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Assessment of soil calcium status in red spruce forests in the northeastern United States

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Abstract. Long-term changes in concentrations of available Ca in soils of red spruce forests have been documented, but remaining questions about the magnitude and regional extent of these changes have precluded an assessment of the current and future status of soil Ca. To address this problem, soil samples were collected in 1992–93 from 12 sites in New York, Vermont, New Hampshire, and Maine to provide additional data necessary to synthesize all available research results on soil Ca in red spruce forests. Sites were chosen to encompass the range of environmental conditions experienced by red spruce. Concentrations of exchangeable Ca ranged from 2.13 to 21.6 $\mathrm{cmol_c\ kg^{-1}}$ in the Oa horizon, and from 0.11 to 0.68 $\mathrm{cmol_c\ kg^{-1}}$ in the upper 10 cm of the B horizon. These measurements expanded the range of exchangeable Ca reported in the literature for both horizons in northeastern red spruce forests. Exchangeable Ca was the largest Ca fraction in the forest floor at most sites (92% of acid-extractable Ca), but mineral Ca was the largest fraction at the three sites that also had the highest mineral-matter concentrations. The primary factor causing variability in Ca concentrations among sites was the mineralogy of parent material, but exchangeable concentrations in the B horizon of all sites were probably reduced by acidic deposition. Because the majority of Ca in the forest floor is in a readily leachable form, and Ca inputs to the forest floor from the mineral soil and atmospheric deposition have been decreasing in recent decades, the previously documented decreases in Ca concentrations in the forest floor over previous decades may extend into the future.

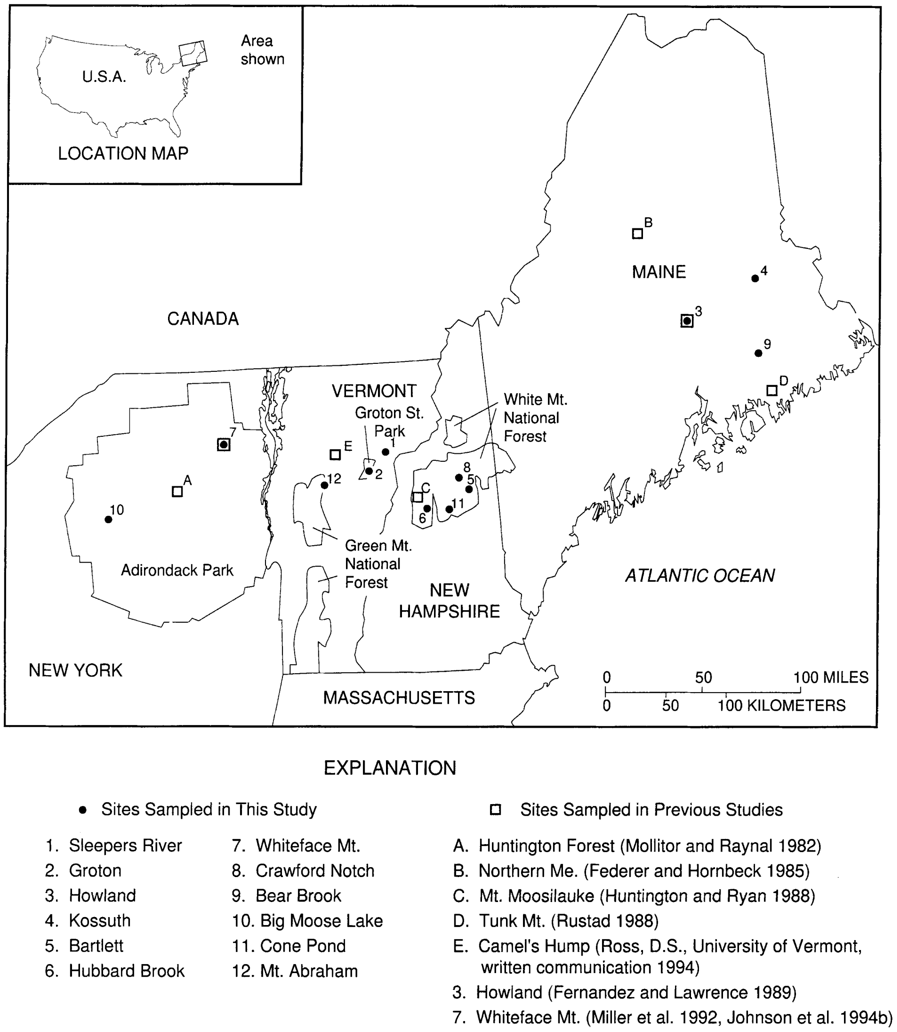
Introduction

Conclusions from the 1995 international conference on acid deposition (Acid Reign 95?) stated that (1) we know with confidence that sulfur deposition has caused the depletion of base cations in soil, and (2) we suspect that soil acidification causes damage to forests by inducing nutrient cation deficiencies (Rodhe et al. 1995). Agreement has not been reached, however, on whether acidic deposition is significantly affecting base cation availability in declining red spruce forests of the eastern United States. Johnson and Fernandez (1992) concluded from a literature review that soils in eastern spruce-fir forests were naturally acidic, therefore acidic deposition was unlikely to cause significant further acidification. In a second literature review, Joslin et al. (1992) concluded that current rates of Ca and Mg leaching in red spruce forests were substantial in relation to exchangeable pools of these elements in both organic and mineral horizons, and that acidic deposition probably contributes to soil acidification by causing more than half of the current leaching losses of Ca in red spruce stands.

Interpretations of acidic deposition effects on soil chemistry vary because natural processes such as plant uptake, mineral weathering, and organic-acid leaching affect available Ca concentrations but are difficult to measure accurately. Studies by Shortle and Bondietti (1992) and Johnson et al. (1994a) nevertheless indicated that available soil-Ca concentrations declined in the Northeast over the past half century. Detailed ecosystem Ca budgets at Whiteface Mountain, New York, (Johnson et al. 1994b) and Cone Pond Watershed, New Hampshire (Bailey et al. 1996) have also indicated recent depletion of available Ca. Furthermore, a study by Lawrence et al. (1995) indicated that the recovery of soil Ca pools in red spruce forests is being hindered by high Al saturation of exchange sites in the mineral soil and increasing Al saturation of exchange sites in the forest floor.

