

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

GREGORY B. LAWRENCE¹, MARK B. DAVID²,
SCOTT W. BAILEY³ & WALTER C. SHORTLE³

¹U.S. Geological Survey, 425 Jordan Road, Troy, NY 12180, USA; ²University of Illinois, W-503 Turner Hall, 1102 South Goodwin Avenue, Urbana, IL 61801, USA; ³USDA Forest Service, Northeastern Experiment Station, Durham, NH 03824, USA

Key words: atmospheric deposition, calcium, forest floor, forest soils, red spruce

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 cmol_c kg⁻¹ in the Oa horizon, and from 0.11 to 0.68 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.

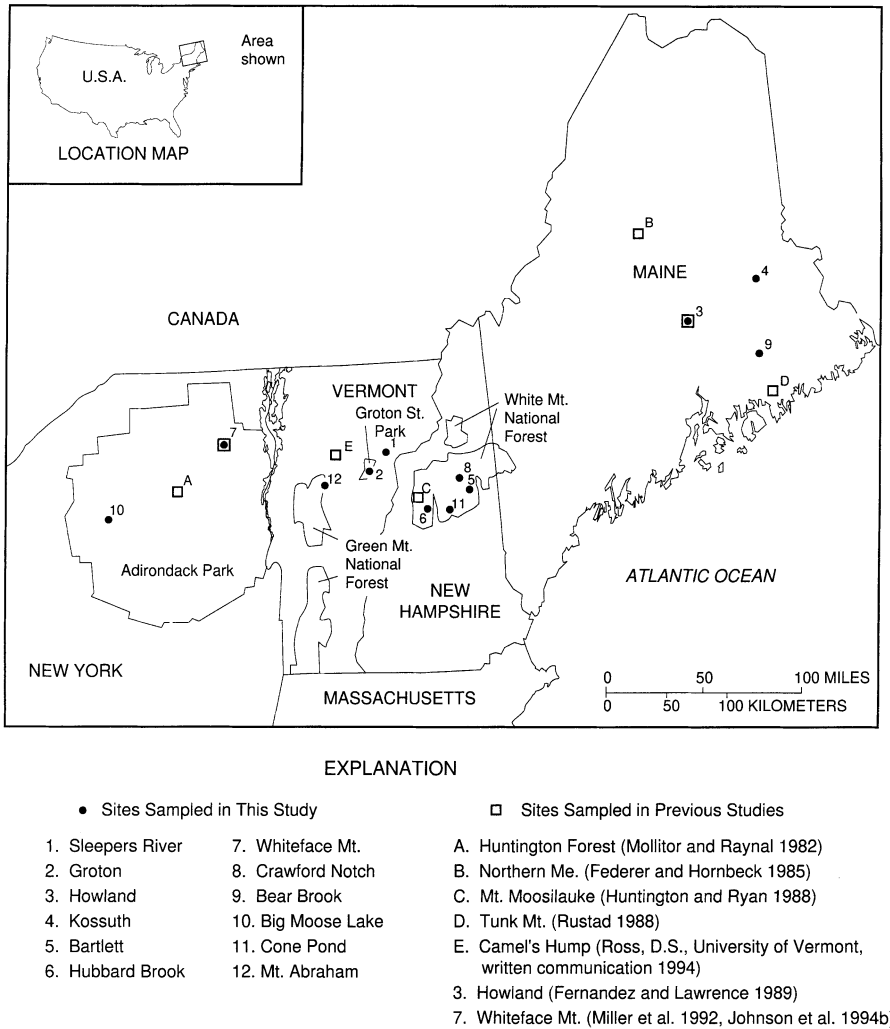


Figure 1. Locations of sites sampled in this study and previous studies since 1980, in New York, Vermont, New Hampshire, and Maine.

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 as 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 NO₃⁻ plus NH₄⁺ estimated from map of Ollinger et al. (1993).

