ASSESSING THE SENSITIVITY OF NEW YORK FORESTS TO CATION DEPLETION FROM ACID RAIN

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Final Report

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Notice

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Abstract

The overall goal of our project was to better understand the sensitivity of forests across New York State to calcium depletion. Both the distribution of Ca sources and the ability of tree species to obtain Ca from these sources are essential to predicting the future health of the forest resource and the value of environmental controls on emissions. In the first phase of this project, we describe the distribution of Ca-bearing minerals across soil parent materials in New York State. Our findings suggest that, to a first order, bedrock controls the spatial distribution of apatite and carbonate in the glacial till in the northeastern USA, as well as the concentration of exchangeable Ca in overlying horizons. The occurrence of carbonates or apatite in parent material contributes to the pool of readily weathered Ca, which mitigates the threat of Ca depletion from repeated forest harvest or acid rain. We compared limed and unlimed plots at four forested sites treated 14-41 years earlier. We found 5-75% more organic matter and N in the limed plots, suggesting that soils may be storing more C and N over time as they acidify. Finally, we measured the concentration of Ca and other elements in leaf litter at the same sites studied in the first phase of the project. Birch and maple species showed the most response to soil variation in Ca; spruce and fir had low Ca across all sites. More research is needed to determine the relative ability of different tree species to access Ca from different soil sources.

Key Words

apatite; calcium; sequential extraction; northern hardwoods

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Table of Contents

Section **Page**

Executive Summary

The degree to which acid rain threatens forest health and productivity depends in part on the ability of soils to supply calcium and other base cations for forest growth. Predictions of Ca depletion have been based on the assumption that only the salt-exchangeable Ca pool is available to plants; the weathering of Ca from parent materials has been believed to be too slow to play a role in mediating the acidifying effects of air pollution on soils. Because of these assumptions, the role of readily weathered Ca-bearing trace minerals, such as apatite and calcite, have been overlooked in assessments of Ca depletion from acid rain. Information about the distribution of Ca sources and the ability of tree species to obtain Ca is essential to predicting the sensitivity of forests across New York State to Ca depletion, with implications for sustainable forest management and air pollution policy.

The overall goal of this project was to better understand the sensitivity of forests across New York State to soil acidification and Ca depletion. Both the distribution of Ca sources and the ability of tree species to obtain Ca from these sources are essential to predicting the future health of the forest resource and the value of environmental controls on emissions. To examine these relationships, we used a series of experiments designed to test the following hypotheses.

- Apatite is more common in soils formed in granitic parent materials than sedimentary ones. Calcite will be present in only small amounts except where limestone is involved.
- Apatite and calcite have been weathered from surface soils to a greater degree than the silicate pools.
- Variation in Ca availability across sites is reflected in plant tissue concentrations.
- Tree species vary in the degree to which they reflect differences across sites.

We also addressed aspects of soil acidification by comparing forest soils that have been undisturbed, but are receiving ambient acidic deposition, with soils that had been treated with lime to reverse the acidification process. We found more organic matter and nitrogen in soils that were not treated. This comparison suggests that soils may be storing more C and N in organic matter over time as they acidify.

Our examination of parent materials in forest soils across New York State demonstrates that the pool of readily weathered Ca can be substantial; this pool has not traditionally been included in assessment of the Ca available to plants. In sites with carbonates or apatite in the parent material, the threat of Ca depletion is probably not as great as previously supposed. It is possible that some tree species or forest types are better than others at accessing nutrients through weathering. More research is needed to determine the degree to which forest management could be used to improve Ca availability to forests via weathering of native soil minerals.

1. Introduction

The plant-available pool of soil Ca has commonly been equated with the salt-exchangeable fraction (NH_4Cl), and the non-exchangeable pool has been assumed to be dominated by slowly weathered silicate minerals (Bailey et al., 1996; Likens et al., 1998). However, an acid leach of soils from a 65-90 year-old northern hardwood stand at the Hubbard Brook Experimental Forest removed a relatively large pool of Ca (65 g Ca/ m2 in E and B horizons and 6 g Ca/ m^2 per cm of depth in the C horizon) (Hamburg et al., 2003). The Ca:P and Ca:Sr ratios suggest that this treatment dissolved the non-silicate mineral apatite ($Ca_5(PO_4)_3OH$), which is in lower abundance but is much more rapidly weathered than silicate minerals. Both apatite and calcite ($CaCO_3$), another Ca-bearing trace mineral, are ubiquitous as small inclusions in the silicate minerals of the soil parent material, as revealed by cathodoluminescence imaging of soil thin sections. The very high Ca/ Sr ratio of this extract is quite characteristic of these non-silicate minerals and could be used for distinguishing the source pools of Ca to various tree species (Blum et al. 2002).

Up to this point, geologically sensitive areas of New York State have been defined as those in which surface waters have been acidified (e.g., April et al., 1986). We contend that this definition has been incomplete in terms of protecting and managing forest health. Areas with few carbonate rocks, such as the Adirondacks and Hudson Highlands, may indeed be most susceptible to acidification of surface waters, and the low buffering capacity of soils may explain the phenomenon of dead lakes (Reuss and Johnson, 1986). But the susceptibility of forest soils to Ca depletion may also depend on the presence of trace minerals such as apatite. At the Hubbard Brook Experimental Forest in New Hampshire, our budgetary calculations revealed that 20% of the Ca now cycling through forest biomass was originally weathered from apatite (Nezat et al., 2004). The focus on feldspars and other Ca-bearing silicate rocks in calculating weathering rates of Ca (Bailey et al., 1996; Likens et al., 1998) is not surprising, given the dominance of silicate minerals in the parent material; but the omission of non-silicate minerals as a Ca source may have seriously overestimated the threat to forest health from acid rain.

Establishing the importance of Ca-bearing minerals in parent materials across New York State, in combination with assessing the ability of various commercially and socially important tree species to obtain Ca from sources such as apatite, will enable us to better predict the susceptibility of forests to Ca limitation across a geologically and ecologically varied landscape.

Objective 1: Soil sources

Based on bedrock geology and the distribution of soil types, 30 sites were selected in New York State for sampling of soils. A sequential extraction procedure was used to quantify the amount of calcium that is exchangeable, readily weathered (such as apatite) and resistant to weathering (such as silicate minerals).

Objective 2: Liming study

Samples collected at sites where Ca was added in liming experiments 14 to 41 years ago were analyzed for C and N in order to determine whether soil acidification might lead to changes in soil C and N storage.

Objective 3: Tree response to soil sources of calcium

At the same sites used in Objective 1, we collected leaf litter from the most dominant species at each site to determine the influence on contrasting parent materials on plant tissue chemistry. We compared the Ca concentrations in leaves to those we measured in the soils.

2. Objective 1: Soil Sources

Reprinted, with permission from Nezat, C.A., J.D. Blum, R.D. Yanai, S.P. Hamburg, and B.B. Park. 2008. Mineral sources of calcium and phosphorus in soils of the northeastern USA. Soil Science Society of America Journal 72(6): 1786–1794

A. Introduction

Understanding mineral sources of calcium in soils of the northeastern USA is important because plant-available Ca has been leached from the soil at accelerated rates for several decades (Lawrence et al., 1999; Likens et al., 1998) possibly resulting in Ca limitation in some forest ecosystems (Horsley et al., 2000; Huntington, 2005; Long et al., 1997). Plagioclase, the dominant Ca-bearing mineral in non-carbonate soils in the region, weathers too slowly to compensate for the Ca lost from the exchangeable pool (Likens et al., 1998; Nezat et al., 2004). Apatite, $Ca_5(PO_4)_3(F,Cl,OH)$, although it is usually present only in trace amounts, may be an important mineral source of Ca because it dissolves several orders of magnitude more rapidly than plagioclase (Oxburgh et al., 1994; Valsami-Jones et al., 1998; Welch and Ullman, 1993). For example, at the Hubbard Brook Experimental Forest, NH, apatite represents <1% of soil mineral mass (12 % of total Ca) yet its dissolution is responsible for at least 20% of the Ca weathered from the soils since the area was deglaciated 14,000 years ago (Nezat et al., 2004). In the Adirondack Mountains, apatite accounts for ~1-8% of the total Ca in some soil parent materials (Yanai et al., 2005).

Apatite is common in igneous, metamorphic, and sedimentary rocks. In igneous rocks, apatite is found in both plutonic and volcanic rocks ranging in chemical composition from felsic to ultramafic (Piccoli and Candela, 2002). In metamorphic rocks, apatite is found in pelitic, carbonate, basaltic, and ultramafic rocks of all metamorphic grades (Spear and Pyle, 2002). Apatite may appear as individual grains or as inclusions in aluminosilicate minerals, such as feldspar and biotite. Apatite is also present in a variety of sedimentary rock types. In clastic rocks, both detrital and authigenic apatite have been found in rocks formed from continental and marine deposits (Bouch et al., 2002; Rasmussen, 1996; Roden-Tice and Tice, 2005). Apatite is also common in carbonate rocks, usually as carbonate-apatite, $Ca_5(PO_4,CO_3OH)_3(F,Cl,OH)$ (Knudsen and Gunter, 2002). Sedimentary rocks may also contain biological apatite such as bones and teeth (Kohn and Cerling, 2002).

