

Seven Decades of Calcium Depletion in Organic Horizons of Adirondack Forest Soils

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We used repeated sampling of the forest floor to determine if there was a net loss of Ca from organic horizons of Adirondack forest soils between 1930 and 2004. In 1984, we established 48 permanent plots in spruce–fir, northern hardwood, and pine stands located in areas sampled by Carl C. Heimburger in the early 1930s. Following Heimburger's protocols and analytical methods, we measured pH and dilute-HCl-extractable Ca in Oe and Oa horizons, and determined that there was a statistically significant decrease in Ca concentration during the 1932 to 1984 interval. In the 36 plots that we could locate in 2004, we again sampled organic horizons. During the >70-yr interval, HCl-extractable Ca concentrations in the Oe and Oa horizons decreased in each forest type ($P < 0.05$). We also measured NH_4Cl -extractable Ca and Al in the 1984 and 2004 samples and found a significant decrease in Ca concentration in the pooled Oe horizons. High-elevation spruce–fir plots showed a Ca loss rate between 1984 and 2004 of 7.6 to 9.8 $\text{kg ha}^{-1} \text{yr}^{-1}$. This compares well with a 4-yr Ca cycling study conducted in an equivalent spruce–fir forest at Whiteface Mt. in the Adirondacks, which showed an annual forest floor Ca loss of 8.4 $\text{kg ha}^{-1} \text{yr}^{-1}$. Based on uptake and anion flux data from the Whiteface Mt. study, we estimated that about 25 to 30% of the 1984 to 2004 forest floor Ca loss in the spruce–fir plots is attributable to leaching driven by atmospheric SO_4^{2-} deposition.

During the past three decades, major research efforts in the northeastern United States and in northern Europe have been aimed at quantifying the impact of anthropogenically generated SO_4^{2-} and NO_3^- on the leaching of base cations from forest soils, and whether or not depletion of exchangeable bases in soil adversely affects forest health (e.g., Johnson and Lindberg, 1992; Eagar and Adams, 1992; Likens et al., 1998). Several studies have addressed base cation depletion in forest soils of the northeastern United States using a variety of approaches including trends in Ca and Al in tree rings, input–output budgets, modeling, and decadal-scale remeasurement. The forests studied in the Northeast are diverse, with different species, age distributions, histories of use, and soil parent materials. There was a variety of results, making it difficult to generalize about which soils have been subject to base cation depletion, and how observed base cation depletion is partitioned among several causes: (i) incorporation in aggrading forest biomass; (ii) leaching loss due to atmospherically deposited SO_4^{2-} and NO_3^- ; (iii) leaching due to internally gener-

ated anions (especially organic anions); and (iv) decreasing Ca deposition in precipitation.

Leaching by organic anions, strong-acid anions SO_4^{2-} and NO_3^- , and sequestration into growing vegetation are generally considered the most important causes of Ca loss from northern forest soils (e.g., Federer et al., 1989; Johnson and Lindberg, 1992; Adams et al., 2000). Whatever the mechanism(s), there have been several reports of forest floor Ca loss in northeastern forests. Bondietti et al. (1990) and Shortle and Bondietti (1992) used Ca and Al in red spruce (*Picea rubens* Sarg.) annual wood increments to infer decreasing soil Ca and increasing soil Al during the 1970s and 1980s in spruce–fir forests of the northern Appalachians. Lawrence et al. (1995, 1997) and Lawrence and Huntington (1999) cited longitudinal studies that suggest widespread base cation depletion in forest soils of the Appalachians during recent decades. Lawrence et al. (1999) documented increased depletion of exchangeable bases along a gradient of increasing acid deposition in the Catskills of southern New York, and linked historic decreases in stream alkalinity to depletion of exchangeable soil base cations. Hedin et al. (1994) and Likens et al. (1996, 1998) showed that the atmospheric deposition of base cations has decreased markedly in the northeastern United States during the past few decades, and that decreases in acid deposition have not kept pace, increasing the possibility of soil Ca depletion. Stoddard et al. (1999) reported a lack of recovery of surface water alkalinities in the Adirondacks and Catskill Mountains as acid deposition was decreasing and inferred that this was due to decreases in Ca deposition or soil Ca depletion.

Johnson et al. (1994b) used 4 yr (1985–1988) of nutrient budget data in a subalpine spruce–fir forest at Whiteface Mt. to determine that Ca loss from the forest floor was

Soil Sci. Soc. Am. J. 72:1824–1830

doi:10.2136/sssaj2006.0407

Received 29 Nov. 2006.

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8.4 kg ha⁻¹ yr⁻¹. This amounted to 2.2% yr⁻¹ of the Ca pool, which, if sustained, would result in a substantial decrease in available Ca in organic horizons in about two decades.

Bailey et al. (2005) used recent and archived samples of four soils on the Allegheny Plateau to show decreases in pH and exchangeable Ca and Mg, and increases in exchangeable Al during a 30-yr interval. The base cation losses they recorded were not accounted for by Ca sequestration in aggrading biomass, and they attributed most of the change to leaching loss. That study represents an extreme case of acidification that is difficult to explain, as losses at two of the four sites exceeded by several-fold amounts that can be accounted for by the combination of sequestration in vegetation combined with reasonable estimates of SO₄²⁻ and NO₃⁻ leaching (Johnson, 2005).

