ca concentration in bulk precipitation during the period of our study is correlated with a decline in particulate matter emissions from industrial

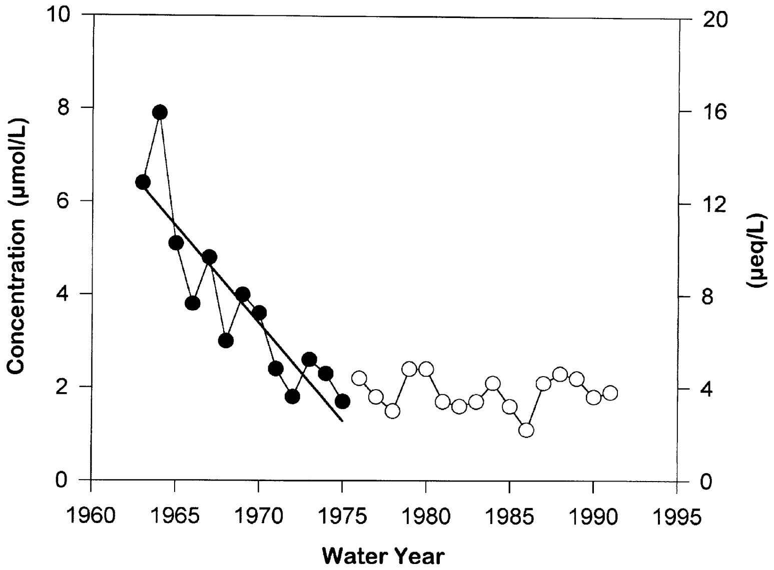


Figure 4. Annual volume-weighted concentrations of Ca in bulk precipitation for W6 at HBEF during 1963–1992. The $r^2 = 0.78$ during 1963–1975 (—●—).

processes (particularly cement production), fuel combustion and solid waste incineration (Likens 1992; US Environmental Protection Agency 1995).

Average monthly concentrations for Ca in bulk deposition varied by 3.6-fold during the year. Concentrations of Ca in precipitation were highest in April, but there was no statistically significant seasonal pattern in the long-term record (Figure 5A). Average volume-weighted concentrations were much more variable during April, May and October than in other months (Figure 5A).

About 30% of annual precipitation accumulates during mid November through mid April each year in a snowpack (Likens & Bormann 1995), which represents a temporary storage of chemicals including Ca. Based on data collected during winter 1972–73, the amount of Ca stored in the snowpack is relatively low compared to its cumulative input in bulk precipitation during the winter (Hornbeck & Likens 1974). This pattern is similar to that for NO_3^- and SO_4^{2-}, but is in sharp contrast to K, where K leached from plant materials is held in the snowpack (Hornbeck & Likens 1974; Likens et al. 1994). For Ca, the cumulative input in bulk deposition during the entire winter was approximately double the amount stored in the snowpack by mid-March. The remainder apparently was leached by winter rains, which were extensive during 1972–73, and by snowmelt water. The mean concentration of Ca in the snowpack was about 2.25 μmol/ℓ (0.09 mg Ca/ℓ), with generally

Table 1. Annual volume – weighted average concentrations of calcium in bulk precipitation for HBEF watersheds.

Water-year	W1	W2	W3	W4	W5	W6	Mean	±sd
1963–64	0.26	0.26	0.26	0.25	0.25	0.26	0.26	<0.005
1964–65	0.32	0.32	0.31	0.32	0.32	0.32	0.32	<0.005
1965–66	0.21	0.21	0.21	0.21	0.21	0.21	0.21	<0.005
1966–67	0.15	0.15	0.15	0.15	0.15	0.15	0.15	<0.005
1967–68	0.18	0.18	0.18	0.18	0.19	0.19	0.18	<0.005
1968–69	0.12	0.12	0.12	0.12	0.12	0.12	0.12	<0.005
1969–70	0.16	0.16	0.16	0.16	0.16	0.16	0.16	<0.005
1970–71	0.15	0.15	0.15	0.14	0.14	0.15	0.14	<0.005
1971–72	0.10	0.10	0.10	0.10	0.10	0.10	0.10	<0.005
1972–73	0.07	0.07	0.07	0.07	0.07	0.07	0.07	<0.005
1973–74	0.11	0.11	0.11	0.11	0.11	0.11	0.11	<0.005
1974–75	0.09	0.09	0.09	0.09	0.09	0.09	0.09	<0.005
1975–76	0.07	0.07	0.07	0.07	0.07	0.07	0.07	<0.005
1976–77	0.09	0.09	0.09	0.09	0.09	0.09	0.09	<0.005
1977–78	0.07	0.07	0.07	0.07	0.07	0.07	0.07	<0.005
1978–79	0.06	0.06	0.06	0.06	0.06	0.06	0.06	<0.005
1979–80	0.09	0.09	0.09	0.09	0.09	0.10	0.09	<0.005
1980–81	0.10	0.10	0.10	0.10	0.10	0.10	0.10	<0.005
1981–82	0.07	0.07	0.07	0.07	0.07	0.07	0.07	<0.005
1982–83	0.06	0.06	0.06	0.06	0.07	0.07	0.06	<0.005
1983–84	0.07	0.07	0.07	0.07	0.07	0.07	0.07	<0.005
1984–85	0.09	0.09	0.09	0.09	0.09	0.09	0.09	<0.005
1985–86	0.06	0.06	0.06	0.06	0.06	0.06	0.06	<0.005
1986–87	0.04	0.05	0.04	0.05	0.04	0.04	0.04	<0.005
1987–88	0.08	0.08	0.08	0.09	0.09	0.09	0.09	<0.005
1988–89	0.09	0.09	0.09	0.09	0.09	0.09	0.09	<0.005
1989–90	0.09	0.09	0.09	0.09	0.09	0.09	0.09	<0.005
1990–91	0.08	0.08	0.08	0.08	0.08	0.07	0.08	<0.005
1991–92	0.08	0.08	0.08	0.08	0.08	0.08	0.08	<0.005
Individual annual mean (mg/ℓ)	0.110	0.110	0.110	0.110	0.110	0.111	0.110	
±sd	0.0617	0.0616	0.0613	0.0610	0.0612	0.0616	0.0614	

low concentrations from December 1972 to late February 1973 and higher concentrations during March and April 1973 (Hornbeck & Likens 1974).

Volume-weighted average annual Ca concentrations in bulk precipitation varied inversely with amount of annual precipitation for the entire period ($r^2 = 0.25$; Figure 6A), but this relation could have been an artifact of declining

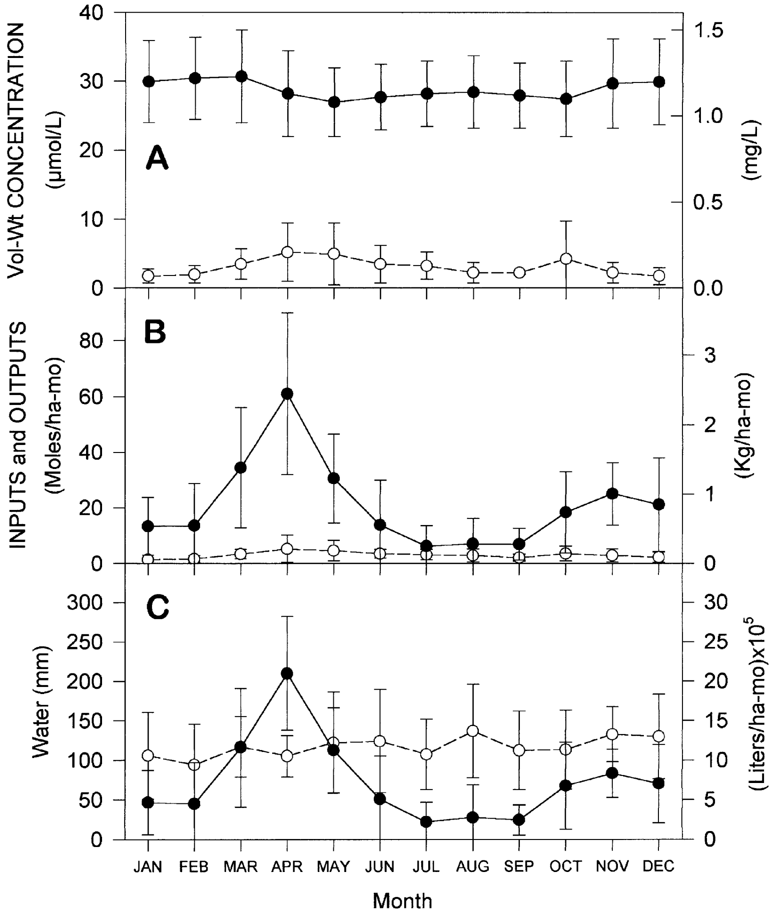


Figure 5. **A**. Monthly volume-weighted concentrations of Ca in bulk precipitation (—○—) and stream water (—●—) for W6 at HBEF during 1963–1992. The vertical bars are ± one standard deviation for the mean value.

B. Monthly inputs of Ca in bulk precipitation (—○—) and outputs of Ca in stream water (—●—) for W6 during 1963–1992. The vertical bars are ± one standard deviation for the mean value.

C. Monthly amounts of precipitation (—○—) and stream water (—●—) for W6 during 1963–1992. The vertical bars are ± one standard deviation for the mean value.

concentrations that followed the initial drought years (Figures 3A and 3C). After 1971, there was no relationship. Annual deposition of Ca was not significantly related to amount of precipitation (Figure 6B).

The annual bulk precipitation inputs of Ca decreased from 1963–64 to mid 1970s and were relatively constant thereafter (Figure 3B; Table 2). These inputs of Ca ranged from 77.3 mol/ha-yr (3.1 kg Ca/ha-yr) in 1964–65 to

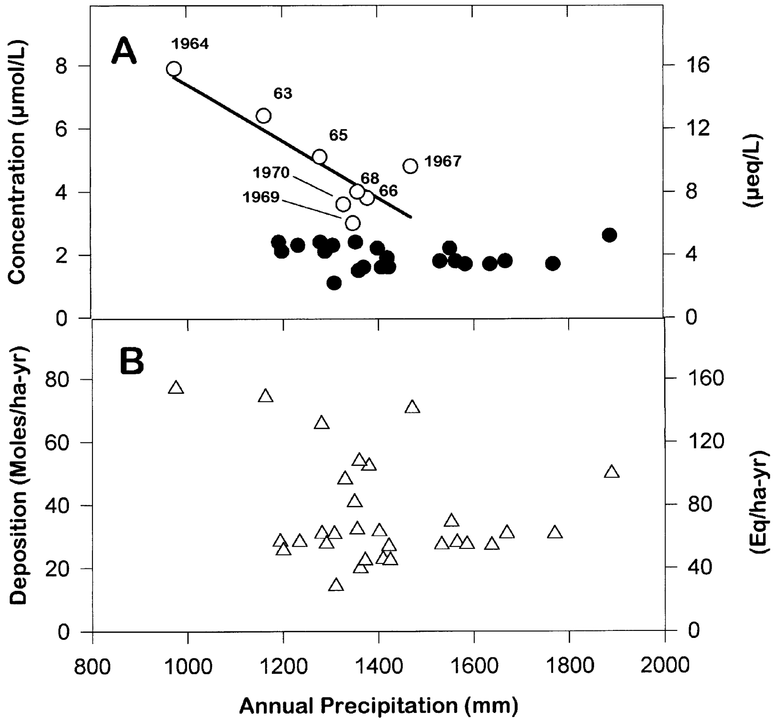


Figure 6. **A**. Relationship between the annual volume-weighted concentration of Ca in bulk deposition and amount of precipitation. The probability for a larger F-ratio for the regression line for 1963–70 is <0.01, $r^2 = 0.71$; and,
B. Annual input of Ca in bulk deposition and amount of precipitation for W6 at HBEF during 1963–1992.

15.0 mol/ha-yr (0.6 kg Ca/ha-yr) in 1986–87, averaging 37.4 mol/ha-yr (1.5 kg Ca/ha-yr; (SD = 0.67) during the period (Table 2).

Monthly inputs of Ca in bulk precipitation were slightly higher during April and May than in other months, but monthly inputs were always small compared to outputs in streamflow. There was no statistically significant difference among monthly inputs on a long-term basis (Figure 5B).

Concentrations and inputs of Ca in bulk precipitation varied little among watersheds within HBEF (Tables 1 and 2). Somewhat larger inputs to Watersheds 6, 5 and 4 reflect a west-to-east gradient in amount of precipitation in HBEF (Federer et al. 1990). Furthermore, Likens et al. (1967) reported that Ca concentrations in bulk precipitation were similar along an elevational gradient within the HBEF. Thus spatial variations in bulk deposition of Ca within the HBEF appear to be minimal.

Table 2. Annual bulk deposition input of calcium to HBEF watersheds.

Water-year	W1	W2	W3	W4	W5	W6	Mean	±sd
1963–64	2.9	2.9	2.9	2.9	2.9	3.0	2.9	0.020
1964–65	3.0	3.0	2.9	3.0	3.0	3.1	3.0	0.044
1965–66	2.5	2.5	2.6	2.6	2.6	2.6	2.6	0.035
1966–67	2.0	2.0	1.9	2.0	2.1	2.1	2.0	0.053
1967–68	2.5	2.5	2.5	2.5	2.7	2.8	2.6	0.123
1968–69	1.5	1.5	1.5	1.6	1.6	1.6	1.6	0.048
1969–70	2.0	2.0	2.1	2.1	2.1	2.2	2.1	0.044
1970–71	1.8	1.8	1.8	1.8	1.9	1.9	1.8	0.055
1971–72	1.2	1.2	1.2	1.2	1.2	1.2	1.2	0.019
1972–73	1.1	1.1	1.1	1.1	1.1	1.1	1.1	0.019
1973–74	2.0	1.9	1.9	2.0	2.0	2.0	2.0	0.023
1974–75	1.1	1.1	1.1	1.0	1.1	1.2	1.1	0.065
1975–76	1.1	1.1	1.1	1.2	1.2	1.2	1.2	0.034
1976–77	1.2	1.2	1.2	1.2	1.2	1.3	1.2	0.028
1977–78	1.0	1.0	1.0	1.0	1.0	1.1	1.0	0.023
1978–79	0.7	0.7	0.7	0.8	0.8	0.8	0.8	0.020
1979–80	1.1	1.1	1.1	1.1	1.1	1.1	1.1	0.026
1980–81	1.2	1.2	1.2	1.2	1.2	1.3	1.2	0.032
1981–82	1.0	1.0	1.0	1.1	1.1	1.1	1.0	0.038
1982–83	0.8	0.8	0.9	0.9	0.9	0.9	0.9	0.026
1983–84	1.0	1.0	1.0	1.1	1.1	1.1	1.0	0.030
1984–85	0.9	0.9	0.9	1.0	1.0	1.0	1.0	0.039
1985–86	0.8	0.8	0.8	0.9	0.9	0.9	0.9	0.026
1986–87	0.5	0.5	0.5	0.6	0.6	0.6	0.6	0.016
1987–88	1.0	1.0	1.0	1.1	1.1	1.1	1.0	0.046
1988–89	1.1	1.1	1.1	1.1	1.1	1.1	1.1	0.021
1989–90	1.3	1.3	1.3	1.4	1.4	1.4	1.3	0.035
1990–91	1.2	1.2	1.2	1.2	1.2	1.2	1.2	0.012
1991–92	1.0	1.0	1.0	1.1	1.1	1.1	1.0	0.027
Total (kg/ha)	40.7	40.6	40.8	41.5	42.0	43.3	41.5	
Annual mean (kg/ha-yr)	1.40	1.40	1.41	1.43	1.45	1.49	1.43	
±sd	0.65	0.64	0.64	0.64	0.66	0.67	0.65	

Bulk deposition vs. wet deposition and dry deposition

Because bulk deposition collectors are continuously open, they collect not only precipitation but also atmospheric particles that are large enough to fall under the influence of gravity (sedimentation). These large particles constitute a part, but not all of the dry deposition of Ca to the ecosystem, which also includes deposition of fine particles. Whether or not bulk deposition is an accurate measure of total (wet + dry) deposition depends on (1) the fraction of dry deposition occurring as sedimenting particles as opposed to fine particles, and (2) how well the sedimentation flux trapped by an open funnel reflects deposition for the entire canopy. Because Ca has no gaseous phase and most of its particulate mass is in particles >2 μm diameter, sedimentation probably dominates the dry deposition flux (Lindberg et al. 1986).

To examine the difference between wet deposition and bulk deposition, we collected bulk deposition and wet-only deposition in side-by-side collectors during 11 years (1979–1989) in a clearing (252-m elevation) near the Robert S. Pierce Ecosystem Laboratory at HBEF (Martin et al. 1997). During this period, mean Ca deposition in the bulk collector (21.9 mol/ha-yr) was significantly greater than the mean deposition to the wet-only collector (17.3 mol/ha-yr, paired t-test $p < 0.05$). The difference of 4.6 mol/ha-yr (21% of the total bulk deposition) may be attributed to sedimentation. If vertical sedimentation were the only deposition mechanism, then bulk deposition collectors would provide a good estimate of total wet + dry deposition to the forest.

Lindberg et al. (1988) have shown that Ca deposition to a horizontal surface, such as a bulk collector, underestimates dry deposition to the forest canopy by a factor of approximately $0.5 \times$ LAI (leaf area index), because of more efficient particle scavenging by the canopy. The LAI of the forest at HBEF is slightly more than 6 (TJ Fahey, unpublished data), suggesting that dry deposition of Ca to the canopy of HBEF might be $3 \times 4.6 = 13.8$ mol/ha-yr, about 80% of the wet-only deposition. In this case, total Ca deposition for 1979–89 would have been about 31 mol/ha-yr, or 1.42 times the bulk deposition. However, all of the sites used in the analysis by Lindberg et al. (1988) had airborne Ca concentrations 3 to 15 times greater than the concentrations at HBEF, so it is unclear whether their canopy scavenging factor would apply to the HBEF.

Another estimate of dry deposition can be made from atmospheric concentrations of Ca measured from 1974 to 1976 using a Lundgren impactor in a clearing at HBEF. The mean air concentration of Ca measured during this period was 2.4 nmol/m^3, about half of which occurred in association with large particles (>3.6 μm in diameter) and half with smaller particles (Eaton et al. 1978). Assuming that the particles in the largest size class were deposited by sedimentation, a reasonable deposition velocity would be the median fall speed for the class, 0.5 cm/s. Assuming that the deposition velocity for the smaller particles was 0.1 cm/s, we calculate a total dry deposition of about 2.1 mol Ca/ha-yr (Table 3), or about 12% of the 1979–1989 annual mean, wet deposition value. This estimate is substantially less than the estimate based on bulk deposition, even without the correction for LAI. Impactors and other

Table 3. Calculation of dry deposition rates based on atmospheric concentrations and deposition velocities. Concentration data from Eaton et al. (1978).

Size class (μm)	Ca concentration (nmol/m^3)	Dep. velocity (cm/s)	Estimated deposition (mol/ha-yr)
3.6–20	1.08	0.5	1.7
0.65–3.6	0.51	0.1	0.16
0.1–0.65	0.86	0.1	0.27
Total	2.45		2.13

suction-inlet sampling devices are known to undersample large particles (Noll et al. 1985), and this undersampling may be responsible for the discrepancy.

For nearby Cone Pond, a predominantly coniferous watershed, Bailey et al. (1996) estimated dry deposition of Ca to be 3 mol/ha-yr (15% of total Ca deposition) using Sr isotopes as a tracer.

Here we will make the conservative assumption that the bulk deposition collectors at HBEF accurately sample both wet and dry deposition of Ca. Using the comparison between wet-only and bulk collectors discussed above, we estimate that 21% of the bulk deposition is from dry deposition, yielding dry deposition estimates of 12 and 6 mol/ha-yr for 1964–69 and 1987–92, respectively.

Supply of Ca from weathering and cation exchange

Calcium is released to the soil solution by the dissolution of Ca-bearing minerals. It is convenient to consider weathering release of Ca an input because it represents the conversion of Ca from the relatively unavailable mineral-bound form to soluble, highly available Ca.

The eastern portion of the HBEF (including the experimental watersheds) is underlain by a complex assemblage of metasedimentary and igneous rocks (Barton et al. 1997). The major map unit is the Silurian Rangeley Formation, consisting of sulfidic mica schist and quartzite with abundant calc-silicate boudins. The western portion of the HBEF is underlain by the Devonian Kinsman Granodiorite, a foliated granitic rock with megacysts of microcline.

A number of Ca-bearing minerals may supply Ca to the forest ecosystem through weathering. These include relatively slowly weathering minerals like plagioclase and biotite, minerals with intermediate weathering rates like garnet (grossular), and more readily decomposed minerals like amphibole (hornblende and actinolite), pyroxenes (mostly diopside) and clinozoisite. All of these minerals are present in at least one of the bedrock lithologies at HBEF, and presumably have been incorporated in glacial till, the soil parent material.

Table 4. Plagioclase content and composition (An_x = percent anorthite content) for bedrock lithology based on petrographic examination and electron-microprobe analysis of thin-sections collected at HBEF (SW Bailey, unpublished data). Numbers in parentheses represent the range reported in the literature for these map units in the White Mountains of New Hampshire. The weathering rate in log (mol/cm^2-sec) is from laboratory studies conducted at pH 5 (Blum & Stillings 1995).

Lithology	% Plagioclase	An_x	Log weathering rate
Calc-silicate	25 (20–45)	90 (70–95)	−13.7
Mica schist	10 (0–20)	20 (15–25)	−15.8
Granodiorite	30 (25–35)	25 (20–30)	−15.7

Some Ca release could occur from a highly weatherable mineral, such as hornblende, which is found in trace quantities at HBEF. However, we believe that most Ca may be supplied by a relatively slow-weathering mineral that is abundant, such as plagioclase. Plagioclase is relatively abundant in HBEF soils, and is the principal Ca-bearing mineral (R April, unpublished data). The plagioclase in local bedrock varies in chemical composition from An_{15} (15% Ca end-member) to An_{95} (Table 4). The average soil plagioclase composition, based on analyses of 12 grains collected from the Bs_2 horizon in W5 is $Ca_{0.19}\ Na_{0.81}\ Al_{1.19}\ Si_{2.81}\ O_8$ (R April, unpublished data).

Dissolution of plagioclase may result in the formation of kaolinite or Al sesquioxides in soils at HBEF. Calcium is not a significant component in the lattice of clays or other secondary minerals formed at HBEF and, therefore, the formation of secondary minerals is unimportant in the biogeochemistry of Ca.

Weathering is only one of several geochemical processes that release Ca to soil solution. Notably, displacement of Ca from soil exchange sites and mineralization of Ca associated with soil organic matter (SOM) may also contribute to solution Ca fluxes. These two processes differ from weathering in that they also may be sinks for Ca in the ecosystem (e.g. when Ca accumulates on the exchanger or when the pool of Ca in SOM increases over time). Unfortunately, it is impossible to discriminate quantitatively the relative importance of weathering, exchange, and mineralization using Ca flux data.

Using similar notation to Likens et al. (1994), we write the mass balance for Ca during a specified time period as:

$$P_{Ca} + W_{Ca} = S_{Ca} + \Delta B_{Ca} + \Delta O_{Ca} + \Delta X_{Ca} + \Delta M_{Ca} \qquad (1)$$

where P is the atmospheric input, W is the weathering release (from primary minerals), S is the stream export, ΔB is the net accumulation in biomass, ΔO is the change in the soil organic matter pool, ΔX is the change in the

Table 5. Soil calcium dynamics for W6 of the HBEF, NH. Values are mol/ha-yr.