Because apatite is easily weathered, the concentrations of apatite in soils are expected to be lower than in the underlying parent material. The depletion of apatite from soil during soil development has been documented in chronosequence studies (Crews et al., 1995; Schlesinger et al., 1998; Walker and Syers, 1976). This depletion of apatite from surface soils accompanied by its persistence at depth has also been documented in relatively young soils (Beck and Elsenbeer, 1999; Blum et al., 2002). In addition, depletion of apatite from surface soils during the initial stages of weathering has been interpreted from the presence of apatite in young detrital lake sediments (< 5000 years old) following deglaciation and its absence in older lake sediments (Filippelli and Souch, 1999). Similarly, carbonate minerals weather very rapidly from soil profiles and are almost always depleted from surface horizons even in extremely young and poorly developed soils (Lichter, 1998; Vandenbygaart and Protz, 1995).

Although apatite is the most important primary mineral source of phosphorus and potentially an important source of Ca, it is not routinely measured in operationally defined plant-available pools. Exchangeable Ca extracted by a neutral salt solution (Hendershot et al., 1993; Robertson et al., 1999) is the most common index of Ca availability. Plant-available P is commonly quantified using anion-exchange resins or a 0.5 M $NaHCO_3$ extraction (Hedley et al., 1982; Schlesinger et al., 1998). Neither of these methods assesses the amount of apatite susceptible to chemical weathering.

A new sequential extraction procedure allows apatite to be distinguished from more weathering-resistant aluminosilicate minerals in soils (Nezat et al., 2007). In recent studies, this procedure revealed that apatite was present in trace amounts in the lower B horizon and C horizon at the Hubbard Brook Experimental Forest, NH (Blum et al., 2002; Nezat et al., 2004) and at other sites in the northeastern USA underlain by granitoid bedrock (Yanai et al., 2005). The distribution of apatite in other soil parent materials across the northeastern USA is not well known.

The first objective of this study was to determine the concentration of Ca and P in easily weathered minerals in soil parent material at 31 sites of various bedrock lithologies across the northeastern USA. Based on our previously published sequential extraction method (Nezat et al., 2007), we defined easily weathered minerals as those that can be removed by a 1 M HNO_3 solution. Using the chemical composition of the 1 M HNO_3 extract, we inferred the concentration of apatite in the parent materials. We divided soil parent materials into three categories based on their underlying bedrock type. Crystalline silicate rocks included non-carbonate igneous and metamorphic rocks such as gneiss, schist and granitoid rocks. Clastic sedimentary rocks included shale, siltstone and sandstone. Carbonate rocks included limestone and dolostone as well as carbonate rocks interlayered with clastic sedimentary rocks.

A comparison of a general geologic map (Fig. 1-1) and soil distributions in the northeastern USA (Web Soil Survey, NRCS) show that bedrock and soil order are roughly correlated in the northeastern USA. That is, spodosols are common on glacial deposits of crystalline silicate bedrock, inceptisols are prevalent on the Alleghany Plateau where clastic sedimentary rocks are the major rock type, and alfisols are located in a narrow belt running east-west across New York where carbonate bedrocks are located. In this study, we limited some of the other variables that affect soil formation (i.e., climate, time for soil development, and topography) by choosing soils in a humid continental climate that have developed on glacial deposits of similar age (left by the last retreat of the Laurentide Ice Sheet) on relatively flat ground.

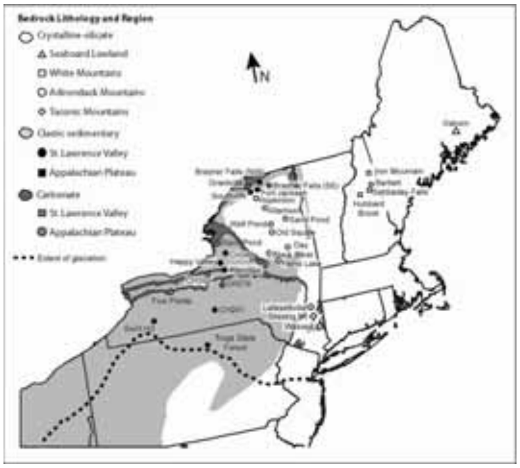


Figure 1-1. Location of samples collected in northeastern USA.

In addition to studying soil parent materials, we examined the occurrence of easily weathered sources of Ca and P in weathered soil horizons. In addition to apatite, some of the P and Ca present in organic matter or adsorbed to aluminum and iron oxides would be included in this easily weathered fraction (Nezat et al., 2007). We expected to find that apatite was depleted from near-surface soils compared to the soil parent material, or C horizon.

Finally, we tested for a relationship between the amount of easily weathered minerals (apatite and carbonate) in the underlying soil parent materials and the exchangeable Ca concentration of surface soil horizons. Although there are other variables that affect exchangeable Ca in soil such as organic matter content and cation exchange capacity, we wanted to examine whether or not exchangeable Ca concentration could be predicted solely from bedrock type.

B. *Materials and Methods*

1. ***Site Selection and Sampling***

Thirty-one study sites were selected in New York, Pennsylvania, New Hampshire, and Maine to include a range of igneous, metamorphic and sedimentary parent materials. In areas covered by ice sheets during the past 20,000 years, which includes all of our study area, the soil parent materials are glacial deposits, mostly glacial till. Because the till generally represents the bedrock within a ~15 km radius in the direction from which the glacier advanced (Bailey et al., 2003; Crowl and Sevon, 1999; Isachsen et al., 2000), we selected sites for sampling based on the bedrock composition at, and north of, each site (Figure 1-1, Table 1-1).

We selected 16 sites underlain by metamorphic and igneous bedrock in Maine, New Hampshire (White Mountains), and New York (Adirondack Mountains and Taconic Mountains). The sampling site in Maine, located in the Seaboard Lowland section of the New England Province, is underlain by granite (Osberg et al., 1985). The bedrock at the four sites in the White Mountains is gneiss, granite and schist (Barton et al., 1997; Lyons et al., 1997). In New York, the Adirondack Mountains are composed primarily of granitoid rocks including charnockite, anorthosite and mangerite but in the northwest region of the Adirondacks, marble, calcsilicate rock and quartzite are also present (Isachsen et al., 2000). The Taconic Mountains in southeastern NY are composed of schist and quartzite (Isachsen et al., 2000).

Table 1-1. Sampling locations in the northeastern USA. The bedrock at each site includes bedrock found up to 10 km northward. The surficial deposits are glacial till at all sites except for Brasher Falls (NW), Fort Jackson, and Southville, which have proglacial lake deposits.

Location	**State**		**Latitude**		**Longitude**		**Bedrock**
Crystalline silicate bedrock							
Osborn	ME	Seaboard Lowland	44°	48'	68°	16'	alkali feldspar granite
Iron Mountain (T30)	NH	White Mtns	44°	9'	71°	14'	pelitic schist
Bartlett Experimental Forest (H1)	NH	White Mtns	44°	3'	71°	17'	granite, syenite
Sabbaday Falls (M6)	NH	White Mtns	44°	0	71°	25'	granite, syenite
Hubbard Brook Experimental Forest	NH	White Mtns	43°	57'	71°	43'	granodiorite, pelitic schist
Hopkinton	NY	Adirondack Mts	44°	31'	74°	36'	charnockite, granitic & quartz syenite gneiss
Altamont	NY	Adirondack Mts	44°	16'	74°	27'	mangerite, syenite gneiss, charnockite, metasedimentary rock, granitic gneiss
Sand Pond	NY	Adirondack Mts	43°	57'	73°	54'	metanorthosite, anorthositic gneiss
Wolf Pond	NY	Adirondack Mts	43°	54'	74°	21'	charnockite, granitic & quartz syenite gneiss
Old Squaw	NY	Adirondack Mts	43°	44'	74°	22'	gabbroic metanorthosite, anorthositic gneiss, mangerite to charnockitic gneiss
Day	NY	Adirondack Mts	43°	20'	74°	3'	biotite & hbl granitic gneiss, metasedimentary rock, migmatite
Black River	NY	Adirondack Mts	43°	34'	74°	51'	metasedimentary rock, granitic gneiss, marble
Ferris Lake	NY	Adirondack Mts	43°	24'	74°	42'	metasedimentary rock, granitic gneiss
Lafayetteville	NY	Taconic Mts	41°	58'	73°	43'	slate, phyllite, schist, dolostone, sandstone
Stissing Mt.	NY	Taconic Mts	41°	56'	73°	41'	slate, phyllite, schist
Wassaic	NY	Taconic Mts	41°	47'	73°	34'	slate, phyllite, schist, marble
Sedimentary bedrock (clastic)							
Brasher Falls (NW)	NY	St. Lawrence Valley	44°	52'	74°	50'	limestone, dolostone
Fort Jackson	NY	St. Lawrence Valley	44°	43'	74°	45'	dolostone, sandstone, siltstone
Southville	NY	St. Lawrence Valley	44°	41'	74°	51'	dolostone, sandstone, siltstone
CH 201	NY	Alleghany Plateau	42°	38'	76°	24'	shale
CH 342	NY	Alleghany Plateau	43°	30'	75°	58'	sandstone, shale
Happy Valley	NY	Alleghany Plateau	43°	27'	76°	2'	sandstone, siltstone, shale
Klondike	NY	Alleghany Plateau	43°	22'	75°	59'	sandstone, shale
Swift Hill	NY	Alleghany Plateau	42°	27'	78°	14'	shale and siltstone
Tioga State Forest, Gleason	PA	Alleghany Plateau	41°	39'	76°	56'	sandstone
Sedimentary bedrock (carbonate)							
Brasher Falls (SE)	NY	St. Lawrence Valley	44°	51'	74°	39'	limestone, dolostone
Grantville	NY	St. Lawrence Valley	44°	51'	74°	55'	limestone, dolostone
Black Pond	NY	Alleghany Plateau	43°	47'	76°	12'	limestone, shale
CH 392	NY	Alleghany Plateau	43°	11'	76°	41'	limestone, dolostone
CH 379	NY	Alleghany Plateau	43°	1'	76°	22'	limestone, dolostone
Rush	NY	Alleghany Plateau	42°	58'	77°	40'	limestone, dolostone