Groton, Vt.: Wet-only values assumed to equal values measured at Sleepers River, Vt. Total NO₃⁻ plus NH₄⁺ 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 Brook, 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.: SO₄²⁻ deposition values are averaged for 1988–92 from Rustad et al. (1994). Wet-only NO₃⁻ plus NH₄⁺ 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 SO₄²⁻ deposition values based on onsite measurements in 1992. Total NO₃⁻ plus NH₄⁺ 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 thylolite	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).

²Bedrock at each site determined by field observation or from cited maps.

³Other rock types potentially present in parent materials determined with model of Bailey and Hornbeck (1992).

⁴Weathering 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.

$$Oe = 1.22(Oa) + 6.08 \quad P < 0.01, n = 30, R^2 = 0.64$$

where: Oe = Oe-horizon concentration of acid-extractable Ca in $\text{cmol}_c \text{ kg}^{-1}$

Oa = Oa-concentration of acid-extractable Ca in $\text{cmol}_c \text{ kg}^{-1}$

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-

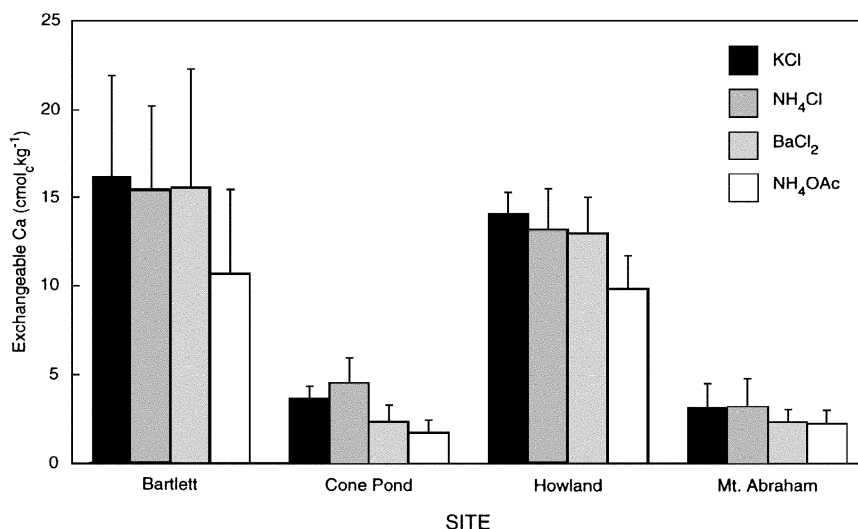


Figure 2. Comparison of exchangeable Ca concentrations in soils from four sites, measured with four different extractants.

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 HNO₃ 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 (KMnO₄), 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 (NH₄OH) to precipitate Fe and Al. Precipitates are then removed by filtration, and ammonium oxalate (NH₄C₂O₄) is added to form a CaC₂O₄ precipitate. The precipitate is then dissolved and titrated with KMnO₄ to form CaSO₄ 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).