Time period	(1) Ca accumulation in biomass	(2) Net Ca output (stream–precip.)	(3) Net soil release of Ca (1) + (2)	(4) Net Na release*	(5) Weathering release of Ca#	(6) Ca depletion
1965–77	430	271	701	241	58–80	621–643
1977–82	262	206	468	207	50–68	400–418
1982–87	6	169	175	215	52–71	104–123
1987–92	103	172	275	236	57–78	197–218

* Net Na release is streamwater Na loss minus bulk precipitation input.
\# Weathering release based on net Na release (Column #4) and the molar Ca:Na ratio in soil plagioclase (0.24) and plagioclase in Kinsman Granodiorite (0.33 at HBEF).

exchangeable pool, and ΔM is the change in the secondary mineral pool. We collect the terms representing fluxes involving soil pools, and call the result “net soil release.” Calcium is insignificant in secondary minerals, as discussed above, so the term ΔM_{Ca} is negligible, and equation (1) becomes:

$$\text{Net soil release} = W_{Ca} + \Delta X_{Ca} + \Delta O_{Ca} = S_{Ca} + \Delta B_{Ca} - P_{Ca} \qquad (2)$$

The net soil release includes the mobilization of Ca via weathering, exchange, and mineralization. Although the flux data cannot be used to distinguish among these processes, we can attempt to quantify them approximately.

For example, we can use Na as an indicator of weathering rates, since: *(i)* it is a negligible component of the soil exchange complex at HBEF (Johnson et al. 1991b); *(ii)* it is not a major nutrient, so is a negligible component of SOM; and *(iii)* it is not a structural component in secondary minerals. Thus, the terms ΔB, ΔO, ΔX, and ΔM in equation (1) are negligible for Na, and the net soil release of Na should equal approximately the weathering release, W_{Na}. Using these assumptions, it appears that the rate of mineral weathering has varied little since 1965 at HBEF (Table 5). Thus, the variations observed in the net soil release of Ca are likely the result of changing dynamics in the exchangeable and SOM pools.

An estimate of Ca release by weathering, W_{Ca}, can be made by multiplying the Na weathering release, W_{Na}, by the Ca:Na ratio of weathering reactants. A range of possible Ca:Na ratios is suggested by the following plagioclase compositions: (1) available soil plagioclase analyses (0.24); plagioclase from the Kinsman granodiorite (0.33); and calcic plagioclase from the Rangeley Formation (9.0) (Table 4). It is desirable to know the distribution of plagioclase compositions, not just the average, as the weathering rate varies exponentially with Ca content (Blum & Stillings 1995).

Clayton (1988) has suggested that the weathering of plagioclase, and possibly other minerals, is non-stoichiometric, with proportionally greater losses of Ca than Na. Also, a Ca:Na ratio as high as 9.0 could be possible if calcic plagioclase were to dominate the weathering reactions at HBEF. Finally, others have found that the weathering of Ca-rich minerals such as calcite, apatite, or hornblende, could explain high Ca:Na ratios in stream water even if the minerals were present in very small amounts (Drever & Hurcomb 1986; April et al. 1986). If any of these situations were present at Hubbard Brook, W_{Ca} would be greater than the maximum estimate of 80 mol/ha-yr in Table 5. However, these scenarios could not reasonably explain the marked interperiod, temporal variations observed in the net soil release of Ca, nor are they consistent with the expected weathering history for such Ca-rich minerals during the past 13,000 yr. Thus, we have used here the lower end of the range (0.24 to 0.33), based on available data, for our calculations (Table 5).

Weathering generally accounts for appreciably less than 50% of the net soil release (Table 5). The remainder must be derived from net losses from the exchangeable pool and/or mineralization of Ca bound in SOM. In either case, depletion of these pools is ecologically significant because it represents the loss of relatively available forms of Ca.

Even if the weathering release of Ca were two or three times greater than the estimates in Table 5, it is clear that significant depletion of soil Ca pools has occurred in the past thirty years at HBEF. We estimate that the total amount of Ca lost from exchange sites and SOM between 1965 and 1992 was 9.9–11.5 kmol/ha. For scale, this amount is greater than the entire exchangeable pool, measured in 1983 (Johnson et al. 1991b); it is 53–61% of the total living biomass pool in 1992 (Table 7); and it is 2.0–2.4 times the forest floor Ca pool in 1969–70, as measured by Gosz et al. (1976).

Bedrock type exerts a profound influence on the net release of Ca (Table 6). Soils at Sleeper's River, VT, which is underlain by calcareous bedrock, released ten times more Ca than the non-calcareous sites. Recent rates of net soil release of Ca at HBEF are comparable to rates at other sites in the northeastern U.S. At the Cone Pond watershed, where the bedrock and till are particularly base-poor (Bailey et al. 1996), the net soil release of Ca was 66–80% lower than at other non-calcareous sites. Note that the net soil release values in Table 6 do not account for the possible net accumulations by forest vegetation, with the exception of HBEF.

Table 6. Rates of net soil release of Ca in forest watersheds of the northeastern U.S. Units are mol/ha-yr.

Site	Bedrock type	Study period	Net soil release	Reference
Fort River, MA	Gneiss	July 1981–Dec. 1982	312	Yuretich & Batchelder 1988
Mundberry Br., MA	Schist	Dec. 1987–Dec. 1988	386	Yuretich & McManamon 1992
Caldwell Cr., MA	Gneiss/granite	1983	217	Batchelder & Yuretich 1992
Biscuit Br., NY	Sandstone/shale	Oct. 1983–Oct. 1985	515	Murdoch 1991
Panther Lake, NY	Granitic gneiss	1978–80	574	April et al. 1986
Woods Lake, NY	Granatic gneiss	1978–80	83	April et al. 1986
Cone Pond, NH	Schist	Oct. 1989–	77	Hyman et al. 1996
Sleeper's River, VT	Calcareous schist	June 1980–May 1982	3380	Thorne et al. 1988
Hubbard Brook, NH	Schist	June 1982–May 1992	259*	This study

* Includes net biomass storage; not included in other sites.

Intrasystem cycling

Living and dead biomass pools and accretion

Calcium accrual in above- and belowground biomass for the forest is calculated for 1965–1992 (also see Likens et al. 1994) and given in Table 7. Allometric equations and plant tissue chemistry have been revised periodically (Siccama et al. 1994; TG Siccama, unpublished data) and the most recent information is used here. Chemical composition of plant tissues is based on Likens & Bormann (1970) and Whittaker et al. (1979), except for lightwood, which has been extensively re-analyzed from tree cores and cross sections to assess temporal and spatial variability (Figures 7, 8 and 9). Lightwood represents some 49% of the above- and belowground biomass (see Whittaker et al. 1974). (We interpret darkwood and lightwood [*sensu* Whittaker et al. 1979] as "heartwood" and "sapwood", respectively).

We utilized foliage chemistry values for 1965 (Likens & Bormann 1970) to calculate Ca accrual because we have no clear evidence of systematic changes in foliar Ca concentration between 1965 and the 1990's. Annual sampling of canopy foliage of the dominant species from 1992–1995 in the forest west of W6 indicated that values reported in 1965 were generally higher than averages in 1992–95: sugar maple: 1965 = 0.60% and 1992–1995 = 0.52%; beech: 1965 = 0.55% and 1992–1995 = 0.51%; yellow birch: 1965 = 0.88% and 1992–1995 = 0.80%. However, large year-to-year differences precluded any conclusion about a long-term, temporal trend. In contrast, highly significant elevation patterns in foliage Ca concentration were observed. In particular, foliar Ca of sugar maple at high elevations (715-m elevation) was significantly lower ($p = 0.008$; 0.382% dry mass, se = 0.03) than in low and mid-elevations (535–625 m; 0.594%, se = 0.03). The same pattern was observed for yellow birch ($p = 0.04$; high elevations: 0.619%, se = 0.14 and mid/low zones: 0.896%, se = 0.06). No elevation trend was observed for beech and no significant between-year differences were detected for any species. The foliage patterns for Ca concentrations are consistent with elevation patterns of decreasing Ca concentrations in HBEF soils (see following sections). Moreover, for sugar maple, observations of unusually high mortality at high elevations (TG Siccama, unpublished data) are suggestive of possible inorganic nutrition stresses.

The three major tree species (yellow birch, American beech and sugar maple) accounted for 90% of the Ca in trees at Hubbard Brook in 1992 (Table 8). Within the trees, the largest Ca pools were found in branches (41%), bark (26%) and roots (19%). Although bole wood contained more than half of the tree mass, it only contained 11% of the Ca. Calcium concentrations in darkwood were considerably higher than in lightwood (Likens & Bormann 1970; TG Siccama, unpublished data).

Table 7. Total above- and belowground biomass and calcium content of live and dead standing trees on W6 of the HBEF.

Size class	Year 1965	1977	1982	1987	1992
			Biomass (Mg/ha)		
Live					
≥9.6	149	218	235	234	237
1.6–9.5 cm dbh	11	–	8	10	12
Dead					
≥9.6	–	10	11	14	15
1.6–9.5 cm dbh	–	–	0.52	0.62	0.45
			Calcium (moles/ha)		
Live					
≥9.6	11106	16266	17574	17442	17736
1.6–9.5 cm dbh	955	–	624	786	1006
Dead					
≥9.6	–	641	705	864	948
1.6–9.5 cm dbh	–	–	26.6	34.3	27.5
			Calcium (kg/ha)		
Live					
≥9.6	445	652	704	699	711
1.6–9.5 cm dbh	38	–	25	31	40
Dead					
≥9.6	–	26	29	35	38
1.6–9.5 cm dbh	–	–	1.0	1.4	1.1

Calcium concentration appears to have varied over the age of lightwood in sugar maple and yellow birch (Figure 7), although there was no relationship between Ca concentration and diameter (dbh) of these trees. We do not know whether the pattern in lightwood reflects changing physiology of trees, redistribution of Ca across the bole during growth, or changes in soil chemistry at HBEF.

There were also significant spatial variations in the Ca concentration of lightwood in these species (Figure 8; Arthur et al. 1997). In particular, trees at the highest elevation (730–760 m) had the lowest concentration of Ca in lightwood. This pattern also reflects the decreasing concentrations and pools of Ca in soils with increasing elevation (see *Forest Floor and Mineral Soil*

Table 8. Calcium content in living tress (>2 cm dbh) of W6 at the HBEF in 1992 (in mol/ha).

Species	Sapwood	Heartwood	Bark	Branches[*]	Leaves	Roots	Total above-ground	Total above and belowground
Sugar maple	772	59	2080	2245	195	865	6216	7081
American beech	694	49	1776	2819	188	1330	6856	8186
Yellow birch	243	92	651	1844	138	813	3780	4593
Balsam fir	25	0	38	38	16	135	251	386
Red spruce	22	0	36	37	13	124	233	356
White birch	70	14	182	446	59	215	986	1200
Other[**]	46	6	83	240	9	77	462	539
Total	1873	220	4845	7669	618	3558	15225	18783
As % of grand total	9.97	1.17	25.80	40.8	3.29	18.9	81.1	

[*] Includes twigs and dead branches.

[**] Other species incude white ash, striped maple, choke cherry, mountain ash, hemlock, red maple and mountain maple.

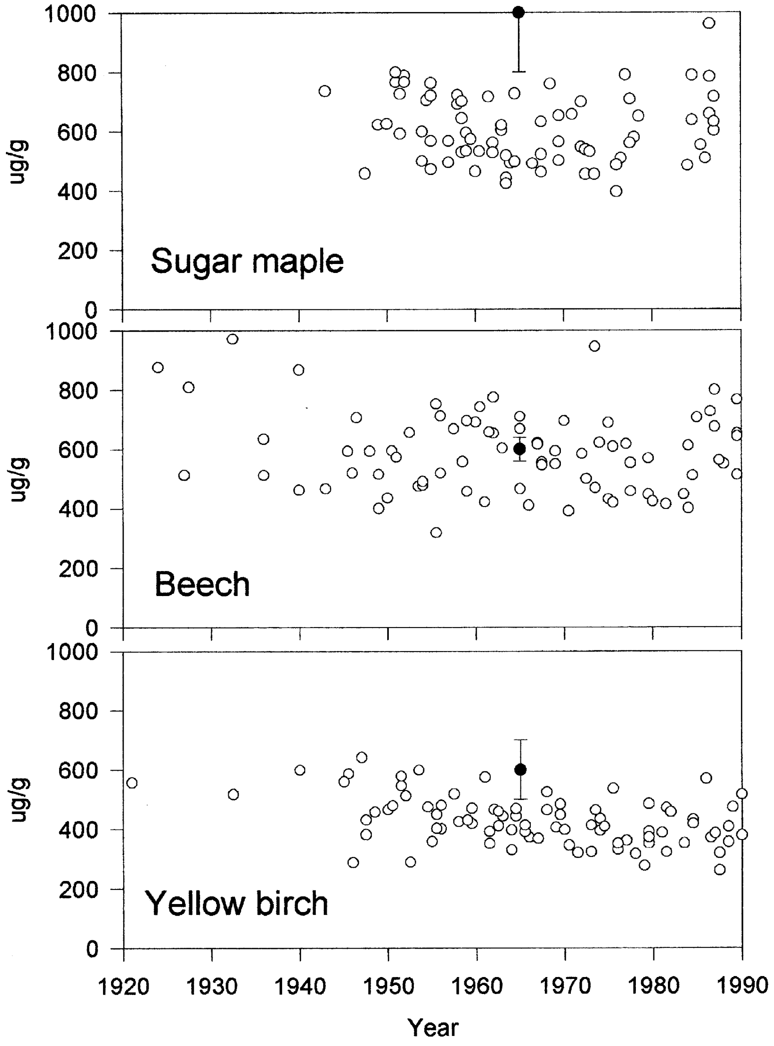


Figure 7. Calcium concentration in lightwood of the three dominant tree species at HBEF. Curved or straight lines show statistically significant patterns of Ca across the boles. Solid points with standard error bars illustrate the original (Likens & Bormann 1970) calcium concentrations reported for lightwood.

Pools and Dynamics). White birch, which is a co-dominant at the highest elevations, also had a significantly lower Ca concentration (393 μg/g, se = 22) than yellow birch at the same elevations (488 μg/g, se = 17).

Interestingly, lightwood in beech trees growing on topographic lows on the landscape, e.g. beds of ephemeral streams, or on flats, had a much higher Ca content than beech trees growing on drier sites (ridges and convex topography;

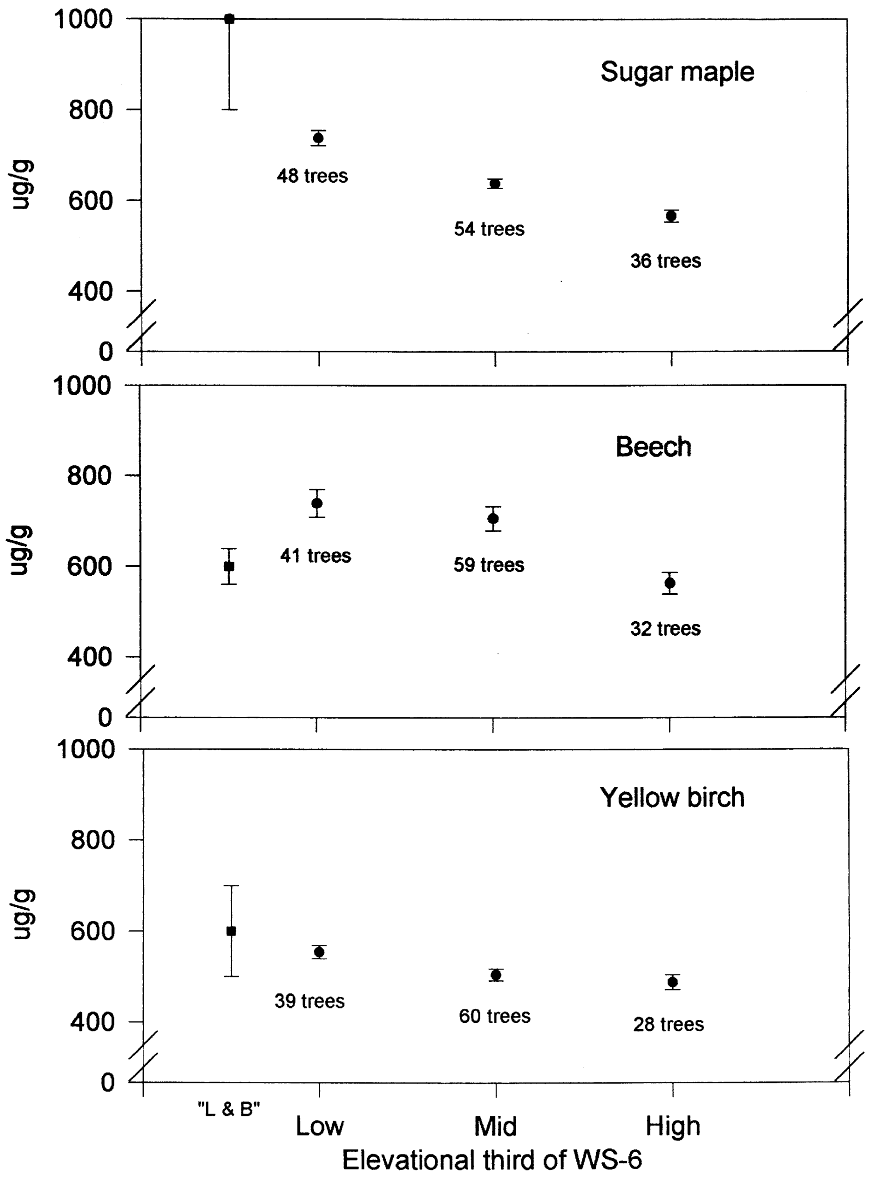


Figure 8. Calcium concentration in lightwood from the three dominant tree species at low (520–600 m), mid (670–730 m) and high (730–760 m) elevations. The closed squares ("L & B") and standard error bars show are the concentrations reported by Likens & Bormann (1970).

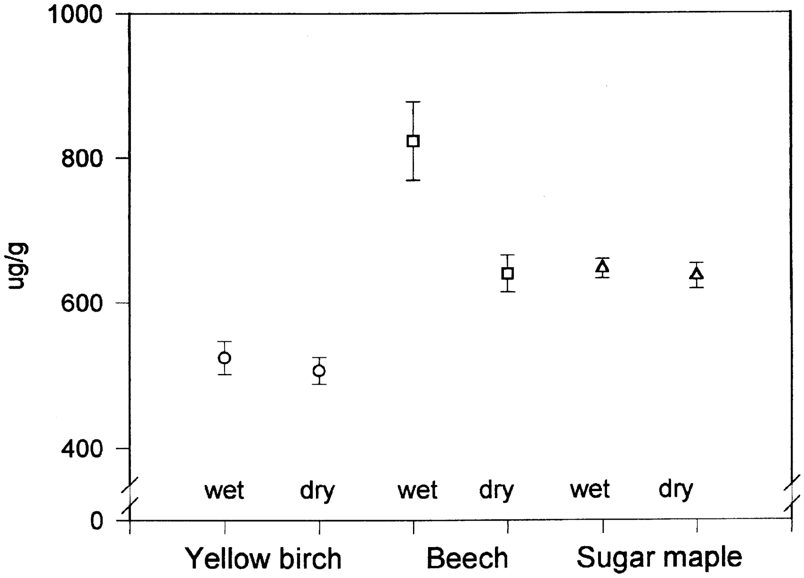


Figure 9. Calcium concentration (± standard error) in lightwood of trees (yellow birch ○, beech □, sugar maple △), from convex topographic features or broad open slopes, areas which are clearly upland (dry sites), and from concave slopes, depressions, flats, along ephemeral stream courses, or adjacent to flowing streams (wet sites). Number of samples, each from a different location: yellow birch, wet = 19, dry = 21; beech, wet = 15, dry = 33; sugar maple, wet = 23, dry = 26.

Figure 9; Arthur et al. 1997). The other major species showed no topographic dependence.

The biomass inventories in 1977 and later, measured standing dead trees in two classes, as standing dead trees (which were dead but retain most of their smaller branches), and as snags (which were broken off above breast height and had lost most of their major limbs). Since no studies of the chemistry of standing dead boles have been reported for the northern hardwood forest (see Likens et al. 1994), the Ca content of the standing dead boles of trees was assumed to be the same as for the live trees.

The Ca content of live trees on an areal basis increased from 1965 to 1980. This net storage in living trees essentially ceased about 1980 (Figure 10). This parallels the decrease in above and belowground biomass increment after about 1980 (Table 7), but the reason for the reduction in growth is not clear. The pool of Ca in standing dead trees is small compared to that in living trees, accounting for 5–7% of the total Ca pool in biomass (Table 7). The biomass of standing dead trees has been increasing since our first inventories of these components in 1977. Between 1982 and 1992, while the

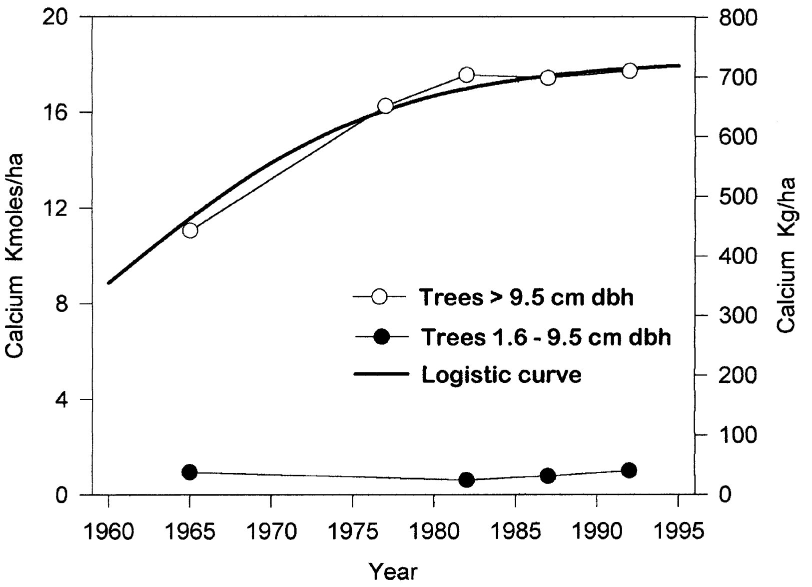


Figure 10. Changes in calcium pools in live tree biomass (above- and belowground) of W6 at HBEF from 1965 to 1992. The equation for the logistic curve is, Ca in biomass (kg/ha) = $\frac{730}{1+\exp(-0.122*(t-45.455))}$ where t is time (yr) since 1915.

living biomass pool was nearly constant, the pool of Ca in larger dead trees (>9.6 cm dbh) increased by 37% (Table 7).

We have estimated the amount of Ca sequestered in the growth of living trees during 1991 to 1992. Radial growth rates were obtained from tree cores taken from the three major species over a wide range of diameters and at three elevations. Relationships of dbh to average radial increment during the previous five years were used to estimate growth rates of the inventoried population in 1992. We then reduced the diameters of all the trees by their estimated one-year growth increments. For tree species other than the three dominants, a relationship based on the average of the three dominant species was used. Allometric estimates of biomass and Ca content were generated for the simulated 1991 tree population. This calculation indicated a sequestration of Ca in currently living trees (above- and belowground $\geq$10 cm dbh in 1992) of 320 mol Ca/ha-yr for biomass accrual of 4.17 tons/ha. Since there has been no net increase in the total biomass and Ca content from 1980 to present, there must have been an equal amount of tree mortality during this period. Thus, about 320 mol Ca/ha-yr is transferred to the standing and downed dead wood and dead root compartment.

Throughfall and stemflow

Throughfall (TF) concentrations of Ca were considerably greater than bulk precipitation at HBEF. The Ca added to TF during passage through the canopy during the growing season originates both from washoff of dry-deposited particles and from leaching of Ca from surfaces on and within the forest canopy. During the 1989–1992 period, volume-weighted mean Ca concentration in TF during the growing season (June–September) was 17.4 μmol/ℓ, about ten times greater than the corresponding concentration in bulk precipitation (1.68 μmol/ℓ). Calcium deposition in TF during this period was 83.7 mol/ha compared to the bulk deposition of 9.8 mol/ha. Assuming Ca deposition in stemflow (SF) to be 9.2% of that in TF (Eaton et al. 1973) or 7.7 mol/ha, total below-canopy deposition during the growing season was 91.4 mol/ha, about nine times the bulk deposition during this period.