Fifteen of the study sites are underlain by sedimentary bedrock and are in the St. Lawrence Valley (northern New York), western New York, and northern Pennsylvania (Figure 1-1). In New York, nine sites are underlain by limestone or dolostone, and five sites are underlain by clastic sedimentary rocks: i.e., sandstone, shale, and/ or siltstone (Isachsen et al., 2000). At three sites in the St. Lawrence Valley, proglacial lake deposits lay over carbonate bedrock but were composed of non-carbonate sedimentary deposits; we reclassified these three sites as clastic sedimentary rock.

One soil pit at each of the sampling locations was excavated to the C horizon. At most of the sites, soil samples were collected from 0-10 cm, 10-20 cm, and 20-30 cm below the top of the mineral soil, and from the bottom of the soil pit in the C horizon. The soils collected from Hubbard Brook Experimental Forest were collected by horizon (Nezat et al., 2004).

2. *Sample Processing*

All samples were dried at 105°C and sieved through a 2-mm screen. Soils were sequentially extracted (Nezat et al., 2007) to identify selected pools of Ca, Mg, and P. The exchangeable fraction was extracted by mixing ~0.5 g of soil with 5 mL of 1M NH_4Cl on a shaker table for ~18 hours at room temperature. To dissolve apatite and carbonates, the residual material was then shaken with 1M HNO_3 acid for 18 hours at 10°C (Nezat et al., 2007). After each extraction, the mixture was centrifuged and the supernatant was collected and filtered through a 0.45 μm membrane. All 1 M NH_4Cl and 1 M HNO_3 extracts were evaporated to dryness on a hot plate and redissolved in 5% HNO_3 acid.

Both the exchangeable and 1 M HNO_3 extractable fractions were then diluted with 2% HNO_3 and analyzed for Ca, Mg, and P concentrations on a Perkin Elmer Optima 3300DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) using a five- to eight-point calibration curve. Analysis of a certified reference material (Soil Solution A, High Purity Standards Inc.) indicated an accuracy of ±5%.

To verify the presence of apatite and explore its relationship with other minerals in crystalline silicate soils, we examined six of the soil parent materials collected from the Adirondack Mountains, NY.

Samples were sieved to obtain the 250 µm to 2 mm size fraction. Subsamples of this fraction were impregnated with epoxy and prepared as polished thin sections. Minerals were identified using an energy dispersive spectrometer (EDS) on a Hitachi S3200N Scanning Electron Microscope (SEM).

3. Data Analysis

To test the null hypothesis that soil chemistry did not differ among bedrock type, a two-tailed Student's t-test, assuming equal variances, was performed on each pair. Because skewness and kurtosis values indicated that data were not normally distributed, data were log transformed before statistical analysis in order to satisfy this requirement for the t-test. The equality of the variances of the groups was tested using an f-test. Significance was tested at $\alpha = 0.05$.

C. Results

1. Identification of Ca- and P-bearing minerals in soil parent materials

We used a 1 M HNO_3 extract of samples from 31 sites to determine which soil parent materials in the northeastern USA contained apatite (Figure 1-2). Because this extract dissolves apatite congruently (Nezat et al., 2007), soil parent materials containing apatite as the primary source of easily weathered Ca and P should have a P:Ca ratio of 3:5, the stoichiometric ratio in apatite.

Most of the soil parent material derived from crystalline silicate rocks had a P:Ca ratio in the 1 M HNO_3 extract close to 3:5 (Figure 1-2b). Calcium concentrations ranged from 0.2 – 41 µmol/ g soil and P ranged from 1.1 – 27 µmol/ g soil, indicating that these soil parent materials varied widely in apatite concentration (0.002 – 0.4% apatite in soil by weight based on Ca concentrations). These soil parent materials did not differ systematically by region. For example, the Adirondacks had sites with the highest and some of the lowest apatite concentrations. Some of the soils derived from crystalline silicate rocks (Osborn, Stissing Mountain, Sabbaday Falls, and Lafayettville) had P:Ca>3:5 suggesting the presence of other P sources in addition to apatite.

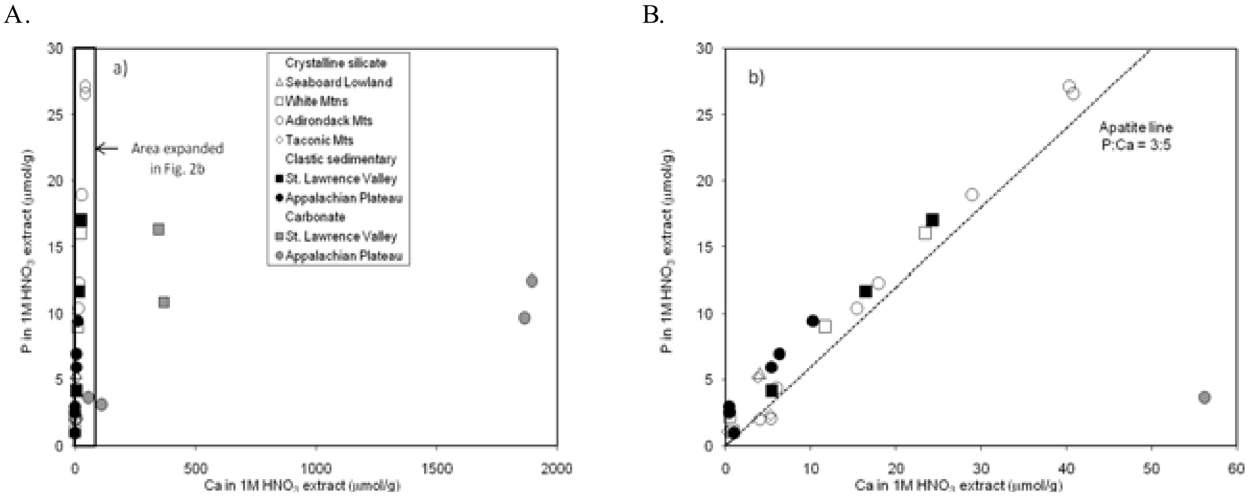


Figure 1-2. Phosphorus versus Ca of 1M HNO$_3$ extract (at 10 °C) of C horizon samples from across the northeastern USA. a) All data. Not surprisingly, carbonate-rich sites have the highest Ca concentrations. b) An enlarged view of Figure 2a at low Ca concentrations. Many of the parent materials derived from crystalline silicate and clastic sedimentary rocks fall near the dashed line that represents the P:Ca ratio of apatite (3:5).

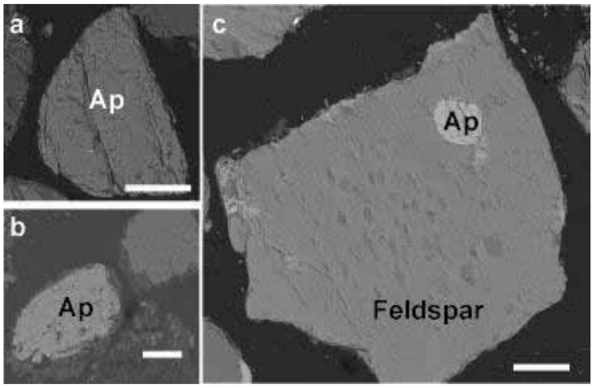
Soils collected from clastic sedimentary sites (located on the Appalachian Plateau) generally had Ca and P concentrations that were not significantly different from the crystalline-silicate soils ($p = 0.22$ for Ca and 0.80 for P). However, the P:Ca ratio was typically greater than 3:5 (Figure 1-2b), suggesting other sources of P besides apatite.

