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Abstract. Loss of base cations from forest soils can be accelerated by acid rain, by forest regrowth following harvest removals, and by declining inputs of base cations from atmospheric deposition. Calcium losses from forest floors have been reported at several sites in the northeastern United States. To test for loss of base cations from forest floors at the Hubbard Brook Experimental Forest in New Hampshire (USA), we analyzed samples collected on seven dates between 1976 and 1997. Calcium and magnesium contents of the forest floor did not decline significantly; a change >0.9%/yr would have been detectable. Concentrations of Ca were 40% higher in 1969–1970 than in the current study, but the difference is partly due to changes in collection methods. Magnesium concentrations were too variable to detect a loss of <47% over the 21-yr interval. To determine whether base-cation losses were associated with forest growth, we resampled a chronosequence of northern hardwood stands in the White Mountains of New Hampshire. The 13 stands did not show consistent changes in Ca, Mg, and potassium over the 15-yr interval. Losses of these cations were most pronounced in stands logged more than 25 yr earlier. Younger stands, contrary to our expectation that rapid forest growth should cause cation depletion, all gained base cations in the forest floor. Early in stand development these forest floors appeared to accumulate biomass along with living vegetation, rather than serving as a net source of nutrients. Finally, in a regional survey of 28 mature stands in the northeastern United States, some lost significant forest-floor Ca and Mg between 1980 and 1990, while others gained. The average change in Ca and Mg content was not significant; a loss of 1.4%/yr would have been detectable. Forest floors in the region are not currently experiencing rapid losses of base cations, though losses may have preceeded the onset of these three studies.

Key words: base-cation depletion; calcium; chronosequence, resampling; forest-floor cations; forest floor, recovery from logging; forest soil; forests, northeastern United States; magnesium; nutrient cycling; potassium.

INTRODUCTION

The export of calcium, magnesium, and potassium in stream water exceeds inputs of these cations in precipitation in a variety of ecosystems (Mann et al. 1988, Federer et al. 1989, Likens and Bormann 1995). The gradual loss of base cations from soils is a natural feature of weathering and pedogenesis. In addition, however, the loss of calcium and other base cations from soils is accelerated by human action, in more and less direct ways.

First, forest harvest removes nutrients as well as biomass from the landscape. Forests in the northeastern United States are regrowing, some because of recent logging activities, some because of extensive land clearing in the past century. Forest harvest can also result in increased nitrification, with accompanying losses of Ca in stream water (Bormann and Likens 1979).

Second, industry and automobiles have increased the deposition of sulfuric and nitric acids in precipitation, which accelerates the acidification of soils and the mobilization of base cations from exchange sites in soil. The leaching of base cations caused by acid deposition is thought to be responsible for declines in forest growth and nutrient status in eastern North America (Baes and McLaughlin 1984, Shortle and Bondietti 1992) and in Europe (Malmer 1976, Ulrich et al. 1980). For example, at Walker Branch, Tennessee, USA, cation leaching from soils is thought to have doubled as a result of acid deposition (Johnson et al. 1988), and declines in exchangeable Mg in soil have been attributed to this leaching (Johnson and Todd 1990). Cation leaching is expected to be most severe at high elevations; sulfate deposition increases by a factor of two from 600 m to 1000 m elevation in the Adirondacks (New York, USA; Miller et al. 1993).

Finally, regulation of industrial emissions has resulted in a reduction of atmospherically deposited nutrients, including base cations (Hedin et al. 1994). De-

position of base cations in precipitation declined dramatically between 1963 and 1975 at the Hubbard Brook Experimental Forest in New Hampshire, USA (Likens et al. 1998); Ca deposition is now only ~30% of what it was 25 yr ago. At current rates of nutrient deposition in precipitation and loss in stream water, Ca is the element first predicted to become depleted in soils in the eastern United States (Johnson et al. 1988, Federer et al. 1989, Hornbeck et al. 1990). Repeated forest harvest would reduce ecosystem stores of Ca even sooner (20–60% in 120 yr; Federer et al. 1989).

The rate of weathering, where it has been estimated independently of stream-water export, is less than the rate of Ca loss from soils to vegetation and stream water (Likens et al. 1996, 1998). A decline in soil stores of exchangeable Ca might therefore be expected. Losses of Ca and Mg have been observed in studies that compare soils measured at different times. In the Adirondacks, ~25% of exchangeable Ca was lost from forest floors between 1930–32 and 1984 (Johnson et al. 1994). At Walker Branch, Tennessee, most of the sites studied suffered losses of exchangeable Ca, Mg, and K in both the forest floor and mineral soil between 1972 and 1982 (Johnson et al. 1988). At Coweeta, North Carolina, USA, mineral soil horizons lost dilute-acid extractable Ca, Mg, and K between 1970 and 1990 (Knoepp and Swank 1994).

The forest floor is an important pool of organic matter and nutrients in those ecosystems in which it accumulates to substantial depths. This organic horizon, like the mineral horizons below, has been observed to decline in concentration and amount of base cations in recent decades (Shortle and Bondietti 1992, Johnson et al. 1994). At the Hubbard Brook Experimental Forest (HBEF) in New Hampshire, we compared samples of forest floor collected in 1970 with those collected in 1987, and found reductions in Ca and Mg concentrations of 35% and 22%, respectively. Likewise, forest floors collected from northern hardwood stands on Camels Hump, Vermont, USA, had 30% lower Ca concentrations in 1990 than 1981, although Mg concentrations increased (T. G. Siccama, *unpublished data*). The forest floor, unlike the mineral soil, can be completely and quantitatively described without labor-intensive and destructive excavations. The forest floor would be valuable as an indicator of ecosystem cation depletion, if it reflected the supply and demand of nutrients by vegetation and the added stress of acidic precipitation and reduced cation deposition.

We undertook three studies of base-cation depletion in forest floors in the northeastern United States, in an effort to describe the extent and degree of base-cation loss and to elucidate the mechanisms responsible for this loss. First, we described in detail the pattern of cation change in forest floors at the HBEF. We measured Ca and Mg in forest-floor samples from seven collection dates ranging from 1976 to 1997, with all samples taken in the same 13-ha watershed. In a chronosequence study, we resampled forest floors in 13 northern hardwoods stands of different ages for which we had archived samples collected 15 yr previously. We hypothesized that young, rapidly growing stands would show the greatest declines in base cations, if cation loss were caused by vegetative demand by forests accumulating biomass and nutrients as they regrow following logging. Alternatively, if cation loss were caused primarily by acid rain or by reductions in atmospheric deposition of base cations, then stands of all ages should show similar rates of decline. Finally, we analyzed archived samples collected in 1980 and 1990 from 28 forested sites located across the northeastern United States, to test for regional changes in base-cation concentrations and amounts.

METHODS

An organic horizon must have >20% organic carbon (Soil Survey Staff 1975), which corresponds to ~40% organic matter (Federer 1982). This criterion should be applied at the lower boundary, but the organic fraction is commonly measured only for the forest floor as a whole. Organic-matter content generally declines with depth; a horizon averaging 40% organic matter could have considerably less than 40% organic matter in its deepest part. To further confuse matters, there is not a universally accepted definition of the forest floor— some investigators include a highly organic mineral horizon, such as an A or A1 (Federer 1982). In sampling forest floors at the Hubbard Brook Experimental Forest (HBEF), we distinguished Oie and Oa horizons, but the so-called Oa horizon often included A material that averaged <40% organic matter. In the chronosequence study, we collected a separate A horizon, which invariably averaged <40% organic matter by stand (R. D. Yanai, M. A. Arthur, T. G. Siccama, and C. A. Federer, *unpublished manuscript*). The regional study used the same sampling methods as the HBEF study, but horizons were not divided.