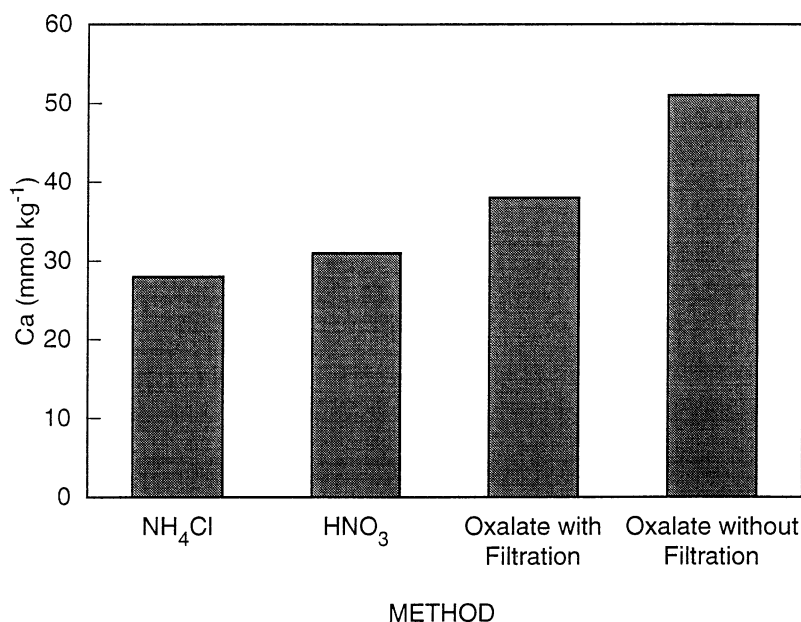


Figure 3. Comparison of acid-extractable Ca concentrations measured by extraction with (1) NH₄Cl, (2) dry ashing-HNO₃ digestion, (3) complexation with oxalate without filtration to remove Al and Fe interference, and (4) complexation with oxalate after filtration to remove Al and Fe interference. Histograms 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 NH₄OAc 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.

Site no. in Fig. 1	Site	Mineral Matter	Exchangeable Ca	Acid-Extractable	
		(%)	($\text{cmol}_c \text{kg}^{-1}$)	Ca Saturation (($\text{cmol}_c \text{kg}^{-1}$) CEC $^{-1}$) 100	Ca [†] (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.

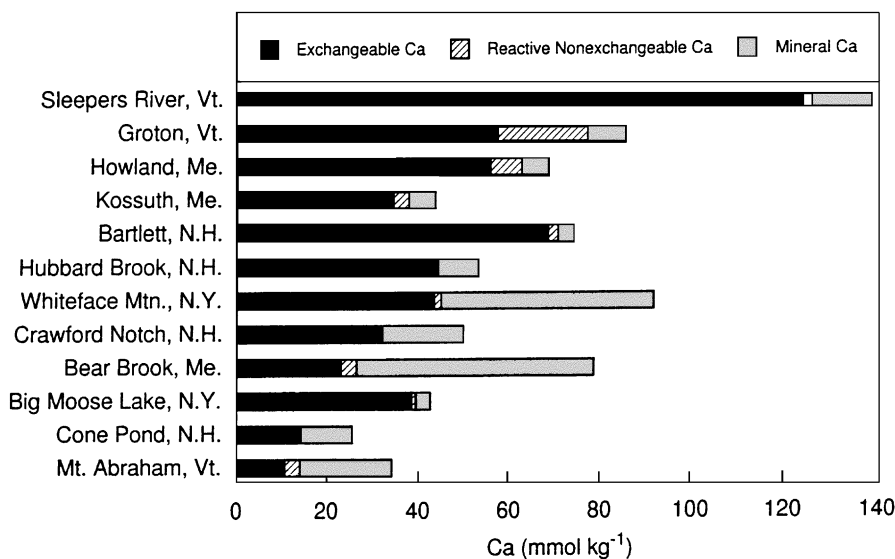


Figure 4. Concentrations of exchangeable Ca, reactive nonexchangeable Ca (acid-extractable Ca concentrations minus exchangeable-Ca concentrations) and mineral Ca (total Ca concentrations minus acid-extractable Ca concentrations) in the Oa horizon of the 12 sites sampled in this study. Site locations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

Table 4. Exchangeable-Ca concentrations as $\text{cmol}_c\text{kg}^{-1}$ 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 ($\text{cmol}_c\text{kg}^{-1}$)	Ca Saturation ($(\text{cmol}_c\text{kg}^{-1})\text{CEC}^{-1}$) 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.