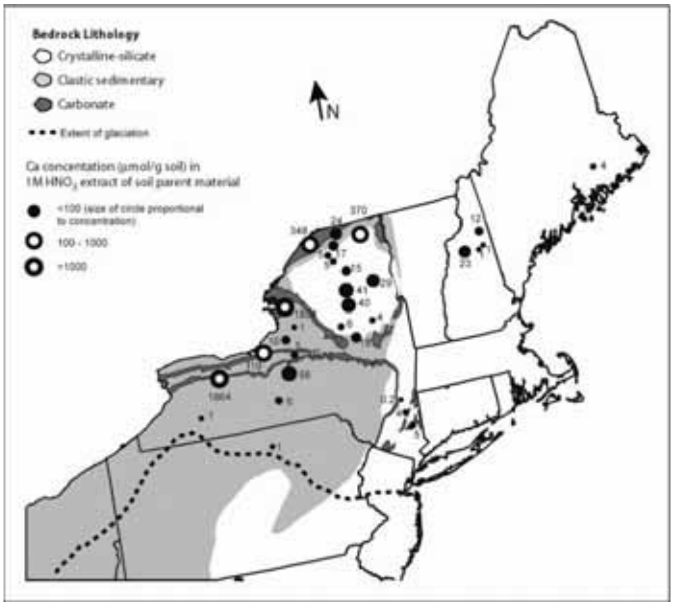
Three sites in the St. Lawrence Valley (Brasher Falls NW, Fort Jackson, and Southville) overlay carbonate bedrock, but are in an area where carbonate-poor glacial lake deposits blanket glacial till. The lack of abundant Ca in the 1 M HNO$_3$ extract and the P:Ca ratio of 3:5 is consistent with the origin of these three soil parent materials as siliclastic glacial lake deposits rather than carbonate-rich glacial till. Field textural analysis confirmed that these soil parent materials were composed of well-sorted sand, which also indicates that they are lakeshore deposits and not glacial till.

Soil parent materials underlain by carbonate bedrock had significantly higher Ca concentrations in the 1 M HNO$_3$ extract than soils derived from crystalline silicate and clastic sedimentary rocks ($p < 0.001$; Figure 2a). These sites also had high concentrations of 1 M HNO$_3$-extractable Mg (252-344 µmol Mg/ g soil) relative to other sites (<75 µmol Mg/ g soil), suggesting the presence of dolomite or high-Mg calcite. Phosphorus was present in these materials at concentrations that did not differ significantly from those at the non-carbonate sites ($p > 0.33$).

To investigate the relationship between apatite and silicate minerals in granitoid parent materials, we examined thin sections of soil parent materials from the Adirondack Mountains. We found apatite either as individual grains (Figure 1-3a), partially included in silicate minerals (Figure 1-3b), or completely included in silicate minerals (Figure 1-3c). Apatite grains ranged from 50 to 300 μm in diameter.

Figure 1-3 (below). Scanning electron microscopy (SEM) images of apatite (abbreviated Ap) in Adirondack soils collected from a) Old Squaw, b) Day, and c) Sand Pond. The scale bar is 100 μm long. Figure 1-4 (right). Calcium concentration in 1 M HNO_3 extract of soil parent materials.





We examined bedrock type as an explanation of the regional pattern in available Ca (1 M HNO_3 extractable) in soil parent material (Figure 1-4). It is clear from the map that the highest Ca availability is located near carbonate bedrock. However, as described above, three of the five sites in the St. Lawrence Valley overlying carbonate bedrock did not contain any evidence of carbonates.

2. *Easily extracted Ca and P in upper soil profiles*

We determined the 1 M HNO_3 extractable Ca and P in the upper soil profile (Figure 1-5). Not surprisingly, carbonate-dominated soils generally had higher Ca concentrations than the soils overlying crystalline silicate or clastic sedimentary bedrock. Generally, the Ca and P concentrations were

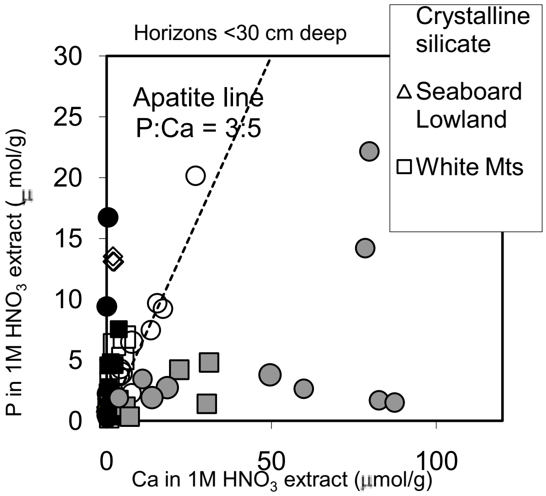


Figure 1-5. Phosphorus versus Ca of 1M HNO$_3$ extract (at 10 °C) of surface soils (<30 cm deep) from across the northeastern USA. Each site is represented by two to three samples collected roughly at 5, 15 and 25 cm.

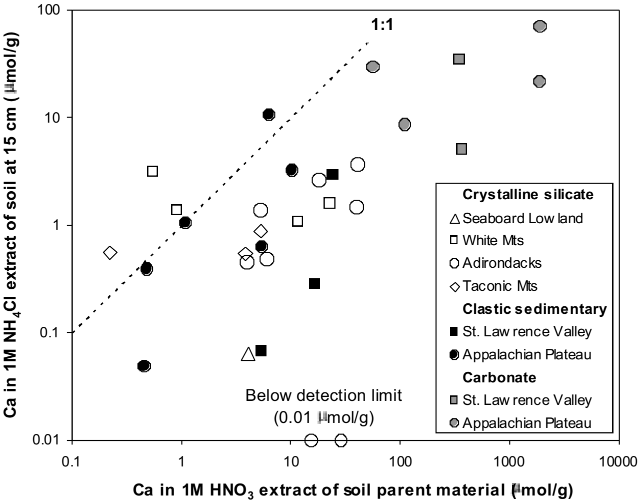


Figure 1-6. Calcium concentration of 1 M NH$_4$Cl extract of soil at 10-20 cm depth versus Ca concentration in 1 M HNO$_3$ extract of soil parent material. The dashed line represents a 1:1 ratio.

lower in the surface soils relative to the parent materials (Figure 1-2) as expected, due to apatite weathering, plant uptake, and leaching. Notable exceptions were Lafayetteville, a crystalline silicate bedrock site, in which the Ca in the 0-10 cm sample was three times that in the C horizon; Swift Hill (clastic sedimentary), in which the P in surface horizons was 16 times that in the C horizon; and Black Pond (Carbonate), in which the P in surface horizons was five times that in the C horizon. These sites are probably cases where the C horizon is not representative of the parent material for the upper portion of the profile. Three additional sites had more modest excesses (up to three-fold) of P concentrations in this extract in the surface soils compared to the C horizon: H1, CH 201, and Stissing Mountain. Excluding these six sites, the concentration of Ca in the surface soils (averaging up to three layers per site), as a fraction of the concentration in the C horizon, was 28% (13 crystalline silicate sites), 22% (four clastic sedimentary sites) and 14% (eight carbonate sites). For P, these fractions were 35% (crystalline silicates), 25% (clastic sedimentary) and 41% (carbonates). The difference between the retention of Ca and P was not significant ($p > 0.4$ in paired t-tests) except in the case of the carbonate sites ($p = 0.03$).

3. Relationship between exchangeable Ca in upper soils and soil parent material

We tested the dependence of soil Ca availability on the type of parent material by comparing the exchangeable Ca concentration at 10–20 cm depth to the Ca in the 1 M HNO_3 extract of the respective soil parent material (Figure 1-6). Not surprisingly, soils formed on carbonate-dominated soils had the highest exchangeable Ca concentrations, whereas soils formed on clastic sedimentary and crystalline silicate rocks had approximately an order of magnitude less exchangeable calcium. The exchangeable Ca at 10–20 cm was correlated with easily extracted Ca in the 1 M HNO_3 extract of soil parent material ($p < 0.001$, $r^2 = 0.52$). This pattern, however, was driven by the high Ca concentrations in the carbonate soils. When the carbonate sites were omitted from the analysis, there was no significant relationship ($p = 0.56$, $r^2 = 0.01$).

D. Discussion

1. Apatite in soil parent materials

The importance of apatite in young soils at the Hubbard Brook Experimental Forest in New Hampshire has previously been reported (Blum et al., 2002; Nezat et al., 2004; Yanai et al., 2005). Because apatite is common in crystalline silicate rocks, we predicted that soil parent materials in other young soils in the northeastern USA that were derived from crystalline silicate rocks would also contain apatite. We identified apatite in most of these soil parent materials based on the similarity between the P:Ca ratio in the 1 M HNO_3 extract and that in apatite (3:5) (Figure 1-2b). Some of the soils derived from crystalline silicate rocks (Osborn, Stissing Mountain, Sabbaday Falls, and Lafayettville) had P:Ca>3:5 suggesting the presence of other P sources in addition to apatite. In fact, the 1 M HNO_3 solution also extracts Ca and P from organic matter and weathering products such as P adsorbed to Al and Fe oxides (Nezat et al., 2007), which are typically a negligible fraction of soil parent materials derived from crystalline silicate rocks. Monazite, another primary phosphate mineral found in crystalline silicate rocks, is less common than apatite and is not likely to be extracted by a 1 M HNO_3 solution (Nezat et al., 2007).