HBEF

The HBEF is located in the central White Mountains of New Hampshire (USA; 43°56′ N latitude, 71°45′ W longitude). Forest-floor samples used in this study were collected in the reference watershed (W6), which ranges in elevation from 550 to 790 m. Most of the watershed is dominated by northern hardwoods, mainly yellow birch (*Betula alleghaniensis* Britton), sugar maple (*Acer saccharum* Marsh), and beech (*Fagus grandifolia* Ehrh.). Balsam fir (*Abies balsamea* (L.) Mill.), red spruce (*Picea rubens* Sarg.), and paper birch (*Betula papyrifera* var. *cordifolia* (Marsh.) Regel) dominate above ~700 m. More detail on the vegetation, soils, and biogeochemistry of the small watershed ecosystems at the HBEF is available in hundreds of publications (e.g., Whittaker et al. 1974, Bormann and Likens 1979, Johnson et al. 1991a, Likens et al. 1994, Likens and Bormann 1995).

Forest-floor samples were first collected in W6 in 1969 and 1970 by Gosz et al. (1976). Later collections in 1976, 1977, 1978, 1982, 1987, and 1992 were all supervised by T. G. Siccama. Continuity in investigators is important because of the subjectivity involved in delineating forest-floor horizons in the field (Federer 1982). At each sampling date, 52–87 plots were located randomly within elevational thirds of the watershed. Rocks and streams were not sampled. At each plot, a 15 × 15 cm square was placed on the soil surface and the block was isolated in place by cutting away the soil surrounding it until mineral soil was exposed. Ideally, the mineral-soil pedestal supporting the forest-floor block was then lifted out and the mineral soil removed from the bottom of the block. In less ideal circumstances, the defined volume of soil was removed from around boulders or large roots. In some years the forest floor was divided into horizons (Oie and Oa, or Oi, Oe, and Oa). Contents were summed and concentrations mass-weighted to allow comparison to undivided samples.

The method used in the earliest collections at the HBEF by Gosz et al. (1976) differed from those used in our studies: Gosz et al. excavated pits to the depth of mineral soil, encountering the boundary between forest floor and mineral soil from the top down instead of from the bottom up.

Chronosequence

The chronosequence consists of 13 stands in the central White Mountains of New Hampshire, all between 310 m and 550 m elevation, and all northern hardwood forests dominated by yellow birch, beech, sugar maple, red maple (*Acer rubrum* L.), and paper birch (*B. papyrifera* Marsh) or, in young stands, pin cherry (*Prunus pennsylvanica* L.f.) (R. D. Yanai, M. A. Arthur, T. G. Siccama, and C. A. Federer, *unpublished manuscript*). They were selected to cover a range of ages since clearcutting when they were first sampled in 1979 and 1980 (Federer 1984). One stand that was over 100 yr old in 1979 was clear-cut in 1986; otherwise the stands are as described by Federer (1984). We relocated all the stands with certainty; in some cases, we exactly relocated the original sampling lines.

We sampled forest floors by the same methods used in the earlier collection. Federer's method differs from that of Siccama in the HBEF study. In each stand, we collected samples along five transect lines. We used a plastic template holding stainless steel pins in a 10 × 10 cm square array to collect blocks of forest floor 0.01 m² in area to the depth of the E or B horizon. The A horizon, where present, was included in the forest-floor sample. The soil containing the block was lifted with a shovel and the block trimmed with a knife and clippers to the dimensions of the pins; mineral soil was removed from the bottom of the block. Thicknesses of the O and A horizons were recorded in the field. Ten forest-floor blocks were composited in each line, for a total of five composited samples per stand. There were no exclusion criteria for sampling points, which were located at 5-m intervals along the lines; rocks and trees were counted as zeros. Buried organic horizons were not collected. Samples were air dried and then sieved to 2 mm for stands first sampled in 1979 and to 6 mm for stands first sampled in 1980. The 6 mm is the better sieve for forest floors, but we applied the same treatment as the archived samples in both collections.

Regional survey

The regional study involved revisiting stands sampled in 1980 (Johnson et al. 1982, Friedland et al. 1984). Thirty stands were relocated and resampled in 1990 (Friedland et al. 1992). Samples from 28 stands were available for our study; they included a range of forest types in addition to northern hardwoods (9 stands): spruce–fir (7 stands), pine–hemlock–hardwoods or other conifer–hardwood mixtures (8 stands), and some oak, pine, and spruce–hemlock types (4 stands). Elevations ranged from 160 to 1160 m. None of the stands had been recently disturbed. Five forest-floor samples were collected from random locations in each stand, using Siccama's method, as described above (see *HBEF*).

Laboratory analyses

Forest-floor samples, once collected, were all analyzed in the same manner. Ground subsamples were ashed and dissolved in 6 mol/L nitric acid and analyzed by inductively coupled plasma spectroscopy (ICP). Accuracy of cation analysis was tested through repeated analysis (10% of all samples) of tissue standards obtained from the U.S. Bureau of Standards. In the chronosequence samples collected in 1979 and 1994, we found a mean Ca concentration of 28.1 ± 0.3 g/kg for citrus leaves (11% lower than the certified value of 31.5 ± 1.0), a mean Mg concentration of 5.2 ± 0.1 (compared to the certified value of 5.4 ± 0.1), and a mean K concentration of 17.8 ± 0.1 (certified value 18.2 ± 0.6) (all are means ± 1 SE). In the samples collected in 1980 and 1995, we found a mean Ca concentration of 14.4 ± 0.13 g/kg for apple leaves (6% lower than the certified value of 15.26 ± 0.15), a mean Mg concentration of 2.71 ± 0.03 (certified value 2.71 ± 0.08), and a mean K concentration of 13.2 ± 0.19 (18% lower than the certified value of 16.1 ± 0.2). To minimize the effect of analytical errors on our comparisons, archived and contemporary samples were analyzed side by side in both the chronosequence and the regional study.

The Ca and Mg extractable by our nitric-acid digest is mostly exchangeable. In a comparison of Oa horizon samples from six sites in the chronosequence, 6 mol/L nitric acid extracted only 14% more Ca and 15% more Mg than did 1 mol/L ammonium chloride. The comparison is important because nonexchangeable cations are less likely to be lost by leaching.

We report concentrations on an ash-free basis (grams of element per kilogram of organic matter [kg_o]) (Federer et al. 1993) because the mineral fraction of the forest floor contributes little to the measured cation content (our extraction procedure does not dissolve primary minerals). The correlation between cation concentration and organic-matter concentration (determined by loss on ignition) in the chronosequence study was 0.76 for Ca, 0.70 for Mg, and 0.51 for K, on a per sample basis ($n = 259$ samples).

To demonstrate that the differences we report are not due to changes in analytical methods or to alteration of the forest-floor samples during storage, we reanalyzed 110 samples from the 1969–1970 collections by Gosz et al. There was no significant difference in Ca or Mg concentrations measured in the archived samples from those in the original analysis (paired t tests, $P = 0.25$ for Mg and 0.40 for Ca).

Statistical analyses

We report means and standard errors of forest-floor properties. For derived variables (cation contents and concentrations per unit organic matter), we calculated products on individual samples and report the mean of the products, not the product of the means. Regressions were conducted on log-transformed variables, as required to normalize the residuals. Linear trends over time were assessed on means by sampling dates. Pairwise comparisons of means were conducted using Fisher's protected least-significant difference. Comparisons of two points in time in which the stand was the experimental unit were based on paired t tests. Comparisons of two points in time in the same stand were based on independent sample t tests, using transect lines as the experimental unit. In addition, for each stand and collection date, we calculated the amount of change that would be detectable by a t test at a specified value of α, assuming equal sample sizes and standard deviations. The detectable difference is $\sqrt{2}t$ SE, where t is a percentile of the t distribution depending on α and sample size and SE is the standard error. For regressions, the SE of the slope can be used to calculate the detectable rate of change (t SE). We used one-tailed t, because we were testing for cation loss over time.