While the aforementioned studies suggest the potential for substantial and biologically important Ca depletion with effects on trees and surface waters, there are other studies that suggest more moderate losses. Johnson et al. (1994a) showed significant decreases in dilute-HCl-extractable Ca from the Oe, Oa, and E horizons, but no change in B or C horizons in a low-elevation, mixed hardwood–softwood forest near Newcomb, NY, in the central Adirondacks. The average Ca depletion from the O and E horizons amounted to 7 kg ha⁻¹ yr⁻¹, all of which could be accounted for by accumulation in the aggrading biomass during the 55-yr interval (Johnson et al., 1994a).

Liu et al. (1992) used the NuCM model to project Ca and Mg depletion of soils at the Huntington Forest (central Adirondacks) to project that soil available Ca and Mg would change by only a few percentage points during the next 65 yr, amounting to an annual loss of about 2 kg Ca ha⁻¹ yr⁻¹ and <1 kg Mg ha⁻¹ yr⁻¹.

Yanai et al. (1999, 2005a,b) studied forest floor Ca in the Adirondack and White Mountains and in Maine and found that spatial variability was a problem in detecting temporal changes in forest floor Ca, and that apatite Ca in the Adirondacks cycled by vegetation may mitigate forest floor Ca loss. Decadal-scale losses of forest floor Ca were hard to verify as a result.

SCOPE AND OBJECTIVES OF THIS STUDY

Long-term monitoring of soil Ca can establish trends in Ca pools and help validate Ca cycling models. Parallel vegetation monitoring combined with detailed studies of causes of mortality can be used to constrain inferences about, and frame studies of the effects of, changing soil nutrient status on tree health. We initiated this study in 1984 by establishing permanent plots in which soils and vegetation could be sampled in the future. In the early 1930s, Carl C. Heimburger's Ph.D. research (Heimburger, 1933) focused on a classification of "forest types" in the Adirondacks, which he defined by the dominant herbs and shrubs. He believed the herbs and shrubs best reflected inherent site quality, which depended on soil characteristics and climate. He dug soil pits, measured horizons, and used the standard analytical methods of his era to measure organic matter content (by loss-on-ignition), pH (by quinhydrone electrode), mineralizable N (by incubation), and 0.2 mol L⁻¹ HCl-extractable Ca (measured using a Ca oxalate titration) in organic horizons. He measured organic matter content and dilute-acid-extractable Ca in mineral horizons as well.

In 1984, Andersen (1988) established permanent plots in locations sampled by Heimburger (1933), sampled organic and

mineral horizons, and processed and analyzed them for pH and 0.2 mol kg⁻¹ HCl-extractable Ca following Heimburger's original methods. Andersen (1988) also compared the results obtained using Heimburger's methods with those obtained using mid-1980s analytical techniques (electrometric pH and Ca in dilute HCl extracts measured by atomic absorption spectroscopy). The 1984 air-dry samples were archived for future use.

For the 1984 study, Andersen located 48 plots distributed widely across the Adirondacks, including high-elevation stands dominated by red spruce and balsam fir [*Abies balsamea* (L.) Mill.], and lower elevation stands dominated by white or red pine (*Pinus strobus* L. and *Pinus resinosa* Ait., respectively) or by northern hardwoods, principally sugar maple (*Acer saccharum* Marsh), American beech (*Fagus grandifolia* Ehrh.), and yellow birch (*Betula allegheniensis* Britt.). Soil characteristics in this region vary with elevation. Most important to this study was that O horizon thickness was directly proportional to elevation. Most of the lower and mid-elevation soils had well-developed spodic horizons (Spodosols), whereas upper elevation soils were a combination of Spodosols and Histosols (Folists) depending on the thickness of the surface organic horizons.

We were able to find 36 of the 48 plots intact in 2004 and compare the 1932, 1984, and 2004 measurements of dilute-acid-extractable Ca, and compare measurements of neutral-salt-extractable Ca in Oe and Oa horizons sampled in 1984 and 2004.

Bedison et al. (2007) reported the 20-yr trends in vegetation from these plots, and those results are relevant to the Ca budget of the forest floor and relevant to claims that depletion of soil Ca is involved in the decline diseases of red spruce and sugar maple in forests of the northeastern United States. Growing trees in these plots continued to sequester base cations while mortality reduced the cation uptake. Initially, mortality does little to restore soil cations because decomposition of the wood and the return of cations to the soil is slow. Standing dead trees present in 1984 had largely fallen over and were in some stage of releasing Ca to the soils, but the rate is not known at this time. The results of the 2004 vegetation measurements in the plots (Bedison et al., 2007) showed considerable mortality in both spruce–fir and northern hardwood plots, while pine-dominated plots (which included several old-field stands) were aggrading rapidly. Across all spruce–fir-dominated plots, live basal area (BA) decreased by an average of 16% ($P < 0.04$). Red spruce live BA decreased by 41% ($P < 0.02$) and balsam fir live BA decreased by 3% (not significant). In the northern hardwood plots, there was no change in overall live BA (45.7 vs. 45.5 m² ha⁻¹ in 2004). American beech live BA increased slightly (but not significantly) in spite of the prevalence of beech bark disease (*Cryptococcus fagisuga* Lind., followed by *Nectria* spp.) while the pooled BA of other major species, sugar maple, yellow birch, and white birch, decreased significantly ($P < 0.05$). In contrast to the spruce–fir and northern hardwood plots, live BA in the pine-dominated plots increased by 19% during the 20-yr interval ($P < 0.01$).