In addition to its presence in igneous and metamorphic rocks, apatite is also found in a variety of sedimentary rocks as detrital, authigenic, or biological apatite (Bouch et al., 2002; Knudsen and Gunter, 2002; Rasmussen, 1996). Although Ca and P were present in the 1 M HNO_3 extract of most of the soil parent materials derived from the sedimentary rocks, the P:Ca ratio for most of these samples was greater than 3:5, indicating other sources of P in addition to apatite. In the region we studied, young soils developed from crystalline silicate and clastic (non-carbonate) sedimentary rocks have similar ranges of easily weathered Ca and P (Figure 1-2b).

Carbonate rocks also contain apatite, often as carbonate-apatite (Knudsen and Gunter, 2002). Because the 1 M HNO_3 extract also dissolves calcite, we used the P concentration to estimate the concentration of apatite in these soil parent materials. Although carbonate-rich soil parent materials contain considerably more 1 M HNO_3-extractable Ca, the concentration of easily weathered P in carbonate parent materials is similar to that found in crystalline silicate and clastic sedimentary parent materials (Figure 1-2a).

The concentration of apatite estimated from the Ca and P concentrations in the 1 M HNO_3 extract may be less than the total because some apatite may occur as inclusions in, and may be completely armored by, weathering-resistant minerals such as biotite, plagioclase and K-feldspar, which are not dissolved by this extract (Nezat et al., 2007). Unlike apatite inclusions, apatite that is present as free grains or partially included in silicate minerals may be exposed to soil solution and release nutrients during weathering. At the Hubbard Brook Experiment Forest, 70% of the total P in the soil parent materials was removed by the 1 M HNO_3 extract (Nezat et al., 2004) indicating that the remaining 30% was from apatite inclusions and other P-bearing minerals such as monazite. In the current study, a range of 10 to 100% of the total P was removed by the 1 M HNO_3 extract from the soil parent materials (data not shown) with no pattern among bedrock type or geographic region. While this extraction method quantifies the amount of apatite that is currently exposed to soil solution, biological, chemical and physical processes are continually occurring in soils and may expose more apatite with time. For example, this method does not account for apatite inclusions that may be accessed by mycorrhizal fungi as they tunnel through silicate minerals (Jongmans et al., 1997; Landeweert et al., 2001). To determine total apatite using this extraction method, soils should be pulverized before extraction. In this study, we extracted untreated soils because we were interested in apatite currently susceptible to weathering.

2. *Easily weathered minerals in upper soil profile*

Although apatite is present in soil parent materials, it can be weathered from surface soils in a few thousand years due to its rapid weathering rate (Crews et al., 1995). Assuming that the original composition of surface soils is similar to the soil parent material and that inputs from atmospheric dust are minor, apatite concentrations in soil should increase with depth due to the decrease in weathering (Schlesinger et al., 1998). At HBEF, apatite was identified in lower B horizons (Blum et al., 2002) suggesting that apatite has not been completely weathered at this depth.

As apatite weathers, P accumulates in organic matter or binds to Al and Fe oxides (Crews et al., 1995; Schlesinger et al., 1998; Walker and Syers, 1976). The 1 M HNO_3 solution releases Ca and P from both of these pools as well as from apatite (Nezat et al., 2007) making it difficult to estimate the concentration of apatite present in these soil horizons. The portion of P concentration loss we report (two thirds in crystalline silicates and three quarters in clastic sedimentary sites) should be a conservative estimate of the portion of apatite weathered, both because of the weathering products appearing in this operationally defined pool and also because of the loss of other elements from the profile. The concentration of an immobile element as an indicator of mass loss, combined with identification of apatite crystals, could give a more exact measure of apatite loss. It has been suggested that P may be more tightly retained than Ca in surface horizons due to high ecosystemic demand relative to its lithologic supply (Jobbágy and Jackson, 2001). However, we did not find a greater fraction of Ca than P lost from the upper part of the profile, relative to the C horizon, except in the carbonate sites.

3. *Effect of soil parent material on exchangeable fraction*

The relationship we found between easily weathered Ca in parent materials and exchangeable Ca in soils is informative because it may give a first-order approach to identifying soils that have high exchangeable Ca concentrations. Where the composition of bedrock is well known, it would be very appealing to use a bedrock map to predict the area most susceptible to Ca depletion and soil acidification.

Nevertheless, there are some limitations to this approach. First, the surficial geology also needs to be considered. Although glacial till is typically derived from local bedrock, other glacial deposits are not. For example, glacial lake deposits located in the St. Lawrence Valley (at Brasher Falls (NW), Southville and Fort Jackson) are carbonate-poor despite the fact that they are underlain by calcareous bedrock. In nearby soils that are underlain by the same bedrock but developed on glacial till (e.g., Brasher Falls (SE) and Grantville), carbonates are present. Second, it is important to keep in mind that there is a wide variation in parent material composition within the broad categories of crystalline silicate and clastic sedimentary rocks, which influences soil mineral and chemical composition (Figure 1-2). To predict the availability of Ca and P to vegetation and the susceptibility of soils to acidification at specific sites would require detailed characterization of the glacial till composition (Bailey and Hornbeck, 1992; Hornbeck et al., 1997), along with an evaluation of the soil capacity to retain exchangeable calcium.

E. Conclusions

Using a new sequential extraction method, we quantified the concentration of "easily-weathered" Ca and P pools, such as apatite and carbonate, in soil parent materials derived from a variety of bedrock types. The similarity between the P:Ca ratio in apatite and the 1 M HNO_3 extract indicates that apatite is the dominant source of P and Ca in this easily-weathered pool of most soil parent materials derived from crystalline silicate rocks. This method also distinguishes the apatite that is exposed to soil solution from that which is completely armored by weathering-resistant silicate minerals, and thus not currently susceptible to weathering.

Although known as the dominant, P-bearing primary mineral in soil, apatite has not been studied as a source of Ca in soils until recently. In this study we show that apatite is present in many parent materials of young soils in the northeastern USA where Ca depletion is a concern. Previous methods of characterizing soil Ca and P do not routinely measure the apatite fraction. Although usually present in trace amounts, apatite dissolves orders of magnitude more rapidly than plagioclase, the dominant Ca-bearing silicate mineral in many soils. To predict changes in plant-available Ca concentrations in soil in response to acid deposition and forest harvesting, it is important to be able to quantify this Ca pool.

3. Objective 2: Liming Study

A. Introduction

Carbon storage in forest soils is of increasing interest because of the need to account for C storage in soils when using forests to offset emissions of CO_2. Recent work linking changes in extractable cations to soil C and nitrogen content raises the possibility that changes in soil Ca pools could in turn influence soil C and N storage.

B. Materials and Methods

Site description: Study sites were located in northeastern America (Table 2-1). The “Bartlett” site is located in the Bartlett Experimental Forest, Bartlett, New Hampshire, in the White Mountain National Forest. In 1963, lime was applied to a 2 ha area at a rate of 1.1 Mg/ ha as part of a study testing for fertilization effects on root biomass (Safford 1974). The “Harvard” site is located in the Harvard Forest, Petersham in north central Massachusetts. Beginning in 1984, lime was applied to a 0.093 ha area in a hardwood stand as part of a study examining the effect of fertilization on mycorrhizal communities (Antibus and Linkins 1992). Applications occurred every two to four weeks from April through October of 1984 and May through August of 1985; the cumulative treatment rate was 15.9 Mg/ ha. The “PMRC” (Proctor Maple Research Center) site is located near Underhill Center, Vermont, USA, on the western slopes of the Green Mountains. In 1990, lime was applied at a rate of 3 Mg/ ha to a 0.15 ha plot along with 400 kg/ ha of a 10:5:1 K:Ca:Mg base cation fertilizer as part of a study on sugar maple response. An additional 2000 kg/ ha of the base cation fertilizer was applied in 1991, for a cumulative rate of 2400 kg/ ha (Wilmot et al 1996). The “Woods Lake” site is located in the west central portion of the Adirondack Park in New York, USA. Two subcatchments of the Woods Lake watershed were treated with 6.9 Mg/ ha of pelletized limestone in October of 1989 to test influence of the resulting acid neutralization effects on the lake (Driscoll et al 1996).

Sampling methods: For treatment and control areas at the Bartlett, Harvard, and PMRC experiments, thirty small (~30cm diameter) soil pits were dug approximately every five meters along systematically located transects spaced to cover the site. Samples were collected from all horizons present down to and including the top of the B horizon, and horizon depths were measured twice, on opposite sides of each pit. Samples for a given horizon were randomly assigned to one of three groups, which were then combined, yielding three composite samples for each horizon from each treatment at each site. At the Woods Lake site, because of the rockiness of the soil, we collected samples from three large pits (~1m diameter) in the limed subcatchment on the northeastern side of the lake and two large pits in the adjacent unlimed subcatchment to the south. Horizon depths were measured at six locations around the perimeter of each soil pit.