These studies raise concerns about the current and future status of Ca availability in northeastern red spruce forests. Despite the number of studies that have evaluated soil Ca in red spruce forests, however, characterization of regional and temporal variability has been limited by uncertainty resulting from the different methods used in these studies. Causes of regional variability have also not been investigated, and the limited ecosystem budget data currently available have not been evaluated in a regional context.

To address these problems, we collected soil samples from twelve red spruce stands selected to encompass the range of environmental conditions experienced by this species in the Northeast. Soil Ca concentrations were determined by the methods most commonly used, and method comparison tests were conducted with other common methods in the literature. The purpose of this paper is to (1) apply results of methods comparisons to relate our survey data to other published data, (2) determine the relative concentrations of major Ca fractions in the forest floor, the primary rooting zone of red spruce, (3) evaluate causes of soil Ca variability across the region, (4) synthesize information obtained from tasks (1) through (3) with other relevant studies to draw conclusions regarding the status of soil Ca in northeastern red spruce forests.



EXPLANATION

● Sites Sampled in This Study

1. Sleepers River
2. Groton
3. Howland
4. Kossuth
5. Bartlett
6. Hubbard Brook
7. Whiteface Mt.
8. Crawford Notch
9. Bear Brook
10. Big Moose Lake
11. Cone Pond
12. Mt. Abraham

□ Sites Sampled in Previous Studies

A. Huntington Forest (Mollitor and Raynal 1982)
B. Northern Me. (Federer and Hornbeck 1985)
C. Mt. Moosilauke (Huntington and Ryan 1988)
D. Tunk Mt. (Rustad 1988)
E. Camel's Hump (Ross, D.S., University of Vermont, written communication 1994)
3. Howland (Fernandez and Lawrence 1989)
7. Whiteface Mt. (Miller et al. 1992, Johnson et al. 1994b)

Figure 1. Locations of sites sampled in this study and previous studies since 1980, in New York, Vermont, New Hampshire, and Maine.

Methods

Site description

Twelve sites were selected to include the four physiographic regions in the Northeast in which spruce forests are common – the Adirondack Mountains of New York, the Green Mountains of Vermont, the White Mountains of New Hampshire, and low- to mid-elevation areas in Maine (Figure 1). To ensure that soils reflected an extended period of conifer influence, criteria for site selection required that: (1) the forest floor be at least 8 cm thick, (2) live red spruce trees be a significant component of the forest canopy, and (3) the stands be uneven-aged, with red spruce trees commonly more than 100 years old. Sites with poorly drained soils were excluded.

The 12 sites range in elevation from 80 m at Howland, Me., to 975 m on Whiteface Mountain, N.Y (Table 1). Annual precipitation at the 12 sites is typically between 90 and 140 cm, of which about one-third falls as snow. The growing season extends from early May through late September at the low-elevation sites and becomes shorter as elevation increases. Bedrock mineralogy differs considerably among the sites (Table 2). Relative Ca-weathering rates (indicated in Table 2 as weathering potential) range from moderately high in areas influenced by the calcareous bedrock in eastern Vermont, to low, in areas underlain by mica schist and quartzite, such Cone Pond. Acidic deposition was lowest at the interior Maine sites (Howland and Kossuth) and was probably highest at the high-elevation sites (Lovett 1994), although total-deposition measurements were available for only one site above 800 m elevation (Whiteface Mt., N.Y.). Obvious dieback of red spruce trees has been underway for more than ten years at Whiteface Mountain, Mt. Abraham, Vt. and Crawford Notch, N.H.; significant dieback is also occurring at Big Moose Lake, N.Y., but is less advanced. The remaining 8 sites vary in crown condition but do not show unusual mortality.

Sample collection and analysis

Soil samples were collected from the faces of nine individual soil pits (grouped in three plots, each with three pits) at eight of the twelve sites in mid-June and late September or early October of 1992 and 1993; four of the twelve sites were sampled only once (early summer or early fall) in each of the two years (Table 1). In each pit, a sample was collected from the middle of the Oa horizon and from the top 10 cm of the B horizon. No samples were collected from deeper in the B horizon because the root density below 10 cm is extremely low at these sites. Thus, a total of 36 samples from each horizon was collected from eight sites and 18 samples from each horizon were collected from four sites. The three individual soil samples from each horizon, in each plot, were combined into one sample and thoroughly mixed before chemical analysis. Horizon depths for the entire profile were also recorded at the time of sampling.

All soil samples were analyzed for exchangeable Ca concentrations by NH_4Cl extraction, and for mineral-matter concentration by loss-on-ignition (Blume et al. 1990). Oa-horizon samples from two collections at each site (18 samples combined into 6 samples for analysis) were analyzed for acid-

Table 1. Site characteristics of red spruce stands sampled in this study. Dashes indicate where data were unavailable.

Site no. in Fig. 1	Site name	No. of times sampled	Elevation (m)	Forest floor thickness (cm)	Atmospheric deposition* (mmol $m^{-2}yr^{-1}$) Wet-only SO_4^{2-}	Total SO_4^{2-}	Wet-only NO_3^-+NH_4^+	Total NO_3^-+NH_4^+
1	Sleepers River	2	680	21.0	17.2	–	35.1	57–65
2	Groton	4	510	9.0	17.2	–	35.1	49–57
3	Howland	4	80	12.6	12.7	22.1	18.2	30.3
4	Kossuth	4	150	9.0	12.7	22.1	18.2	32–40
5	Bartlett	4	480	15.6	26.5	–	51.0	–
6	Hubbard Brook	2	720	14.1	20.3	22.8	36.0	43.9
7	Whiteface Mt.	2	975	12.3	25.3	41.8	46.9	89.2
8	Crawford Notch	4	810	13.7	28.8	–	55.3	–
9	Bear Brook	4	395	12.0	17.9	33.8	29.8	–
10	Big Moose Lake	4	550	23.9	25.8	–	52.0	–
11	Cone Pond	4	585	11.7	24.5	30.1	51.1	–
12	Mt. Abraham	2	945	10.6	28.4	–	52.8	–

* *Sleepers River, Vt.*: Wet-only values obtained by onsite bulk measurements in 1992 and therefore could overestimate wet-only deposition somewhat. Total NO_3^- plus NH_4^+ estimated from map of Ollinger et al. (1993).