In this study, we investigated changes in Ca concentrations and estimated amounts in the Oe and Oa horizons. In the Adirondacks and the northern Appalachian Mountains of neighboring states, the forest floor is a quantitatively important reservoir of plant-available Ca, and has been studied often to assess trends in base cations (Yanai et al., 1999, 2005a,b). In the high-elevation spruce–fir forest at Whiteface Mt., NY, 70% of the exchangeable Ca is in the O horizons, compared with 30% contained in the mineral horizons (Johnson et al., 1994b). In the northern hardwood forest at the Huntington Forest in the central Adirondacks, the forest floor contains 33% of the exchangeable

Ca and Mg (Johnson and Lindberg, 1992). Thus the pool of forest floor Ca is nutritionally important in these forests.

MATERIALS AND METHODS

Site Locations

In 1930 to 1932, Heimburger (1933) described soil profiles and collected samples of each horizon at >100 sites in the Adirondacks as part of a study designed to identify different “forest types,” their associated soil characteristics, and the potential for timber production. He selected sites that were “more or less well-drained uplands” in “more or less original and undisturbed forested areas.” Ultimately he identified 21 forest types, which he differentiated by the dominant herbs and shrubs.

In 1984, Andersen (1988) used Heimburger’s descriptions of a physiographic feature (i.e., Lake Arnold), the trails on the 1898 series of USGS topographic maps that Heimburger used, elevation (determined in both studies by altimeters set principally at points where trails crossed streams), and Heimburger’s lists of the overstory trees and understory plants to locate plots in areas that matched the sites that Heimburger sampled. While there were no known biases in selecting the 1984 plots, this sample is neither random nor systematic, so we confine the conclusions to this set of plots. On the other hand, we know of no reasons why this sample is not a good representation of spruce–fir, northern hardwood, and pine stands across the Adirondacks.

Plots and Soil Samples

In 1984, we established circular vegetation plots (usually 20 m diameter) and measured the diameter at breast height of all live and dead stems >2 cm. Following Heimburger (1933), we sampled soils in a large excavation (~1 by 1 m) in or adjacent to the plot. Horizons were measured on the pit faces and sampled from several places within each horizon. Plot centers were marked by fiberglass or plastic stakes for future relocation, and the locations of the soil pits were referenced to the center stakes. The remaining air-dry samples from 1984 were stored in glass jars with lined lids.

In 2004, we sampled soils at 36 plots that had remained intact during the 20-yr period. We divided the plots into three forest types based on the species composition of the canopy: subalpine spruce–fir, northern hardwood, and pine (Bedison et al., 2007). We sampled the forest floor by collecting five 15- by 15-cm blocks. We collected five samples in 2004 since we wanted a basis for determining reasonable estimates of Ca amounts in the Oe and Oa horizons that would allow suitable comparisons in the future. Following Heimburger (1933), who sampled F (Oi) and H (Oe) horizons, and Andersen (1988), the Oi horizon (fresh litter) was brushed away, a template was placed on the top of the Oe horizon, and the blocks were isolated by removing the surrounding material well into the mineral soil. The isolated block was inverted and the mineral soil removed to the base of the field-defined Oa horizon.

Table 1. Mean organic matter fraction in Oe and Oa horizons determined by Heimburger (1933), Andersen (1988) and this study, with standard errors in parentheses.

Horizon	n	Organic matter content		
		1932	1984	2004
— % , oven-dry weight —				
Oe	32	86 (3) a†	89 (1) a	87 (2) a
Oa	23	64 (5) a	69 (4) a	67 (3) a

† Values in a row followed by the same letter are not significantly different ($P > 0.05$, paired *t*-test).

The difficulty of separating organic horizons the same way at different times has been noted by others (Federer, 1982). We designated Oe and Oa horizons in the field based on color, fiber content, and in the case of Oa1 and Oa2 horizons, the degree of granulation. Table 1 summarizes the organic matter content (organic matter percentage, oven-dry weight, measured as loss-on-ignition) of the Oe and Oa horizons sampled in the three studies. There were no significant differences in the average organic matter percentage of the Oe and Oa horizons sampled in the different investigations, and we take this to mean that there were no substantial differences in horizon designation across the three studies.