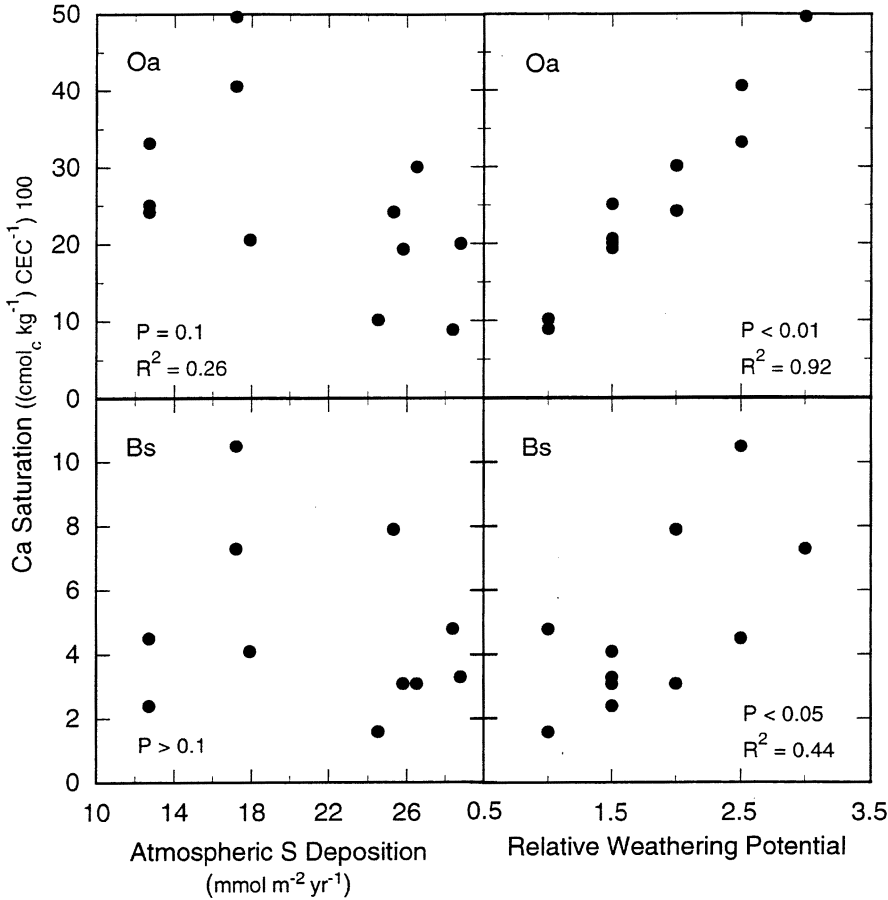


Figure 5. Ca saturation as a function of atmospheric deposition and relative weathering potential in Oa and Bs horizons.

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. (1992) and Johnson et al. (1994b) did not separate the Oe horizon from the Oa horizon, the O-horizon