We calculated annual fluxes in TF + SF by assuming that bulk precipitation is the flux for the leafless period. This calculation yields an annual TF + SF flux of 110 mol/ha-yr, which is likely to be an underestimate because there can be net leaching of Ca from the canopy in winter. The annual bulk precipitation flux for the same period (1989–1992) is 29 mol/ha-yr, yielding a ratio of (TF+SF)/bulk deposition of 3.8. This is well within the range for this ratio from 91 throughfall studies summarized by Parker (1983), for which the mean ratio was 2.86 with a standard deviation of 2.25. For 17 sites in the Integrated Forest Study (Johnson & Lindberg 1992), the mean ratio of TF + SF/(bulk or wet deposition) was 4.1 with a standard deviation of 3.0. As mentioned above, bulk deposition includes wet deposition from rainfall as well as most of the particulate dry deposition. Using our estimate discussed above, in which 21% of the bulk deposition was attributable to dry deposition in the bulk collector ($9.8 \times 0.21 = 2.1$ mol/ha), then the total TF + SF deposition to the forest floor during the growing season (91.4 mol/ha) was composed of 7.7 mol/ha (8.4%) wet deposition and 2.1 mol/ha (2%) dry deposition, with the remainder (81.6 mol/ha, 89%) derived from leaching of Ca from the canopy (Figure 11). Because of the uncertainty in the dry deposition calculations, this breakdown of the sources of Ca in TF must be considered approximate; nonetheless, it seems likely that canopy leaching was the dominant source. This pattern contrasts with extensively studied forests in Tennessee, for which leaching contributed between 42 and 58% of the total TF + SF flux, and dry deposition dominated wet deposition as an atmospheric input (Lovett et al. 1985). In other forests in North America and Europe, Ca leaching from the canopy contributed from 13 to 64% of the total TF + SF flux (Johnson & Lindberg 1992). Most of these sites had much higher airborne Ca concentrations than occur at HBEF, however. In the nearby Cone Pond watershed, Bailey (1994)

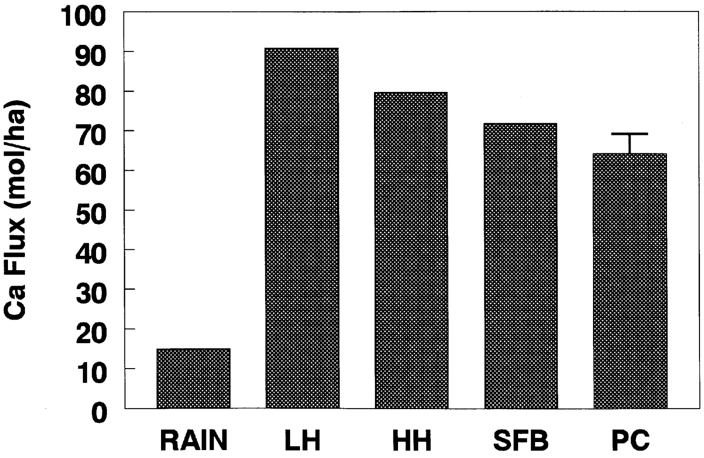


Figure 11. Flux of Ca in bulk deposition (rain) and in throughfall under different forest types at HBEF. Forest types are LH, HH, SFWB, and PC = pin cherry (successional northern hardwood). Data are for single sites except for PC, which is a mean of 4 sites (standard error shown) for June through September of 1989–1992.

used Sr-isotope ratios to estimate that 84% of the TF + SF was derived from canopy leaching, which agreed well with our estimate of 89% for HBEF.

In 1992, tree leaves were estimated to contain 618 mol Ca/ha (Table 8). Thus, the estimated annual rate of canopy leaching of Ca represents about 13% of this leaf Ca pool. Essentially all of this foliar Ca pool eventually would reach the forest floor as litter in the autumn, since resorption of Ca is negligible (see below).

The net Ca flux in throughfall (NTF = TF flux minus bulk precipitation flux) varied significantly among forest types within HBEF, with the mature northern hardwood forest type having greater NTF of Ca during the growing season than either the higher elevation SFWB stands or the northern hardwood forest regenerating from clear cutting, which is dominated by pin cherry (Figure 11; Lovett et al. 1996).

Eaton et al. (1973) measured Ca in TF+SF during the growing season of 1969, and found much higher concentrations and fluxes than observed currently. Expressed on an annual basis, the TF+SF flux in 1969 was 220 mol/ha, compared to 110 mol/ha in 1989–1992. The decrease in atmospheric deposition of Ca (some 30 mol/ha) can account for about 27% of this difference. Other possible factors include decreases in acid deposition (resulting in less Ca leaching from foliage) (Likens et al. 1996), decreases in foliar Ca content, decreases in the "leachability" of the foliar Ca pool, and decreases in plant uptake associated with depletion of Ca in the forest floor, particularly at higher elevations.

Litterfall

A comprehensive study of litterfall was done in 1968–69 on W6 by Gosz et al. (1973). Flux of Ca to the forest floor in aboveground litterfall averaged 1015 mol/ha-yr, with higher fluxes for the deciduous forest zone (1128 mol/ha-yr) than the upper-elevation, SFWB zone (831 mol/ha-yr), matching the pattern for K (Likens et al. 1994). The proportion of litterfall Ca flux associated with perennial tissues (31.5%) was much higher than for K (11.5%) because of the relatively high concentration of Ca in wood and bark.

As has been observed in deciduous trees elsewhere (e.g. Kramer & Kozlowski 1979), the Ca content of foliage for trees at HBEF increases throughout the growing season, reaching the highest concentration at the time of leaf fall in the autumn (Likens & Bormann 1970; Gosz et al. 1972). This seasonal pattern for Ca contrasts with those of nitrogen (N) and phosphorus (P), both of which undergo a large decrease in foliar content during leaf senescence late in the growing season. These seasonal trends of nutrient contents are strong evidence that, unlike N and P, Ca is not withdrawn (resorbed) from senescing leaves and moved into the perennial parts of trees. The relative immobility of Ca in phloem, the route of transport from leaves (Kramer & Kozlowski 1979), and deposition in middle lamellar pectates of leaves prevents resorption.

A greater fraction of the Ca that is acquired by vegetation each year for physiological processes is returned to the forest floor via leaf fall than is the case for N or P (Ryan & Bormann 1982). The estimated cycling of Ca to the forest floor via canopy leaching (82 mol/ha) is about 8% of the litterfall return (1091 mol/ha). Thus, at HBEF cycling of Ca between plants and soil is dominated by plant uptake of Ca from the soil and loss in leaf litter to a degree that is greater than for N and P because plants are not able to translocate Ca internally.

The past 25 years of forest succession apparently have not been accompanied by any marked changes in litterfall Ca flux. For example, deposition of leaf litter in the forest immediately west of W6 averaged 2.60 Mg/ha-yr for 1992–94 compared with 2.61 Mg/ha-yr for W6 in 1968–69. Moreover, Ca concentrations in freshly-fallen leaf litter of the dominant deciduous species during the earlier period were in the same range as for the more recent measurements, except for lower values in the HH zone, and particularly for sugar maple.

A major interval of overstory mortality and consequent branch and stem fall will result in increased litterfall flux of Ca. Mortality of sugar maple increased significantly during 1982–1992 at higher elevations, which ultimately will increase litterfall.

Root processes

The belowground biomass of trees is classified conventionally into two categories, fine roots and woody roots. The former are highly dynamic with short lifespans and high metabolic activity in the acquisition of soil resources. The latter are roots that develop secondary thickening, live longer, and become the largest permanent structures of the tree. These roots, including the root crown that directly underlies the bole, are the woody roots.

The Ca content of the lateral root system of HBEF (i.e. excluding root crowns) has been estimated on the basis of quantitative sampling of woody roots ($>$1-mm diameter) from soil pits in 1983 (Fahey et al. 1988) and from more recent soil coring studies (Fahey & Hughes 1994). The lateral root pool of Ca is about 2570 mol/ha, with 204 mol/ha in the fine root compartment. The proportion of lateral root Ca within fine roots (7.9%) is much lower than for K (15.5%) because of the relatively high Ca concentrations in woody tissues. Because the Ca concentration in fine roots is much higher in the forest floor (0.267% ash-free weight) than in the mineral soil (0.143% AFW), a large proportion of the fine root Ca pool (61%) is contained in the forest floor roots. This pattern is consistent with the higher exchangeable Ca concentrations observed in forest floor soils, compared to mineral soils (see *Forest Floor and Mineral Soil Pools and Dynamics*, below). Based upon allometric equations derived following whole-root-system excavations (Whittaker et al. 1974), the Ca content of the total root system of living trees ($>$2 cm dbh) in W6 is estimated at about 3560 mol/ha (Table 8). The difference between this value and the lateral root estimate represents Ca in root crowns (about 990 mol/ha). Fahey et al. (1988) previously summarized the technical problems of measuring woody root biomass at HBEF and concluded that the combination of soil pits and root excavations provided accurate estimates of these pools.

Recent studies using ingrowth cores and *in situ* screens (Fahey & Hughes 1994), as well as mini-rhizotron observation tubes (TJ Fahey, unpublished data), provide a quantitative basis for estimating Ca fluxes associated with the growth and turnover of fine roots at HBEF. Although we have no basis to revise our previous estimate of fine root turnover (5.08 Mg/ha-yr; Fahey & Hughes 1994), our mini-rhizotron observations strongly suggest that median, fine-root longevity is significantly longer for mineral soil roots (over 1 year) than forest floor roots (about 8 months). Thus, the flux of Ca associated with turnover of fine roots in the forest floor is considerably higher than for the mineral soil both because of higher Ca concentrations and more rapid turnover. We estimate a total annual Ca return to the soil from fine root turnover of 270 mol/ha-yr, with 190 mol/ha-yr contributed to the forest floor and 80 mol/ha-yr to the mineral soil. This fine root turnover value of Ca is about three times higher than the value for exudation by roots (90 mol/ha-yr)

Table 9. Summary of soil physical characteristics and exchangeable Ca pools by depth for W5 of the HBEF (Johnson et al. 1991a,b).

Horizon	Thickness cm	Dry wt mass kg/m^2	LOI %	OM mass kg/m^2	Bulk density Mg/m^3	Exchangeable ca kmol/ha
Oi + Oe	6.9*	2.2	87.1	2.0	–	–
Oa	–	6.5	51.6	3.4	–	1.85
0–10 cm	8.8	48.8	13.5	6.0	0.64	1.95
10–20 cm	8.6	52.3	11.2	5.4	0.74	1.0
>20 cm	32.9	216.0	8.4	16.6	0.85	1.9
Mineral soil	50.3	317.0	–	28.0	–	4.8
Total	57.2	326.0	–	33.4	–	6.6

* total forest floor thickness (Oi + Oe + Oa)

estimated by Smith (1976), but only about 25% of the aboveground litterfall value at HBEF.

A prolonged delay in the release of Ca from dead fine roots would be inferred from evidence on Ca release from root litter following the whole-tree harvest of W5 at HBEF. Even after two years of decay, little flux of Ca from decaying roots was observed (Fahey et al. 1988). However, direct observations of rapid disappearance of fine roots from *in situ* screens (Fahey & Hughes 1994) and mini-rhizotron tubes (TJ Fahey, unpublished data) suggest that such a delay does not occur for roots decaying *in situ* in the forest at HBEF. Finally, relatively large fluxes are associated with the death of woody roots because of their high concentrations of Ca. For example, assuming the average longevity of 1- to 20-mm diameter roots is about 5 yr (Schoettle & Fahey 1994), then Ca flux for this compartment would be about 170 mol/ha-yr. Most of the larger woody roots probably return to detrital pools only upon tree death.

Forest floor and mineral soil pools and dynamics

In the Spodosols at HBEF, the forest floor or O horizon is an important nutrient reservoir (Tables 9 and 10). Calcium enters the forest floor in the soluble form in direct precipitation and throughfall, and is supplied in litter (above- and belowground) and root exudates. As litter decomposes, Ca is solubilized and released to soil solution. Because Ca is leached from litter less rapidly than K, and immobilized to a lesser extent by microbes than N, the turnover of Ca in the forest floor, although relatively rapid, is slower than K and faster than N (Table 13; Gosz et al. 1976).

Table 10. Summary of horizon thickness, loss on ignition (LOI) and exchangeable Ca concentrations in soils of W5 of the HBEF (after Johnson et al. 1991a,b).

Horizon	Thickness cm	LOI %	Exchangeable Ca $\mathrm{cmol_c/kg}$
Oa	6.9*	51.8	6.75
A	0.03	14.8	0.58
E	2.7	4.6	0.41
Bh	3.9	13.8	0.63
$\mathrm{Bs_1}$	4.8	13.6	0.35
$\mathrm{Bs_2}$	35.5	8.1	0.17
C	–	3.8	0.08

* total forest floor thickness (Oi + Oe + Oa)

Gosz et al. (1976) estimated the total Ca pool in the forest floor of W6 as 4840 mol/ha in 1969–70. In 1983, Johnson (1989) determined that the total forest floor Ca pool on W5 was 7930 mol/ha. The difference between these estimates is due partly to differences in sampling and analytical methodologies (Likens et al. 1994). Johnson sampled somewhat deeper and used a more aggressive extraction procedure, resulting in greater forest floor mass estimates and greater total metal concentrations than reported in Gosz et al. (1976).

Gosz et al. (1973) measured the rate of release of Ca and other elements from decomposing plant tissues at HBEF. They found that the concentration of Ca in decomposing tissues was relatively constant. Thus, the release of Ca followed closely the mass loss of litter. After 12 months, 27–56% of the Ca had been lost from hardwood leaf litter, while about 30% of the original Ca was lost from woody litter. Arthur et al. (1993) reported that 14% of the Ca remained in dead boles 23 years after they were felled on W2. Loss of Ca from decaying root tissue is more difficult to assess, but also appears to be rapid (see *Root Processes,* above).

A significant fraction of the Ca in the forest floor is relatively available to plants and microorganisms. The pool of exchangeable Ca in the Oa horizon was estimated as 1850 mol/ha or 23% of the total Ca in the horizon (Johnson 1989; Johnson et al. 1991b). In contrast, less than 5% of the total K in the Oa horizon was in the exchangeable form. The Oa horizon contained about 28% of the exchangeable Ca in the solum, despite the fact that it represents only 2% of the soil mass (Table 11; Johnson et al. 1991a,b). Exchangeable Ca concentrations were greatest in the Oa horizon (mean = 6.75 $\mathrm{cmol_c/kg}$).

Federer et al. (1989) estimated the total pool of Ca in the fine earth (<2 mm) fraction of HBEF soils “to the bottom of the root zone” to be 250,000 mol/ha. The pool of exchangeable Ca is much smaller (6500 mol/ha; Johnson et al. 1991b) than the total Ca pool, but more reactive. Exchange reactions in soils have been shown to be relatively fast with reaction times of seconds or minutes (cf. Sparks 1989). Thus, the exchangeable Ca pool may react rapidly to changing solution conditions, and to buffer changes in Ca concentrations.

Calcium is the principal base cation on the soil exchanger on both a mass and equivalence basis. The pool of exchangeable Ca is about 4 times larger on an equivalence basis than the pools of exchangeable Mg and K (exchangeable Na is negligible; Johnson et al. 1991b). Nevertheless, in the acidic Spodosols at the HBEF, Ca only occupies 6.4% of the exchange sites, with Al occupying the majority of the sites. In the mineral soil, mean exchangeable Ca concentrations ranged from 0.08 cmol_c/kg in the C horizon to 0.63 cmol_c/kg in the Bh horizon (Table 10). Calcium occupied 39% of the exchange sites in the Oa horizon, compared to 5% in the mineral soil. Average Ca saturation in the mineral soil ranged from 12% in the E horizon to 3.8% in the C horizon.

Exchangeable Ca concentrations in HBEF soils were significantly correlated with organic matter content, measured by loss-on-ignition at 500 °C (Exch. Ca [cmol_c/kg] = $-0.645 + 0.132$ *OM[%]; $r^2 = 0.73$). However, this regression relationship is of limited predictive value because it results in negative estimates of exchangeable Ca concentrations when the organic matter content is less than 5%. When the Oa horizon and mineral soils are considered separately, the relationships, although significant, were considerably weaker (forest floor: $r^2 = 0.15$; mineral soil: $r^2 = 0.17$). Inclusion of other soil properties, notably pH and cation exchange capacity (CEC), did not significantly strengthen the relationships. Soils at HBEF typically have very low clay content ($<5\%$ by weight), and thus clays contribute little to exchange capacity.

There are significant spatial variations in pools of Ca in the forest floor and mineral soil at the HBEF. The forest floor in the SFWB zone at higher elevations contained significantly less total and exchangeable Ca than in the largely deciduous zones at lower elevation (Johnson et al. 1997). Total Ca in the forest floor of the SFWB zone was 4830 mol/ha, compared to 7040 mol/ha in the HH zone, and 10700 mol/ha in the LH zone. The pools of exchangeable Ca in the Oa horizon were 980 mol/ha in the SFWB zone, 1820 mol/ha in the HH zone, and 2300 mol/ha in the LH zone. These spatial patterns existed despite the fact that the forest floor in the SFWB zone contained significantly greater organic matter than the HH and LH zone soils (Johnson 1994). The low Ca pools in the forest floor of the SFWB zone are consistent with the lower Ca inputs in litter (Gosz et al. 1972), lower tissue Ca concentrations in conifer tree tissues compared to deciduous trees (Likens & Bormann 1970; Lang et al. 1982), lower concentration in lightwood of all dominant tree species

(Figure 8), and lower net throughfall in the SFWB zone (see *Throughfall and Stemflow*, above). Also, differences in forest floor Ca pools between HH and LH zones correspond with foliar Ca content for sugar maple and yellow birch at these elevations. Elevational differences in forest floor Ca undoubtedly reflect differences in pools and concentrations of available Ca elevationally across the watershed.

Exchangeable Ca in the mineral soil is the major pool of available Ca at the HBEF. The pools of exchangeable Ca were also significantly smaller in the SFWB zone than in the mineral soil of lower elevation zones. In the SFWB zone, the pool of exchangeable Ca in the mineral soil was estimated as 2800 mol/ha, compared to 4160 mol/ha in the HH zone, and 6300 mol/ha in the LH zone (Johnson et al. 1997). These differences are only partly explained by differences in soil mass, which increases downslope. Exchangeable Ca concentrations also showed a striking spatial pattern, with the lowest concentrations generally observed in soils at highest elevations (Figure 12).

Thus, it appears that exchangeable Ca concentrations and pools in the experimental watersheds at HBEF are controlled by a complex of interacting factors including elevation, physical properties of soils (including drainage) and forest vegetation, all of which vary systematically across the landscape.

The pool of Ca in the forest floor at HBEF has declined since 1965 (Yanai et al. 1993; Lawrence et al. 1995; Likens et al. 1996). When appropriately weighted by mass, the concentration of Ca in the Oi and Oe soil layers in 1969–70 was 0.661% (Gosz et al. 1976). In 1983, the mean Ca concentration in the combined Oi + Oe layer was 0.563%.

To explore this comparison further, we edited the data from Johnson (1989) in an attempt to make them comparable with the data from Gosz et al. (1976). The mean loss-on-ignition (LOI) for the Gosz et al. (1976) H horizon samples (roughly equivalent to the current Oa designation) was 71% (JR Gosz, personal communication, 1978). By sampling deeper, Johnson (1989) found a mean LOI of 51.6%. To make these data comparable, we deleted the 32 Oa horizon samples from the Johnson (1989) data set with the lowest LOI values. The mean LOI of this reduced data set was 70.8%, comparable to the Gosz et al. (1976) value. The corresponding mean Ca concentration of the Oa horizon was 0.247%, compared to the value of 0.296% reported by Gosz et al. (1976). Assuming that forest floor mass has remained constant (TG Siccama, unpublished data), it appears that the pool of Ca in the Oi + Oe layers declined by about 15% between 1969–70 and 1983, while the decline in the Oa horizon was about 16%. Based on these estimates the annual rate of Ca depletion from the forest floor would have been 60 mol/ha-yr during this period.

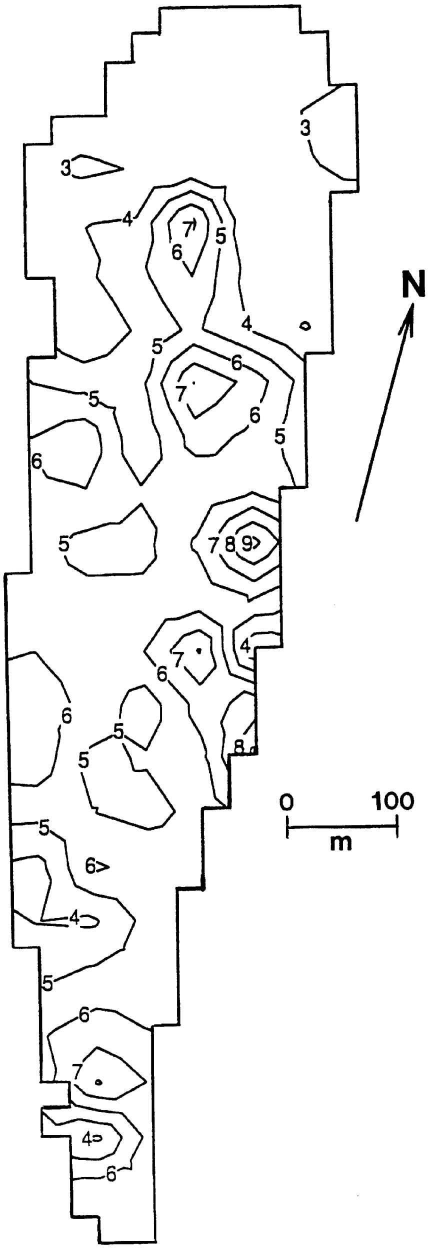


Figure 12. Calcium saturation in mineral soils of W5 of HBEF, computed as the percent of effective CEC (1M NH_4Cl) satisfied by Ca.

The pool of exchangeable Ca in the soil (6500 mol/ha) is not, by itself, sufficient to supply the Ca found in living biomass at HBEF (18700 mol/ha; Table 8). This condition also is evident in other forests in eastern North America (e.g. Weetman & Webber 1972; Smith et al. 1986; Johnson & Todd 1990), contributing to the argument that soil Ca depletion eventually may affect forest dynamics in areas subjected to intensive forestry (Federer et al. 1989). The ratio of biomass Ca to exchangeable Ca is greatest in the SFWB zone (4.3) and lowest in the LH zone (2.3). Interestingly, net accumulation of Ca in live biomass has ceased in the SFWB zone, but continues at a slow rate in the LH zone (Johnson et al. 1997).

Patterns in soil solution chemistry

Soil solution Ca concentrations generally were high in Oa horizon soil water and decreased as waters percolated through the mineral soil (Figure 13). This pattern likely was due to high inputs of Ca to the forest floor from throughfall and stemflow, and mineralization of aboveground and root litter. Calcium draining the forest floor was sequestered in the mineral soil. A number of processes undoubtedly contribute to the decline in Ca concentrations in drainage water as it passes through the soil profile. Most prominent of these are root absorption and retention on the soil exchange complex (as discussed below).

Differences in soil water Ca occurred between study sites at different elevations (Figure 13). Mean concentrations of Ca in Oa horizon leachate were low in the high elevation SFWB zone (23 μmol/ℓ) and HH zone (23 μmol/ℓ) and decreased in the mineral soil (to 14 μmol/ℓ in SFWB Bs_2 horizon leachate and 7.2 μmol/ℓ in HH Bs_2 horizon leachate). Thus, the decline in soil water Ca concentrations from the forest floor to the mineral soil was more pronounced in the HH zone than the SFWB zone. In contrast, Ca concentrations were higher throughout the soil profile in the LH zone than at the higher elevation sites. From the Oa horizon (mean concentration 34 μmol/ℓ), concentrations of Ca increased in the Bh horizon (mean concentration 47 μmol/ℓ) and then decreased with depth in the lower mineral soil (27 μmol/ℓ in the Bs_2 horizon).