RESULTS

HBEF

Organic matter concentrations in the forest-floor samples from the Hubbard Brook Experimental Forest (HBEF) averaged 54%. Organic-matter concentrations decreased with depth in the forest floor, from an average of 80% in the Oie to 41% in the Oa horizon. Many of our Oa horizon samples had <40% organic matter, reflecting the inclusion of mineral material. The proportion of Oa samples with <40% organic fraction ranged from 0.10 to 0.44; the median proportion was 0.29.

Calcium concentrations declined with depth in the forest floor even when adjusted for the change in organic fraction; we report concentrations on an organic-matter basis (Fig. 1, Table 1). The Oi horizon, or litter layer, had a Ca concentration of 7 g/kg_o and the Oe had a concentration of 4 g/kg_o in the samples from 1978, when they were collected separately. On most sampling occasions, the Oi and Oe were collected together. The Ca concentration of the Oie averaged 4.2 g/kg_o, higher than the average concentration in the Oa (1.8 g/kg_o). The concentrations of the combined O horizons averaged 3.1 g/kg_o. Magnesium concentrations, unlike Ca concentrations, were higher in the Oa than in the Oie horizons (0.61 compared to 0.48 g/kg_o) (Fig. 2).

There were significant differences in the measured mean mass of the forest floor among years ($P < 0.001$), with higher values in 1976 and 1992 (Table 1). There were also significant differences in mean organic fraction ($P < 0.001$), with lower values in 1976 and 1992 and higher values in 1977 and 1997. Because of the decrease in organic fraction with depth, the most massive samples tended to have lower organic fraction (correlation of -0.36 significant at $P < 0.0001$ over 472 O-horizon samples). The organic mass of the forest floor, which is proportional to both the mass and the organic fraction collected, was much less variable than either (Fig. 3) and there was not a significant effect of time on means by date ($P = 0.11$). None of these variables (total mass, organic fraction, or organic mass) showed a significant linear change with time in univariate regression ($n = 7$ sampling dates).

There was some significant variation in mean Ca and Mg concentrations with time between 1976 and 1997 ($P = 0.06$ for Ca and $P < 0.001$ for Mg). Calcium concentrations were highest in the 1987 samples, while Mg concentrations were high in the 1976 samples and low in the 1977 samples. There was no significant effect of time on Ca or Mg concentrations in linear regression ($P = 0.68$ and $P = 0.88$, respectively; $n = 7$ sampling dates).

The amount of Ca in the forest floor is obtained by multiplying concentrations and masses. Because the concentrations of Ca are higher in the Oie, more of the Ca in the forest floor is held there than in the Oa (Fig. 1), although the mass of the Oa is greater (Table 1). As in the case of organic mass, the Ca content of the forest floor is less sensitive to variation in sampling depth than is the organic-matter concentration or Ca concentration. There was not significant variation in the Ca content of the forest floor between sampling dates ($R^2 = 0.009$ and $P = 0.62$), and the decrease with time over all collections was not significant ($P = 0.26$ in linear regression, $n = 7$ sampling dates). Magnesium contents differed more between sampling dates ($R^2 = 0.05$, $P = 0.05$), with a high value in 1976 and a low value in 1987 (Fig. 2). The decrease with time in Mg contents over all collections was not significant ($P = 0.85$ in linear regression).
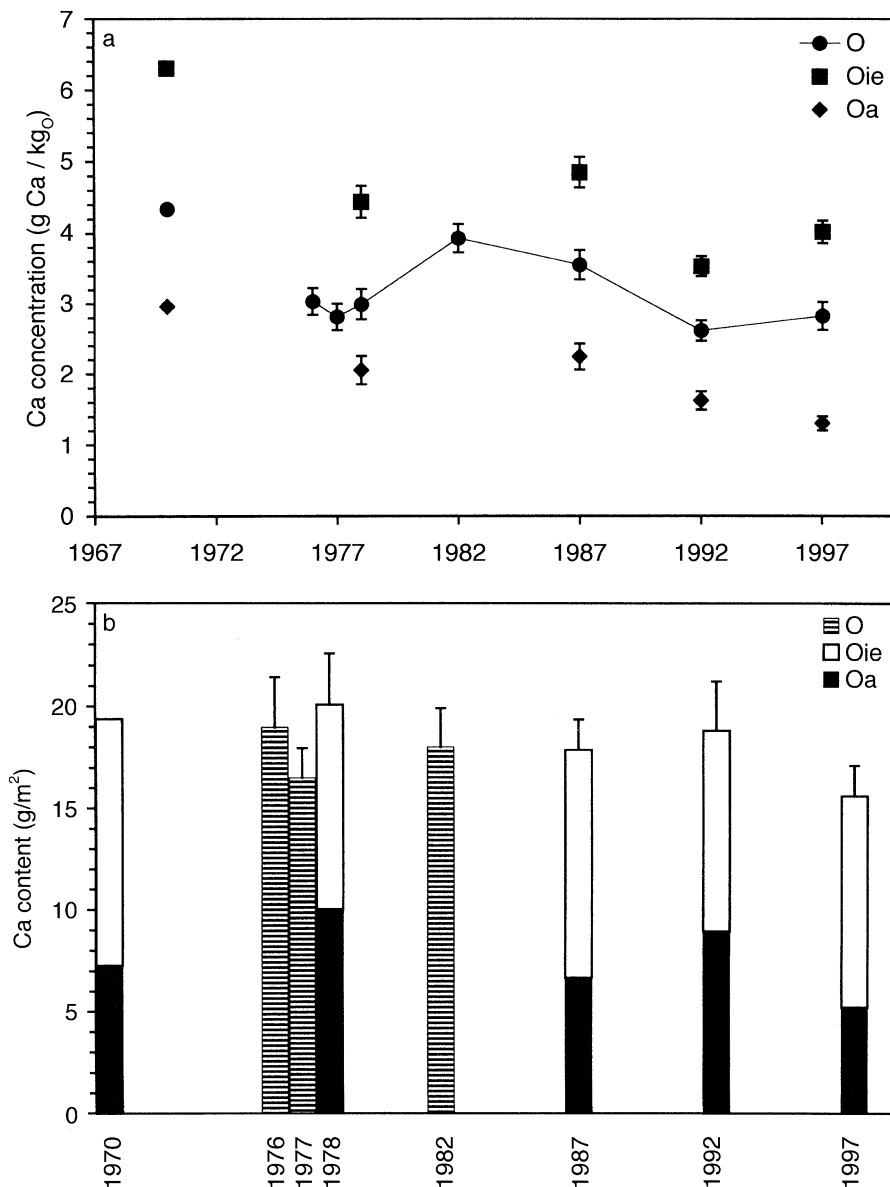
FIG. 1. (a) Concentrations and (b) amounts of Ca in forest floors collected at different times from Hubbard Brook Experimental Forest (HBEF; New Hampshire, USA) reference watershed W-6, by soil horizon. The values for 1970 are the means of collections from June 1969 and May 1970 reported by Gosz et al. (1976). Data in (a) are means ± 1 SE; error bars in (b) are + 1 SE for the O horizon.