Groton, Vt.: Wet-only values assumed to equal values measured at Sleepers River, Vt. Total NO_3^- plus NH_4^+ estimated from map of Ollinger et al. (1993).

Howland, Me.: All values determined by onsite measurements in 1988–92 by methods given in McLaughlin et al. (1996).

Kossuth, Me.: All values assumed to equal those measured at Howland, Me.

Bartlett, N.H.: Precipitation amount estimated by model of Dingman (1981). Chemical concentrations assumed to be average of values measured at Hubbard Book, N.H. and Cone Pond, N.H. in 1992.

Hubbard Brook, N.H.: Wet-only values from National Atmospheric Deposition Program (NADP) site at Hubbard Brook, N.H. for 1992 (NADP 1993). Total values determined from average air concentrations for 1989–90 at Hubbard Brook National Dry Deposition Network site.

Whiteface Mountain, N.Y.: All values represent average for 1986–90 (Miller et al. 1993).

Crawford Notch, N.H.: Precipitation amount estimated by model of Dingman (1981). Chemical concentrations assumed to be average of values measured at Cone Pond, N.H. and Hubbard Brook, N.H. in 1992.

Bear Brook, Me.: SO_4^- deposition values are averaged for 1988–92 from Rustad et al. (1994). Wet-only NO_3^- plus NH_4^+ deposition values from NADP site at Acadia National Park, Me., 1992 (NADP 1993).

Big Moose Lake, N.Y.: Values represent average of NADP sites at Bennett Bridge and Huntington Forest, N.H., 1992 (NADP 1993).

Cone Pond, N.H.: Wet-only deposition values measured with bulk collector and thus may overestimate wet-only deposition somewhat. Total SO_4^{2-} deposition values based on onsite measurements in 1992. Total NO_3^- plus NH_4^+ assumed to equal the value measured at Hubbard Brook, N.H. in 1992.

Mt. Abraham, Vt.: Precipitation amount estimated from model of Dingman (1981). Chemical concentrations assumed to equal average values measured at Whiteface Mountain, N.Y. 1986–90 (Miller et al. 1993).

Table 2. Geology and relative weathering potential of study sites. The range in weathering potential given at several of the sites reflects uncertainty in parent material composition. Mineralogic analyses of most sites were unavailable.

Site no. in Fig. 1	Site[1]	Bedrock[2]	Other Influences on Parent Material[3]	Weathering Potential.[4]
1	Sleepers River, Vt.[a]	metapelite	calcareous schist	3
2	Groton, Vt.[a]	granite	calcareous metapelite	2–3
3	Howland, Me.[b]	pelite and sandstone	possibly calcareous sandstone	2–3
4	Kossuth, Me.[b]	pelite	sandstone and thyolite	1–2
5	Bartlett, N.H.[c]	granite	metapelite and quartzite	2
6	Hubbard Brook, N.H.[c]	metapelite and quartzite	amphibolite and mixed granitic	2
7	Whiteface Mt., N.Y.[d]	anorthosite	granitic gneiss	2
8	Crawford Notch, N.H.[c]	metapelite and quartzite	mixed granitic rocks	1–2
9	Bear Brook, Me.[b]	sulfidic/carbonaceous pelite	granite and calcareous sandstone	1–2
10	Big Moose Lake, N.Y.[d]	granitic gneiss	mixed metasedimentary	1–2
11	Cone Pond, N.H.[c]	metapelite and quartzite	mixed granitic rocks	1
12	Mt. Abraham, Vt.[a]	metapelite	quartzite	1

[1] (a) Doll et al. (1961).
(b) Osberg et al. (1985).
(c) Lyons et al. (1986).
(d) Fisher et al. (1971).
[2] Bedrock at each site determined by field observation or from cited maps.
[3] Other rock types potentially present in parent materials determined with model of Bailey and Hornbeck (1992).
[4] Weathering potential estimated from following scale:
4 – High, controlled by carbonate substrate
3 – Moderately high, controlled by carbonates included in a predominantly silicate substrate
2 – Moderately low, controlled by silicates with high Ca content and(or) relatively high reaction rates
1 – Low, controlled by silicates with low Ca content.

extractable-Ca concentrations by the method of Friedland et al. (1984), and Oa samples from one collection at each site (nine samples combined into 3 samples) were analyzed for total Ca concentrations by neutron activation (Parry 1991). Because neutron activation provides complete recovery of Ca, all forms of Ca in the soil sample are measured. Mineral Ca concentrations were calculated as the difference between total Ca concentrations and acid-extractable Ca concentrations; reactive nonexchangeable-Ca concentrations were calculated as the difference between concentrations of acid-extractable Ca and exchangeable Ca.

Acid-extractable Ca content of the forest floor was estimated from concentration measurements for the Oa horizon, thickness measurements of the Oe and Oa horizons, bulk density estimates determined by the model of Federer et al. (1993), and estimated concentrations of Ca in the Oe horizon, determined by the following regression equation that relates Ca concentrations in Oa horizons to those in Oe horizons.

$$Oe = 1.22(Oa) + 6.08 \quad P < 0.0l, n = 30, R^2 = 0.64$$

where: Oe = Oe-horizon concentration of acid-extractable Ca in $\mathrm{cmol_c\ kg^{-1}}$

Oa = Oa-concentration of acid-extractable Ca in $\mathrm{cmol_c\ kg^{-1}}$

To develop the regression equation, concentrations of exchangeable Ca were measured in both Oa and Oe samples at three sites (Big Moose, Groton and Hubbard Brook), on one date. Separating the Oe horizon from the Oa horizon during sampling can be difficult because their appearance is similar (Federer 1982), but Oe concentrations of Ca are reported to be consistently higher than Oa concentrations in our comparison, as well as other studies that report values for both horizons (Mollitor & Raynal 1982; Federer & Hornbeck 1985; Huntington & Ryan 1988; Rustad & Cronan 1995). Because the regression doesn't include the sites with the highest and lowest average Ca concentrations, the forest floor pool sizes must be considered approximate.