These patterns in soil water Ca likely are related to elevational differences in the depth and base status of surficial materials, and chemical interactions in soil water, notably with aluminum. Soil depth generally decreases with increasing elevation at HBEF. Also, lower exchangeable Ca pools are observed in upper elevations, consistent with the lower soil solution Ca concentrations at the upper elevations (see *Forest Floor and Mineral Soil Pools and Dynamics*).

Elevational differences in other soil water solutes also may contribute to the patterns in Ca leaching from the soil. Soil water in the SFWB zone

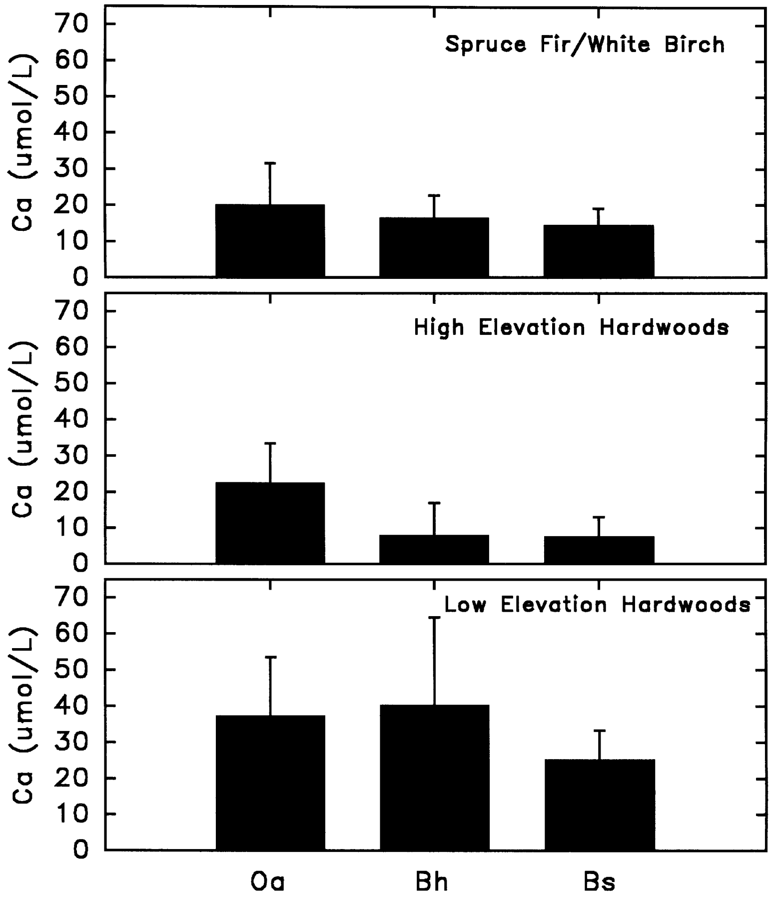


Figure 13. Means and standard deviations of concentrations of Ca in soil water by horizon and elevation zone for W6 at HBEF during 1984–1992 (monthly samples). SFWB is a spruce-fir-white birch stand at 750 m; HH is a deciduous stand at 730 m, and LH is a deciduous stand at 600 m elevation.

was characterized by high concentrations of dissolved organic carbon (DOC) and organic anions throughout the profile. In contrast, within the HH zone, elevated DOC and organic anions draining the Oa horizon were immobilized readily within the mineral soil (see McDowell 1982). Elevated release and dissociation of organic acids within more coniferous stands probably contribute to the mobilization of Ca from soil cation exchange sites and/or from mineral dissolution. At the LH site, soil water pH and HCO_3^- concentrations were higher than observed at the higher elevation sites. These conditions coincided with higher concentrations of exchangeable Ca in the soil and undoubtedly facilitated the leaching of Ca.

Seasonal variations in concentrations of soil water Ca might be anticipated at HBEF, with lower concentrations during the growing season resulting from vegetation uptake and storage. No discernible seasonal pattern in soil water Ca, however, was evident at any of the elevational sites or in any soil horizons monitored (CT Driscoll, unpublished data).

Losses of calcium from the watershed-ecosystem

Dissolved losses in stream water – concentrations, trends and patterns

Streamwater concentrations of Ca are higher than are concentrations of bulk precipitation because they include additional inputs from dry deposition, cation exchange, mineralization of organic matter and weathering, as well as concentration through evapotranspirational water loss. The long-term, volume-weighted mean concentration of Ca in stream water was 28.4 μmol/ℓ (1.14 mg Ca/ℓ). Annual, volume-weighted mean concentrations of Ca in stream water have ranged from a low of 21.2 μmol/ℓ (0.85 mg Ca/ℓ) in 1991–92 to a high of 40.7 μmol/ℓ (1.63 mg Ca/ℓ) in 1969–70 (Figure 3A; Table 11).

Average monthly concentrations of Ca in stream water were relatively constant from month to month with no discernible seasonal pattern (Figure 5A). This absence of a seasonal pattern mirrors that in soil solution. Some 24% of the annual average output of Ca in streamflow occurs during April and 50% occurs during the combined snowmelt runoff months of March, April and May (Figure 5B). Input of Ca in bulk deposition is distributed evenly throughout the year (Figure 5B); thus, the accumulation of snow throughout the winter and its melting play a major role in the uneven seasonal output of Ca via streamflow during the year.

Annual volume-weighted average concentrations in stream water were variable, but generally increased from 1963–64 to 1968–69, then decreased sharply until about 1983–84, and have remained relatively constant thereafter (Figures 3A, 14; Table 11). Time-series analyses of stream Ca concentrations by the SKT procedure showed a statistically significant decrease ($p < 0.0001$; median slope -0.53 μmol/ℓ-yr). For the period 1970–1983, the median slope was somewhat greater, -0.61 μmol/ℓ-yr.

Annual gross outputs of Ca consistently exceeded bulk precipitation inputs during 1963–1992 (Figure 3B). Only during the drought year of 1964–65 did bulk precipitation inputs (77.3 mol/ha; 3.1 kg/ha) approach stream outputs (120 mol/ha; 4.8 kg/ha) (Figure 3B). Annual outputs in stream water increased variably from 1963–64 to 1973–74, then decreased to 1984–85 and remained relatively constant (although more variable than concentrations) thereafter (Figure 3B; Table 12).

Table 11. Annual volume – weighted average concentrations in stream water for HBEF watersheds.

Water-year	W1	W2	W3	W4	W5	W6	Mean[1]	±sd
1963–64	1.83	2.11	1.92	2.56	1.74	1.53	1.76	0.17
1964–65	1.48	1.40	1.64	1.51	1.10	0.97	1.36	0.28
1965–66	1.62	**1.82**	1.62	1.85	1.51	1.37	1.54	0.12
1966–67	1.63	**6.44**	1.55	1.81	1.43	1.27	1.48	0.15
1967–68	1.67	**7.56**	1.61	1.79	1.43	1.29	1.52	0.17
1968–69	1.66	**5.99**	1.59	1.87	1.50	1.30	1.52	0.15
1969–70	2.17	6.23	2.03	2.35	1.76	1.63	1.94	0.23
1970–71	2.03	4.02	2.09	**2.30**	1.69	1.46	1.86	0.28
1971–72	1.87	2.19	2.09	2.81	1.62	1.44	1.80	0.27
1972–73	1.80	1.83	1.68	**2.45**	1.53	1.36	1.61	0.19
1973–74	1.83	1.73	1.64	2.31	1.55	1.36	1.61	0.19
1974–75	1.83	1.73	1.63	**1.93**	1.57	1.39	1.62	0.18
1975–76	1.72	1.65	1.53	1.75	1.48	1.28	1.51	0.18
1976–77	1.61	1.53	1.43	1.49	1.37	1.19	1.41	0.17
1977–78	1.45	1.63	1.37	1.54	1.29	1.11	1.31	0.15
1978–79	1.35	1.53	1.29	1.51	1.23	1.05	1.23	0.13
1979–80	1.48	1.61	1.38	1.60	1.28	1.15	1.34	0.14
1980–81	1.45	1.66	1.37	1.63	1.29	1.12	1.31	0.14
1981–82	1.26	1.54	1.19	1.56	1.13	0.97	1.14	0.12
1982–83	1.18	1.50	1.16	1.58	1.12	0.95	1.10	0.10
1983–84	1.07	1.42	1.09	1.54	**1.15**	0.87	1.01	0.10
1984–85	1.08	1.39	1.13	1.58	2.62	0.93	1.04	0.08
1985–86	1.03	1.31	1.07	1.52	2.27	0.88	0.99	0.09
1986–87	1.04	1.42	1.14	1.72	1.44	0.92	1.03	0.09
1987–88	1.05	1.45	1.12	1.74	1.33	0.92	1.03	0.08
1988–89	1.11	1.44	1.20	1.76	1.37	0.97	1.09	0.09
1989–90	1.13	1.53	1.16	1.93	1.32	0.96	1.08	0.09
1990–91	1.08	1.52	1.14	1.98	1.32	0.87	1.03	0.12
1991–92	1.00	1.39	1.07	1.77	1.33	0.85	0.98	0.09
Individual annual mean (mg/ℓ)	1.47	2.36	1.45	1.85	1.47	1.15	1.35	0.15
±sd	0.34	1.76	0.31	0.35	0.32	0.23	0.29	0.06

Mean[1] and ±sd for W1, W3, and W6 only
bold: Values from years during experimental treatments

Gross annual outputs in stream water were positively and significantly (r^2 = 0.50 for all data) related to amount of annual streamflow during 1963–1992 (Figure 15). This relationship was somewhat surprising, considering the substantial long-term decline in stream Ca concentration (Figures 3A,

Table 12. Annual stream output of calcium from forested and disturbed HBEF watersheds.

Water-year	W1	W2	W3	W4	W5	W6	Mean[1]	±sd
1963–64	11.9	15.0	12.4	18.0	11.5	10.7	11.6	0.7
1964–65	6.5	7.0	7.2	7.5	6.1	4.8	6.2	1.0
1965–66	11.0	**14.5**	11.5	13.9	11.2	10.4	10.9	0.4
1966–67	12.4	**77.1**	11.9	15.2	11.7	10.8	11.7	0.7
1967–68	14.5	**93.1**	14.0	16.7	13.6	12.2	13.6	1.0
1968–69	14.1	**69.4**	13.3	17.3	12.6	11.7	13.0	1.0
1969–70	18.1	68.7	16.6	20.5	14.1	14.1	16.3	1.6
1970–71	14.8	39.6	15.9	**18.7**	12.8	12.1	14.3	1.6
1971–72	12.8	18.2	14.9	22.4	11.2	10.7	12.8	1.7
1972–73	17.2	19.6	16.2	**26.4**	15.1	14.0	15.8	1.3
1973–74	24.5	26.2	21.9	35.3	21.3	19.0	21.8	2.2
1974–75	14.0	15.5	12.3	**17.1**	12.4	11.2	12.5	1.1
1975–76	20.5	21.6	18.1	23.1	17.4	15.2	17.9	2.2
1976–77	14.0	14.3	11.4	14.1	11.6	10.1	11.8	1.6
1977–78	13.8	17.3	12.3	16.1	12.1	10.9	12.3	1.2
1978–79	11.0	13.6	10.5	13.1	9.9	8.9	10.2	0.9
1979–80	10.6	12.1	9.6	11.6	9.0	8.2	9.4	1.0
1980–81	10.9	12.8	10.1	12.5	9.5	8.7	9.9	0.9
1981–82	13.5	17.5	12.8	17.6	11.4	10.0	12.1	1.5
1982–83	9.5	12.3	9.3	13.0	8.6	7.7	8.9	0.8
1983–84	10.7	14.7	10.8	15.9	**11.0**	8.7	10.1	1.0
1984–85	7.0	9.1	7.3	10.5	21.0	6.2	6.8	0.5
1985–86	9.1	11.8	9.2	13.9	21.1	8.0	8.8	0.6
1986–87	7.8	11.2	9.1	13.5	11.4	7.6	8.2	0.6
1987–88	7.5	10.2	8.0	13.0	9.8	7.1	7.5	0.4
1988–89	7.0	9.4	7.7	11.4	9.4	6.9	7.2	0.4
1989–90	10.9	16.4	11.7	20.0	14.1	10.1	10.9	0.7
1990–91	11.4	17.4	12.4	21.7	15.0	9.8	11.2	1.1
1991–92	8.0	12.3	9.0	15.2	12.0	7.4	8.1	0.7
Total (kg/ha)	354.8	697.9	347.4	485.4	367.7	293.1	331.8	
Annual mean (kg/ha-yr)	12.2	24.1	12.0	16.7	12.7	10.1	11.4	
±sd	4.1	22.3	3.4	5.4	3.6	2.9	3.4	

Mean[1] and ±sd for W1, W3, and W6 only
bold: Values from years during experimental treatments

14). Indeed, within this highly significant ($p = <0.0001$) long-term pattern, there were interesting and important changes with time (Figure 15). Initially (1963–75), the output-streamflow relationship had a relatively steep slope (Y

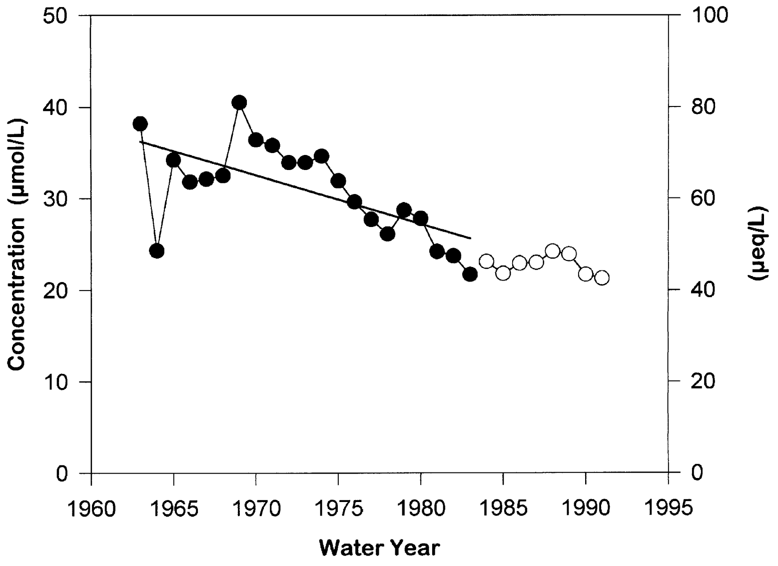


Figure 14. Annual volume-weighted concentrations of Ca in stream water of W6 at HBEF during 1963–1992. The $r^2 = 0.42$ during 1963–1983 and 0.94 during 1969–1983 (●).

= 0.34X + 0.4; $r^2 = 0.89$). The slope was lower in 1976–80 (Y = 0.25X + 23.1; $r^2 = 0.85$), and even lower in 1981–93 (Y = 0.21X + 10.3; $r^2 = 0.82$). With units of mol/ha/mm-yr, the regression slopes reflect the temporal changes in annual Ca concentrations in stream water. In each period, the correlation was high, suggesting relatively constant stream Ca concentrations (see also Figure 14). Overall, these tight but changing relationships with time, likely reflect changes in the fluxes of acid anions and the depletion of the labile Ca pool in the soil.

Net annual flux of Ca (stream output – bulk deposition input) in stream water is related strongly to the amount of annual streamflow ($r^2 = 0.64$; Figure 16).

Elevational patterns in streamwater chemistry

Although not significantly different, arithmetic averaged, annual (based on monthly collections during 1982–1992) concentrations of Ca were relatively high at the highest elevation stream sampling site (mean concentration 17.8 μmol/ℓ) (Figure 17). Stream Ca concentrations decreased as waters drained from this SFWB zone and entered the HH zone, to a mean value of 12.5 μmol/ℓ at 660 m. Mean concentrations of Ca then increased with decreasing elevation to the highest value, 22 μmol/ℓ, at the weir, at 540 m.

These elevational patterns in Ca concentrations were consistent with concentrations in the mineral soil water (Figure 13). Concentrations of Ca in

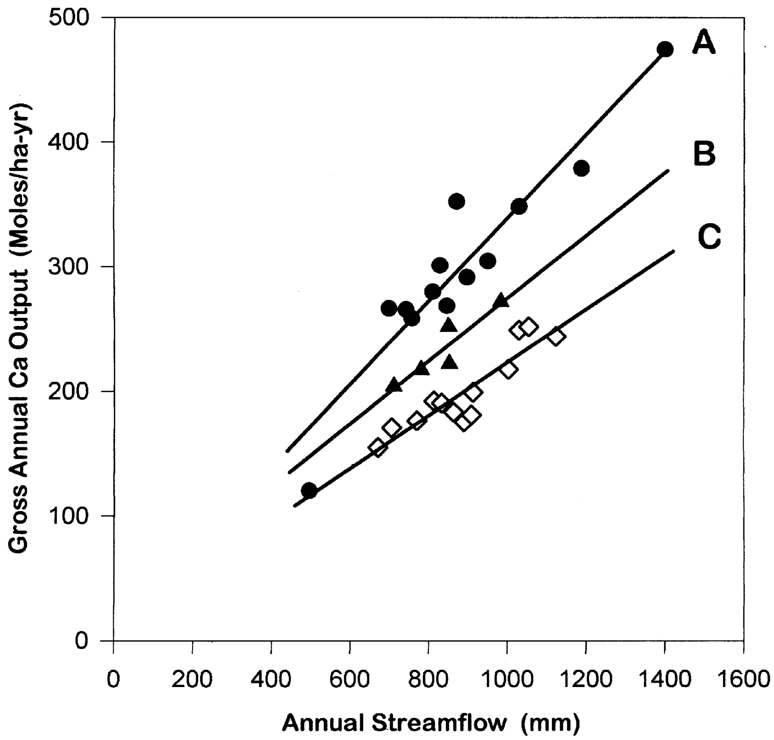


Figure 15. Relationship between the gross, annual output of Ca in stream water and the amount of streamflow for W6 at HBEF. Symbols indicate: ● 1963–64 to 1974–75 (A); ▲ 1975–76 to 1979–80 (B); ◊ 1980–81 to 1992–93 (C). See text for details.

Table 13. Estimates of residence times (Tn) of calcium in the forest floor and mineral soil of the Hubbard Brook Experimental Forest during 1987–1992.

	Input (mol/ha-yr)							
	Pool size (mol/ha)	Above-ground litter	Stemflow + through-fall	Root litter	Root exudates	Oa hor. leachate	Total	Tn (yr)
Forest floor:								
Exchangeable	1850	1015	110	202*	41*	–	1370	1.4
Total	7930	1015	110	202	41	–	1370	5.8
Mineral soil:								
Exchangeable	4850	–	–	238	49	361	648	7.5
Total	250,000	–	–	238	49	361	648	390

* same assumptions as in Likens et al. 1994

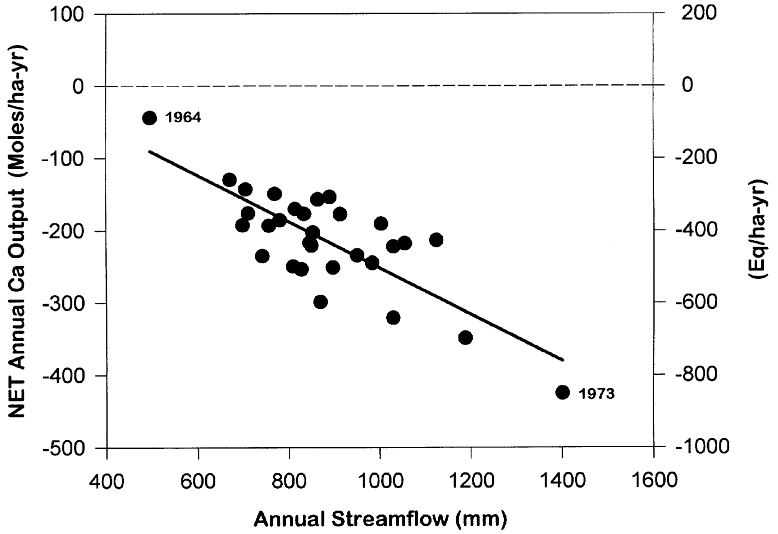


Figure 16. Annual net Ca output (bulk precipitation input – streamwater output) for W6 at HBEF during 1963–1992. Negative fluxes indicate that the watershed-ecosystem is a net source of Ca.

Bs_2 soil waters and stream water were high in the high elevation SFWB zone, decreased in the HH zone and increased in the lower elevation LH zone. Like soil water concentrations, these stream patterns likely reflect elevational variations in concentrations of naturally occurring organic acids and the exchangeable Ca concentrations of mineral soil. Stream water draining the SFWB zone was characterized by high concentrations of DOC and organic anions, and low pH. Elevated concentrations of organic acids in the SFWB zone probably facilitated the mobilization of Ca from soil, despite the relatively low concentrations of exchangeable Ca. Concentrations of DOC decreased and pH increased markedly in the stream reach of the HH zone, and as a result, organic acid leaching was diminished. Lower concentrations of organic anions, coupled with low concentrations of exchangeable Ca in the mineral soil resulted in lower concentrations of Ca in stream water. At lower elevations in the watershed, stream pH and Ca concentrations increased, while DOC concentrations decreased further. The soils in this lower zone contain appreciably larger exchangeable Ca pools (see *Forest Floor and Mineral Soil Pools and Dynamics*, above), and tend to be deeper, resulting in greater contact times between soil and percolating water. Thus, elevated stream pH and Ca concentrations can be explained by leaching of exchangeable Ca and enhanced weathering of Ca-bearing minerals in the different zones (Johnson et al. 1997).

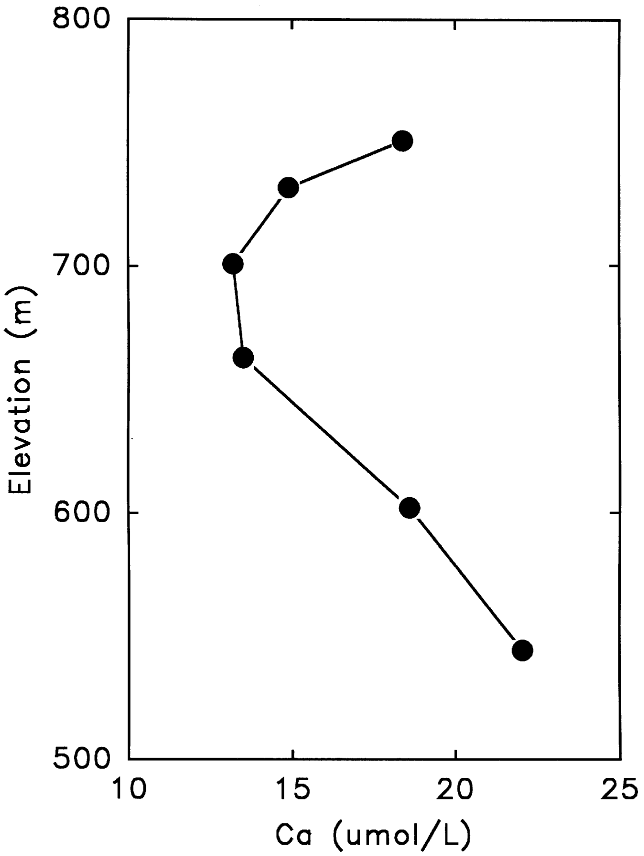


Figure 17. Arithmetic mean annual concentrations of Ca in stream water at sites along an elevational gradient within W6 at HBEF during 1982–92.

As observed in soil solutions, seasonal patterns were not evident in Ca concentrations at any elevational stream sites (CT Driscoll, unpublished data).

Particulate losses in stream water

The particulate matter transported from watershed-ecosystems at HBEF was partitioned into three categories: suspended and bed-load materials collected in the ponding basin at the mouth of the gauged watershed-ecosystem, suspended material collected in a 1-mm mesh net from water passing through the gauging weir, and suspended material collected on a 0.45-μm pore filter from samples collected behind a net at the weir (Bormann et al. 1969). During an 8-yr period (1965–66 through 1972–73), material collected in the ponding-basin represented more than 77% of the total particulate matter. Organic particulate matter comprised some 33% of the total particulate matter transported (Likens et al. 1977). About 74% of the Ca lost in particulate matter was contained in inorganic particules (Bormann et al. 1974). We assume that these proportions were similar throughout 1963–1992 and that Ca was transported accordingly in this particulate matter.