Position on the watershed is a significant predictor of Ca and Mg in the forest floor (Arthur et al. 1999). Calcium concentrations and contents were significantly lower at higher elevations at every collection date ($P < 0.01$ in all cases). Magnesium concentrations and contents declined with elevation at most sampling dates, not always significantly. The organic fraction was always higher at high elevation, but the mass of the forest floor tended to be lower; the organic mass generally decreased with elevation (significant for two of the sampling dates at $P < 0.05$). The greatest losses

of base cations might be expected in the high-elevation spruce–fir area, but there were not significant declines with time in samples collected from the spruce–fir zone, nor in any of four other vegetation zones defined by species composition and elevation.

The sampling methods at the HBEF were the most intensive of our three studies, involving from 52 to 87 blocks, each 15 × 15 cm, at each sampling date. The forest floor is so variable, however, that even with this intensity of sampling, it is difficult to detect small changes over time. A regression of the means at the

TABLE 1. Properties of forest floors in Hubbard Brook Experimental Forest (HBEF, New Hampshire, USA) experimental watershed W6 over time.

Hori-zon	Year	n	Organic fraction (%)	Mass (kg/m²)	Organic mass (kg/m²)	Concentration (g/kg$_o$)†		Content (g/m²)	
						Ca	Mg	Ca	Mg
O	1969–1970	n.a.	76	n.a.	4.7	4.3	0.51	19.4	2.3
	1976	59	47 ± 3	18.1 ± 2.2	6.5 ± 0.6	3.0 ± 0.2	0.80 ± 0.12	19.0 ± 2.4	5.6 ± 0.9
	1977	57	59 ± 3	13.3 ± 1.9	7.0 ± 0.7	2.8 ± 0.2	0.47 ± 0.04	16.5 ± 1.5	3.1 ± 0.4
	1978	52	54 ± 2	13.2 ± 0.6	6.9 ± 0.6	3.0 ± 0.2	0.53 ± 0.04	20.1 ± 2.5	3.8 ± 0.5
	1982	65	57 ± 2	11.0 ± 0.7	6.3 ± 0.5	3.9 ± 0.3	0.57 ± 0.03	22.9 ± 2.6	3.3 ± 0.3
	1987	70	53 ± 2	13.0 ± 2.0	6.3 ± 0.8	3.6 ± 0.2	0.54 ± 0.03	17.4 ± 1.5	3.2 ± 0.5
	1992	80	48 ± 2	16.8 ± 1.3	7.7 ± 0.6	2.6 ± 0.1	0.58 ± 0.04	18.8 ± 2.4	4.4 ± 0.5
	1997	87	60 ± 2	11.5 ± 0.9	6.3 ± 0.5	2.8 ± 0.2	0.59 ± 0.04	15.7 ± 1.5	3.8 ± 0.4
Oie	1969–1970	n.a.	91	n.a.	2.1	6.6	0.52	12.1	1.0
	1978	52	84 ± 1	3.0 ± 0.2	2.5 ± 0.2	4.4 ± 0.3	0.43 ± 0.03	10.1 ± 0.9	1.0 ± 0.1
	1987	70	72 ± 2	3.9 ± 0.3	2.8 ± 0.2	4.8 ± 0.3	0.53 ± 0.03	11.2 ± 0.9	1.3 ± 0.1
	1992	80	80 ± 1	3.3 ± 0.2	2.6 ± 0.1	3.5 ± 0.5	0.48 ± 0.05	9.9 ± 0.6	1.2 ± 0.1
	1997	87	83 ± 1	3.4 ± 0.2	2.8 ± 0.1	4.0 ± 0.2	0.47 ± 0.03	10.4 ± 0.7	1.2 ± 0.1
Oa	1969–1970	n.a.	65	n.a.	2.6	3.0	0.52	7.3	1.27
	1978	51	43 ± 2	10.2 ± 1.1	4.4 ± 0.5	2.0 ± 0.2	0.60 ± 0.05	9.9 ± 1.9	2.7 ± 0.5
	1987	65	41 ± 2	9.1 ± 2.0	3.5 ± 0.7	2.2 ± 0.2	0.58 ± 0.05	6.7 ± 1.0	1.9 ± 0.5
	1992	78	38 ± 2	13.4 ± 1.3	5.1 ± 0.6	1.6 ± 0.1	0.66 ± 0.07	8.9 ± 2.1	3.3 ± 0.5
	1997	87	40 ± 2	8.1 ± 0.8	3.5 ± 0.4	1.3 ± 0.1	0.61 ± 0.06	5.2 ± 1.0	2.5 ± 0.4

Notes: Data are means ± 1 SE. Values for 1969–1970 are those reported by Gosz et al. (1976). Some values are not available (n.a.) for 1969–1970 because of how samples were combined and reported.

† Grams of element per kilgram of organic matter.

seven sampling dates is the appropriate test for a trend in cation loss over time. Based on the standard error of the slope and $\alpha = 0.05$, a decrease of 19% in Ca content or 25% in Ca concentration would have been detectable over the 21-yr period. For Mg the rate of loss required to be detectable at $\alpha = 0.05$ would be 62% for content and 47% for concentration. In a comparison of only two points in time, the change in Ca concentration that would be detectable at $\alpha = 0.05$ ranged from 16% to 20% over the dates we sampled; the average detectable change was 19%. Somewhat larger changes would be needed, on average, to be significant for Mg than for Ca and for contents than for concentrations.

Chronosequence

Calcium was the dominant base cation in the forest floors in the chronosequence of 13 northern hardwood stands. Mean concentrations of Ca by stand ranged from 3.1 to 15 g/kg$_o$ (Table 2) with a mean concentration of 10 g/kg$_o$. Magnesium concentrations averaged 1.4 g/kg$_o$ and K concentrations averaged 1.7 g/kg$_o$. Concentrations were quite variable within stands, despite compositing 10 samples in each of the five lines collected in each stand; coefficients of variation within stands averaged 32% for Ca, 28% for Mg, and 24% for K. The variation in cation concentrations among stands was larger than the variation within stands: coefficients of variation among stands ranged from 36% for Ca to 88% for Mg.

The goal of resampling the chronosequence was to quantify changes in base-cation status in forest floors

over the 15-yr interval. Change in the distribution or storage of cations is indicated by the cation contents (amount per unit area). Calcium contents declined in 6 of the 13 stands in the chronosequence (Fig. 4). In four of these the decline was statistically significant (Table 2). The changes in Mg and K contents over time were very similar to those of Ca. Contrary to our prediction, losses were not greatest in the youngest stands, where biomass accretion was highest; in fact, the five youngest stands had most of the cases of increased forest-floor cation contents. The average changes in base-cation concentrations and contents across the chronosequence were not significant.