As a final step, exchangeable Ca concentrations in the Oe horizon were assumed to equal acid- extractable concentrations. This assumption was based on results of Oa horizon analyses, which indicated that acid-extractable Ca concentrations, averaged among the 12 sites, were only 8% higher than exchangeable-Ca concentrations. The values we report for acid-extractable Ca content of the forest floor also do not include the Oi horizon.

Comparisons with data from other studies

We conducted a literature search to locate all data collected since 1980 on Ca concentrations in the forest floor and upper B horizon of red spruce stands in the Northeast. Data included for comparison represented mature, uneven-aged stands (to ensure that the stands had not been clearcut) that were primarily coniferous and had a significant red spruce component. Because the previous studies had used a variety of extractants to measure Ca concentrations in soil, we conducted two methods tests on Oa horizon samples from four sites; two sites with relatively high Ca concentrations (Bartlett, N.H. and Howland, Me.), and two sites with relatively low Ca concentrations (Cone Pond N.H., and Mt. Abraham, Vt.). In the first test, extractants used to measure exchangeable Ca were compared. Three samples from each site were extracted with (1) NH_4Cl (Blume 1990), (2) $BaCl_2$ (Ross et al. 1991), (3) KCl (Rustad & Cronan 1995) and (4) NH_4OAc (Blume et al. 1990). Concentra-

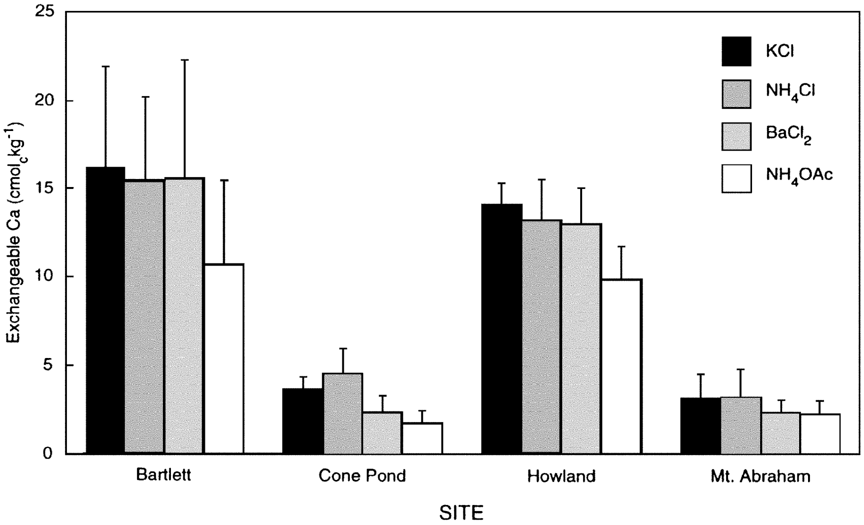


Figure 2. Comparison of exchangeable Ca concentrations in soils from four sites, measured with four different extractants.

tions of Ca in extracts were measured by flame-aspiration atomic-absorption spectrophotometry (AAS).

In the second test, methods used to measure acid-extractable Ca were compared. Three samples from each site were analyzed by (1) dry ashing and extraction with 6 M HNO_3 with measurement by AAS, in accordance with the method of Friedland et al. (1984), (2) extraction with 0.2 M HCl and titrimetric measurement with potassium permanganate ($KMnO_4$), after pH adjustment and filtration to remove Al and Fe interferences, in accordance with the method of Valmari (1921), and (3) the Valmari method without filtering to remove Al and Fe interferences. In the Valmari method Ca is recovered after acid extraction by raising the pH to 6.0–6.8 with ammonium hydroxide (NH_4OH) to precipitate Fe and Al. Precipitates are then removed by filtration, and ammonium oxalate ($NH_4C_2O_4$) is added to form a CaC_2O_2 precipitate. The precipitate is then dissolved and titrated with $KMnO_4$ to form $CaSO_4$ until a faint pink color is observed.

Method (1) was used to analyze the samples we collected in the regional survey, and is commonly used for analysis of metals in organic soils. Method (2) was used by Heimburger (1934) in an assessment of soils in the Adirondack Mountains of New York, and method (3) was used in a resampling of Heimburger's plots (Andersen 1988; Johnson et al. 1994a).

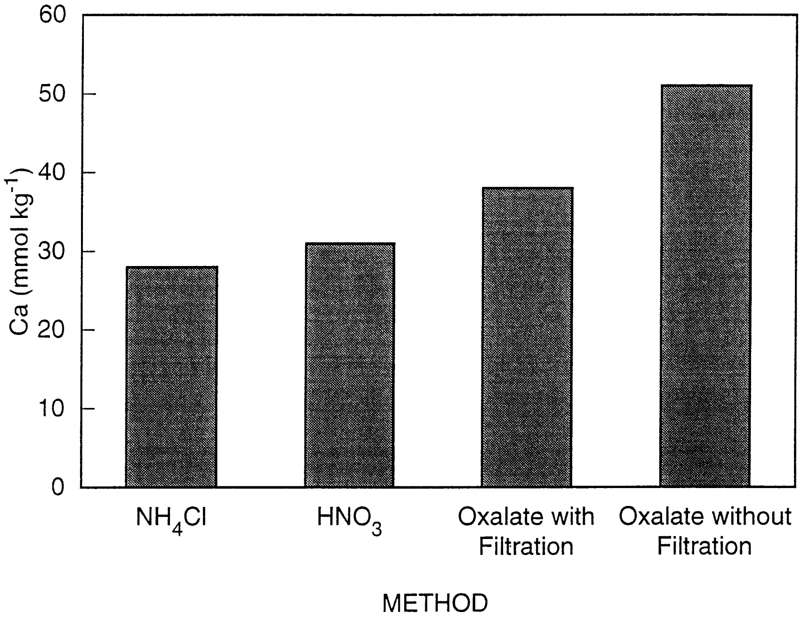


Figure 3. Comparison of acid-extractable Ca concentrations measured by extraction with (1) NH_4Cl, (2) dry ashing-HNO_3 digestion, (3) complexation with oxalate without filtration to remove Al and Fe interference, and (4) complexation with oxalate after filtration to remove Al and Fe interference. Histograms are the mean of nine different soil samples that represented a range of concentrations from each of four red spruce stands, determined by each of the four methods. Because of the large concentration range (and standard error) among the nine samples, only methods 1 and 4 yielded statistically different results. Average coefficient of variation for eight duplicate analyses done with method (1) was 7.9%; average coefficient of variation for four duplicate analyses done with method (2) was 4.3%; average coefficient of variation for one triplicate analyses done with method (3) was 8.8%; average coefficient of variation for one triplicate analyses done with method (4) was 26%.