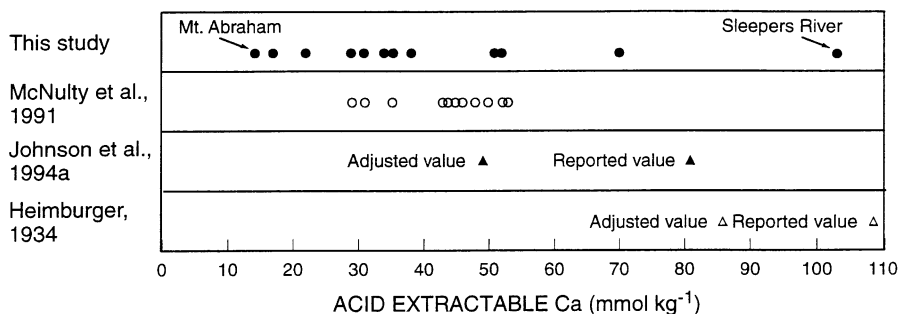


Figure 6. Acid-extractable Ca concentrations in Oa horizons of red spruce stands in the northeastern US measured in this study and the studies of McNulty et al. (1991), Johnson et al. (1994a), and Heimbürger (1934). Values from this study of McNulty et al. (1991) represent means of individual sites; the values from Johnson et al. (1994a) represents the mean of 59 samples collected throughout the Adirondack Mountains of New York; the values from Heimbürger (1934) represent the mean of 38 samples collected throughout the Adirondack Mountains of New York. Values reported by Johnson et al. (1994a) and Heimbürger (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 Heimbürger, 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 Heimbürger (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	Concen- tration ($\text{cmol}_e\text{kg}^{-1}$)
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 Heimbürger). The method used by Heimbürger (1934) overestimated acid-extractable Ca concentrations by 25%, relative to the modern dry ashing-HNO₃ method. Only at Sleepers River did we measure higher exchangeable Ca concentrations than the adjusted average reported by Heimbürger 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. 1995). 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.

Acknowledgements

The authors thank I. J. Fernandez, D. S. Ross, and G. M. Lovett, for supplying unpublished data from their sites, and J. Liu and M. Graham for comparison of extraction methods. We also thank J. W. Hornbeck and D. A. Burns for their reviews of the manuscript. This work was supported by the USDA Forest Service Northern Global Change Research Program.

References

- Andersen SB (1988) Long-term changes in the acid-base status of forest soils in the Adirondacks of New York. Ph.D. Dissertation. Univ. Pennsylvania, pp 521
- Bailey SW, Driscoll CT & Hornbeck JW (1995) Acid-base chemistry and aluminum transport in an acidic watershed and pond in New Hampshire. *Biogeochemistry* 28: 69–91
- Bailey SW, Hornbeck JW, Driscoll CT and Gaudette HE (1996) Calcium inputs and transport in a base-poor forest ecosystem as interpreted by Sr isotopes. *Water Resources Research* 32: 707–719.
- Bailey SW & Hornbeck JW (1992) Lithologic composition and rock weathering potential of forested, glacial-till soils. USDA Forest Service Research Paper NE-662 Northeastern Forest Experiment Station, Radnor, Pennsylvania
- Blume LJ, Schumacher BA, Schaffer PW, Cappo KA, Papp M, Van Remortel RD, Coffey DS, Johnson MG & Chaloud DJ (1990) Handbook of methods for acid deposition studies: laboratory analyses for soil chemistry US Environmental Protection Agency. EPA/600/4-90/023 Environmental Monitoring Systems Laboratory, Las Vegas, Nevada
- Couture S (1995) Response of the Laflamme Lake watershed, Quebec, to reduced sulphate deposition (1981–1992). *Can. J. Fish. Aquat. Sci.* 52: 1936–1995
- Cronan CS & Grigal DF (1995) Use of calcium/aluminum ratios as indicators of stress in forest ecosystems. *J. of Env. Qual.* 24: 209–226
- Cumming BF, Davey KA, Smol JP & Birks HUB (1994) When did acid-sensitive Adirondack Lakes (New York, USA) begin to acidify and are they still acidifying? *Can. J. Fish. Aquat. Sci.* 51: 1550–1568
- Dingman SL (1981) Elevation: a major influence on the hydrology of New Hampshire and Vermont, USA. *Hydrol. Sci. Bul.* 26: 399–413
- Doll CG, Cady WM, Thompson JB & Billings MP (1961) Centennial geologic map of Vermont. Vermont Geological Survey, Scale 1:250,000
- Driscoll CT, Fuller RD, Santore RC & Lawrence GB (1987) The speciation of ions in acidic solutions. Proceedings of the International Soil Congress, July 1986, Hamburg, West Germany, pp 59–62
- Federer CA (1982) Subjectivity in the separation of organic horizons of the forest floor. *Soil Sci. Soc. Am. J.* 46: 1090–1093
- Federer CA (1994) BROOK90, a simulation model for evapotranspiration, soil water and streamflow. Version 3.0 Freeware Computer Program and Documentation, USDA Forest Service, Durham, New Hampshire
- Federer CA & Hornbeck JW (1985) The buffer capacity of forest soils in New England. *Water Air Soil Pollut.* 26: 163–173
- Federer CA, Hornbeck JW, Tritton LM, Pierce RS & Smith CT (1989) Long-term depletion of calcium and other nutrients in eastern US forests. *Environ. Manag.* 13: 593–601
- Federer CA, Turcotte DE & Smith CT (1993) The organic fraction-bulk density relationship and the expression of nutrient content in forest soils *Can. J. For. Res.* 23: 1026–1032
- Fernandez IJ & Lawrence GB (1989) A preliminary report on element cycling and the potential effects of atmospheric deposition in a low elevation, commercial northeast spruce-fir ecosystem. Internal Report, USDA-FS Northeastern Forest Experiment Station, Radnor, Pennsylvania
- Fisher DW, Isachsen YW & Rickard LV (1971) Geologic Map of New York New York State Museum and Science Service. Number 15, Scale 1:250,000
- Friedland AJ, Johnson AH, Siccama TG & Mader DL (1984) Trace metal profiles in the forest floor of New England. *Soil Sci. Soc. Am. J.* 48: 422–425
- Hedin LO, Granat L, Likens GE, Buishand TA, Galloway JN, Butler TJ & Rodhe H (1994) Steep declines in atmospheric base cations in regions of Europe and North America. *Nature* 367: 351–367
- Heimbürger CC (1934) Forest-type studies in the Adirondack Region Cornell University Agriculture Experiment Station Memoir 165 Cornell University, Ithaca, New York