Changes in the base-cation contents of the forest floor were calculated from the concentrations per unit soil mass and the soil mass per unit area; these numbers are not sensitive to the measured depth or organic fraction of the samples. The latter measures can be used, however, to help elucidate the processes responsible for the observed changes in cation contents. Gains or losses of cations per unit area are due to changes in cation concentration per unit organic matter or to changes in the amount of organic matter per unit area, which can in turn be attributed to changes in bulk density, depth, or organic fraction of the forest floor (Table 2). Declining cation concentrations contributed to every case of declining Ca and Mg content and most cases of declining K content. Among the older stands, the one that gained in base-cation content did so mainly due to increased depth of the forest floors collected. In the middle-aged stands, concentrations decreased more consistently than did contents, usually because of in-
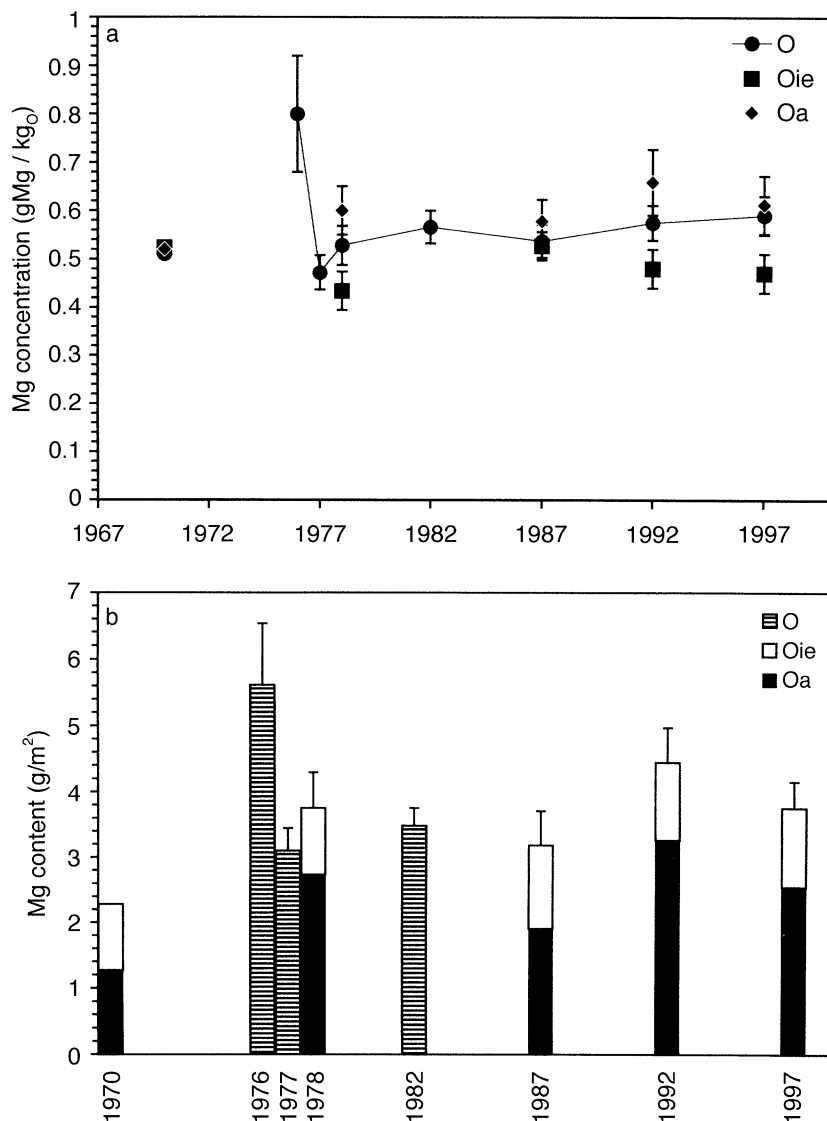
FIG. 2. (a) Concentrations and (b) amounts of Mg in forest floors collected at different times from HBEF W-6. Format and data are as in Fig. 1.

creases in the organic fraction. Increases in mass (due mainly to increases in depth) in the four youngest stands contributed to their increased base-cation contents; in the three youngest stands, concentrations of base cations also increased (except for K in the youngest stand).

The amount of change in cation concentrations required to produce a difference detectable at $P = 0.05$ ranged from 21% to 57%, depending on the stand and the cation. Mean detectable differences were larger than in the Hubbard Brook study, because the samples were smaller and fewer and were pooled to reduce the analytical load, giving $n = 5$ observations per stand. Using the 13 stands in the chronosequence in a paired

t test, detectable differences were 18% for Ca, 33% for Mg, and 26% for K contents.

Regional survey

About half of the 28 stands in the regional survey decreased in the amount of Ca and Mg in the forest floor between 1980 and 1990, while the rest increased (Fig. 5). The average change across all 28 sites was positive but not significant for Ca and Mg contents and concentrations. Mass and organic mass were also not systematically different over time across all stands (paired t tests, $n = 28$ sites). Organic fraction increased significantly ($P = 0.04$) between the two sampling dates, but the change was small (from an average of
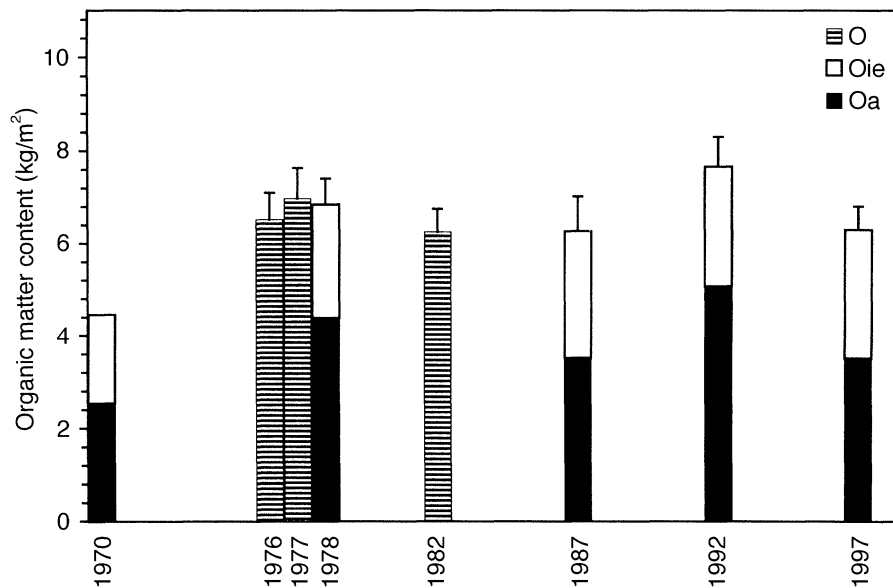
FIG. 3. Organic-matter content of forest floors collected at different times from HBEF W-6. Format and data are as in Fig. 1.

64% in 1980 to 68% in 1990). The magnitude of change in Ca or Mg contents that would be significant at α = 0.05 was 14% for both Ca and Mg. Concentration changes would be statistically detectable at 29% for Ca and 26% for Mg.

The amount of change required to produce a detectable loss in cation contents for an individual stand was large, averaging 72% for Ca and 160% for Mg, because only five samples were collected in each stand. Two of the Ca losses and one of the Mg losses were significant; one of the Ca and three of the Mg increases were significant. Magnesium concentrations were more variable than Ca concentrations. The higher variation in the 1990 than the 1980 Mg concentrations was probably due to analytical methods rather than spatial variation in the field. Forest type did not explain the pattern of cation gains and losses.

The two cations showed similar behaviors to one another despite differing strongly across stands: concentrations of Ca and Mg were positively correlated at both collection times (correlation of 0.63 and 0.69), and the concentration changes were also correlated (0.68). The gains and losses in forest-floor Ca contents were correlated with changes in Ca concentrations rather than with changes in mass or organic-matter content.

DISCUSSION

The goal of analyzing samples collected over a period of 21 yr at the Hubbard Brook Experimental Forest (HBEF) was to describe changes in Ca and Mg concentrations and content since the previous measurement of forest-floor chemistry in 1969–1970 (Gosz et al. 1976). Concentrations of Ca, but not Mg, were higher in samples collected in 1969–1970 than in those col-

lected from 1976 to 1997 (Figs. 1 and 2). The 1969–1970 forest-floor collections are not, however, directly comparable with the current study. The organic fraction of the Oa horizon in the 1970 samples was always >40% and averaged 65%, much higher than in the subsequent collections (Table 1). Since the organic fraction decreases with depth in the forest floor, the lower organic fraction of the later samples suggests that we included more soil from deeper, more mineral, horizons than did Gosz et al. in 1969–1970. A difference in the depth of sampling could bias the estimate of Ca concentrations, because Ca concentrations decline with depth, as described above (see *Results: HBEF*). The higher Ca concentration of the 1969–1970 samples (Fig. 1) might be at least partly explained by shallower sampling, with material from the upper, more Ca-rich part of the forest floor contributing a greater fraction of the weighted average forest-floor concentration. In a similar comparison, differences in Pb collected from the forest floor between 1966 and 1980 were attributed to changes in sampling techniques, which resulted from sampling to different depths (Friedland et al. 1984).