Results

Methods comparisons

Comparison of methods for determining exchangeable Ca indicated no statistically significant differences ($p < 0.05$) among concentrations obtained with the four extractants, although concentrations obtained by NH_4OAc extraction were 20% lower on average than those obtained with the other extractants (Figure 2). On the basis of these results, we included data from other studies for comparison if one of the four extractants was used to measure exchangeable Ca. The three methods for determining acid-extractable Ca yielded larger differences than the exchangeable Ca measurements (Figure 3). Concentrations obtained with the oxalate titrimetric method without filtration were 67%

higher than concentrations measured with the dry ashing-HNO_3 extraction and AAS detection, and the oxalate titrimetric method with filtration was 25% higher than the HNO_3 extraction and AAS detection. Extraction with NH_4Cl yielded lower concentrations that were 10% lower than the HNO_3 extraction for the soils used in this test.

Regional survey data

At the 12 sites that we sampled in 1992–93, mineral matter constituted from 14% to 40% of Oa horizon mass, and concentrations of exchangeable Ca in the Oa horizon varied among the 12 sites by a factor of 10 (Table 3). The eastern Vermont sites (Sleepers River and Groton) had the highest Ca concentrations and the central Vermont site (Mt. Abraham) had the lowest. Other than the high concentrations in eastern Vermont, Ca concentrations showed no consistent geographical relations; the concentration at Big Moose Lake in the western Adirondack Mountains was similar to that at Kossuth in eastern Maine, whereas, in the White Mountains of New Hampshire the concentration at the Bartlett site was almost twice the concentration measured at nearby Crawford Notch. When exchangeable Ca was expressed as a percent of CEC (Ca saturation), concentrations ranged from 9.1% at Mt. Abraham to 51% at Sleepers River.

Acid-extractable Ca content of the forest floor also varied by a factor of 10 among the 12 sites; Sleepers River, Vt., had the highest content, and Mt. Abraham, Vt. had the lowest content (Table 3). Because Ca content reflects forest-floor thickness as well as concentration, the content value for Big Moose Lake, N.Y., was among the highest of the 12 sites even though the exchangeable-Ca concentration for this site was among the lowest.

Exchangeable-Ca concentrations in the upper B horizon were less varied than in the Oa horizon, and were 1 to 2 orders of magnitude lower (Table 4). The geographic relations for the upper B horizon also differed somewhat from the those for the Oa horizon: for example, Whiteface Mountain, N.Y. and Mt. Abraham, Vt., which had lower concentrations of exchangeable Ca in the Oa horizon than most sites, had among the highest concentrations in the upper B horizon. In contrast, Bartlett, N.H. had a relatively high exchangeable Ca concentration in the Oa horizon, but the second lowest in the upper B horizon. Cone Pond had relatively low concentrations of exchangeable Ca in both horizons. All sites had Ca saturation values of 13% or less, with Cone Pond exhibiting the lowest value; 1.6%.

Exchangeable Ca was the largest fraction of total Ca in the Oa horizon at all sites except Whiteface Mountain, N.Y., Bear Brook, Me., and Mt. Abraham, Vt., where mineral Ca (total Ca concentration minus acid-extractable Ca concentration) was the largest fraction (Figure 4). These three sites also had the

Table 3. Mineral matter concentrations, exchangeable-Ca concentrations as $\text{cmol}_c\text{kg}^{-1}$ and exchangeable-Ca concentrations as a percent of CEC in the Oa horizon, and acid-extractable Ca content of the forest floor (Oe plus Oa horizons) for the 12 study sites. each mineral matter and exchangeable Ca value is a mean that represents 36 samples that were collected individually, then combined into 12 samples for analysis, except where indicated. Each value for acid-extractable Ca content is a mean that represents 18 samples that were collected individually, then combined into 6 samples for analysis. Standard errors are in parentheses.

		Mineral Matter	Exchangeable Ca	Ca Saturation	Acid-Extractable Ca†
Site no. in Fig. 1	Site	(%)	($\text{cmol}_c\ \text{kg}^{-1}$)	(($\text{cmol}_c\ \text{kg}^{-1}$) CEC^{-1}) 100	(mol ha^{-1})
1	Sleepers River, Vt.*	14(3.4)	22 (3.1)	51	29,300
2	Groton, Vt.	18(2)	14(1.17)	41	9,330
3	Howland, Me.	16(1.5)	11(1.03)	34	7,750
4	Kossuth, Me.	21(3.3)	6.3(1.00)	24	5,690
5	Bartlett, N.H.	14(2)	11(1.92)	31	11,700
6	Hubbard Brook*	15(3)	7.9(1.99)	25	8,070
7	Whiteface Mt., N.Y.*	32(7.2)	6.3(1.69)	26	7,360
8	Crawford Notch	16(2)	6.8(1.20)	21	7,120
9	Bear Brook, Me.	35(3.4)	5.3(1.01)	21	5,190
10	Big Moose Lake, N.Y.	19(4.2)	6.4(0.82)	20	10,300
11	Cone Pond, N.H.	15(2)	3.5(0.60)	10	3,920
12	Mt. Abraham, Vt.*	40(4)	2.1(0.30)	9.1	3,910

† Standard errors could not be calculated for Ca content values because measurements of soil depth could not be individually related to soil concentration values.

* For these sites, each value represents 18 samples that were collected individually, then combined into 6 samples for analysis.

highest mineral-matter concentrations in the forest floor (Table 3). Reactive-nonexchangeable Ca (acid-extractable Ca concentration minus exchangeable Ca concentration) was either absent or only a minor component of total Ca at all sites except Groton, Vt., where the concentration of this form of Ca was about twice the concentration of mineral Ca. Averaged for the 12 sites, acid-extractable Ca was comprised of 92% exchangeable Ca and 8% reactive-nonexchangeable Ca.