The amount of particulate matter transported from hillslopes at HBEF is highly dependent upon stormflow events (e.g. Bormann & Likens 1979; Bormann et al. 1969, 1974; Likens & Bormann 1995). Losses of Ca in particulate matter were small compared to those in dissolved form. For example, during 1966–67 through 1969–70 streamwater losses of Ca in particulate matter were 5.7 mol/ha-yr (0.23 kg/ha-yr), whereas the net loss of dissolved Ca (streamwater loss – bulk deposition input) was 242 mol/ha-yr (9.7 kg/ha-yr).

Biotic flux

Burton & Likens (1975) reported that the standing crop of Ca was 0.69 mol/ha (27.5 g/ha) in mammals, 0.30 mol/ha (11.9 g/ha) in salamanders and 0.17 mol/ha (6.9 g/ha) in birds at HBEF during the early 1970's. Sturges et al. (1974) estimated that the maximum net loss of Ca from watershed-ecosystems via birds during 1969 and 1970 was 0.075 mol/ha-yr (3.0 g/ha-yr). All of these values are small, as compared to a net loss of 230 mol/ha-yr (9200 g/ha-yr) and 5.7 mol/ha-yr (230 g/ha-yr) in dissolved and particulate Ca, respectively during 1969–70, a rather average hydrologic period (Figure 2C). The bird population during this period was relatively large (see Likens 1992). Nevertheless, the transport of Ca across watershed-ecosystem boundaries at HBEF by animals (e.g. birds and mammals) was quite small (e.g. Sturges et al. 1974), primarily because large mammal populations were small during the study period (e.g. Siegler 1968; Pletscher 1982, 1987). Biotic fluxes could increase in the future as numbers of moose (*Alces alces*) currently are increasing at HBEF. Among the major elements, the standing crop and flux of Ca in animal populations are exceeded only by C, H, O and N at HBEF.

General discussion/budgetary considerations

Environmental concerns about Ca biogeochemistry arise from its dual role as an essential macronutrient and as a principal base cation in most natural waters. Calcium is the dominant cation in stream waters at HBEF (Likens & Bormann 1995), and streamwater outputs of Ca exceed atmospheric inputs throughout the year (Figure 3B, Table 14). During 1963–1992, streamwater outputs of Ca averaged 252 ± 72.3 mol/ha-yr, whereas bulk precipitation inputs averaged 37.4 ± 17.5 mol/ha-yr (Table 14).

Table 14. Annual input-output budgets for calcium in Watershed 6 of the Hubbard Brook Experimental Forest, New Hampshire.

Water-year	Precip. input	Stream output	Net gain (+) or loss (−)
1963–64	74.2	266.8	−192.6
1964–65	77.0	120.6	−43.6
1965–66	65.7	258.8	−193.0
1966–67	52.3	268.7	−216.4
1967–68	70.6	304.8	−234.2
1968–69	40.9	291.7	−250.8
1969–70	54.0	352.6	−298.7
1970–71	48.1	301.3	−253.2
1971–72	30.9	265.9	−235.0
1973–73	28.0	348.5	−320.5
1973–74	49.9	474.6	−424.7
1974–75	30.8	280.1	−249.3
1975–76	30.7	379.2	−348.5
1976–77	31.5	252.0	−220.5
1977–78	27.4	271.9	−244.5
1978–79	19.9	222.3	−202.4
1979–80	28.4	204.1	−175.7
1980–81	32.1	217.4	−185.2
1981–82	27.4	249.2	−221.8
1982–83	22.8	192.5	−169.8
1983–86	27.2	217.6	−190.4
1984–85	25.6	155.1	−129.6
1985–86	22.3	199.4	−177.1
1986–87	14.2	190.8	−176.5
1987–88	27.7	176.7	−149.0
1988–89	28.3	170.9	−142.7
1989–90	34.6	251.9	−217.4
1990–91	30.9	244.0	−213.2
1991–92	26.9	183.6	−156.7
Mean	37.3	252.2	−214.9
±sd	16.6	72.7	70.6
Max	77.0	474.6	−43.6
Min	14.2	120.6	−424.7

Values in moles/ha-yr (1 mole/ha-yr = 0.04 kg/ha-yr)

The uncertainty in estimating dry deposition has only a very small effect on the calculation of net flux of Ca from this watershed-ecosystem. Our high and low estimates of Ca dry deposition were 2.1 and 13.8 mol/ha-yr (see *Bulk*

Deposition vs. Wet Deposition and Dry Deposition, above). The difference between these estimates would vary the current net Ca output (211 − 29 = 182 mol/ha-yr; Figure 18B) from this ecosystem by only 6%. In other ecosystems subject to higher loads at airborne dust, uncertainty in dry deposition estimates could be crucial for calculation of the mass balance, but for HBEF the effect appears to be minor.

The Ca budget for HBEF shows that the biomass and soil pools are large relative to atmospheric inputs and streamwater losses. Thus, changes in the distribution and cycling of Ca in the forest ecosystem may impact forest productivity, soil fertility and water quality. Currently most (92%) of the Ca in the forest ecosystem is in the soil, with only 8% bound in living and dead biomass (Figure 18B). However, much of the soil Ca is bound in minerals, unavailable for plant uptake. If the soil exchangeable Ca pool were reduced significantly, available Ca for biomass uptake could become critical for growth. Concentrations of Ca in bulk precipitation have decreased markedly since 1955–56 (Junge & Werby 1958; Figure 4). During our study, average atmospheric deposition of Ca decreased from 61 to 29 mol/ha-yr (Figure 18). Likewise, the average annual loss of dissolved Ca in stream water decreased from 249 mol/ha-yr in 1964–69 to 205 mol/ha-yr in 1987–92. Annual net uptake of Ca by forest vegetation also declined sharply, from 202 mol/ha-yr in 1964–69, to 54 mol/ha-yr in 1987–92. Thus, total annual streamwater output was 1.3 times greater than net biomass accretion in 1964–69, and 3.9 times greater in 1987–92 (Figure 18).

With these data, we can assess the magnitude of annual biocycling of Ca. During 1987–92, we estimate the gross uptake of Ca in trees to be approximately 1709 mol/ha-yr, based on estimates of root exudation (90 mol/ha-yr), fine root turnover (270), woody root turnover (170), litterfall (1015), canopy leaching (110), and net biomass accrual (54) (Figure 18B). Of the annual gross uptake by vegetation, only 3% is stored while the other 97% is returned to the soil. Gross uptake (1967 mol/ha-yr) during 1964–69 was 15% greater than in 1987–92, and net storage represented about 10% of gross uptake of Ca.

The relatively large gross uptake of Ca clearly shows the importance of biocycling to the Ca cycle. Some 7 to 8 times more Ca is cycled through trees than is lost from the ecosystem in stream water during a year. Also, the gross uptake represents about 26–30% of the entire exchangeable Ca pool in the soil (6500 mol/ha), suggesting that Ca turns over rapidly in the soil as well (see Table 13). Based on the total output of Ca from the soil (gross uptake by trees + stream loss), the turnover time of exchangeable Ca in the solum is about 3 years. This estimate is only approximate because the exchangeable

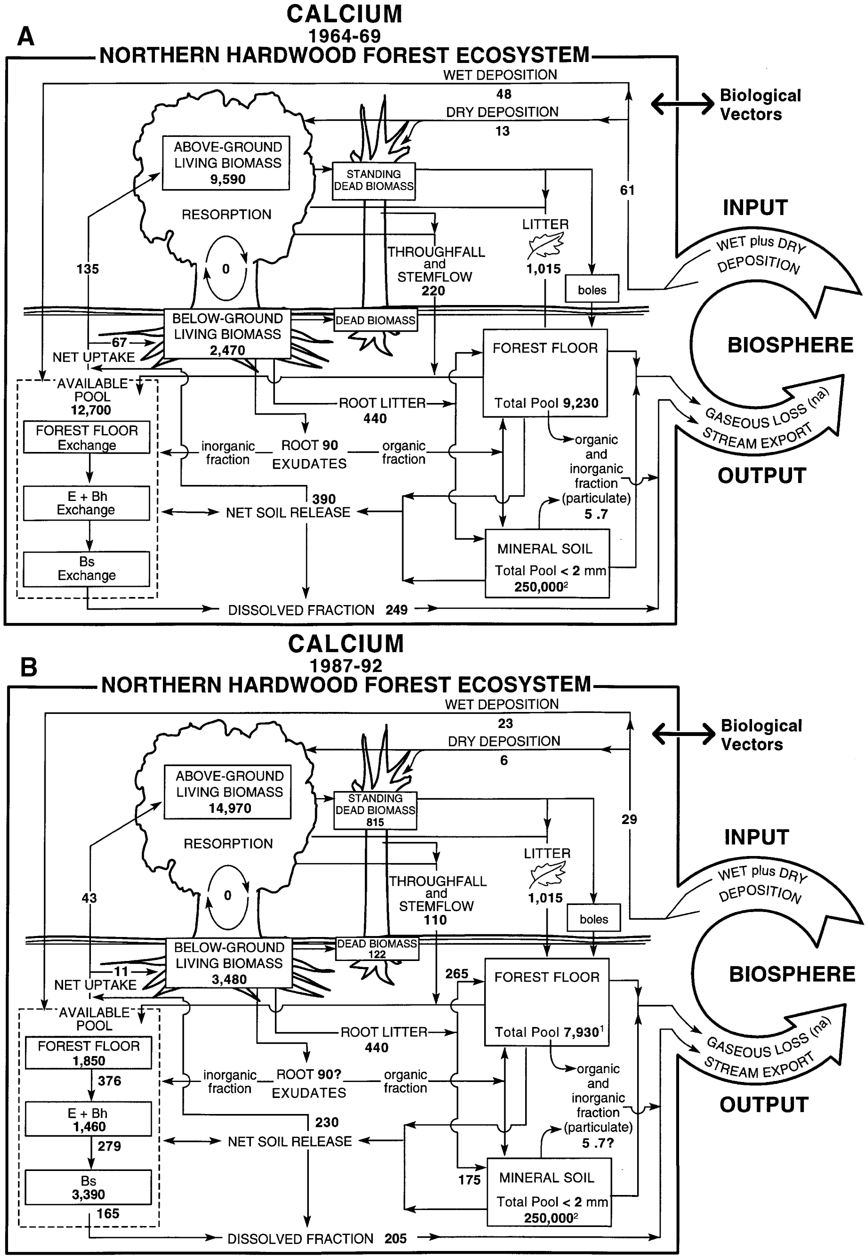


Figure 18. Ecosystem pools (boxes) and fluxes (arrows) of Ca for W6 at HBEF. Average values in mol/ha or mol/ha-yr for periods specified. Values for 1964–69 are shown in **A** (values are modified from Likens et al. 1977; root and aboveground litter, root exudates and mineral soil assumed to be same in 1987–1992), while **B** shows the Ca cycle in 1987–92 (above- plus belowground biomass is average of 1987 and 1992 values, belowground assumed to be 20% of aboveground; Net uptake values are based on the difference in biomass storage between 1982 and 1992; [1])Total forest floor pool from Johnson 1989, [2])Total mineral soil pool from Federer et al. 1989.

Ca pool appears not to be at steady state (see *Supply of Ca from Weathering and Cation Exchange*).

Despite the large internal pools and fluxes of Ca within the forest ecosystem, relatively small amounts of Ca are lost in stream water at HBEF during an annual cycle (see also, Likens et al. 1967, 1977, 1985; Bormann & Likens 1979; Likens & Bormann 1995). The net flux in drainage waters results from the balance of processes supplying Ca in atmospheric deposition, those retaining or releasing Ca from the soil (cation exchange, mineralization of organic matter and mineral weathering), and storing of Ca in living and dead biomass within the forest ecosystem. Therefore, on short time scales (weekly, monthly, seasonal), streamwater fluxes vary based on the timing of plant activities, hydrologic flowpaths and weather. Plant uptake and transpiration are low in the autumn, winter and early spring. In spring, temperatures and leaching rates increase when the snowpack melts while plants are largely dormant. During this period, Ca output in stream water reaches its annual peak (Figure 5B). By late April, spring ephemeral plants begin to sequester Ca (Muller 1978), and by late May, most of the forest vegetation is fully active, resulting in two important biotic effects: (1) plant uptake of Ca increases, (2) transpiration by vegetation increases dramatically, reducing the amount of soil water. Losses of Ca in stream water during the summer period are the lowest in the annual cycle. In the fall, plant uptake and transpiration decrease and leaves are shed by deciduous vegetation. Lower uptake and reduced transpiration, coupled with leaching of Ca from fresh litter result in somewhat elevated Ca losses (Figure 5B). Finally, with soil cooling in late fall and early winter, and with significant accumulation of atmospheric input in the snow pack, biotic processes (uptake, transpiration and mineralization) slow, and soil water flow declines due to snowpack accumulation, all resulting in somewhat smaller Ca losses in winter than in the fall.

Current inputs to the available nutrient compartment are partitioned as follows: net soil release, 50%, leaching from canopy, 24%, root exudates, 20%, and atmospheric deposition, 6% (Figure 18B). Fluxes of Ca increase as precipitation passes through the canopy and forest floor, then decrease while passing through mineral soils to the stream (Figure 18B). Foliar leaching, scavenging of dry deposition and mineralization of Ca in the forest floor can explain these increases in Ca concentrations. However, the causal mechanisms underlying the immobilization of Ca in mineral soils are unknown. This pattern could reflect deep root uptake by forest vegetation and subsequent biological cycling, or more likely, the removal from soil solution by cation exchange in the mineral soil. However, exchangeable Ca pools have been consistently and significantly depleted in the past 40 years or so (estimated to be $>$42,000 eq/ha ($>$21,000 mol/ha) during 1940–1995; Likens et al. 1996).

Direct or indirect leaching by acid rain is thought to be the mechanism causing the depletion of Ca from surface soil pools, but the sink for this Ca is not clear, particularly given the recent declines in biomass storage and streamwater outputs. Long-term measurements of Ca in Mirror Lake, near the mouth of the Hubbard Brook Valley, have not shown statistically significant temporal trends in Ca concentration (GE Likens, unpublished data). Potential sinks could be immobilization by cation exchange in the lower mineral soil (see Figure 18B) and/or differential species uptake and storage in the changing mix of canopy species and dead biomass pools (see e.g. Figure 7). For example, sugar maple, the tree species with the highest Ca concentration, has shown a 5% to 30% increase in mortality between 1982 and 1992 in the HH zone.

The low values of cation exchange capacity (∼5 cmol_c/kg) and percent base saturation (∼12%) of HBEF mineral soil (Driscoll et al. 1989; Likens et al. 1994) result in small exchangeable Ca pools, and are indicative of high sensitivity of these soils to acid deposition from the atmosphere (e.g. Reuss & Johnson 1986) and to intensive forest harvest practices (Federer et al. 1989). Furthermore, the rate of supply of Ca to drainage water is low at HBEF because this pool of exchangeable base cations is small and the abundances and/or weathering rates of Ca-bearing minerals are low. Because cation exchange and weathering are largely responsible for the generation of acid-neutralizing capacity (ANC) in stream water and the neutralization of external and internal inputs of acidity (e.g. Johnson et al. 1981; Driscoll & Likens 1982; Likens et al. 1996), the continued depletion of Ca from HBEF soils, especially from the exchangeable pool, will result in further soil acidification and declines in stream Ca concentrations.

Effects of acid rain on Ca biogeochemistry

Anthropogenic acid rain began *per se* about 1950–1955 in the northeastern U.S. (e.g. Cogbill & Likens 1974). Although the continuous records of bulk precipitation and streamwater chemistry at HBEF are the longest in North America by some 15 years, they began only in 1963. Data for 1955–56 (Junge & Werby 1958), show that annual concentrations of Ca in wet-only precipitation were about 2 times higher than bulk precipitation in 1963–64 and approximately 6.6 times the average value for 1988–1992 at HBEF. Unfortunately, Junge & Werby (1958) did not report pH values.

The volume-weighted annual pH of bulk precipitation at HBEF has varied from 4.05 to 4.3 during 1963–1992, with minimum values for individual storms as low as 2.85. The average pH of rain during June through September of 1964–69 was 4.04, whereas during 1987–92 it was 4.27. Calcium leaching from the canopy, and thus net throughfall of Ca, is affected strongly by acidic deposition, as has been shown by experimental studies on seedlings (e.g. Wood & Bormann 1975) and on mature trees (Lovett & Hubbell 1991). Despite the fact that Ca is much less mobile within the plant than K, Ca is much more susceptible to increased leaching from acid rain (Lovett & Hubbell 1991). This difference in leaching probably results because Ca is held on exchange surfaces within and on the foliage and branches. For sugar maple, one of the dominant species at HBEF, acid rain of pH 3.8 doubled the foliar leaching of Ca, relative to rain of pH 5.0 (Lovett & Hubbell 1991). This same study found no significant effect of acidity on K leaching. The effect of acidity on Ca leaching likely varies among species and forest types. Multiple regression analysis has shown that pH of rain events is the second most important factor (after precipitation amount) explaining the event-to-event variability in Ca NTF at HBEF, and that the regression coefficients vary among forest types, with the mature northern hardwood forests showing greater sensitivity to acid-induced foliar leaching than the SFWB or pin cherry stands (Lovett et al. 1996).

Concentrations of Ca in stream water generally increased during the first seven years (1964–70) of our study, peaked in 1969–70 and declined thereafter (Figures 3A, 14). The output of base cations ($C_\beta = Ca^{2+} + Mg^{2+} + K^+ + Na^+$) in stream water is strongly related to the output of strong acid anions ($SO_4^{2-} + NO_3^-$) (Figure 19). In particular, the concentration of Ca in stream water was strongly related to the concentration of SO_4^{2-} in stream water ($Y = 0.84X - 19.9$; $r^2 = 0.64$) during 1963–92 (Figure 20C), and the output of Ca was even more strongly related to SO_4^{2-} output ($Y = 0.62X - 125$; $r^2 = 0.83$; Figure 20D). Concentration and output of Ca also were significantly correlated with concentration of NO_3^- ($Y = 0.36X + 20.8$; $r^2 = 0.69$) and streamwater output of NO_3^- ($Y = 0.96X + 323$; $r^2 = 0.73$) (Figure 20A,B). The streamwater outputs of Ca, SO_4^{2-} and NO_3^- all were strongly dependent on amount of water, with 1963–65 being drought years and 1973–74 being the wettest year on record (Figures 3C, 20C,D). Chloride does not affect these relations because it represents only 9.0% of atmospheric inputs and 9.1% of streamwater outputs of strong acid anions at HBEF.

Significantly, the time path of changes in volume-weighted, mean annual streamwater Ca, SO_4^{2-} and NO_3^- concentrations follows a hysteresis pattern (Figure 21), as does C_β (Likens et al. 1996). The SO_4^{2-} in stream water at HBEF was estimated for pre-industrial revolution (PIR) times, circa 1800, at about 20 μeq/ℓ (Brakke et al. 1989; Christophersen et al. 1990; Sullivan et al. 1990; Sullivan 1991) and NO_3^- concentrations at 5 μeq/ℓ for a total concentration of 25 μeq/ℓ for $SO_4^{2-} + NO_3^-$, with an ANC of about 20 μeq/ℓ. These values would produce an estimate for C_β of about 45 μeq/ℓ (Likens et al. 1996) and for Ca of about 20 μeq/ℓ in PIR (Figure 21).

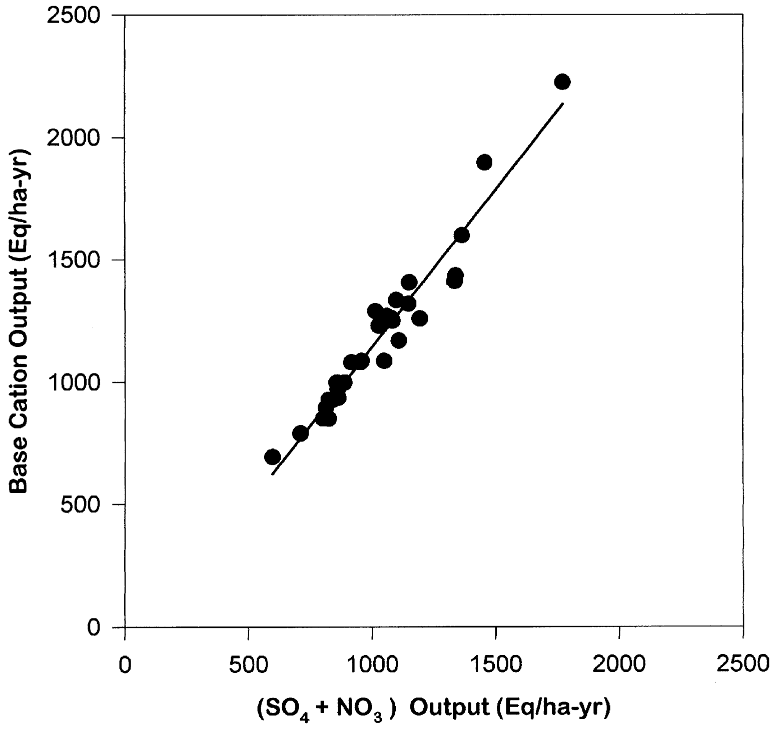


Figure 19. Relation between annual output of base cations ($Ca^{2+} + Mg^{2+} + K^{+} + Na^{+}$) and strong acid anions in stream water from W6 during 1963–64 through 1992–93; $r^2 = 0.94$.

A major and consistent response to deforestation and clearcutting within the White Mountain region is for nitrate concentrations and acidity of soil water and stream water to increase due to increased nitrification (e.g. Likens et al. 1970; Bormann & Likens 1979; Martin & Pierce 1980; Martin et al. 1986). Thus, the deforestation experiment of W2 (yielding the most pronounced response in pH and NO_3^-) provided an experimental test of the effect of increased input of H^+ on concentration and flux of Ca in stream water in response to anthropogenic acidification. The hysteresis response of Ca concentrations in W2 to changes in NO_3^- and SO_4^{2-} concentrations following deforestation (Figure 22) was similar in pattern (although concentration change was more pronounced) to the long-term response to acid rain in W6 (Figure 21). In other areas predictions about cation leaching may be more complicated depending upon soil type and the relative amounts of NO_3^- and SO_4^{2-} (Kölling & Prietzel 1995). The changing inputs of NO_3^- and SO_4^{2-} in precipitation with time (Likens & Bormann 1995) may complicate these interrelationships even further.

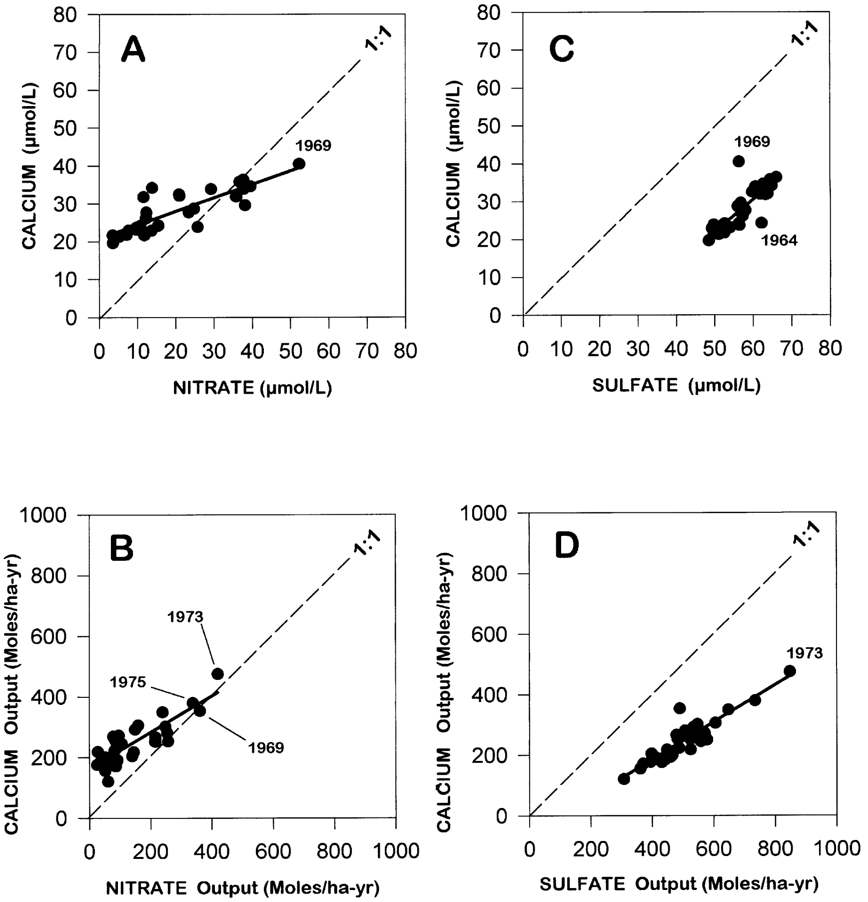


Figure 20. Relation between concentration of calcium and nitrate in stream water (A, $r^2 = 0.69$), output of calcium and nitrate in stream water (B, $r^2 = 0.64$), concentration of calcium and sulfate in stream water (C, $r^2 = 0.73$) and ouptut of calcium and sulfate in stream water (D, $r^2 = 0.83$) of W6 of the HBEF.