Table 2-1. Description of study sites and treatments.

Location	Treatment	Forest Type	Years since treatment
Bartlett	1 Mg/ ha dolomite	Northern Hardwood	41
Harvard	16 Mg/ ha limestone	Northern Hardwood	20
PMRC	1) 3 Mg/ ha lime 2) 2400kg/ ha 10:5:1 K-Ca-Mg	>85% Sugar Maple	14
Woods Lake	7 Mg/ ha $CaCO_3$	Mixed Hardwood	15

Sample analysis: Samples from all experiments were air dried and sieved to 2 mm before chemical analysis. Organic matter content was measured by loss on ignition after combustion at 450 °C for 16-18 hours. For total N, a subsample was ground using a Wig-L-Bug (Crescent Dental MFG, Co.) and analyzed using a Carbon-Nitrogen elemental analyzer (model NC2100).

Data analysis: We used paired t-tests to compare soil properties (nitrogen and organic matter concentrations and contents) between treatments by horizon within site. The sum of nitrogen and organic matter across horizons was compared between treatments with a t-test paired by site.

C. Results and Discussion

Limed and unlimed sites had different horizon thicknesses (Figure 2-1). At PMRC, the E horizon was absent from the limed sites. Earthworms or other soil organisms are known to prefer less acid soils, and bioturbation disrupts the process of podzolization responsible for the formation of the E and Bh horizons.

Soil organic matter concentrations declined with depth (Figure 2-2), as expected. By definition, an organic horizon should have 20% organic C or 40% organic matter mass. The Oa horizon at PMRC was marginal; the other sites had O horizons clearly above and mineral horizons clearly below this threshold.

The limed soils had greater organic matter concentrations than untreated soils in the Oe (P = 0.002) and Oa (P = 0.09) horizons; differences in other horizons were not statistically significant. Patterns in N concentrations with depth and across sites were similar to those of organic matter (Figure 2-3). The limed plots had significantly lower N concentrations than the controls in the Oe horizon (P = 0.03). The differences were not significant in the other horizons.

The bulk density of these soil horizons was not known; rock volume can occupy a significant fraction of the soil volume in sites such as these (Park et al. 2007). We compared the sites and treatments with an index proportional to the concentration and the depth of each horizon, which ignores possible variation in bulk density. Since the rock volume would not change with liming treatment, this should be a good indicator of differences in C and N content (Figure 2-4 and 2-5). In most cases, the liming treatments had less C and N than the controls, but these differences were not very statistically significant. The lowest P values for a t-test by horizon across sites was for the Oe horizon (P = 0.06 for N and P = 0.07 for organic matter).

Finally, we summed the indices of C and N contents over all the horizons, which showed greater C and N storage in untreated than limed plots. For N, Bartlett, Harvard, PMRC, and Woods Lake had 6%, 52%, 79%, and 5% more N in the untreated plots, assuming constant bulk density with depth, including rock volume. For organic matter, Bartlett, Harvard, PMRC, and Woods Lake had 12%, 76%, 63% and 5% more organic matter in the untreated plots, based on this index. Summing the horizons introduces the assumption that bulk density is constant with depth, while organic horizons likely have lower bulk density in the fine fraction. Since the mineral soil is likely to have a higher rock volume, and we lacked data to correct for this, our approach assumes that these two sources of error balance one another or that the net error is negligible.

If liming reverses the trends caused by anthropogenic soil acidification, then this comparison suggests that soils may be storing more C and N in organic matter over time as they acidify.

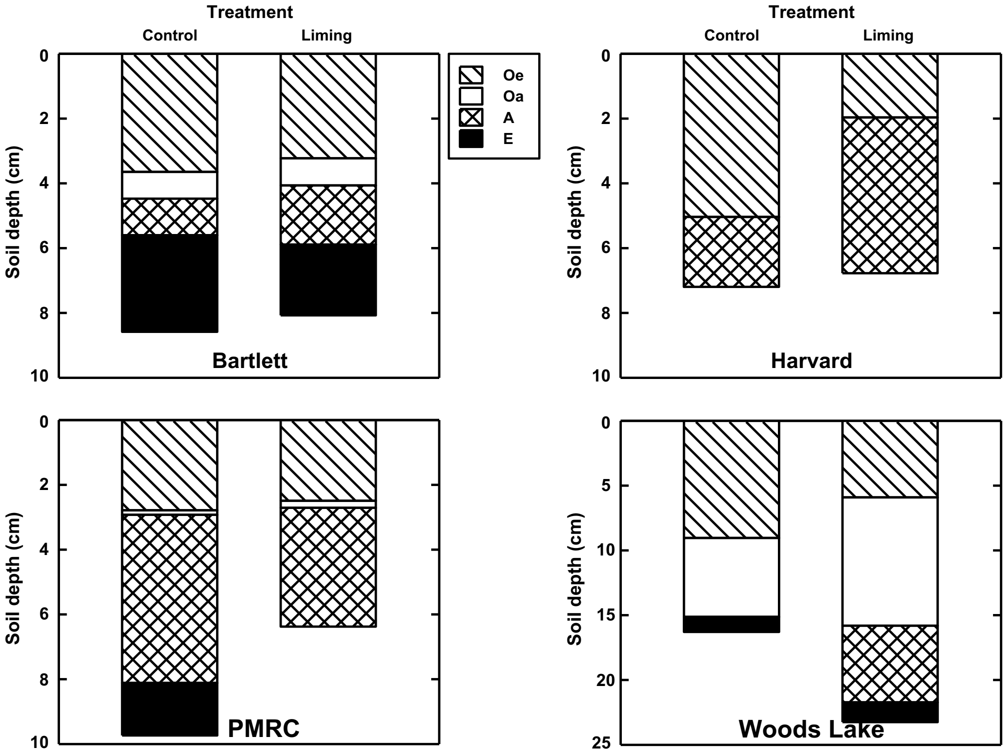


Figure 2-1. The depth of soil horizon between control and liming treatments at three sites. Data from the Woods Lake site are not presented here because of the small number of samples.

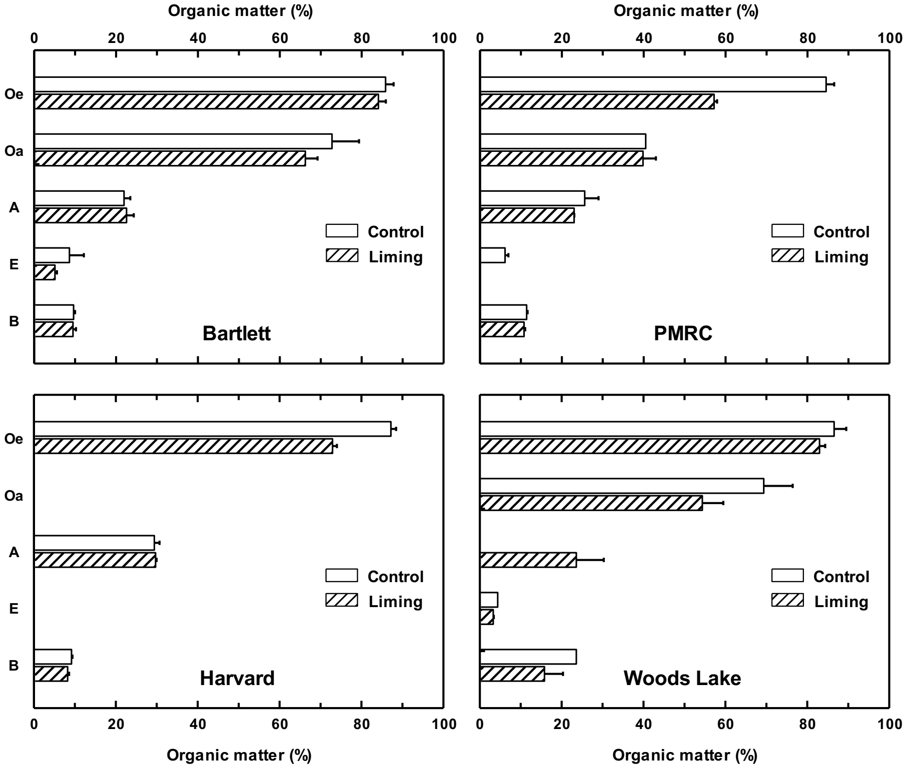


Figure 2-2. Soil organic matter concentration at the four study sites.