Calcium saturation was weakly related to atmospheric wet S deposition in the Oa horizon and unrelated to atmospheric wet S deposition in the Bs horizon (Figure 5). Calcium saturation was, however, related to relative weathering potential in both the Oa and Bs horizon.

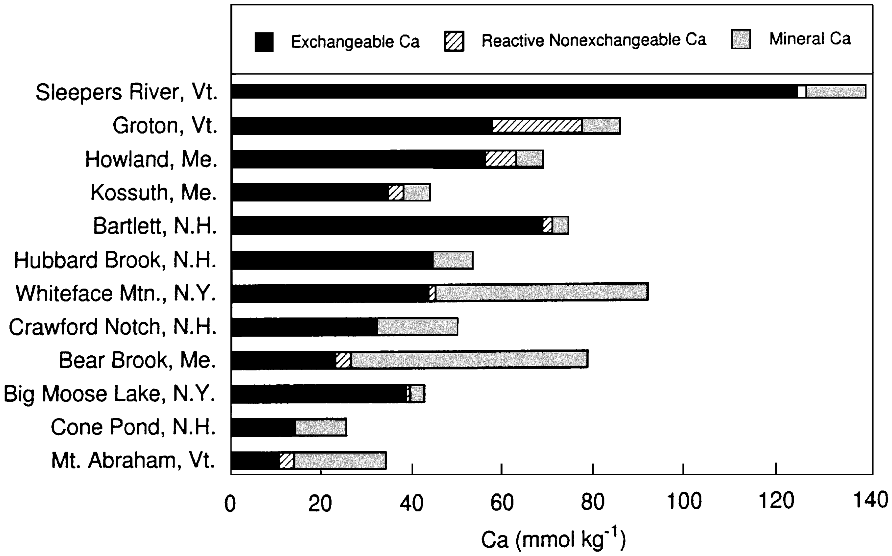


Figure 4. Concentrations of exchangeable Ca, reactive nonexchangeable Ca (acid-extractable Ca concentrations minus exchangeable-Ca concentrations) and mineral Ca (total Ca concentrations minus acid-extractable Ca concentrations) in the Oa horizon of the 12 sites sampled in this study. Site locations are shown in Figure 1.

Table 4. Exchangeable-Ca concentrations as $\mathrm{cmol_c kg^{-1}}$ and as a percent of CEC and in the upper 10 cm of the B horizon. Each exchangeable Ca value is a mean that represents 36 samples that were collected individually, then combined into 12 samples for analysis, except where indicated. Standard errors are in parentheses.

Site no. in Fig. 1	Site	Exchangeable Ca ($\mathrm{cmol_c kg^{-1}}$)	Ca Saturation ($\mathrm{((cmol_c kg^{-1})CEC^{-1})}$ 100
1	Sleepers River, Vt.*	0.68(0.09)	6.9
2	Groton, Vt.	0.32(0.18)	13
3	Howland, Me.	0.19(0.04)	3.8
4	Kossuth, Me.	0.19(0.05)	2.6
5	Bartlett, N.H.	0.18(0.05)	3.4
6	Hubbard Brook*†	–	–
7	Whiteface Mt., N.Y.*	0.57(0.11)	7.3
8	Crawford Notch	0.30(0.03)	3.1
9	Bear Brook, Me.	0.32(0.04)	4.1
10	Big Moose Lake, N.Y.	0.37(0.06)	3.1
11	Cone Pond, N.H.	0.11(0.01)	1.6
12	Mt. Abraham, Vt.*	0.41(0.11)	4.0

*For these sites, each value represents 18 samples that were collected individually, then combined into 6 samples for analysis.

†Insufficient B horizon for sample collection at this site.

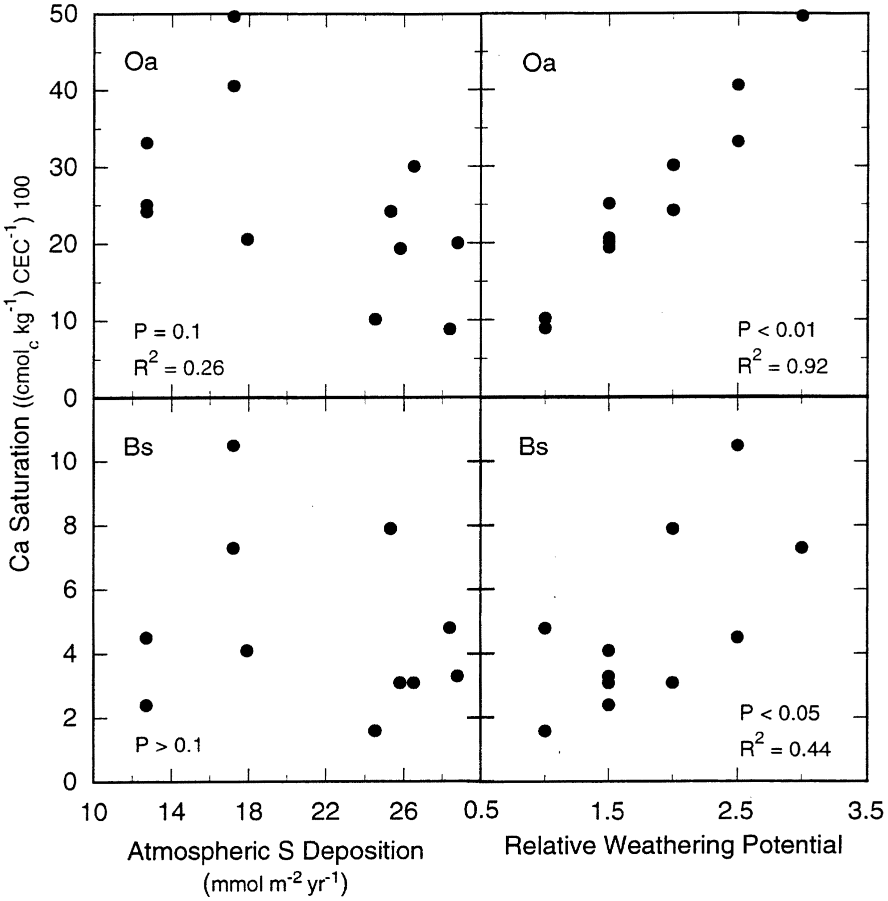


Figure 5. Ca saturation as a function of atmospheric deposition and relative weathering potential in Oa and Bs horizons.