Air-dried 2004 samples were prepared for analysis following the methods used by Heimburger (1933) and Andersen (1988). The Oe horizons were sieved through 5-mm stainless steel screens, and Oa horizons were sieved through a 2-mm screen in all three studies, with the <5- and <2-mm fractions used for the analyses. Following Heimburger (1933), Andersen (1988) split the Oa horizon into Oa1 and Oa2 subhorizons where there was a distinct difference in the content of granular aggregates, with the Oa2 horizons being distinctly “greasier.” In 2004, we sampled the Oa1 and Oa2 horizons as a single Oa horizon. Accordingly, we composited the 1984 Oa samples for analysis, using amounts of the Oa1 and Oa2 horizons proportional to the depths measured in the field in 1984. Likewise, to compare Heimburger’s O horizons to the 1984 and 2004 values, we weighted his published Ca concentrations by the depths of the H1 (Oa1) and H2 (Oa2) horizons that he measured.

Organic Matter, pH, and Calcium Measurements

The organic matter content of the sieved fractions was estimated by loss-on-ignition (LOI) overnight at 550°C after oven drying at 95°C for the 1932 and 1984 samples. In 2004, air-dried samples were ashed, then corrected for the difference between oven-dry and air-dry weights.

We measured the pH of the archived 1984 samples and the 2004 samples in H₂O in a 1:1 (v/v) slurry using a combination glass electrode. Samples were stirred and allowed to sit for 20 min before the pH was measured. This procedure was repeated and the average of the two measurements used if the second measurement differed from the first. We note here that Andersen (1988) showed that electrometric pH gave acceptably comparable values to those obtained by a quinhydrone electrode (Heimburger’s method), but for reasons explained below, we believe that changes in pH during 20 yr of storage precluded meaningful pH comparisons.

Comparability of the Ca determination methods is one of the most important aspects of this study. With regard to possible errors in the Ca determination, Andersen (1988) provided data related to the potential for artifacts and how the laborious wet-chemical method for Ca determination might be subject to errors from the lack of Al removal and the loss of Ca during the many steps of washing salts or precipitates from filter paper to beakers. The key results are presented here to demonstrate that if the 1930s Ca oxalate method is done carefully, the results for extractable Ca are essentially the same as those obtained using the best available technology in 1984 and in 2004. In the 1984 study, we measured HCl-extractable Ca in organic horizons following Heimburger’s (1933) extraction procedures and analytical method (Andersen, 1988; Johnson et al., 1994b). The Ca oxalate procedure Heimburger used (Association of Official Agricultural Chemists, 1925, 1935) is a time-consuming and complex process involving several steps and filtrations. In the current investigation, we extracted Ca with 0.2 mol kg⁻¹ HCl as Heimburger did, but measured Ca in the extract by inductively coupled plasma–atomic emission spectroscopy (ICP–AES).

Andersen (1988) tested Heimburger's method using the 1984 Oa, Oe, and mineral horizon samples by measuring Ca in the HCl extracts by atomic absorption spectrophotometry (AAS) as well as by Heimburger's method. Figure 1 shows that, with a few exceptions, AAS and the Ca oxalate procedure gave nearly identical values. As we no longer have the spectrophotometer that we used to generate the comparison shown in Fig. 1, we compared elemental analyses obtained from that instrument with the results obtained by ICP-AES. The results for forest floor Ca determined by our ICP-AES match the results obtained on our AAS approximately 20 yr before (Fig. 1 insert). Thus we believe that the Ca values we report here for the 1984 and 2004 samples are comparable to Heimburger's values obtained in the early 1930s. Calcium values are reported on an oven-dry weight basis for the three studies.

In addition to the evolution of analytical technology, there have been changes in the preferred methods for determining soil chemical properties. During the past two decades, many forest soils projects have reported base cations extracted with a neutral salt, most often NH_4Cl . For comparability with recent Adirondack forest soil studies, we measured exchangeable Ca in the 1984 and 2004 studies extracted with $1 \text{ mol L}^{-1} \text{NH}_4\text{Cl}$. Air-dry 2.0-g samples were extracted with 50 mL of $1 \text{ mol L}^{-1} \text{NH}_4\text{Cl}$ during a 12-h period using a vacuum extractor. The extracts and reagent blanks were analyzed for Ca on a PerkinElmer Plasma 400 (PerkinElmer Corp., Norwalk, CT) using standard procedures. Results are reported on an oven-dry weight basis. Calcium values determined in the NH_4Cl extracts were generally 55 to 80% of those determined in the HCl extracts.

In 1985 to 1988, we evaluated forest floor Ca pools and fluxes in a detailed study of nutrient cycling in the spruce-fir forest at 1000 m on Whiteface Mt., NY (Johnson et al., 1994b). The 1984 to 2004 comparisons of extractable Ca in the 11 spruce-fir sites we sampled offered an opportunity to compare the measured loss with the rate calculated from the 4-yr mass balance study in an equivalent spruce-fir forest.