Mass-balance analysis

The sources and sinks of Ca for the watershed-ecosystem were apportioned (Figure 23) from 1940 to 1963 based on estimated values, and from 1963 to the present, based on our ongoing measurements. Calcium release from weathering was assumed to be constant prior to 1963 at the average value calculated during 1963–1993 of 53 mol/ha-yr, and is considered a conservative estimate (see section on *Supply of Ca from Weathering and Cation Exchange*). Net decrease in the rate of storage of Ca in biomass since 1973 was estimated from a logistic curve fitted to data from 1965–1992 (Figure 10). Extending back from 1973 to 1940, storage was assumed to be a constant linear accumu-

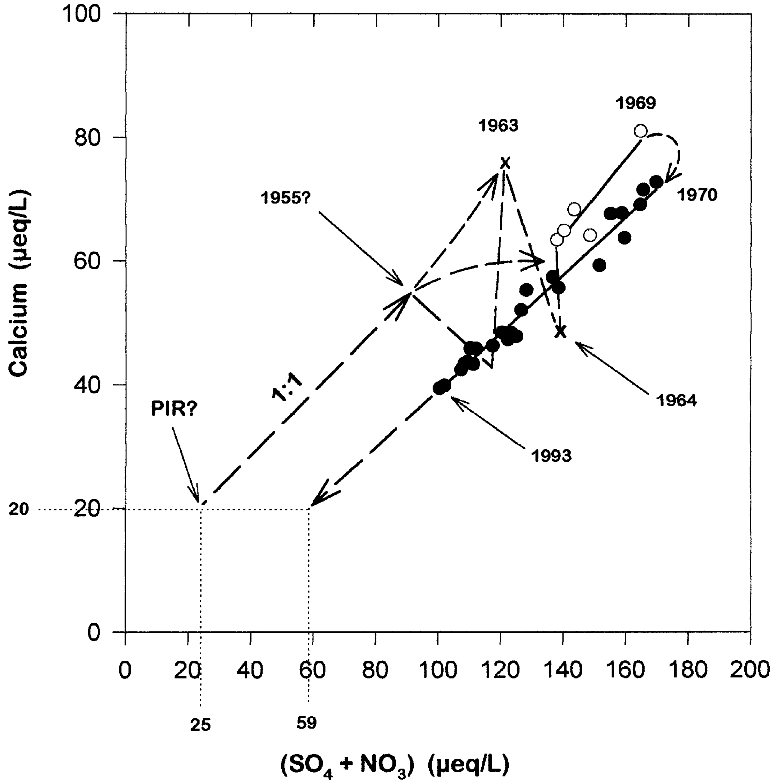


Figure 21. Relation between the annual, volume-weighted average concentration of Ca^{2+} and sum of SO_4^{2-} + NO_3^- in stream water from W6 of the HBEF during 1964–65 through 1993–94. The linear regression for data from 1965–66 through 1969–70 (○) is $Y = 0.63X - 23.8$; $r^2 = 0.84$, and for 1970–71 through 1993–94 (●) is $Y = 0.47X - 8.1$; $r^2 = 0.97$, all in μeq/ℓ. The 95% confidence intervals for these two regression lines do not overlap. PIR = pre-industrial revolution, circa 1800. Data for SO_4^{2-} and NO_3^- during PIR and 1963–64 and Ca^{2+} for PIR are estimated (for PIR see text; Ca^{2+} was 76.3 μeq/ℓ in 1963, but anions were not measured). Values from PIR to 1955 were estimated from a 1:1 linear extension of the relationship at PIR, and assuming an ANC of 20 μeq/ℓ (Likens et al. 1996). The value of 59 for acid anions represents 50% of 1980 value for SO_4^{2-} plus 5 μeq/ℓ of NO_3^-.

lation (359 mol/ha-yr; Bormann & Likens 1979). For bulk deposition inputs, we used measured values after 1963. Prior to 1963, a linear trajectory was used to 1955, and that value (175 mol/ha-yr; Junge & Werby 1958) was used for 1940 to 1955. Bulk deposition samplers underestimate the dry portion of total atmospheric deposition (see *Bulk Deposition vs. Wet Deposition and Dry Deposition*), but no quantitative, temporal data on dry deposition are available to enable us to estimate values prior to 1963. Thus, we made no correction to the bulk deposition values or to the 1955–56 value (Figure 23) and as such

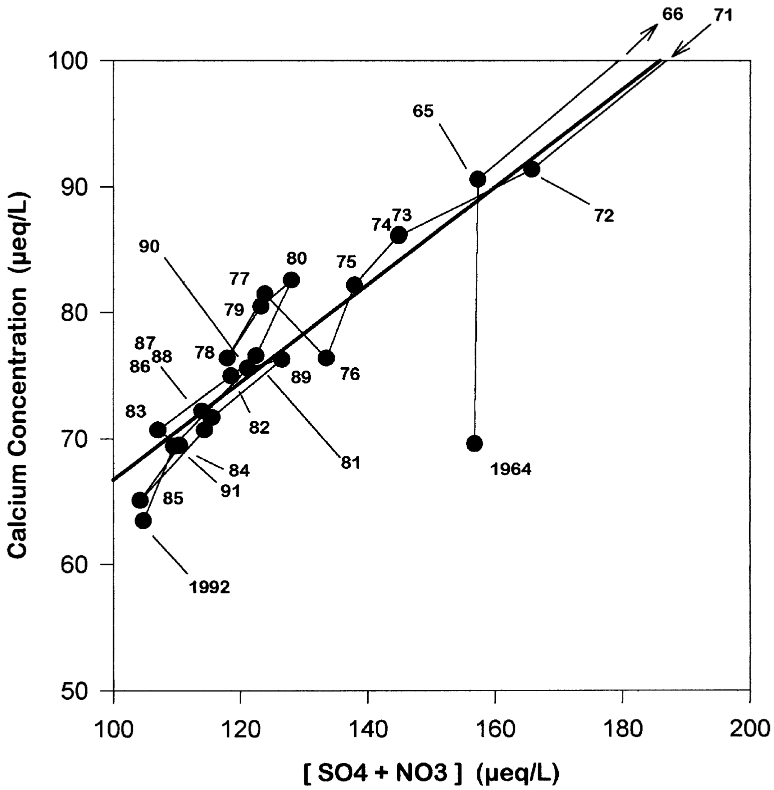


Figure 22. Relation between annual, volume-weighted average Ca concentration and sum of SO_4^{2-} + NO_3^- in stream water from W2, which was deforested in winter of 1965–66. The regression line for 1963–1992 is Ca = 0.39 [SO_4^{2-} + NO_3^-] + 27.9, $r^2 = 0.99$.

they would represent conservative estimates of input. Streamwater Ca output was based on a relationship with historical SO_2 emissions and concurrent SO_4^{2-} concentration + 5 μeq/ℓ of NO_3^- (Likens & Bormann 1995).

Concentrations of strong acid anions and Ca in stream water are assumed to have increased slowly after PIR to about 1940 and then more rapidly thereafter due to increased atmospheric inputs of strong acids (Figures 21 and 23). As the more labile pool of C_β in soil was depleted (mid 1950's to mid 1970's), the concentration of Ca in stream water decreased (1970–1994; Figures 14, 21 and 23). Our initial measurements in 1963 may have captured the end of the phase of rapidly increasing acidification of soil and drainage water, and marked depletion of labile Ca in the soil (Figure 21). The different trajectories of concentration response shown between 1955 and 1963 (Figure 21) reflect this possible "shock effect" of acid rain inputs on the ecosystem.

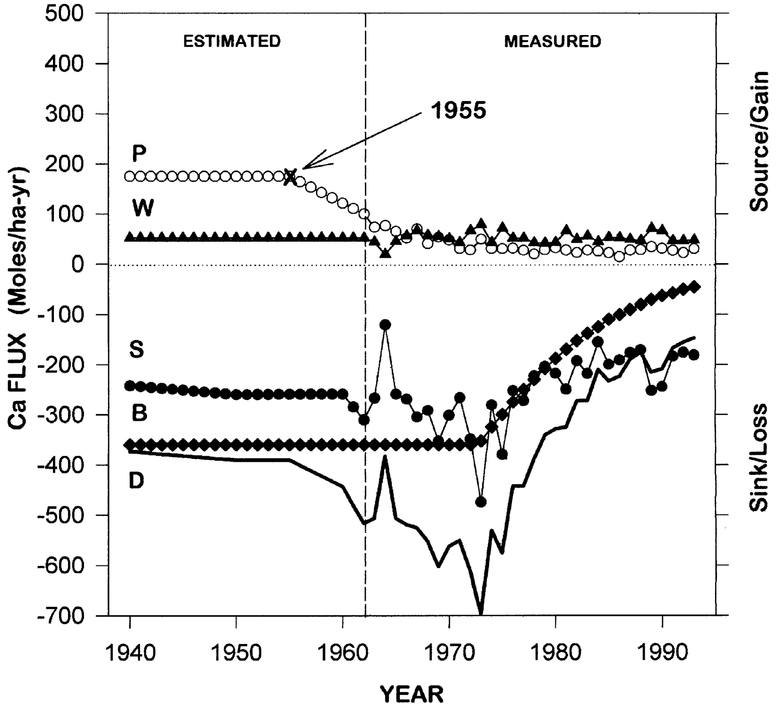


Figure 23. Annual fluxes of calcium for W6 of the HBEF during 1940–1963 (estimated) and 1963–1994 (measured). P (○) is bulk precipitation input, W (▲) is weathering release, S (●) is streamwater loss, B (◆) is net biomass storage and D (—) is net release from labile soil pools (exchangeable + organically bound), obtained by difference. Data for P during 1955–56 are from Junge & Werby (1958). (Modified from Likens et al. 1996.)

The change in Ca as compared to C_β with time in both bulk precipitation and stream water (Figure 24) suggests that Ca was especially responsive to acid rain inputs. Initially, the Ca to C_β ratio in stream water was highly variable (1964–1970) suggesting little ecosystem regulation of leaching of Ca. This period was followed by a period of relentless decline in the Ca:C_β ratio (1970–1989), and finally a leveling off in the ratio at what currently suggests a new steady-state (1989–1993). The smaller decline in Ca:C_β in bulk precipitation with time is significant, but the mechanism for the change is elusive.

The increase in streamwater concentration of Ca during the 1960’s (Figures 3A, 14) corresponds with high, but decreasing inputs of Ca from atmospheric deposition and large net losses from the soil complex; whereas declining concentrations of Ca in stream water thereafter coincide with smaller atmospheric inputs and decreases in biomass storage and net soil loss (Figure 23). We estimate that annual atmospheric input of Ca during 1940–1955

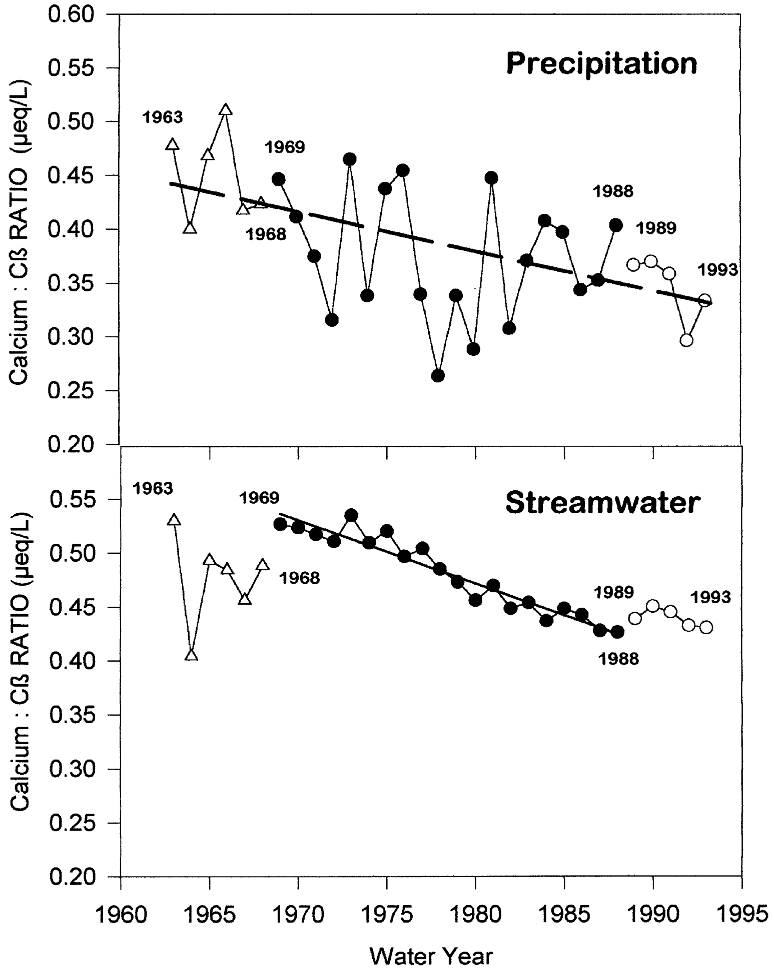


Figure 24. Ratio of calcium to sum of base cations ($C_\beta = Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}$) for bulk precipitation and stream water for W6 of the HBEF. The statistically significant ($p < 0.003$) regression line for bulk precipitation during 1963–1993 is $Y = -0.0037X + 7.6$, $r^2 = 0.29$; and for stream water during 1969–1988 is $Y = -0.0059X + 12.1$, $r^2 = 0.92$.

was 7 times greater than during 1976–1993, and average annual soil loss during 1955–1975 was 1.9 times greater than during 1976–1993. Increased atmospheric deposition of strong acids, decreased atmospheric deposition of Ca, and forest growth until 1982 all appear to have contributed to a large depletion of Ca in the soil. We estimate the total depletion of Ca from labile soil pools during 1940–1995 to be 42,250 eq/ha (21,125 mol/ha) (Figure 23). If Ca concentrations in bulk precipitation were as low during 1940–1995, as they are currently (3.6 μeq/ℓ), the estimated depletion of labile soil Ca would have been 50,400 eq/ha. In contrast, assuming that Ca concentrations in bulk precipitation remained elevated throughout 1940–1995, similar to values observed in 1955–56 (25 μeq/ℓ), the estimated soil depletion of Ca would have been 34,400 eq/ha (Likens et al. 1996). As a result, reductions in atmospheric deposition of Ca associated with particulate emission control (Likens & Bormann 1974; Likens 1992; Hedin & Likens 1996) contributed some 20% of the apparent depletion of soil Ca at HBEF.

Prior to the mid 1950's, depletion of Ca from the soil exchange complex was approximately equal to net biomass storage, and bulk precipitation plus weathering release nearly balanced streamwater loss on an average annual basis. After the mid 1950's, soil depletion of Ca was much larger (1.4 times during 1955–75 and 2 times during 1976–93) than net biomass storage, and streamwater loss was much larger (2.2 times during 1955–75 and 2.7 times during 1976–93) than bulk precipitation input plus weathering release (Figure 23). Bulk precipitation input provided some 29% of the Ca required in the ecosystem to balance net biomass storage plus streamwater loss prior to the mid 1950's; however, during 1955–75 bulk precipitation input decreased to meet only 8% of the demand, with net soil release increasing to 77% of total ecosystem demand (Likens et al. 1996). Overall depletion of Ca from the soil complex during 1940–1995 was very large as compared to Ca stored in the biomass or especially the available pools in the soil (Figures 18, 23).

Calcium is rapidly cycled in soils at HBEF (Table 13). Especially notable is the low residence time (Tn) for total forest floor Ca (5–8 years). Such a low value indicates that rapid depletion of this pool is possible. Assuming that depletion has been occurring at HBEF since the 1940's, nearly 10 turnovers would have occurred. Similarly, the low Tn for exchangeable Ca in the mineral-soil, suggests that rapid depletion of that pool is also plausible.

After 1963, the average stream pH increased slightly (pH 4.85 in 1963 to 5.01 in 1993), but the ANC has remained consistently negative (currently about -6 μeq/ℓ). Prior to the mid-1950's ANC in stream water probably was positive. Based on an evaluation of the long-term changes in the acid-base status at the HBEF, the current rate of decrease in concentrations of strong acid anions and the corresponding changes in Ca in stream water at the HBEF, it has been predicted (Likens et al. 1996) that ANC will become positive again around autumn 1999 (Figure 21). We eagerly await the chance to test this hypothesis. Even with major reductions in emissions of SO_2 anticipated from the 1990 Clean Air Act Amendments (to about 50% of 1980 values), it is unlikely that the acid-base status of stream water will return to PIR levels in the foreseeable future (Figure 21; Likens 1992; Likens et al. 1996).

The large depletion of C_β (primarily Ca) from the soil has delayed appreciably the rate of recovery of streamwater pH and ANC in response to decreases in emissions of SO_2 that have occurred since 1970 (see Likens 1992). If the current trajectory of recovery (Figure 21) were to continue (which is unrealistic), streamwater concentrations of Ca would not reach PIR values for several decades. If Ca concentrations in stream water were to return to PIR levels, acid anions still would be 30 to 40 μeq/ℓ higher than PIR values (Figure 21). To balance a further decline in acid anion concentrations would require maintenance of Ca concentrations at PIR or higher levels. Because the long-term trajectories are parallel (Figure 21) recovery to PIR levels seems unlikely. Increases in streamwater Ca concentrations would require major increases in weathering rates and/or atmospheric deposition and/or forest dieback (Figure 23). To generate large amounts of available Ca again, the ecosystem would need to be further acidified or fertilized.

As a result, our analysis suggests that forest ecosystems at HBEF are much more susceptible to continuing atmospheric inputs of strong acids than expected based on long-term patterns of sulfur biogeochemistry alone. The long-term hysteresis pattern in streamwater chemistry suggests that ecosystem acidification may be reversible, but only very slowly and with major lingering effects on ecosystem biogeochemistry and forest productivity (Likens et al. 1996).

Calcium depletion and forest biomass accumulation

It is unclear whether existing sources of available Ca are sufficient to sustain harvest of forests similar to the HBEF. Much of the Ca liberated by weathering of primary minerals will be increasingly distant from high root and associated mycorrhizal densities in the surface soil. Assuming a long-term average weathering release of Ca of 53 mol/ha-yr, 2650 mol/ha would be released during the next 50 yr. At present (i.e. 1987–1992) input rates, atmospheric deposition would supply another 1450 mol/ha in this 50-yr period. Thus, weathering release and atmospheric input could supply only 27% of the Ca necessary to replace the 14,970 mol/ha in aboveground tree biomass. Even complete depletion of the exchangeable Ca pool (6500 mol/ha) could not make up the difference. Therefore, our data suggest that intensive logging may not be sustainable at HBEF. Possible mitigating factors include: *(i)* trees may be able to draw upon soil Ca pools more strongly bound than exchangeable Ca; *(ii)* long-term weathering release is poorly known, and may be higher; and *(iii)* current tree Ca concentrations might reflect some type of "luxury" rather than necessary consumption (if so, a regrowing forest might make more efficient use of the Ca available). Unexpectedly, accumulation of annual forest biomass for the watershed-ecosystem has declined to a small rate since 1982 (Figure 10; Likens et al. 1994). This decline in growth might be the result of Ca depletion from the soil, where Ca may have become limiting to growth (see Federer et al. 1989; Shortle & Bondietti 1992; Likens et al. 1996). This topic is currently under intensive study at the HBEF (see also, *Comparison of Ca Loss by Forest Harvest and Acid Rain*, below).

Acid rain has impacted forest watersheds that are sensitive to inputs of strong acids throughout eastern North America (e.g. Landers et al. 1988). These watersheds generally are characterized by shallow deposits of surficial materials, soil minerals with slow rates of chemical weathering and low concentrations and pools of exchangeable bases in the soil (April & Newton 1985; Driscoll 1991; Eilers & Selle 1991). The geochemical consequences of acid deposition to forest watersheds include depletion of labile pools of nutrient cations (Kirchner 1992; Bailey et al. 1996) and the mobilization of elevated concentrations of aluminum (Al) from soil to drainage waters (Cronan & Schofield 1979, 1990). Other studies from eastern North America and Europe also have shown limited recovery of surface water chemistry from decreases in atmospheric deposition of sulfur and/or depletion of soil pools of base cations (Dillon et al. 1987; Morgan 1990; Kirchner 1992; Driscoll et al. 1995; Bailey et al. 1996; Kirchner & Lydersen 1995; Wesselink et al. 1995; Christophersen et al. 1990; Bishop & Hultberg 1995).

There is growing concern that depletion of available Ca and associated increases in Al in the rooting zone will slow growth and decrease the stress tolerance of trees (Cronan & Grigal 1995). In a detailed review, Cronan & Grigal (1995) concluded that Ca:Al ratios in soils and plants were useful to indicate the stresses associated with acid deposition and harvest in forest ecosystems. Plants exhibit deleterious effects following exposure to ionic Al either through: *(i)* antagonistic interference of cation assimilation or *(ii)* irreversible damage of cells due to interactions with certain biomolecules (Haug 1984; Sucoff et al. 1990; Cronan & Grigal 1995). Roots strongly sorb Al by cation exchange (Foy 1984). Aluminum competes with other cations, most prominently Ca, for root exchange sites (Shortle & Steinen 1988). The presence of Al associated with root surfaces interferes with the assimilation of Ca and Mg by plants (Clarkson & Sanderson 1988; Schroder et al. 1988). Limitations of Ca or Mg uptake associated with elevated concentrations of Al may have critical consequences to plants. For example, Ca is an essential component of the cell wall and is important in the function of calmodulin and membrane-bound enzymes. Shortle and colleagues (Bondietti et al. 1990; Shortle & Bondietti 1992) observed that the Ca content of tree rings relative to the binding capacity for Ca increased in the mid 1960's and then decreased sharply thereafter at several sites in the eastern U.S. They attributed these changes to increased mobility of C_β, including Ca, in surface organic soils by acid rain followed by depletion of the labile, exchangeable pool of C_β in the soil. Interestingly, the Ca content of the prominent understory species, wood

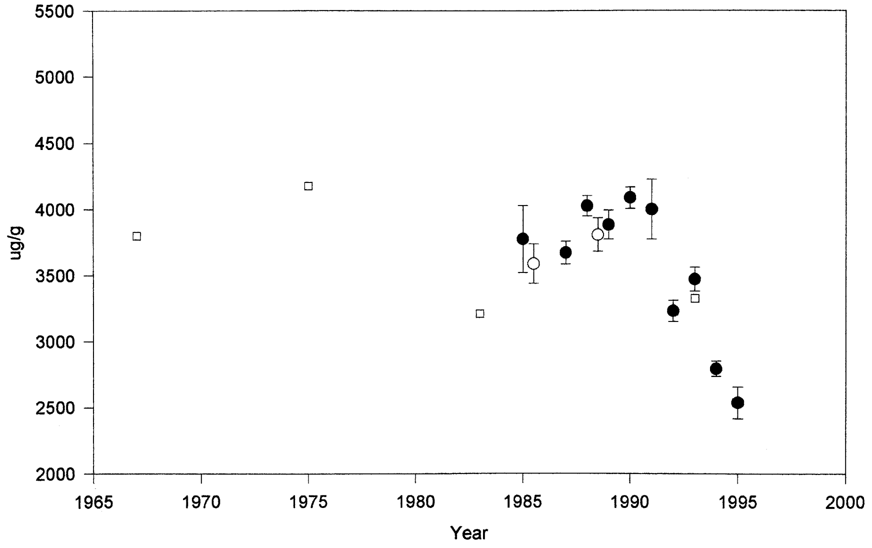


Figure 25. Concentration of calcium in wood fern (*Dryopteris spinulosa*) fronds from LH zone west of W6 at the HBEF. Symbols are: ● annual replicate samples beginning in 1984, ○ reanalyses of earlier collections, and ☐ individual samples from the same general area of forest collected at several times.

fern (*Dryopteris spinulosa*), at HBEF has decreased significantly since about 1990 (Figure 25).