Comparisons with other studies

All the comparable data for exchangeable Ca concentrations from other studies in northeastern red spruce stands were within the ranges we measured, except the concentration for the O2-horizon in the Adirondack Mountains of N.Y., reported by Mollitor and Raynal (1982), (which was lower than our lowest value, measured at Mt. Abraham, Vt.; Tables 3, 5). If Mollitor and Raynal (1982) had used NH_4Cl rather than NH_4OAc to extract Ca, they probably would have obtained a somewhat higher value. Because the studies of Fernandez and Lawrence (1989), Miller et al. (l992) and Johnson et al. (1994b) did not separate the Oe horizon from the Oa horizon, the O-horizon

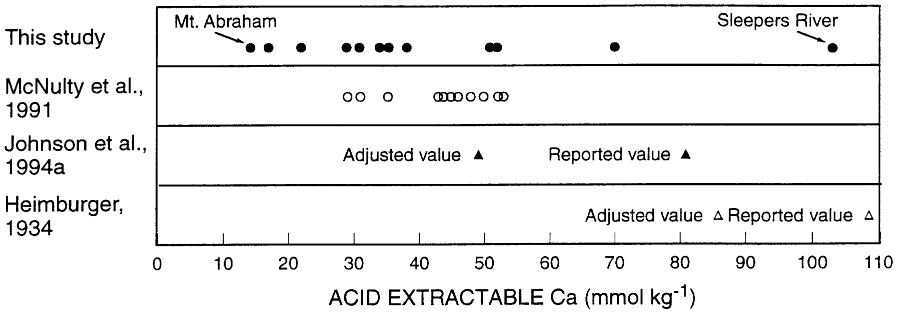


Figure 6. Acid-extractable Ca concentrations in Oa horizons of red spruce stands in the northeastern US measured in this study and the studies of McNulty et al. (1991), Johnson et al. (1994a), and Heimburger (1934). Values form this study of McNulty et al. (1991) represent means of individual sites; the values from Johnson et al. (1994a) represents the mean of 59 samples collected throughout the Adirondack Mountains of New York; the values from Heimburger (1934) represent the mean of 38 samples collected throughout the Adirondack Mountains of New York. Values reported by Johnson et al. (1994a) and Heimburger (1934) have been adjusted for method bias. To express Ca concentrations on a soil mass basis loss-on ignition values of 0.90 were assumed for the data from the McNulty et al. study and the Johnson et al. study.

concentrations reported in Table 4 probably lie between the values that would have been obtained for the separate horizons.

Concentrations of acid-extractable Ca measured in our study in 1992–93, ranged from 13.9 mmol kg^{-1} at Mt. Abraham to 103 mmol kg^{-1} at Sleepers River (Figure 6). This range encompassed values reported by McNulty et al. (1991) for eleven red spruce stands in New York, Vermont, New Hampshire and Maine, and the average for 59 samples collected throughout the Adirondack Mountains of New York by Johnson et al. (1994a). The data included from the Johnson et al. (1994a) study were only from sites with an original soil pH of less than 4.0 (as measured by Heimburger, 1934), presumably soils influenced by conifers. With the exception of Sleepers River and Groton, concentrations measured in our study and that of McNulty's fall between 10 and 55 mmol kg^{-1}. When adjusted for method bias, the value of Johnson et al. (1994a) falls in the upper part of this range. The mean value reported by Heimburger (1934) for 38 conifer stands in the Adirondack Mountains was slightly higher than the value we measured at Sleepers River. When adjusted to account for method bias, this value was similar to the value reported by Johnson et al. (1994a), but higher than all other measurements except Sleepers River.

Table 5. Concentrations of exchangeable Ca in soil samples from O and B horizons in red spruce forests of the northeastern U.S. from studies since 1980.

Site label in Fig. 1	Study	Extractant	Horizon or depth below the forest floor	Concentration ($\mathrm{cmol_c kg^{-1}}$)
A	Mollitor and Raynal (1982)	1 M NH_4OAc*	O1	2.32
			O2	1.07
			B21h	0.14
B	Federer and Hornbeck *1985)	1 M NH_4OAc*	Oe	15.2
C	Huntington and Ryan (1988)†	1 M NH_4Cl	Oie	10.2
			Oa	4.4
			0–10 cm	0.62
D	Rustad, 1988	1 M KCl	O1	13.9
			O2	7.79
			Bh	0.18
E	Ross, D.S., written commun., 1994‡	0.1 M $BaCl_2$	Oa	7.0
3	Fernandez and Lawrence (1989)§	1 M NH_4Cl	O	9.7
			0–7 cm	0.13
7	Miller et al. (1992)	1 M NH_4Cl	O	10.4
			ABhs	0.4
7	Johnson et al. (1994b)	1 M NH_4Cl	O	13.6

* Extractant buffered to pH 7.0.

† For organic horizons, concentrations are means of samples collected at four elevations. For mineral soils, concentrations are means of samples collected at two elevations. Mineral soils include E horizon when present.

‡ Ross, D.S., Department of Plant and Soil Science, The University of Vermont, Burlington, Vt., 05405-0082.

§ Did not include E horizon when present.

Discussion

Through our selection of specific sites that represented the variability of factors influencing Ca availability in northeastern red spruce forests, we expanded the range of Ca concentrations that had previously existed in the literature. The range was expanded primarily by inclusion of the Sleepers River site, where soils had the highest concentrations of exchangeable Ca in both the Oa and Bs horizons. This site is strongly influenced by a bedrock formation comprised of calcareous schist that weathers at a greater rate than any of the parent materials found at the other sites we sampled. High concentrations of exchangeable and acid-extractable Ca in the Oa horizon, and exchangeable Ca in the Bs horizon, reflect the influence of the relatively high rate of Ca input from weathering at this site.