Determination of a change (or lack thereof) in forest floor mass is a key component in determining the change in Ca amounts. There were no forest floor mass determinations done in 1932 or 1984, but LOI and depth were measured. We measured depth, mass, and LOI on the 2004 samples, and we resampled the network of sites in 2005 to 2006 using 0.5- by 0.5-m quantitative excavations. We had, then, two data sets with forest floor depth, mass, bulk density (BD), and LOI that we could use to calculate the 1932 and 1984 forest floor mass. The depth-mass relationships and LOI-BD relationships determined from our samples have R^2 values of 0.7 to 0.8 (data not shown). We assumed that those relationships did not change during the 75-yr period of study. Using either the LOI-BD or depth-mass relationship from the 2004 or 2005 to 2006 data, we calculated that there was no significant difference in organic matter mass in the forest floor between any of the sampling periods, and no trend toward increased mass or thickness between 1932 and 2004 to 2006. Similarly, there was no difference in Oe and Oa thickness (data not shown) or organic matter percentage across the 1932, 1984, and 2004 to 2006 samples. The

different options for calculating forest floor Ca mass in 1932 and 1984 all gave similar results. Here we present the values obtained using the 2004 depth vs. mass relationships.

Statistics

Based on the 1984 to 1932 comparisons (Johnson et al., 1994a), which showed reduced pH and Ca, we used a one-tailed Student's paired sample *t*-test to determine if the mean values of pH and acid-extractable and neutral-salt-extractable Ca were lower (at $\alpha = 0.05$) in the post-1930s samples. Since some samples from the 1984 set had been used up and several sites lacked an Oe or Oa horizon, we had complete data for all sampling periods for 27 Oe horizons. Most of the pine sites had no Oa horizons so there were 21 Oa horizons with complete data for all three studies. In comparisons using the pine Oe HCl-extractable Ca data, Ca values were log transformed to meet the requirement of normality. The NH_4Cl -extractable Al values were skewed toward high values, so we report the median Al concentrations, and used the Mann-Whitney test to determine if there were significant differences in the median values between 1984 and 2004 (at $\alpha = 0.05$).

Comparing forest floor Ca mass values is desirable to determine how the measured Ca loss in the spruce-fir stands between 1984 and 2004 compares with the forest floor Ca loss rate determined in the Whiteface Mt. spruce-fir forest Ca cycling study (Johnson et al., 1994b). Estimating errors for the forest floor Ca mass values is problematic, however. A formal error is difficult to assign to the forest floor mass values because they were estimated from regressions where the residuals were not randomly distributed. Propagating any estimate of error through the calculation of forest floor Ca mass and summing the Oa and Oe horizons to get an overall forest floor Ca loss produces unrealistically large error estimates. These are the same problems shared by most nutrient budget and nutrient flux

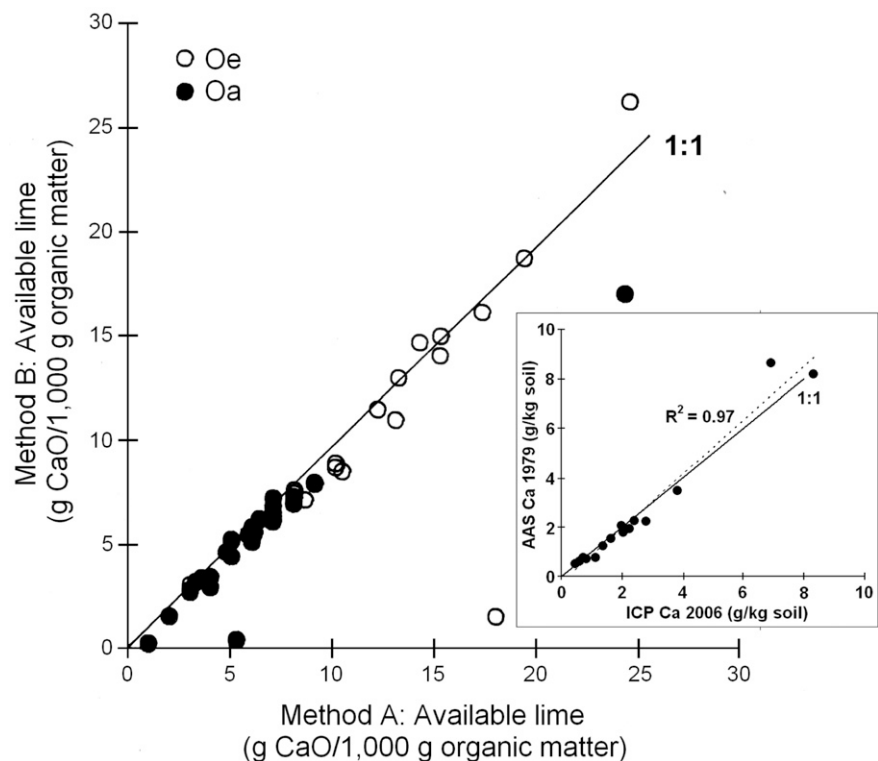


Fig. 1. Calcium in organic-horizon HCl extracts measured by the Ca oxalate precipitation procedure (Method A) and by atomic absorption spectroscopy (Method B; Andersen, 1988). The insert shows the equivalence of forest floor Ca measured in 1978 by atomic absorption spectrophotometry and again in 2006 using inductively coupled plasma-atomic emission spectroscopy.