In an area of southern Finland impacted by high sulfur deposition, Häsänen & Huttunen (1989) found depletion of Ca in tree rings from *Pinus sylvestris* L. during the second half of the 1900's, which they attributed to "natural" factors without explanation. At the same time, they attributed increases in Al, K and Rb concentrations to effects of acid deposition.

A second mechanism of Al toxicity is associated with plant assimilation. It is generally thought that Al is excluded from plant uptake (Taylor 1987, 1991). However if Al were assimilated by plants, it would interact with the plasmalemma and bind with biomolecules such as: *(i)* phospholipids, *(ii)* nucleotides and nucleic acids, *(iii)* ADP, ATP or ATPases, *(iv)* enzymes such as acid phosphatases or *(v)* calmodulin. Due to these interactions, Al potentially affects energy transfer, nutrient dynamics, membrane transport and cell division (Sucoff et al. 1990; Cronan & Grigal 1995).

Based on laboratory and field experiments involving several species, Cronan & Grigal (1995) concluded there was a 50% risk that soil-solution Ca:Al molar ratios of ≤ 1 would have deleterious effects on tree growth and nutrition. This risk increased to nearly 100% when the Ca:Al molar ratio was ≤ 0.2. They also suggested that a series of factors could serve as indicators of forest stress, including: *(i)*% base saturation $<15\%$ of effective cation exchange capacity (CEC_e); *(ii)* the presence of elevated concentrations of strong acid anions, *(iii)* Ca:Al molar ratios ≤ 1.0 in soil solutions; *(iv)* molar Ca:Al of ≤ 0.2 in fine roots, and *(v)* molar ratios ≤ 12.5 in foliar tissue. Based on long-term soil solution measurements at the HBEF, the mean molar $Ca:Al_i$ (Ca to monomeric-inorganic Al) ratio for SFWB stands was 1.27 in Oa soil solutions, decreasing to 0.40 in Bh and 0.27 in Bs soil solutions. In HH stands, the mean $Ca:Al_i$ molar ratio was 1.21 in Oa horizon solutions, decreasing to 0.59 in Bh solutions and 0.39 in Bs horizon solutions. Thus, these values in the B horizons at HBEF are within the range suggested by Cronan & Grigal (1995) to have adverse effects on forest growth.

Galloway et al. (1983) hypothesized that atmospheric inputs of strong acids facilitate the displacement of exchangeable base cations from soil, resulting in the acidification of soil and surface waters. Several investigators have reported significant depletion of exchangeable nutrient cations from forest soils, but have attributed this depletion largely to accumulation of biomass (Johnson et al. 1988a; Johnson et al. 1994; Knoepp & Swank 1994). We and Likens et al. (1996), and Bailey et al. (1996) also show marked depletion of Ca from labile soil pools from the HBEF and nearby Cone Pond watershed, but in contrast to the earlier studies, we have shown that ecosystem Ca depletion cannot be explained by biomass accumulation, but rather is the result of elevated leaching from soil. In both of these New Hampshire studies, the rate of Ca depletion from forest soil was greatly in excess of the supply of Ca from weathering and atmospheric deposition. Moreover, unlike other published studies, these New Hampshire sites are characterized by elevated concentrations of Al in mineral soil solutions (Driscoll et al. 1985, 1994; Bailey et al. 1995).

Atmospheric inputs are an important source of Ca to forest ecosystems where weathering rates are low (Likens et al. 1967; Hedin et al. 1994; Likens & Bormann 1995). Using Sr as a surrogate for Ca, Miller et al. (1993) reported that about half of the forest floor Ca in a high elevation spruce stand was atmospheric in origin. Bailey et al. (1996) also reported similar results for the Cone Pond watershed. It has been suggested that declines in atmospheric deposition of Ca associated with controls on atmospheric emissions of particulates may contribute to ecosystem depletion of Ca (Driscoll et al. 1989; Hedin et al. 1994; Likens et al. 1996). However, based on mass-balance calculations, we found that only about 20% of the depletion of Ca at the HBEF could be explained by decreases in atmospheric inputs of Ca during 1940 to 1995 (Likens et al. 1996).

Recently, Lawrence et al. (1995) speculated that the mobilization of Al by acid deposition is linked to depletion of base cations, particularly Ca, in the forest floor. Northern temperate and boreal forests develop thick forest floors due to relatively cool temperatures, which limit rates of microbial decomposition. The forest floor is an important pool of nutrients for northern hardwood forests (Gosz et al. 1976; Bormann & Likens 1979) and contains over 40% of the fine root biomass (Fahey & Hughes 1994). Lawrence et al. (1995) suggested that enrichment of Al in the forest floor could be caused by plant uptake and subsequent litter input, and/or by water originating from the mineral soil, containing elevated concentrations of Al, and entering the forest floor by a variety of mechanisms. This added Al can displace nutrient cations, particularly Ca, from the soil exchange complex, and cause the forest floor to become enriched in exchangeable Al (Mulder et al. 1991). Lawrence et al. (1995) reported marked decreases in exchangeable and acid-extractable Ca, and increases in acid-extractable Al in Oa-horizon soils from 1969–70 to 1987–92 at the HBEF. Because of the high affinity of Al for exchange surfaces, increases in exchangeable Al will limit retention of nutrient cations input from throughfall, litter and direct precipitation to the forest floor.

Response of Ca biogeochemistry to disturbance by forest cutting

Stream chemistry

Different forest cutting practices have been evaluated through whole-watershed experiments at HBEF (e.g. Bormann & Likens 1979; Likens et al. 1970; Martin & Hornbeck 1989). Watershed 2 (W2) was experimentally deforested in the winter of 1965–66 without removal of forest products, and regrowth was inhibited with herbicides until the summer of 1969 (Bormann & Likens 1979). This experiment was not designed to simulate a commercial clear cut, but rather to assess experimentally the role of vegetation in the biogeochemistry of the northern hardwood forest ecosystem. Very large losses of NO_3^-, H^+ and Al^{n+} occurred in drainage water from W2 during the three years after cutting when regrowth was suppressed (1966–69), primarily as a result of increased decomposition of organic matter and nitrification (e.g. Bormann & Likens 1979; Bormann et al. 1968; Likens et al. 1969, 1970, 1978). This deforestation experiment and subsequent vegetation regrowth beginning in 1969 had large impacts on Ca biogeochemistry (Figures 22, 26, 27).

Concentrations of Ca increased about 5.4-fold in stream water during the devegetated period (Figure 26) and stream outputs of dissolved Ca increased by 13.4-fold as compared to 1964–65 (Figure 27). Particulate losses of Ca, both organic and inorganic, for the water-years 1966–1970 were 5.7 mol/ha-yr (0.23 kg/ha-yr) for W6, the reference watershed, versus 41 mol/ha-yr (1.64 kg/ha-yr) for W2, a 7.1-fold increase (Bormann et al. 1974). Net dissolved losses during the same period were 242 mol/ha-yr (9.7 kg/ha-yr) for W6 versus

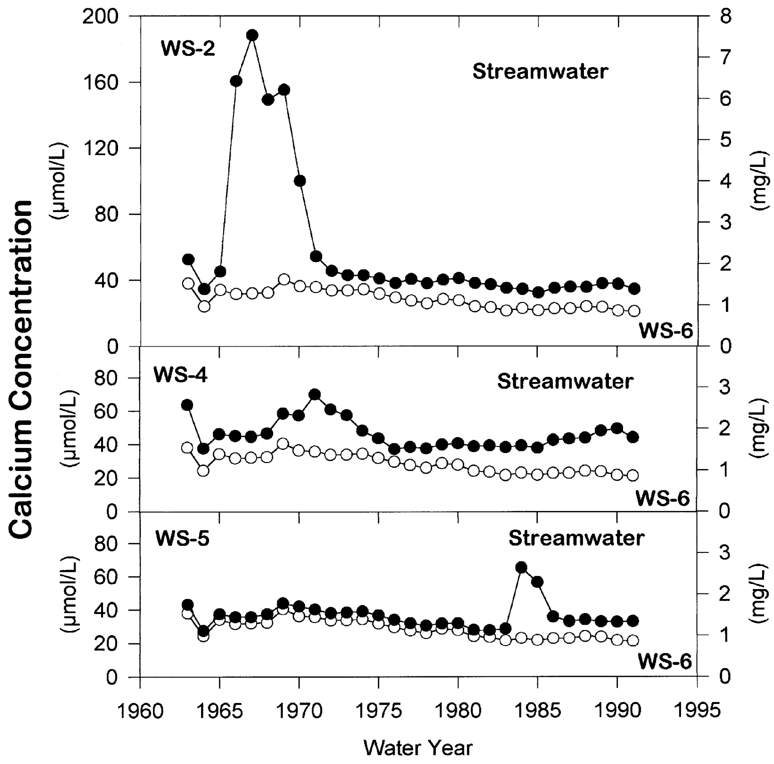


Figure 26. Concentrations of Ca in stream water in experimentally treated Watersheds 2, 4 and 5 (—●—), and uncut 6 (—○—) at HBEF (see text for details of treatments).

1869 mol/ha-yr (74.9 kg/ha-yr) for W2, a 7.7-fold increase (Bormann et al. 1974). Relative changes in the losses of dissolved and particulate fractions due to the loss of vegetation cover and the breakdown of ecosystem retention properties were similar (Bormann & Likens 1979; Bormann et al. 1974; Likens et al. 1978).

Even before vegetation regrowth began in summer 1969, dissolved stream outputs of Ca had decreased, apparently due to declines in nitrification (Bormann & Likens 1979), which had provided the mobile anion, NO_3^-, for the streamwater loss of cations from W2 (Likens et al. 1970). After cessation of the herbicide treatment in 1969, uptake by regrowing vegetation caused further, marked declines in stream Ca concentrations (Figure 26). By 1971–72, stream Ca export was much lower, although still somewhat higher than for W6 (Figure 27).

Other timber harvesting experiments at HBEF include a strip-cut of W4, a block clear-cut of W101 (an ungauged watershed) and a whole-tree harvest of W5 (e.g. Likens & Bormann 1974; Lawrence et al. 1987; Martin & Hornbeck

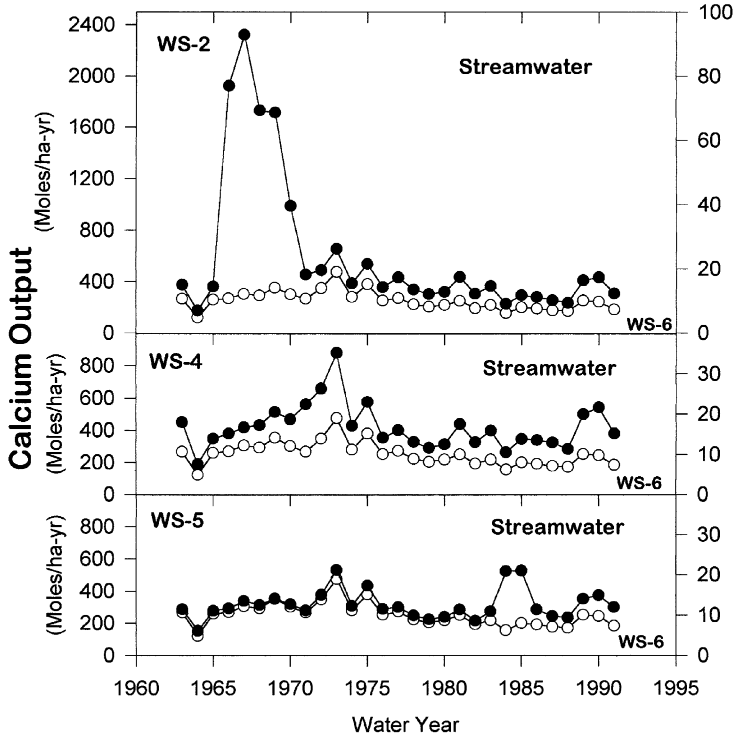


Figure 27. Outputs of Ca in stream water from experimentally treated Watersheds 2, 4, and 5 (—●—) and in uncut 6 (—○—) at HBEF (see text for details of treatment).

1989; Johnson et al. 1991a). The strip-cut experiment involved cutting W4 in 25-m wide strips, which paralleled the general watershed contours. The first third was cut in 1970, the second in 1972, and the final third in 1974. A small buffer area of trees was left uncut adjacent to the stream channel. Watershed 101 was clear-cut as a block in 1970, and W5 was logged by a commercial, whole-tree clear-cut in 1983–84. In all three of these watersheds timber products were removed.

Stream concentrations of Ca increased in response to all forest cutting treatments and declined during regrowth (Figure 26), but there were distinct differences in the magnitudes of Ca loss immediately after clear cutting in these experiments. The loss of Ca was very high following the W2 devegetation experiment. This loss was likely due to the release of Ca from mineralization of organic matter and displacement from the soil exchange complex by high concentrations of H^+ and Al^{n+} in soil water, coupled with suppression of vegetation regrowth by herbicide. Hydrogen ion and NO_3^- were generated by increased nitrification, and loss of dissolved Ca in stream water was

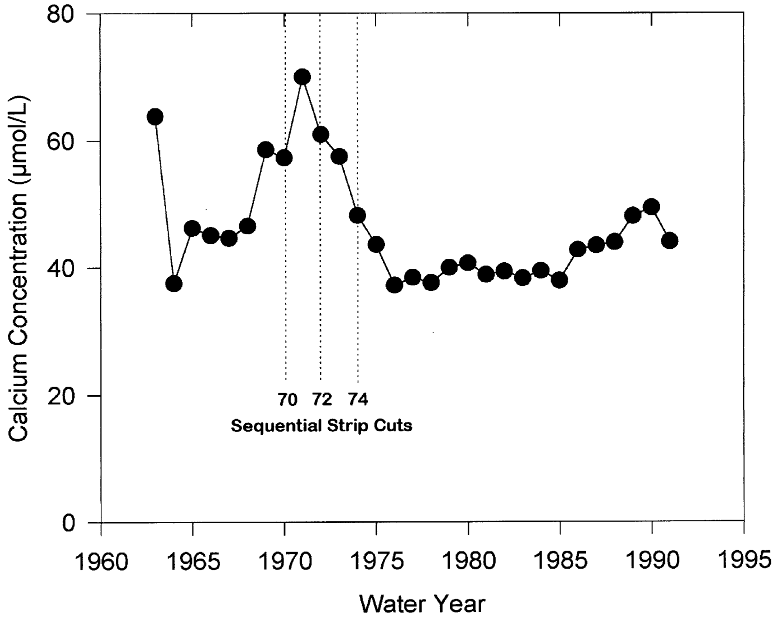


Figure 28. Changes in calcium concentration (volume-weighted averages) in stream water from W4 of the HBEF following sequential strip-cutting treatments during 1970, 1972 and 1974.

correlated strongly (r^2 = 0.95) with loss of NO_3^- (Likens et al. 1970). In the strip-cut of W4, concentrations of Ca increased from 1969–70, peaking in 1971–72 and declined thereafter (Figure 28), but the increases in stream Ca concentrations were much lower than observed in W2; the maximum, annual volume-weighted concentration of Ca was <80 μmol/ℓ (Figure 28).

In the whole-tree harvest of W5, stream concentrations of Ca peaked two years after the manipulation (annual volume-weighted concentration in 1984–85 was 65.5 μmol/ℓ). Concentrations of Ca markedly decreased about 3 years after the clear-cut. However, in all three experiments, stream concentrations of Ca did not decline to reference values by 1992 (Figure 26; Table 9).

Watershed mass balance

To evaluate and contrast the extent of Ca loss for each of the clearcutting treatments at HBEF, mass balances were compared for the 8 yrs following disturbance (Figure 29). These mass balances include bulk precipitation inputs, stream loss and biomass removal associated with the treatment. In this analysis the devegetation and herbicide (W2), block-cut (W101), strip-cut (W4) and whole-tree harvest (W5) treatments were compared to the reference watershed (W6).

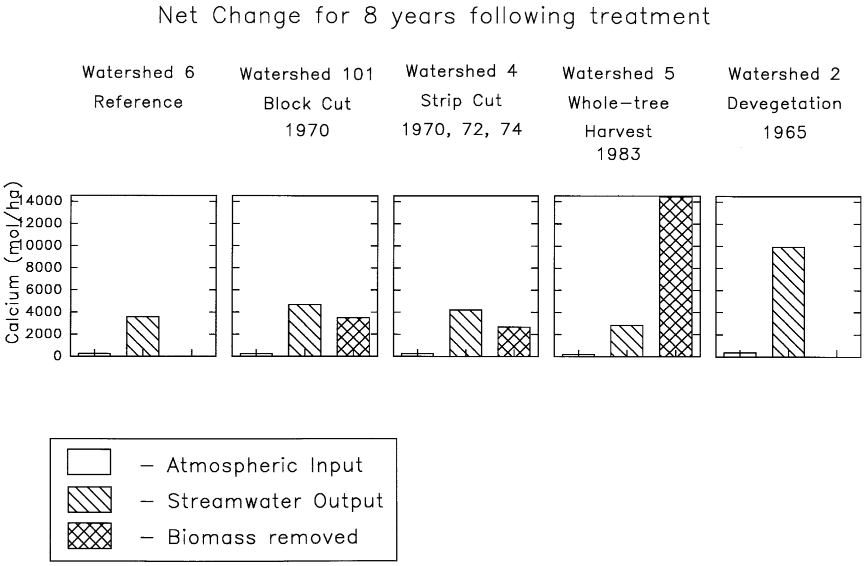


Figure 29. Mass balances for Ca during the 8-yr period immediately following forest cutting by various procedures. Bars show precipitation inputs, stream output and biomass removed by harvesting in a strip-cut (W4; 1970–78), a block clear-cut (W101; 1970–78), a whole-tree clear-cut (W5; 1983–91) and an experimental devegetation (W2; 1966–74). Data from the reference watershed (W6; 1983–91) are also shown.

Aboveground biomass and nutrient content were estimated for W2 (Table 15; Reiners 1992) and W5 (TG Siccama, unpublished data) using a combination of allometric equations and clipped plots. Belowground Ca was estimated from the ratio of aboveground to belowground Ca for the herb, shrub and tree stratum as reported by Whittaker et al. (1979). Release of Ca from logging debris on W2 and W5 was estimated from Ca content of the debris and literature information on mineralization of woody detritus (Arthur et al. 1993; Foster & Lang 1982; Gosz et al. 1973; Harmon et al. 1986; Onega & Eickmeier 1991). Although the behavior of Ca during decay of coarse woody debris appears to vary among species and size classes of woody tissue (e.g. Arthur et al. 1993), the error resulting from the simplifying assumption that Ca release parallels dry weight loss is probably not large because deviations one way or the other (i.e. faster or slower Ca release than weight loss) usually are not large (Foster & Lang 1982; Gosz et al. 1973). We assumed release of 15% of the Ca content of bole wood and bark in yr 1–3 and an additional 45% in yr 4–8. For Ca in branches, we assumed release of 60% in yr 1–3 and an additional 30% in yr 4–8. Finally, from our detailed studies of root decay following clearcutting at HBEF (Fahey & Arthur 1994; Fahey et al. 1988), we estimated Ca release from tree roots on W2 and W5. It is notable

Table 15. Changes in calcium content of vegetation of W2, Hubbard Brook Experimental Forest through succession. Aboveground data are means of 70 plots distributed evenly across the watershed. Belowground are estimated as fixed percentages of aboveground nutrient contents as follows. Trees and sapling belowground = 41% aboveground, shrubs = 53%, herbs = 14%. Data are in g calcium/ha (1 mole/ha = 40 g/ha).

	Year 1 (1969)			Year 2 (1970)			Year 3 (1971)		
Stratum	Above	Below	Total	Above	Below	Total	Above	Below	Total
Herbs	683	96	779	1,176	165	1,341	1,850	259	2,109
Shrubs	848	449	1,297	1,379	731	2,110	4,385	2,324	6,709
Saplings	0	0	0	589	241	830	4,919	2,017	6,936
Trees	0	0	0	0	0	0	0	0	0
Total	1,531	545	2,076	3,144	1,137	4,281	11,154	4,600	15,754

	Year 5 (1973)			Year 11 (1979)			Year 20 (1988)		
Stratum	Above	Below	Total	Above	Below	Total	Above	Below	Total
Herbs	3,328	466	3,794	2,607	365	2,972	3,900	546	4,446
Shrubs	10,671	5,656	6,157	6,157	3,263	9,420	2,351	1,246	3,597
Saplings	17,681	7,221	24,834	26,412	10,829	37,241	18,682	7,660	26,342
Trees	0	0	0	32,516	13,332	45,848	93,779	38,449	132,228
Total	31,612	13,343	44,955	67,692	27,789	95,481	118,712	47,901	166,613

that Ca appears to be retained more tightly in belowground than aboveground detritus.

During this 8-yr analysis, the whole-tree harvest of W5 showed the greatest loss of Ca, 17,300 mol/ha, with 84% and 16% in biomass removal and stream outflow, respectively (Figure 29). In comparison, stream losses from W6 during this period were 3580 mol/ha. The devegetation and herbicide treatment in W2 also resulted in high losses of Ca (9950 mol/ha), occurring entirely as stream losses (all cut vegetation was left on the watershed). The two other commercial treatments resulted in considerably lower Ca losses than the whole-tree harvest and devegetation and herbicide treatments. The strip-cut (W4) showed the smallest Ca loss of the four treatments (6900 mol/ha). Stream losses of Ca were similar in the strip-cut and the whole-tree harvest, but only 3480 mol Ca/ha were removed with biomass from the strip-cut compared to 14,530 mol Ca/ha removed with biomass in the whole-tree harvest. The strip-cut did not appreciably reduce stream losses of Ca in comparison to the other commercial harvest treatments. Slightly greater stream losses of Ca were evident in the block clear-cut, than the other commercial treatments. This increase may be due to the fact that W101 is

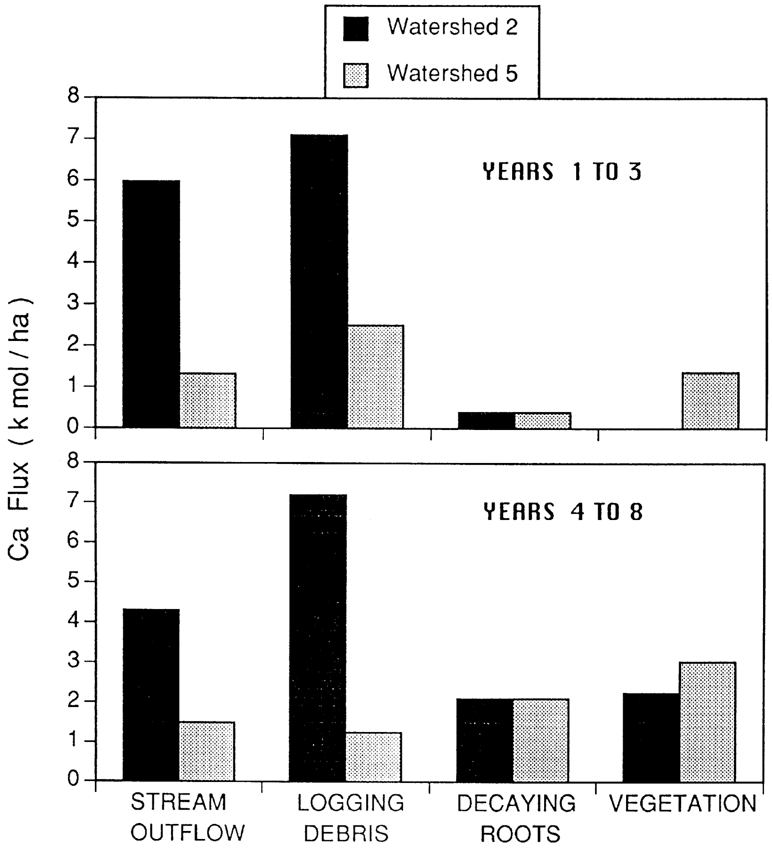


Figure 30. Comparisons of Ca fluxes, including stream outflow, estimated release from logging debris and dead roots, and storage in regrowing vegetation in W2 and W5 for the period 1–3 and 4–8 years after deforestation.

situated on a lower slope than W4 or W5 and is characterized by thicker deposits of glacial till.