- Huntington TG & Ryan DF (1988) Soil chemical properties in the spruce-fir zone at Mt. Moosilauke in New Hampshire. In: Proc of the US/FRG research symposium: effects of atmospheric pollutants on the spruce-fir forests of the eastern United States and Federal Republic of Germany. Burlington, Vermont, 18–23 Oct 1987. USDA Forest Service General Technical Report NE-120 Northeastern Forest Experiment Station, Broomall, Pennsylvania, pp 191–198
- Johnson AH, Andersen SB & Siccama TG (1994a) Acid rain and soils of the Adirondacks. I. Changes in pH and available calcium. *Can. J. For. Res.* 24: 193–198
- Johnson AH, Friedland AJ, Miller EK & Siccama TG (1994b) Acid rain and soils of the Adirondacks III Rates of soil acidification in a montane spruce-fir forest at Whiteface Mountain, New York. *Can. J. For. Res.* 24: 663–669
- Johnson DW & Fernandez IJ (1992) Soil mediated effects of atmospheric deposition on eastern US spruce-fir forests. In: Eager C & Adams MB (eds) *Ecology and decline of red spruce in the eastern United States*. Springer-Verlag, New York, pp 235–270
- Joslin JD, Kelly JM & Van Miegroet H (1992) Soil chemistry and nutrition of North American spruce-fir stands: evidence for recent change. *J. Environ. Qual.* 21: 12–30
- Kuhn AJ, Bauch J & Schroeder WH (1995) Monitoring uptake and contents of Mg, Ca and K in Norway spruce as influenced by pH and Al, using microprobe analysis and stable isotope labeling. *Plant Soil* 168–169: 135–150
- Lawrence GB, David MB & Shortle WC (1995) Aluminum mobilization as a mechanism for calcium depletion in organic forest soil horizons. *Nature* 378: 162–165
- Likens GE, Driscoll CT & Buso DC (1996) Long-term effects of acid rain: response and recovery of a forest ecosystem. *Science* 272: 244–246
- Lyons JB, Bothner WA, Moench RH & Thompson JB (1986) Interim geologic map of Maine. Maine Geological Survey, Scale 1:500,000
- McLaughlin JW, Fernandez IJ & Richards KJ (1996) Atmospheric deposition to a low-elevation spruce-fir forest, Maine, USA. *J. Environ. Qual.* 25: 248–259
- McLaughlin SB, Tjoelker MB & Roy WX (1993) Acid deposition alters red spruce physiology: laboratory studies support field observations. *Can. J. For. Res.* 23: 380–386
- McNulty SG, Aber JD & Boone RD (1991) Spatial changes in forest floor and foliar chemistry of spruce-fir forests across New England. *Biogeochemistry* 14: 13–29
- Miller EK, Friedland AJ, Arons EA, Mohnen VA, Battles JJ, Panek JA, Kadlecsek J & Johnson AH (1993) Atmospheric deposition to forest along an elevational gradient at Whiteface Mountain, NY, USA. *Atmos. Environ.* 27A: 2121–2136
- Miller EK, Huntington TG, Johnson AH & Friedland AJ (1992) Aluminum in soil solutions from a subalpine spruce-fir forest at Whiteface Mountain, New York. *J. Environ. Qual.* 21: 345–352
- Mollitor AV & Raynal DJ (1982) Acid precipitation and ionic movements in Adirondack forest soils. *Soil Sci. Soc. Am. J.* 46: 137–141
- NADP [National Atmospheric Deposition Program] (1993) NADP/NTN Annual Data Summary Precipitation Chemistry in the United States 1992. Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, Colorado, pp 480
- NAPAP [National Acid Precipitation Assessment Program] (1992) National Acid Precipitation Assessment Program Report to Congress. US Government Printing Office Washington. DC
- Ollinger SV, Aber JD, Lovett GM, Millham SE, Lathrop RG & Ellis JM (1993) A spatial model of atmospheric deposition for the northeastern US. *Ecological Applications* 3: 459–472
- Osberg PH, Hussey AM & Boone GM (1985) Bedrock geologic map of Maine. Maine Geological Survey, Scale 1:500,000
- Parry SJ (1991) Activation Spectrometry in chemical analysis. In: Winefordner JD & Kolthoff IM (eds) *Chemical analysis*, vol. 119. John Wiley and Sons, NY
- Reuss LO (1983) Implications of the Ca-Al exchange system for the effect of acid precipitation on soils. *J. Environ. Qual.* 12: 591–595