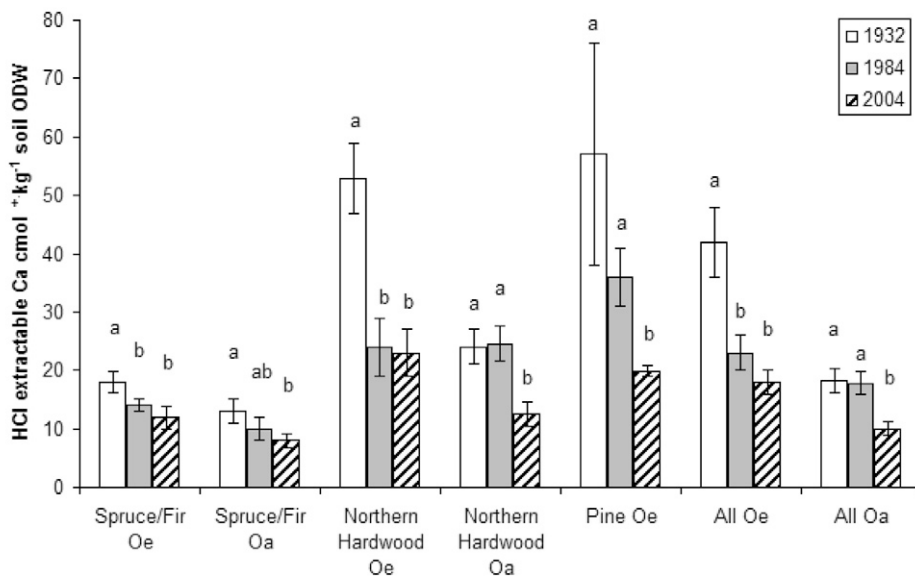


Fig. 2. The 0.2 mol L⁻¹ HCl-extractable Ca from the forest floor organic horizons in 1930 to 1932, 1984, and 2004. Values identified by the same letter are not significantly different ($P < 0.05$); ODW is oven-dry weight.

calculations and, accordingly, we present the calculated forest floor Ca mass values as the best estimate of forest floor Ca in each forest type for each sampling year, without an error estimate.

RESULTS AND DISCUSSION

Measurements of pH and Calcium

When the air-dry 2004 and archived 1984 samples were analyzed in 2005, there was a significant difference in pH, with the 2004 samples having higher values by an average of approximately 0.3 pH units. In 1984, we did not measure pH on air-dry samples, rather we determined pH as Heimburger did, only on field-moist samples. This omission has important implications for this study and for other studies that involve soil samples stored for decades. Since we do not know the air-

dry pH of the 1984 samples shortly after they were collected, the difference in pH we observed in this study could be due to an increase in pH in the field between 1984 and 2004, or a decrease in the pH of the 1984 samples during storage. The inference of an increase in pH in the field conflicts with the consistent evidence of decreasing Ca between 1984 and 2004 discussed below. For analytical verification, we conducted the Ca and pH analyses a second time with the same result—higher pH and lower Ca in the 2004 samples.

There is clear evidence in the literature that the pH of air-dry, acid soils decreases during decades of storage. Billett et al. (1990) found an average pH decrease of 0.5 units in 37 yr. Prodromon and Pavlatou-Ve (1998) found a -0.3 pH change in 20 yr, and Blake et al. (2000) found a -0.2 to -0.4 pH change in 27 yr. Similarly, there was a decrease in the pH of Pennsylvania soils of -0.1 to -0.5 pH after 30 yr of storage if the original pH was about 5.0 or below (Bailey et al., 2005). The mechanism(s) causing the pH change are unknown at present. Regarding Ca, Blake et al. (2000) found no significant change in exchangeable Ca and Mg during a 22-yr period, and we are unaware of any other studies of acid forest soils stored for decades that have shown changes in measures of extractable cations during storage. Based on the available studies, we conclude that the best interpretation of our pH measurements is that the pH of the 1984 samples decreased during storage. Further study is justified to determine if this is a problem that will affect decades-long comparisons using the many soil samples that have been archived during the past two or three decades across North America and Europe.

Changes in Calcium

During the 72-yr time interval since Heimburger's original study, dilute-acid-extractable Ca concentrations decreased significantly (Fig. 2). From 1984 to 2004, the decreases averaged about 10 to 15% but were generally not significant due to high variability and small sample sizes. Neutral-salt-extractable Ca showed either consistent 20-yr trends toward lower Ca or significant ($P < 0.05$) decreases in Ca concentration, depending on how the data are grouped (Fig. 3). Estimates of forest floor Ca amounts (Tables 2 and 3) indicate annual losses averaging