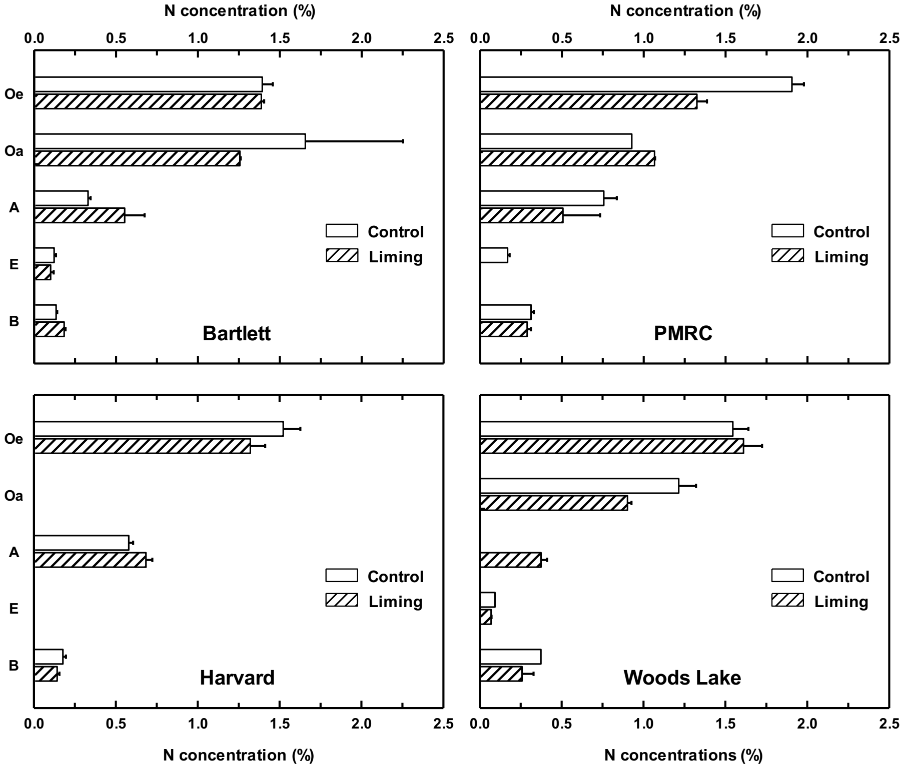


Figure 2-3. Nitrogen concentrations at the four study sites.

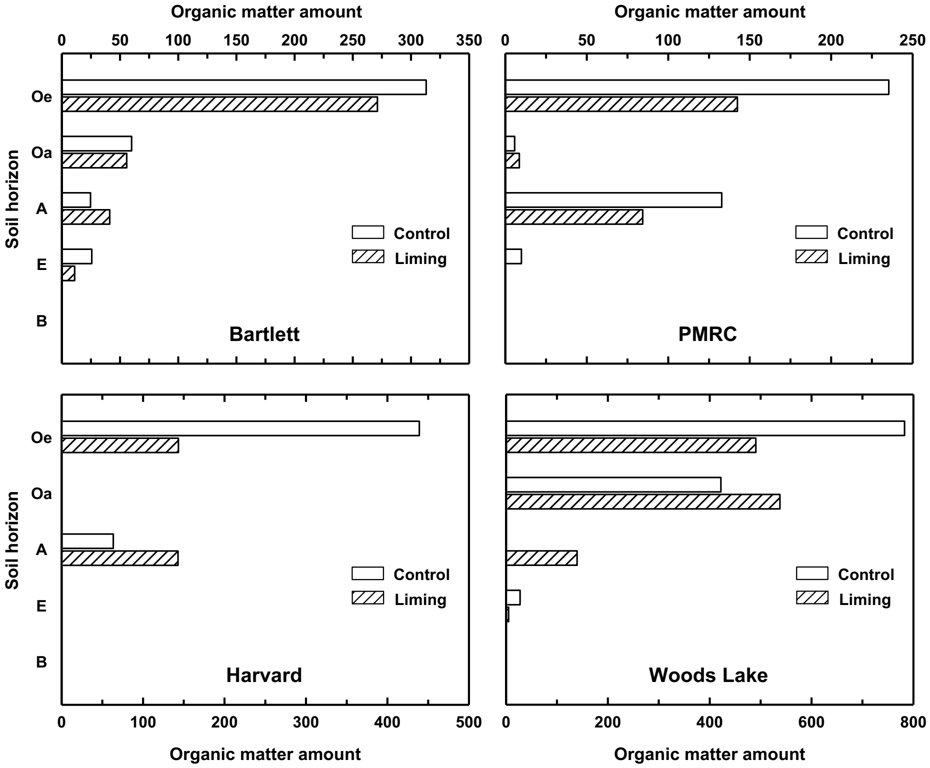


Figure 2-4. An index of organic matter contents at four study sites (proportional to both concentration and horizon thickness)

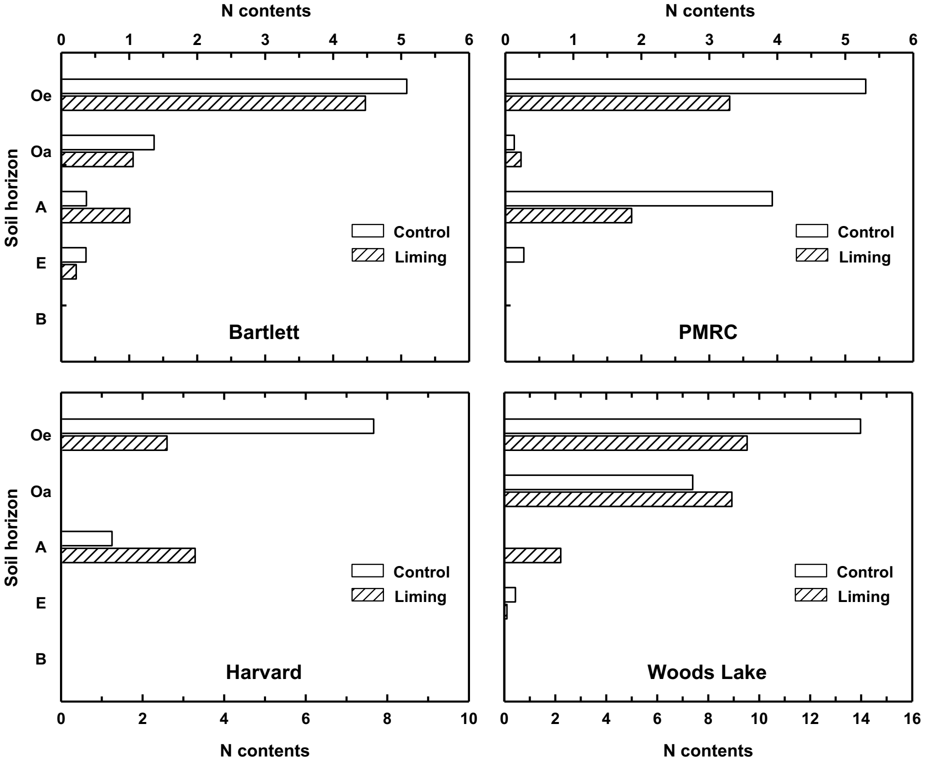


Figure 2-5. An index of N contents at four study sites (proportional to both concentration and horizon thickness)

4. Objective 3: Tree Response to Soil Sources of Calcium

A. Introduction

The land cover of New York State is primarily forest: 61% or 18.6 million acres (Alerich and Drake 1995). The northern hardwood cover-type is the most common across the state, covering 54% of timberland area; no other type covers more than 12% (Alerich and Drake 1995). Northern hardwoods are characterized by sugar maple, American birch and yellow birch. Red maple, black cherry, balsam fir and red spruce are common associates (Eyre 1980). Pin cherry and white (paper) birch are common only in young stands (Eyre 1980).

Our previous observations of litter chemistry and changes over time in forest floor Ca concentrations, and snail abundance in stands of different ages in New Hampshire northern hardwoods, led us to believe that young stands were mobilizing Ca from the mineral soil at a faster rate than older stands (Hamburg et al. 2003; Yanai et al. 2005). One possible explanation for this pattern is a successional change in species composition. The young stands we studied had a significant component of pin cherry, which drops out after about thirty years of stand development (Yanai et al. 2000). In the current study, we had the opportunity to study a wider variety of tree species than in our New Hampshire sites. We also had a wider variety of soil types, as described under Objective 1. The objective of this study was to compare litter samples of dominant species over a variety of sites to determine whether species differed in their response to the availability of soil Ca and other elements.

B. Sample collection and processing

In a subset of the stands represented in Table 3-1, we collected leaf litter from the dominant tree species: red maple, sugar maple, beech, pin cherry, white birch, and yellow birch (Figure 3-1). We compared freshly falling litter to leaves collected at the end of the fall season from permanent litter collectors. We determined that the Ca and Sr chemistry of leaves is not affected by the length of time they remain on the ground, in contrast to K, which is readily leached from leaves after they fall (Figure 3-1). This comparison supports the use of leaf litter to characterize tissue chemistry (Blum et al. 2008).