Analysis of the principal sources and sinks of Ca for W2 and W5 during the first 8 yrs after cutting revealed the likely causes of the contrasting behavior noted above. This recovery period was divided into two intervals, the first (yr 1–3) corresponding to the herbicide treatment of W2, and the second (yr 4–8) to the period of maximum vegetation accumulation (Figure 30). Clearly, most of the difference in streamflow output of Ca between W2 and W5 resulted from the contrasting treatments (Figures 27, 29, 30).

The balance between the Ca supply by release from logging debris and roots and measured Ca sinks in vegetation and stream outflow were compared (Figure 30). In both W2 and W5 the detrital Ca sources appear to be large enough to supply the measured sinks, and the differences in Ca outflow between the watersheds can be explained largely by the much higher Ca release from logging debris on W2. Vegetation accumulation of Ca on W5 accounted for roughly one-third of the 4.5-fold lower Ca loss during the first three years after cutting. During years 4–8, most of the nearly 3-fold higher Ca loss on W2 probably was due to release from logging debris, as the difference in vegetation accumulation of Ca was surprisingly small (Figure 30). As noted previously by Likens et al. (1994) another possible contribution to the differences in element losses between W2 and W5 could be more rapid mineralization of residual organic matter on the forest floor in W2. However, these calculations (Figure 30) suggest that differences in vegetation uptake and Ca release from logging debris may have been sufficient to account for the observed patterns.

As the most abundant base cations circulating in the forest ecosystems at HBEF, it is interesting to compare and contrast the behavior of Ca and K following the treatment of W2 and W5. Potassium normally is regarded as a much more mobile cation than Ca and one that both circulates more rapidly through the vegetation and is released more quickly from detritus. The most prominent difference in behavior between Ca and K was the much more rapid release of K from decaying roots and the resulting contribution of root decay to K loss during the first three years after cutting (Likens et al. 1994; Romanowicz et al. 1996). Despite this difference, a comparison of Ca and K losses between the initial period (yr 1–3) and the next 5 yrs indicated no tendency for lower initial Ca outflow; that is, the ratios of yr 1–3 to yr 4–8 streamflow losses for Ca (1.40 in W2) and for K (1.43) were very similar. This behavior probably is explained by the high Ca content of branches (Table 8) and their relatively rapid decay (Gosz et al. 1973), which resulted in high initial Ca release from logging debris.

Differences in the molar ratio of Ca to K in stream outflow between W2 and W5 also illustrate the roles of detrital release and vegetation uptake in regulating element behavior after disturbance. Initially after cutting the Ca:K ratio in stream outflow was higher for W2 (2.6) than for W5 (2.2) probably because of higher detrital release on W2, but also perhaps because of the elimination of vegetation regrowth on W2. Ryan & Bormann (1982) observed that foliar biomass was substantially restored to levels approaching predisturbance in as little as 5 years following clear cutting of W101, indicating that the dominant part of the Ca cycle involving uptake of Ca from soil, incorporation into foliage and return in leaf litter can be restored quickly by regrowing vegetation. Fahey et al. (1991) noted that Ca:K ratios of recovering vegetation usually increase with time after forest cutting because of increasing proportions of relatively Ca-rich woody tissues. Later, in yr 4–8 the pattern was reversed (higher Ca:K in W5 outflow) possibly because the Ca:K ratio of the detrital source increased markedly from yr 1–3 (Ca:K = 1.8) to yr 4–8 (Ca:K = 4.5).

Comparison of Ca loss by forest harvest and acid rain

Federer et al. (1989) suggested that biomass harvest and leaching losses of Ca could deplete the total soil and biomass pools of Ca in forests of the eastern U.S. by 20–60% within 120 yr. These long-term depletions could result in a Ca deficiency and/or enhance Al toxicity of vegetation in base-poor forest ecosystems. The whole-tree harvest of W5 resulted in the removal of 14,400 mol/ha Ca in biomass. Moreover, stream losses of Ca in W5 exceeded values for the reference watershed (W6) for 1986–91 by 100 mol/ha-yr. If elevated stream losses were to persist over a 65-yr rotation period, the total stream loss of Ca in excess of values for W6 would be 6500 mol/ha. Based on this analysis, the losses of Ca due to a whole-tree harvest over 65 years would be associated largely with biomass removal (69% of total). Johnson et al. (1988b) compared harvest and leaching losses of Ca and other nutrient cations for 10 whole-tree harvest studies. For these sites, leaching losses of Ca ranged from 1500 to 732,000 mol/ha during the harvest rotation period, while harvesting loss of Ca ranged from 3500 to 35,000 mol/ha. The values of Ca loss for the W5 whole-tree harvest were generally within this range of values, particularly for biomass removal. Leaching losses of Ca from W5 were somewhat low compared to most of the studies reported by Johnson et al. (1988b). The sum of Ca losses due to elevated stream export and harvesting (21,000 mol/ha) for a 65-yr rotation period is much greater than the pool of exchangeable Ca at the HBEF (6500 mol/ha; stream and harvest losses 322% of exchangeable Ca). The sum of these losses also represents a significant fraction of the total Ca pool (250,000 mol/ha).

Values of stream and harvest loss associated with whole-tree harvest of W5 can be compared to our estimates of the depletion of Ca from labile soil pools for 1940–1995 (21,125 mol/ha; see *Effects of Acid Rain on Ca Biogeochemistry*), which was associated largely with leaching losses accelerated by inputs of acid rain. Our analysis suggests that both clearcutting losses and accelerated leaching of Ca by acid rain are capable of depleting ecologically significant pools of Ca from base-poor forest ecosystems such as HBEF. At HBEF both disturbances are comparable in magnitude. The magnitude of Ca loss due to whole-tree harvest and acid rain leaching would vary from site-to-site depending on the base status of soil, inputs of atmospheric deposition and the logging practice utilized. In forests of eastern North America, Ca losses associated with clear cutting will be superimposed on losses associated with acid rain, exacerbating an already significant disturbance to base-poor forest ecosystems.

This synthesis of biogeochemical studies from the HBEF has shown that there is considerable variability in the flux and cycling of Ca across the area of the watershed-ecosystem considered here as well as over the landscape of the White Mountains. Calcium is the major base cation associated with the soil exchange complex and in drainage waters at HBEF, although concentrations are low relative to other sites (e.g. Stumm & Morgan 1970). As a result, the supply of Ca is the major mechanism neutralizing inputs of acidity from natural internal processes (e.g. production of organic acids) and atmospheric deposition (Driscoll & Likens 1982), and is critical in regulating the acid-base status of base-poor forest ecosystems such as HBEF. The biogeochemistry of Ca ultimately is controlled by the supply of this element (from weathering and atmospheric deposition). The supply of Ca, in turn, has important consequences on the structure and function of the forest watershed-ecosystem and associated aquatic ecosystems, and their response to disturbances (e.g. atmospheric pollution, clear cutting).

Soils near the ridges of the HBEF are thin, with areas of exposed bedrock and boulders. There is little surface area to expose weatherable minerals which supply Ca and little matrix to hold cations, like Ca, or water. With decreasing elevation and increasing drainage area, there is increasing depth of glacial till. Increasing till depth allows for the development of deeper soil and associated CEC, and greater supply of Ca from weathering. This spatial pattern in the supply and retention of Ca across the landscape is the major factor regulating the elevational variation in the acid-base status of forest watersheds at HBEF, and their associated ecosystem characteristics. Spatial variation in the acid-neutralizing capacity (ANC) of drainage waters within the Hubbard Brook Valley is controlled largely by concentrations of Ca, the major base cation, since concentrations of SO_4^{2-} are relatively uniform in drainage waters (Johnson et al. 1981; Lawrence et al. 1986). For example, headwaters in the SFWB zone exhibit chronically acidic conditions (ANC = $-96\ \mu eq/\ell$) due to very low concentrations of Ca. With increasing drainage area and soil depth at lower elevations, streamwater ANC values increase, approaching near positive values at the weir ($-5\ \mu eq/\ell$) and reaching positive values in the main Hubbard Brook at the base of the Valley ($55\ \mu eq/\ell$). This pattern of increases in streamwater ANC with decreasing elevation and increasing drainage area is controlled largely by increasing Ca concentrations.

We attribute the elevational variations in stream Ca concentrations to the combined effects of the biota on net uptake, to differences in hydrologic flowpaths and to spatial variations in soil chemistry. At the highest elevation stream sites (Figures 13, 17) soils are shallow and flowpaths of water are near

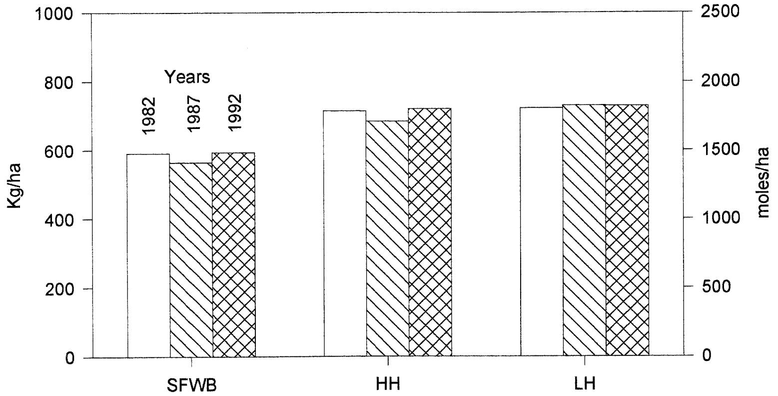


Figure 31. Calcium content of the live tree biomass (above + belowground) on W6 in 1982, 1987 and 1992. SFWB = the upper elevation (ca. 760 m) stand dominated by spruce, fir and white birch; HH = the high deciduous stand (ca. 700 m) dominated by beech, sugar maple and yellow birch on shallow-to-bedrock soils and somewhat exposed topographically; LH = the lower elevation mixed deciduous (ca. 600 m) stand on deeper soils dominated by sugar maple, beech and yellow birch.

the surface. At lower elevation sites, deposits of glacial till are thicker and facilitate deeper, hydrologic flowpaths.

The effects of this spatial pattern on the supply of Ca are evident as pools and concentrations of exchangeable Ca are low at high elevations within the experimental watersheds and increase with decreasing elevation. Low concentrations of Ca in drainage water and on the soil exchange complex coincide with low concentrations of Ca in foliage of sugar maple and yellow birch, smaller living biomass pools of Ca (Figure 31), and lower concentrations of Ca in throughfall at high elevation. High elevation soils exhibit greater drought stress than deeper, lower elevation soils. In response to these conditions at high elevation, plants exhibit lower Ca uptake and appear to be more tolerant of short-term droughts. Vegetation at high elevation has low Ca content in its litter and thus recycles less Ca to the forest floor. This biotic feedback under infertile conditions exacerbates the low Ca availability within the SFWB zone.

High elevation zones within the experimental watersheds are more susceptible to acidic deposition than more base-rich, lower elevation zones. Coinciding with highly acidic drainage waters, concentrations of inorganic monomeric Al are elevated at high elevation (Johnson et al. 1981; Lawrence et al. 1986). Chronically acidic conditions within such stream reaches are not suitable for many aquatic species (e.g. Baker & Christensen 1991). Elevated concentrations of Al in soil solutions may also facilitate the depletion of Ca from cation exchange sites within the forest floor and upper mineral soil within high elevation zones of the watersheds (Lawrence et al. 1995; see *Effects of Acid Rain on Ca Biogeochemistry*). It seems likely that vegetation within high elevation zones, which already is exposed to a high stress environment because of lower water availability, low nutrient availability, colder temperatures and increased wind velocity, would be particularly vulnerable to additional stress associated with depletion of already low Ca pools and low ratios of Ca to Al. With decreasing elevation, rates of Ca supply by weathering increase and the effects of atmospheric inputs of strong acids on aquatic ecosystems and forest vegetation are diminished somewhat.

Measurements of streamwater chemistry at the base of the watershed-ecosystem are an attempt to integrate this biogeochemical and ecological complexity from a functional ecosystem perspective, and to develop a management perspective for a reasonable-sized area (e.g. Bormann & Likens 1967; Likens & Bormann 1995). Where the base of the watershed is located has important implications for mass-balance calculations and for extrapolations to different spatial scales (e.g. Driscoll & Likens 1982; Johnson et al. 1997). Nevertheless, W6 is quite similar to other south-facing watersheds within the Hubbard Brook Valley (Tables 1, 2, 11 and 12; Likens & Bormann 1995) and these watersheds generally appear to be representative of forest watersheds in northern New England (Likens & Bormann 1995). By and large, the fundamental chemical signature for the landscape has been determined in these headwater watershed-ecosystems. Calcium is the dominant cation in headwater streams of the HBEF, and in higher order streams all the way to the Atlantic Ocean, except were locally disturbed by humans (GE Likens, JS Eaton, KM Postek, unpublished data). It is important to note, however, that a significant concurrent decline in Ca concentrations ($-0.54\ \mu$mol/ℓ-yr) in the main Hubbard Brook has been observed since the mid 1970's (Figure 32), and that this decline is related significantly ($p = <0.001$) to a decline in concentrations of $SO_4^{2-} + NO_3^-$ during this period ($r^2 = 0.47$).

What are the causes for this patterning of Ca distribution and biogeochemistry in W6? The patterns of Ca distribution are related ultimately to two sources: atmospheric deposition and the distribution of soil and rock minerals. Further, patterns are modified over time by redistribution of Ca by biological activity, soil formation processes and disturbance, including windthrow and erosion.

The biotic and abiotic interactions in pattern development are complicated and often of a "chicken or egg" nature. For example, there is a clear pattern on the scale of a few meters within W6 of different soil Ca contents associated with different tree species (Johnson 1989; TG Siccama and MA Arthur, unpublished data). Such patchiness does not indicate whether vegetation modified the soil chemistry over time or whether the soil chemistry determined

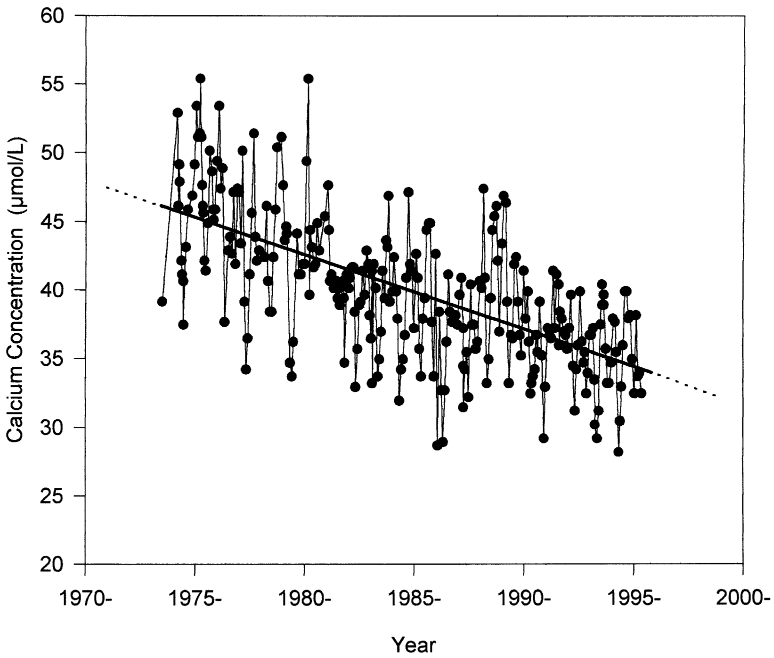


Figure 32. The long-term decline of calcium concentrations in stream water collected from Hubbard Brook near the mouth (235 m elevation) of the Hubbard Brook Valley. At this site, Hubbard Brook is a fourth-order stream, draining some 3000 ha. The regression, based on monthly samples from 1973 to 1995, is Ca (μmol/ℓ) = -0.0014X + 47.9; ($p < 0.0001$ for a larger F-ratio) and the $r^2 = 0.41$.

which species would be successful at specific locations (e.g. Stone 1975). Hutchinson (1948–50) proposed such “circular causal systems in ecology” and biogeochemistry almost 50 years ago. Such issues are critical in the evaluation of alternate management policies and currently are under intensive study at the HBEF.

Increased depletion of exchangeable base cations, especially Ca and Mg, have been reported in soils under alder (*Alnus rubra* Bong.) stands in the northwestern U.S., in contrast to soils under coniferous, forest species in the region (Franklin et al. 1968; van Miegroet & Cole 1988). This increased depletion is thought to be the result of increased acidification of the soil caused by the biological activity of the alders.

To address these questions at the HBEF, we are planning a long-term, experimental watershed manipulation using a Ca amendment. We expect the effects of this experimental manipulation to reverberate throughout the complex, watershed-ecosystem (Figure 33), and to provide answers useful for a clearer understanding of the Ca biogeochemistry and for the management.

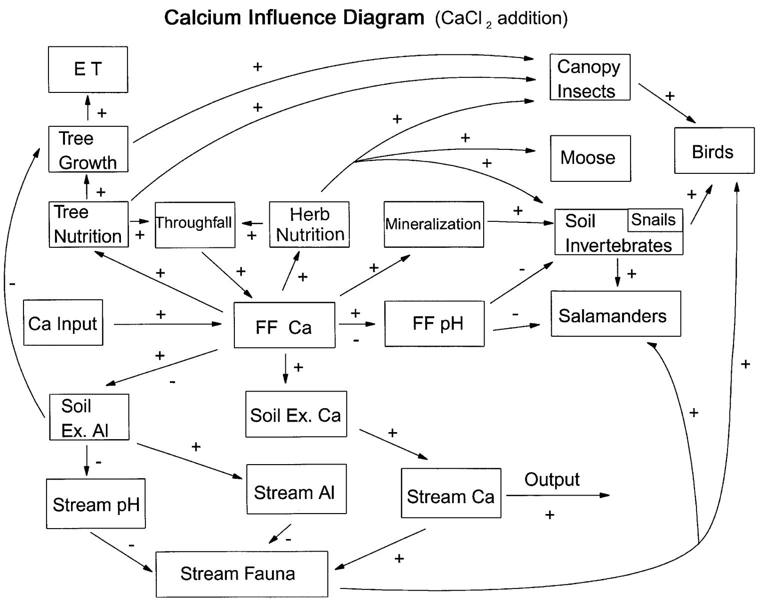


Figure 33. Diagram of the potential influence and interactions following a long-term experimental addition of $CaCl_2$ to a forest, watershed-ecosystem at the HBEF.

Other formulations of a Ca addition, e.g. $Ca(NO_3)_2$ or $CaCO_3$, undoubtedly would result in different effects within such forest, watershed-ecosystems. It is important to gain an understanding about these different management alternatives for such disturbed, forest landscapes in eastern North America.

Summary and conclusions

- Large declines were observed in both annual volume-weighted concentrations and flux of Ca in precipitation and stream water at the HBEF. Declines in concentration extended from 1963 through about 1975 in precipitation, and to about 1985 in stream water.
- On an annual basis, streamwater outputs always exceeded bulk precipitation inputs. On a monthly basis, streamwater concentrations and fluxes always exceeded precipitation concentrations and fluxes, although fluxes were not statistically different during the low streamflow months, particularly June, July, August.
- Annual volume-weighted concentration of Ca in bulk precipitation was inversely related to annual amount of precipitation during 1963–1970; otherwise there was no relation between annual concentration or deposition and amount of precipitation.

- Dry deposition of Ca may represent up to 20% of the total atmospheric deposition of Ca, but it is difficult to measure accurately.
- The intrasystem cycling of Ca is dominated by vegetation uptake and return to the soil via litterfall.
- Concentration of Ca in precipitation and stream water does not vary significantly from month to month; thus, monthly streamwater output is determined by amount of streamflow.
- Concentrations of Ca in soil solutions tended to be higher in the Oa soil horizon and at lower elevations of W6.
- The pool of Ca in live tree biomass increased from 1965 through 1982, but was relatively constant thereafter.
- The Ca concentration of yellow birch wood decreased from 1920 to 1990, and decreased in sugar maple with increasing elevation at HBEF. The foliage of these two species was enriched in Ca at lower elevations.
- Compared to the large quantities of Ca found in abiotic and biotic pools within the ecosystem and the major exchanges occurring among these pools, relatively little Ca is lost in stream water at the HBEF.
- The flux of Ca by biological vectors across watershed-ecosystem boundaries is negligible at the HBEF.
- Ca leaching from the forest canopy is accelerated by acid rain.
- Atmospheric inputs of strong acids to the HBEF have markedly depleted labile pools of Ca from the forest ecosystem, primarily from the forest floor.
- Concentrations of Ca have been depleted selectively in both bulk precipitation and stream water relative to C_β (the sum of Ca^{2+} + Mg^{2+} + Na^+ + K^+) during the study period.
- Due to the depletion of calcium from the soil complex, the fundamental relationship between gross annual output in stream water and annual streamflow has changed systematically with time.
- Generation of acidity and NO_3^- from nitrification following deforestation of W2 provided experimental verification of the effects of acid rain inputs of acidity and mobile anions on depletion of Ca and other base cations from the soil complex.
- Clearcutting disturbance releases large amounts of Ca to stream water, and even larger amounts can be lost from the ecosystem through products removed in whole-tree harvest. Elevated concentrations of Ca in stream water persist for several years depending on the type of disturbance and rate of biotic recovery.
- Following large-area disturbances in northern hardwoods, such as by clearcutting, foliar biomass recovers to levels approaching pre-disturbance in as little as 5 years. As a result, the dominant annual cycle of Ca

between soil and vegetation uptake from the soil and return in leaf litter can be restored quickly.

- A lower content of Ca was observed with increasing elevation for most of the components of the watershed-ecosystem: Concentrations of Ca in throughfall, soil water, and stream water; Exchangeable Ca of the Oa horizon, and to a depth of 20 cm in the soil, was about 2 times higher near the base of the watershed than near the top; Calcium in foliage of sugar maple and yellow birch were about 1.5 times higher at lower elevations than at higher elevations; Annual bulk precipitation input of Ca is about the same over the elevational gradient, whereas dry deposition probably is somewhat higher with increasing elevation (Lovett & Kinsman 1990). Cloudwater inputs to HBEF are minimal (Weathers et al. 1988).
- Comparing ecosystem processes for Ca from 1964–69 to 1987–92, net annual biomass storage has decreased by almost 75%, atmospheric deposition is less than half, throughfall and stemflow is about half, stream export of dissolved Ca has decreased by about 20%, and net soil release has decreased by about 40% of the 1964–69 values. These changes appear to reflect the changing inputs of acid rain to the ecosystem, depletion of base cations by leaching from acid rain, and decreasing rates of living biomass accretion. Even with these changes, watershed-ecosystems were a consistent net source of Ca to downstream ecosystems throughout the study.

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