The organic mass of the forest floor was lowest in 1969–1970 (Fig. 3), again suggesting that Gosz et al. collected samples to lesser depths than we did at the later dates. For Mg, the small mass collected resulted in Mg contents per unit area much lower than any between 1976 and 1997. For Ca, the high concentrations in 1969–1970 were enough to compensate for a bias towards sampling higher in the profile, as Ca contents were not lower than the more recent measures (Fig. 1). The approximate equivalence of Ca contents in 1969–1970 with the later collections suggests that the high

TABLE 2. Properties of forest floors in the chronosequence of northern hardwood stands, sampled at two points in time.

Year		Year sampled	Depth (cm)	Bulk density (Mg/m³)	Organic fraction (%)	Organic mass (kg/m²)
logged	thinned					
1875	⋯	1979	7.9 ± 0.5	0.12 ± 0.01	68 ± 2	8.7 ± 0.5
		1994	9.4 ± 1.6	0.11 ± 0.003†	70 ± 2	7.9 ± 0.7
1875	1936	1979	10.5 ± 0.5	0.16 ± 0.01	55 ± 3	7.0 ± 0.5
		1994	10.1 ± 0.8	0.12 ± 0.01*	55 ± 7	7.0 ± 1.5
1910	⋯	1980	8.7 ± 0.9	0.14 ± 0.02	54 ± 3	6.3 ± 0.7
		1995	14.0 ± 1.4*	0.13 ± 0.01	51 ± 2	9.5 ± 1.0*
1934	1954	1979	6.9 ± 1.0	0.15 ± 0.01	45 ± 4	4.7 ± 0.7
		1994	5.5 ± 0.6	0.13 ± 0.02	52 ± 5	3.5 ± 0.5
1939	⋯	1979	7.8 ± 0.7	0.18 ± 0.02	39 ± 3	5.2 ± 0.6
		1994	7.6 ± 0.6	0.17 ± 0.004	48 ± 2*	6.1 ± 0.6
1948	⋯	1980	n.a.	n.a.	26 ± 2	3.6 ± 0.3
		1995	9.8 ± 1.8	0.11 ± 0.05	40 ± 2*	3.6 ± 0.5
1949–1950	⋯	1980	n.a.	n.a.	45 ± 4	5.3 ± 0.6
		1995	9.5 ± 1.3	0.14 ± 0.10	49 ± 3	6.4 ± 1.0
1958	⋯	1980	6.4 ± 0.4	0.14 ± 0.01	45 ± 5	4.0 ± 0.2
		1995	7.0 ± 0.9	0.12 ± 0.03	41 ± 5	3.2 ± 0.3*
1967	⋯	1979	6.1 ± 0.4	0.16 ± 0.01	47 ± 2	4.6 ± 0.3
		1994	6.5 ± 0.7	0.15 ± 0.11	53 ± 4	4.9 ± 0.6
1970	⋯	1980	4.8 ± 1.0	0.19 ± 0.04	35 ± 4	3.0 ± 0.5
		1995	6.7 ± 0.6	0.18 ± 0.05	36 ± 2	4.2 ± 0.5
1976–1977	⋯	1980	6.2 ± 0.3	0.13 ± 0.01	46 ± 2	3.8 ± 0.4
		1995	7.8 ± 0.7	0.12 ± 0.02	45 ± 2	4.4 ± 0.7
1979–1980	⋯	1980	6.4 ± 0.8	0.15 ± 0.02	48 ± 3	4.8 ± 0.8
		1995	8.0 ± 1.6	0.16 ± 0.04	44 ± 5	5.2 ± 0.9
1983	⋯	1979	8.5 ± 0.3	0.14 ± 0.01	52 ± 2	6.0 ± 0.3
		1994	7.3 ± 0.8	0.14 ± 0.15	57 ± 4	5.5 ± 0.8

Note: Data are means ± 1 SE; n.a. = not available.
† $P < 0.10$ for difference over time (i.e., relative to preceding entry in column).
* $P < 0.05$ for difference over time (i.e., relative to preceding entry in column).

concentrations are not completely explained by a shallower sampling scheme.

The repeated sampling of the chronosequence allowed us to test whether losses of base cations in forest floors were related to stand development. We had hypothesized that if acid rain were the cause of loss, base-cation contents would decrease in all stands. Alternatively, if forest growth were responsible for cation depletion, losses should have been greatest in the youngest, most rapidly growing stands. Instead of either of the expected patterns, we found that most young stands (cut since 1967) had gained base cations in the forest floor over the 15-yr interval, while middle-aged stands (cut between 1934 and 1958) showed the greatest cation depletion (Fig. 4). The factors contributing to cation gains in the young stands were evidently more than enough to offset any losses caused by acid deposition and forest regrowth. It is possible that displacement of base cations by acid cations (hydrogen and possibly aluminum ions (Lawrence et al. 1995)) was responsible at least in part for the losses in the stands over age 30,

but the causes of loss cannot be attributed from this data set alone.

The observed cation accumulation in forest floors of the young stands (those cut since 1967) was unexpected. The increased mass and organic-matter content of these stands (Table 2) contradicts the presumed pattern of organic-matter decline following logging (Covington 1981, R. D. Yanai, M. A. Arthur, T. G. Siccama, and C. A. Federer, *unpublished manuscript*). Decreased leaf and woody-litter inputs, increased decomposition rates, and losses of dissolved organic matter have been supposed to cause losses of organic matter from forest floors after logging. In addition, contemporary logging practices can result in considerable disturbance to the forest floor (Martin 1988). In the case of a whole-tree harvest experiment in New Hampshire, mounded and buried organic matter was enough to account for the observed loss of forest floor in harvesting (Ryan et al. 1992). In some cases, forest-floor organic matter has increased in the first years after logging (Hendrickson et al. 1989).

TABLE 2. Extended.