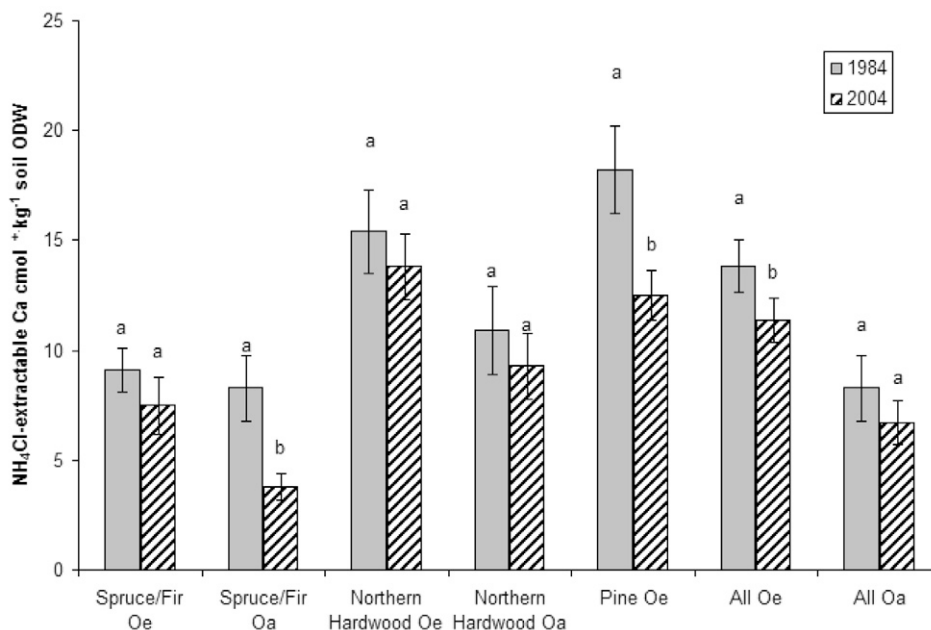


Fig. 3. The 1 mol L⁻¹ NH₄Cl-extractable Ca from the forest floor organic horizons in 1984 and 2004. Values identified by the same letter are not significantly different ($P < 0.05$); ODW is oven-dry weight.

Table 2. The HCl-extractable Ca in the forest floor (Oe and Oa combined) in 1930 to 1932, 1984, and 2004.

Forest type	Content			Loss rate	
	1932	1984	2004	1932–2004	1984–2004
	kg ha ⁻¹ , oven-dry weight			— kg ha ⁻¹ yr ⁻¹ —	
Spruce–fir	871	612	416	-6.3	-9.8
Northern hardwood	709	598	362	-4.8	-11.8
Pine (Oe only)	482	292	198	-3.7	-4.7

0.5 to 2% of the total forest floor Ca per year, depending on forest type and time period.

The spruce–fir plots showed Ca loss ranging from 7.6 to 9.8 kg Ca ha⁻¹ yr⁻¹. Given the potential for large uncertainties in mass-balance nutrient cycling studies, and the variability of forest floor mass and chemistry, the rates compare well with those from the spruce–fir Ca budget study at Whiteface Mt., NY (annual Ca loss of 8.4 kg ha⁻¹ yr⁻¹ from the forest floor, Fig. 4; Johnson et al., 1994b). The Whiteface Mt. nutrient cycling study site is very comparable to the spruce–fir sites we report on here. It is located about 40 km away from the nearest of the spruce–fir plots used in this study, at the same elevation, and has the same vegetation, climate, and soil conditions as 10 of the sites we sampled.

The Ca loss measured in this study is well within the range that can be accounted for by vegetation sequestering soil Ca and leaching loss attributable to organic anions, NO₃⁻, and SO₄²⁻. In the Whiteface Mt. budget study (Johnson et al., 1994b), uptake of Ca accounted for 45% of the annual loss from the forest floor. For the remaining 55%, leaching accounted for by the flux of organic anions and SO₄²⁻ were about equal, whereas Cl⁻ and NO₃⁻ fluxes were negligible (Johnson et al., 1994b). These estimates are probably representative of the 1984 to 2004 period, although there were probably small differences in cation uptake due to decreasing live biomass, decreased Ca deposition, and decreased SO₄²⁻ leaching related to lower S emissions. Accordingly, we estimate that about 25 to 30% of the Ca loss from the subalpine spruce–fir forest floor between 1984 and 2004 was due to SO₄²⁻ deposition and leaching.

There is one other comparison worth noting. Johnson et al. (1994a) determined HCl-extractable Ca loss from organic and mineral horizons and Ca uptake in vegetation between 1932 and 1986 in 17 plots in a mixed hardwood–softwood forest near Newcomb, NY. That forest is similar in elevation to the northern hardwood plots sampled in this study and has many similar species but with a higher softwood compo-

Table 3. The NH₄Cl-extractable Ca in the forest floor (Oe and Oa horizons combined) in 1930 to 1932, 1984, and 2004.

Forest type	1984 content	2004 content	Loss rate
	kg ha ⁻¹ , oven-dry weight		
Spruce–fir	421	270	-7.6
Northern hardwood	437	310	-6.4
Pine (Oe only)	174	133	-2.1

nent [*Abies balsamea* (L.) Mill., *Picea rubens* Sarg. and *Tsuga canadensis* (L.) Carr.]. The Ca loss rate from Oa and Oe horizons in that study was 3.4 kg ha⁻¹ yr⁻¹, similar to the 1932 to 2004 loss rate (4.8 kg ha⁻¹ yr⁻¹) measured in this study, but lower than the calculated rate for the 1984 to 2004 interval.

Table 4 shows that there was a trend toward increased exchangeable Al, which was significant for the Oe horizons grouped by forest type. Increases in exchangeable Al concentration were similar in magnitude to the decreases in exchangeable Ca concentration.