- Rodhe H, Grennfelt P, Wisniewski J, Agren C, Bengtsson B, et al. (1995) Summary statement from the 5th International Conference on Acidic Deposition Science and Policy. Goteborg, Sweden. *Water Air Soil Pollut.* 85: 1–14
- Ross DS, Bartlett RJ & Magdoff FR (1991) Exchangeable cations and the pH independant distribution of cation exchange capacities in Spodosols of a forested watershed. In: Wright RJ et al. (eds) *Plant-soil interactions at low pH*. Kluwer Academic Publishers, the Netherlands, pp 81–92
- Rustad LE (1988) The biogeochemistry of aluminum in a red spruce forest floor in Maine. Ph.D. Thesis, University of Maine, Orono, Maine, 197 p
- Rustad LE & Cronan CS (1995) Biogeochemical controls on aluminum chemistry in the O horizon of a red spruce (*Picea rubens* Sarg.) stand in central Maine, USA. *Biogeochemistry* 29: 107–129
- Rustad LE, Kahl JS, Norton SA & Fernandez IJ (1994) Underestimation of dry deposition by throughfall in mixed northern hardwood forests. *J. Hydrol.* 162: 319–336
- Shortle WC & Bondietti EA (1992) Timing, magnitude and impact of acidic deposition on sensitive forest sites. *Water Air Soil Pollut.* 61: 253–267
- Shortle WC & Smith KT (1988) Aluminum-induced calcium deficiency syndrome in declining red spruce trees. *Science* 240: 1017–1018
- Valmari J (1921) Beitrage sur chemischen bodenanalyse. *Acta Forestalia Fennica* 20, pp 67