Concentration (g/kg$_o$)			Content (g/m^2)		
Ca	Mg	K	Ca	Mg	K
3.6 ± 0.2	0.38 ± 0.02	0.9 ± 0.1	31 ± 2	3.2 ± 0.1	7.6 ± 0.8
3.1 ± 0.1	0.35 ± 0.02	0.7 ± 0.04	24 ± 2†	2.7 ± 0.1†	5.7 ± 0.3†
6.3 ± 0.4	0.68 ± 0.11	1.2 ± 0.1	44 ± 2	4.7 ± 0.3	8.3 ± 0.6
5.3 ± 0.6	0.63 ± 0.23	1.3 ± 0.2	34 ± 6	4.1 ± 0.9	8.0 ± 1.5
7.3 ± 0.7	0.96 ± 0.21	1.1 ± 0.1	45 ± 6	6.3 ± 1.8	7.3 ± 1.0
6.9 ± 0.9	1.11 ± 0.07	1.4 ± 0.1	64 ± 9	10.3 ± 0.5	12.6 ± 1.1*
6.8 ± 0.4	0.77 ± 0.06	1.7 ± 0.2	32 ± 5	3.5 ± 0.4	8.2 ± 1.8
5.7 ± 0.6	0.56 ± 0.02*	1.2 ± 0.03*	20 ± 4	2.0 ± 0.3*	4.4 ± 0.7†
6.1 ± 0.3	0.67 ± 0.06	1.3 ± 0.1	32 ± 4	3.5 ± 0.6	6.5 ± 0.9
4.7 ± 0.4	0.48 ± 0.03*	1.0 ± 0.1*	28 ± 2	2.9 ± 0.1	6.0 ± 0.3
14.9 ± 1.0	5.89 ± 0.85	6.3 ± 0.9	53 ± 6	21.5 ± 4.1	23.1 ± 4.4
12.2 ± 5.7	2.75 ± 0.38*	3.2 ± 0.3*	41 ± 2	9.3 ± 0.8*	11.3 ± 1.8†
9.2 ± 0.5	2.14 ± 0.26	2.1 ± 0.3	47 ± 3	10.3 ± 1.0	10.6 ± 1.3
8.8 ± 0.5	1.88 ± 0.33	1.9 ± 0.3	54 ± 7	12.5 ± 4.0	12.6 ± 3.7
9.9 ± 1.1	1.17 ± 0.07	1.3 ± 0.1	39 ± 3	4.7 ± 0.4	5.3 ± 0.2
7.4 ± 0.6†	0.93 ± 0.08†	1.6 ± 0.1	24 ± 2*	3.0 ± 0.3*	4.9 ± 0.2
7.1 ± 0.6	0.73 ± 0.04	1.3 ± 0.1	32 ± 2	3.4 ± 0.1	6.0 ± 0.5
7.5 ± 0.7	0.73 ± 0.07	1.2 ± 0.2	36 ± 3	3.6 ± 0.4	5.9 ± 0.8
7.5 ± 0.9	2.40 ± 0.39	2.6 ± 0.3	22 ± 5	7.2 ± 1.5	8.0 ± 1.5
7.1 ± 0.6	2.95 ± 0.44	2.4 ± 0.3	30 ± 4	9.3 ± 1.7	10.0 ± 1.4
8.4 ± 2.9	1.85 ± 0.38	2.0 ± 0.4	29 ± 9	6.7 ± 1.1	7.2 ± 1.2
13.6 ± 0.9	2.45 ± 0.36	2.4 ± 0.3	60 ± 11†	9.9 ± 0.5*	9.9 ± 0.6†
7.3 ± 1.1	0.70 ± 0.09	0.9 ± 0.1	36 ± 10	3.1 ± 0.4	4.3 ± 0.6
8.1 ± 0.7	0.95 ± 0.14	1.5 ± 0.3	43 ± 10	5.0 ± 1.1	7.8 ± 1.9
6.6 ± 0.3	0.70 ± 0.06	1.3 ± 0.1	37 ± 4	4.3 ± 0.6	7.9 ± 1.0
7.5 ± 0.8	0.80 ± 0.06	1.2 ± 0.1	39 ± 3	4.4 ± 0.7	6.6 ± 1.4

In addition to accumulating organic matter in the forest floor following logging, the young stands also showed increased concentrations of base cations per unit organic matter (Fig. 4). Changes in species composition and nutrient availability with stand development might contribute to higher concentrations shortly after disturbance (Covington 1981). Changes in litterfall chemistry may accompany stand development even within species. Studies of litterfall amount and chemistry in this chronosequence will reveal the importance of this contribution to changes in forest-floor chemistry.

The losses of base cations in the older stands in the chronosequence may be explained by changes in the same factors: litter quality may decrease over time with changes in nutrient availability, species composition, and woody litterfall. It is impossible from this data set to distinguish these factors from acid rain as a cause of cation loss in these stands. Results from the intensively sampled stand at the HBEF were consistent with the stands of similar age in the chronosequence: decreases in concentrations of Ca were more pronounced than were the changes in contents. The 28 stands in the regional survey were not characterized by age, but none were very young. The absence of significant mean losses in these stands deters us from the general conclusion that mature stands are suffering widespread declines in cation concentrations in the forest floor.

A previous study of a chronosequence of forest floors in this region reported Ca concentrations (Covington 1981); these data do not show a pattern of Ca increasing from young to middle-aged stands and declining with age in older stands. In our chronosequence, as well, the pattern of cation content or concentration as a function of stand age, without repeated sampling, does not suggest the pattern we observed by resampling the stands. Chronosequences contain a covariate (time of treatment) that can be confused with time since treatment, the intended independent variable. In the case of forest floors, historic changes in logging methods make time of treatment an important variable (R. D. Yanai, M. A. Arthur, T. G. Siccama, and C. A. Federer, *unpublished manuscript*). In addition, other sources of variation between stands cannot be distinguished from the effect of stand age when only one point in time is sampled. The best way to control these factors is by repeated sampling, as illustrated in this study. This method was used by Mattson et al. (1987) for slash
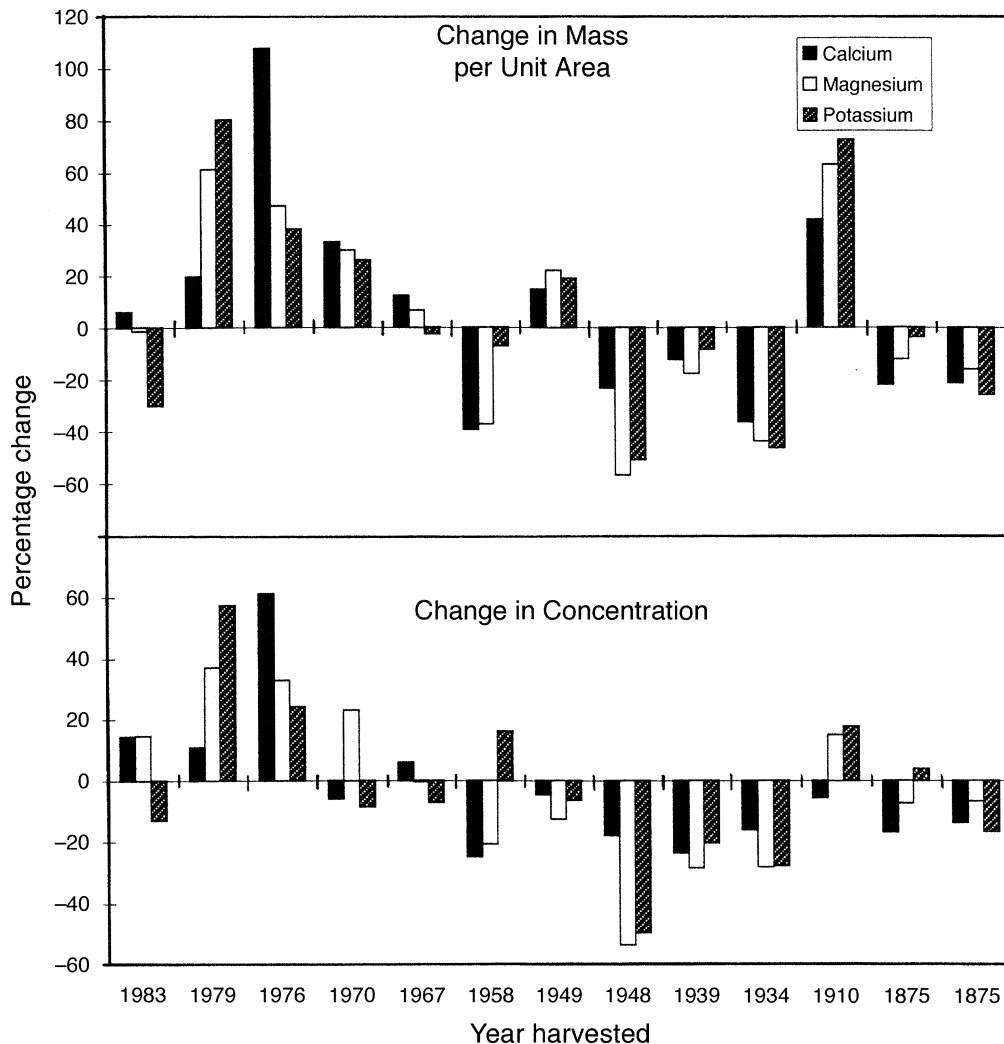
FIG. 4. Changes in forest floors from 13 northern hardwood stands of different ages measured over a 15-yr interval.

and by Covington et al. (1991) to show changes in soil nitrogen following slash burning. In at least one case, resampling a chronosequence has shown that a pattern believed to be due to stand development was instead due to a fertility gradient across sites (Turvey and Smethurst 1988).