SUMMARY

During the past 20 yr, exchangeable Ca changes in the Oe and Oa horizons of about 15% were observed when all sites were pooled. Combined with the HCl-extractable Ca trends between 1930 and 1984, we conclude that Ca loss from the forest floor has proceeded at a moderate rate for seven decades in these plots. The relative importance of decreased Ca deposition, leaching, and uptake as contributors to the forest floor Ca loss observed in this study is difficult to determine with precision. The majority of the Ca loss from the forest floor appears to be due to the

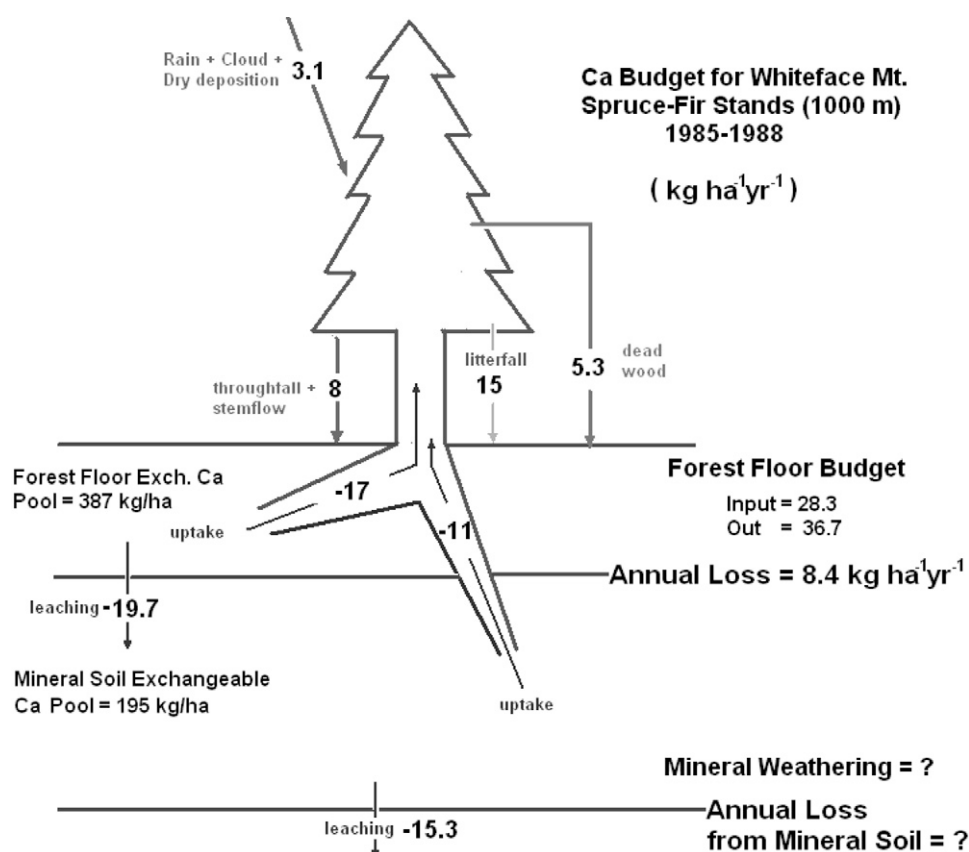


Fig. 4. Calcium budget for the forest floor in a spruce–fir forest on Whiteface Mt., NY (after Johnson et al., 1994b).

Table 4. Median values for NH₄Cl-extractable Al in O horizons in 1984 and 2004.

Forest type	Horizon	n	1984 content	2004 content
			cmol _c kg ⁻¹ oven-dry weight	
Spruce/fir	Oe	10	3.6 a†	8.4 b
	Oa	10	17.7 a	16.7 a
Northern hardwood	Oe	16	1.6 a	3.1 b
	Oa	13	3.7 a	5.5 a
Pine	Oe	6	1.4 a	4.5 b
All	Oe	32	2.3 a	3.5 b
	Oa	24	5.4 a	9.0 a

† Values in a row followed by the same letter are not significantly different ($P > 0.05$, Mann-Whitney test).

natural stand processes of organic anion leaching and uptake by growing vegetation, with 25 to 30% due to SO₄²⁻ leaching. An important unknown for the future of forest floor chemistry in the subalpine spruce–fir stands is the fate of Ca bound in the large mass of dead spruce (and to a lesser extent fir) that has accumulated as downed and standing dead stems. Based on the data of Johnson et al. (1994b) and the change in live and dead stems recorded by Bedison et al. (2007) in these plots, Ca sequestered in dead wood may represent 15 to 20% of the available Ca capital for the spruce–fir forest. The rate at which the Ca is returned to the soil and the mechanisms controlling the release and dispersion of Ca merit study to determine how effective this might be in offsetting some of the projected future Ca losses.

ACKNOWLEDGMENTS

We thank K. Johnson, A. Pike, and K. Schu for their help in the field, and K. Taylor, M. Dranoff, and M. Boyer for their help in the laboratory. This study was supported by grants from the A.W. Mellon Foundation, New York, NY, and the Northeastern States Research Cooperative.

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