In general, site-to-site variations were attributable more to local differences in soil mineralogy than spatial variations in acidic deposition, as suggested by the correlation between Ca saturation and relative weathering potential in both Oa and Bs horizons. Although acidic deposition was not the primary cause of variations among sites, it can, however, explain why Ca saturation was more strongly related to relative weathering potential in the Oa horizon than the Bs horizon. When base saturation is less than 20%, soil solution is strongly buffered by release of exchangeable Al, and leaching of base cations is minimized (Reuss, 1983). The Ca saturation of the Bs horizon at all 12 sites was less than 14%, but in the Oa horizon, Ca saturation was above 20% at most sites. Acidic deposition may have lowered the base saturation of the Bs horizon to levels at which parent materials of these sites become less clearly reflected in Ca saturation than in the Oa horizon, where high root activity helps reduce Ca loss through recycling.

The difference in geographic relations of exchangeable Ca concentrations between the Oa horizon and the Bs horizon can be attributed to the influence of CEC. In the Bs horizon CEC was lower and more variable than in the Oa horizon. When exchangeable Ca was expressed as a percent of CEC, geographic relations for both the Oa and Bs horizons were similar.

Stand condition was an additional factor that probably affected our measurements of exchangeable-Ca concentrations in the forest floor. Extensive dieback of red spruce trees was evident at Mt. Abraham, Vt., Whiteface Mountain, N.Y., Crawford Notch, N.H., and Big Moose Lake, N.Y., at the time of sampling. The return of large amounts of woody material to the forest floor may have been a significant input to exchangeable-Ca pools at these sites. At Whiteface Mountain, Johnson et al. (1994b) estimated that Ca input to the forest floor from mortality was about one-third the input from litterfall. This estimate was based on a long-term average annual mortality rate of 1.3%, although a rate of 3% was measured at this site for the period 1985–1990 (Johnson et al. 1994b). Regeneration is also occurring at these sites so, to some degree, uptake is offsetting the input of Ca to the forest floor from dead branches and bolewood. Correlating stand condition to the site-to-site differences we measured in exchangeable Ca concentrations was not possible because neither the time of onset nor the rate of dieback and regeneration were monitored at most of the sites. These factors would be required to evaluate effects of previous Ca cycling on current exchangeable pools.

Although considerable variability was caused by local influences, comparison of our regional characterization and methods analysis to the results of Heimburger (1934) do not alter the conclusion indicated by the combined studies by Johnson et al. (1994a, b), Shortle and Bondietti (1992), Lawrence et al. (1995) and Bailey et al. (1996), that there has been a regional decline in available Ca concentrations in red spruce forests in the second half of this century. Results of the methods analysis indicate that the decrease in Ca concentrations identified by Johnson et al. (1994a) may have actually been somewhat greater than that demonstrated by their comparison. Measurements of Johnson et al. (1994a) indicated concentrations of acid-extractable Ca that were 67% greater than if the positive interference from Fe and Al had been removed (as was done by Heimburger). The method used by Heimburger (1934) overestimated acid-extractable Ca concentrations by 25%, relative to the modern dry ashing-HNO_3 method. Only at Sleepers River did we measure higher exchangeable Ca concentrations than the adjusted average reported by Heimburger in 1934.

The sensitivity of ecosystem Ca pools to future disturbance is a function of the speciation of soil Ca, and at most sites Ca is stored in the forest floor primarily as exchangeable Ca, the form most readily leached. Reactive-nonexchangeable Ca (Ca primarily bound in organic matter) is a minor fraction at all sites, and mineral Ca availability is limited by weathering rates and mineral matter content of the forest floor. Although leaching losses of Ca caused by atmospheric deposition of sulfuric acid may decrease if sulfur emissions continue to decline (NAPAP, 1992), the recently discovered trend of increasing concentrations of exchangeable Al in the forest floor may offset this effect (Lawrence et al. 1995). The capacity of the forest floor to store Ca in an exchangeable form may also be decreased by increasing saturation of exchange sites by Al (Lawrence et al. l995). If a regional decrease in available Ca does continue, the rate will be influenced by local factors such as weathering rates and forest condition, and to a lesser extent, within-region variability of acidic deposition.

Conclusions

Considerable variability exists in the concentrations of exchangeable and acid-extractable Ca concentrations in the soils of northeastern red spruce forests, primarily due to the influence of local variations in the mineralogy of parent material. The major form of Ca in Oa horizons was exchangeable, indicating that the pool sizes of Ca in this horizon are responsive to changes in processes such as atmospheric deposition and forest growth.

Maintaining concentrations of available Ca is important to the health and productivity of forests. Dieback and growth declines which have occurred throughout the range of red spruce trees have been linked to stress caused by Ca deficiency (Shortle & Smith, 1988; McLaughlin et al. 1993), and decreases in available Ca could impact forest harvesting and management. Reduction of forest productivity from decreased availability of Ca has been cited as a forest-management concern that may need to be addressed in the future by lengthening harvesting rotations or by liming (Federer et al. 1989).

Soil Ca pools may be an important factor in determining surface-water quality in parts of the northeastern U.S. and southeastern Canada. The pH of acidified lakes in the Adirondack Mountains of New York (Cumming et al. 1994) and a stream at the Hubbard Brook Experimental Forest, N.H (Likens et al. 1996), have shown minimal responses to decreases in atmospheric deposition of SO_4^{2-} that have been underway since the 1970's. The decrease in SO_4^{2-} deposition at the Hubbard Brook site was accompanied by a decrease in streamwater concentrations of base cations. Similarly, Laflamme Lake in Quebec showed no improvement in alkalinity through the 1980's despite reductions in sulfate deposition due to a concurrent decrease in Ca and Mg concentrations in the lake (Couture 1995).

Considerable effort has been spent trying to answer the question of whether or not acidic deposition is the primary cause of documented decreases in available soil Ca concentrations. Answering this question, however, may not be critical to address the future status of Ca in soils and surface waters. Recent studies have documented three processes that can reduce available soil Ca pools; (1) retention of weathering-derived Ca in the mineral soil will be limited by high Al saturation on the soil exchanger and high Al to Ca ratios in solution that inhibit root uptake of Ca (Cronan & Grigal 1995), (2) a trend of decreasing atmospheric deposition of Ca has been identified in both North America and Europe (Hedin et al. 1994), and (3) Lawrence et al. (1995) identified a trend of increasing Al saturation in the forest floor, which reduces the capacity of this horizon to store Ca in an available form. Projection of future trends of available Ca pools will need to incorporate these processes.

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