A different danger in experimental design is illustrated by our early comparison of two sample collections at the HBEF. Studies of change in soils over time are often based on only two points in time (Johnson et al. 1988, Johnson et al. 1994, Knoepp and Swank 1994). When only two sampling dates are compared, and they prove to be significantly different, we naturally infer a linear trend with time. It takes more than two points to indicate the degree of temporal variation in the sample, whether it be due to short-term changes in the population or to difficulties in sampling. In the case of sampling forest floors, we know the separation of horizons to be subjective in the field (Federer 1982).

In our studies, the same investigators were present at each sampling occasion, reducing the risk that different investigators might make different judgements. Even with the same investigators, however, it is possible to make different judgements over time. For example, in wetter soil, grains of mineral material are more difficult to distinguish from the organic matter, and the organic-matter fraction may thereby be overestimated in the field. The 1976 and 1992 samples at the HBEF were collected under particularly wet conditions, and they have especially low organic fractions. From the seven sample collections at this site, it is possible to pick pairs that differed significantly in different directions. For example, Ca concentrations were higher in 1987 than 1977, but lower in 1997 than 1987 (Fig. 1, Table 1).

There are two additional limitations inherent in the timing of these studies. First, the onset of accelerated leaching by acid rain preceeded the earliest sampling
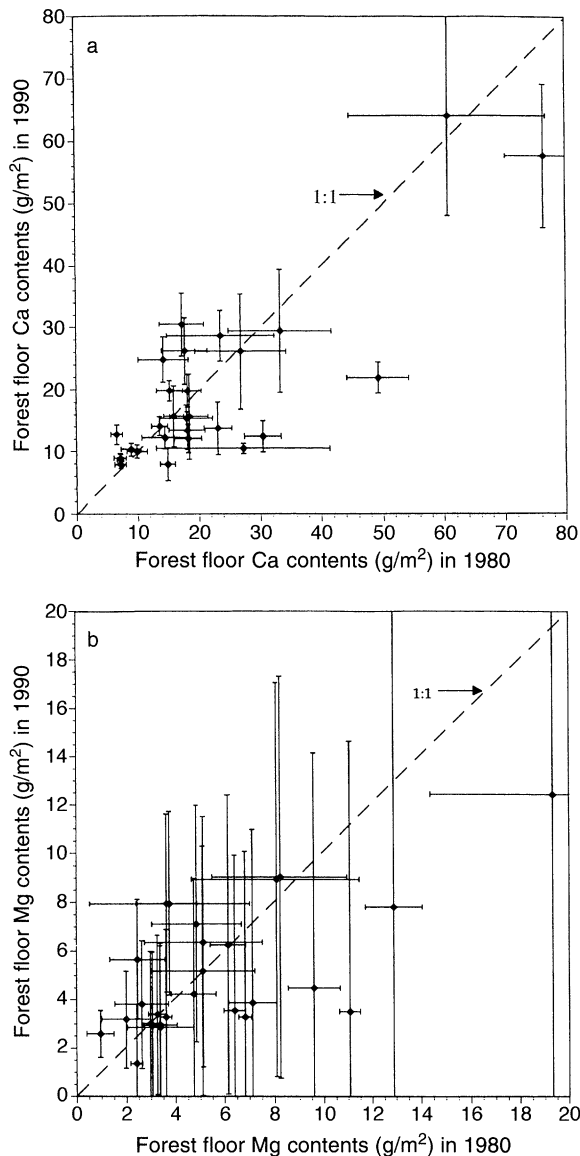
FIG. 5. (a) Ca and (b) Mg contents of forest floors in 28 stands in the northeastern United States. Data are means ± 1 SE.

Ca and Mg in spruce-dominated forest floors than did studies conducted after 1970 (Shortle and Bondietti 1992).

Second, the resolution of temporal change we could detect was determined by our sampling interval. In the chronosequence, where we could test for effects of logging disturbance, this time interval was 15 yr. Our results do not reveal changes in forest-floor chemistry in the first few years after logging. At HBEF, exchangeable Ca, Mg, and K in the forest floor all decreased by ~40% in the first 3 yr after whole-tree harvest (Johnson et al. 1991b). Concentrations had returned to preharvest conditions by 8 yr after whole-tree harvest (Johnson et al. 1997). The rapid rise and fall of cation export in stream water (Bormann and Likens 1979) indicates that ecosystem pools lose nutrients most rapidly in the first few years following disturbance. If the contributing pools are slash and root decomposition, these fluxes should affect forest-floor chemistry. On the other hand, mineral soils may contribute to nutrient export in ways that bypass the forest floor, so that increased export in stream water may not be coupled with losses from the forest floor.

While the forest floor is subject to some of the same processes as the mineral soil, it may be a mistake to assume that it indicates patterns of cation accumulation and loss in the mineral soil. For example, regrowing vegetation is a sink for nutrients, and the soil is the major source pool. The rate of cation accumulation in living biomass can be calculated and compared to observed rates of cation loss from soils (Johnson et al. 1994, Johnson et al. 1988). Losses from mineral soil, however, may not be reflected in parallel losses from the forest floor. In our chronosequence study, the patterns of forest-floor mass and nutrient accumulation in the early stages of stand development resemble the aggradation of living biomass during the same time period. In these cases the behavior of the forest floor may be better understood as part of biotic rather than pedogenic cycles. In contrast, in mid-successional and older stands, it is clearly possible for the forest floor to serve as a source of nutrients while the vegetation is still a sink.

Conclusions

Spatial heterogeneity makes it difficult to detect small changes in base cations in the forest floor. In all three of our studies, changes were too small to be statistically detectable, averaging $<0.9-1.4\%$/yr for Ca contents in the last 10–21 yr. Our measurements do not address changes that took place prior to our studies. It is possible that acid rain will continue to cause accelerated losses of base cations from forest floors, but if so, effects will take many years to become evident. Slow rates of recovery will be equally difficult to detect. More-precise determinations are probably uneconomical: our studies involved the collection of over

in our studies. Models show that cation losses from soils should have been greatest in the 1970s. Control of emissions has reduced the inputs of acids since that time (EPA 1996). Calcium concentrations in precipitation at HBEF decreased fairly steadily from 1965 through 1983, and then increased slightly from 1983 through the early 1990s (Likens et al. 1998). In addition, reductions in exchangeable bases in soil contribute to reduced rates of loss (Kirchner and Lynderson 1995). Because our studies were initiated in 1976, 1979, and 1980, we cannot assume that we have captured the greatest cation losses that might be attributable to changes in atmospheric deposition. Studies conducted before 1950 reported much more exchangeable

2000 forest-floor samples over a period of 21 yr and nearly 900 chemical analyses.

Our results suggest guidelines for future measurements of forest-floor chemistry. Care should be taken to compare similar horizons, because of systematic variation with sampling depth. Measurements at multiple sites and several points in time are important to reduce the risk of erroneously assigning change over time to variation caused by other sources, such as sampling methods or site factors. Finally, archived samples will be essential for detecting unanticipated changes over long time periods.

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