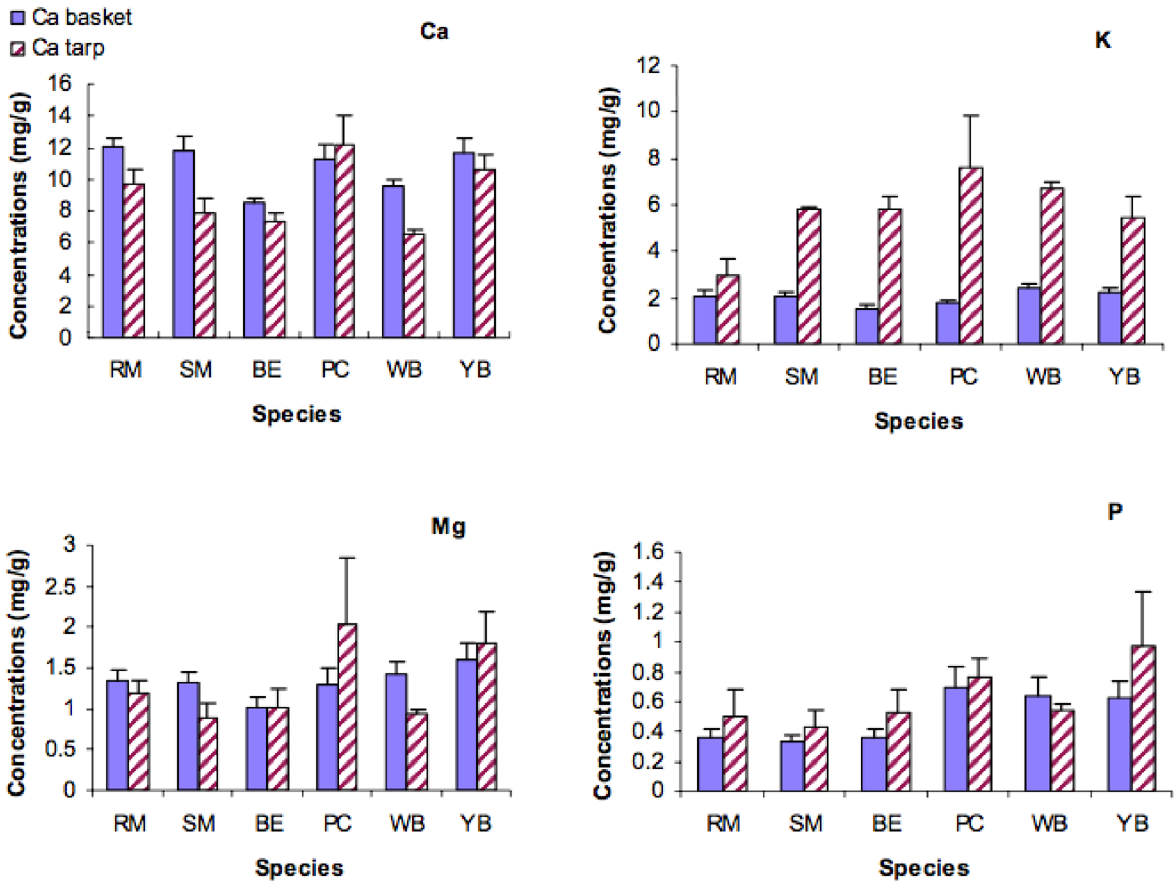


Figure 3-1. Nutrient concentration in leaf litter by species and collection method. "Tarp" is the method for collecting fresh litter samples during rain-free periods, while "baskets" collected leaves all fall.

Tissue analysis

Samples of litter (0.4 to 1 g dry weight) were digested in concentrated nitric acid using high pressure microwave digestion at 200°C and then diluted to a 10% nitric acid solution for analysis using ICP-OES, as described above for soil analyses.

C. Results

The sites were grouped into three classes of parent material, as described under Objective 1. Four sites had soils derived from crystalline silicate (grantoid) rocks, eight sites were formed from clastic sedimentary rocks derived from silicates, and seventeen sites were developed from carbonate rocks (Table 3-1).

Table 3-1. Classification of sites by parent material type.

Name	County	Bedrock	Soil Parent Materials
Happy Valley	Oswego	Sandstone and shale	Sedimentary clastic
Klondike	Oswego	Sandstone and shale	Sedimentary clastic
Black River	Herkimer	Silicate (?)	Crystalline silicate
Ferris Lake	Hamilton	Marble (?)	**Sedimentary clastic**
Southville	St. Lawrence	Limestone and dolostone	**Sedimentary clastic**
Fort Jackson	St. Lawrence	Limestone and dolostone	**Sedimentary clastic**
Brasher Falls (SE)	St. Lawrence	Limestone and dolostone	Sedimentary carbonate
Brasher Falls (NW)	St. Lawrence	Limestone and dolostone	**Sedimentary clastic**
Grantville	St. Lawrence	Limestone and dolostone	Sedimentary carbonate
Black Pond	Jefferson	Limestone and dolostone	Sedimentary carbonate
Lafayetteville	Dutchess	Slate or Phyllite	Crystalline silicate
Stissing Mt.	Dutchess	Slate or Phyllite	Crystalline silicate
Wassaic	Dutchess	Slate or Phyllite	Crystalline silicate
Five Points Road	Monroe	Limestone and dolostone	Sedimentary carbonate

The average elemental concentrations of soils developed on these three bedrock types are given in Table 3-2, with three soil extractions reported for each of three soil horizons. The cold nitric acid leach dissolves carbonates and apatite not occluded by silicates (Nezat et al. 2007). Leaf litter elemental concentrations are given in Tables 3-3.

We characterized soil Ca at each site with multiple extracts from multiple soil horizons. Figure 3-2 shows litter chemistry on the y axis graphed against soil extraction and soil horizon. The carbonate sites stand out with high Ca in all horizons and extracts. These soil measures are correlated with one another, but some differences are apparent. For many combinations of horizon and extractant, the crystalline silicates and clastic sedimentary soils had similar Ca concentrations. However, in the A horizon, the sedimentary soils had higher exchangeable Ca than the soils developed in crystalline silicate parent material. The pattern is reversed in the hot nitric extract of the B horizons, where the crystalline silicate sites have more Ca, on average, than the sedimentary sites. The leaf Ca concentrations of eight species or species groups was averaged for each of the three soil categories of soil parent material. Birch species, red maple, and other hardwoods (Table 3-3) had the highest Ca in leaf litter in the carbonate sites and showed the most response to soil type (steepest slopes in Figure 3-2). We found that birch species, red maple and sugar maple showed the most response to soil variation in Ca. Spruce and fir had low Ca across all sites. It is not yet clear from this analysis that any soil horizon or extract is a better predictor of leaf Ca.

D. Recommendations for future work

Because of the range of properties in parent materials, the effect of parent material on foliar concentrations should be analyzed with soil as a continuous variable (Ca availability as defined by the sequential extraction procedure) in multivariate regression. The analysis by classes of sites is a good start and represents the final product of the funded project. Additional publications can be expected to result from future work on these questions. We plan to use strontium isotopes and the ratio of calcium to strontium to determine the relative importance of atmospheric deposition, silicate weathering, and trace minerals as Ca sources to different tree species or forest types.

Table 3-2. Soil elemental concentrations by analysis method, bedrock type, and soil horizon.

Sequential				Al (*u*mol g^{-1})		Ba (*u*mol g^{-1})		Ca (*u*mol g^{-1})		Fe (*u*mol g^{-1})		K (*u*mol g^{-1})		Mg (*u*mol g^{-1})	
extracts	Horizon	Bedrock	n	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
Exchangeable	A	Silicate	4	0.10	0.03	0.10	0.03	0.67	0.16	0.02	0.01	0.89	0.20	0.19	0.10
		Clastic	8	5.17	2.41	5.17	2.41	8.66	5.22	0.30	0.13	2.33	0.71	2.04	0.96
		Carbonate	17	0.05	0.02	0.05	0.02	32.14	6.33	0.01	0.00	0.87	0.18	7.39	1.20
	B	Silicate	17	0.67	0.39	0.67	0.39	0.39	0.07	0.14	0.10	0.56	0.05	0.06	0.02
		Clastic	12	2.21	1.27	2.21	1.27	0.78	0.21	0.19	0.10	0.49	0.08	0.23	0.07
		Carbonate	27	0.22	0.13	0.22	0.13	19.55	5.56	0.10	0.06	0.49	0.08	5.19	1.82
	C	Silicate	4	0.23	0.15	0.23	0.15	0.42	0.18	0.02	0.02	0.38	0.07	0.08	0.05
		Clastic	4	0.28	0.08	0.28	0.08	1.98	1.29	0.16	0.09	0.39	0.11	0.91	0.61
		Carbonate	12	0.11	0.02	0.11	0.02	28.08	7.34	0.02	0.01	0.46	0.07	7.86	1.78
Cold HNO$_3$	A	Silicate	4	62.69	15.47	62.69	15.47	1.28	0.50	20.98	5.48	0.51	0.18	2.25	1.63
		Clastic	8	64.06	9.04	64.06	9.04	4.93	3.13	36.45	8.40	0.80	0.16	0.87	0.31
		Carbonate	17	62.00	11.47	62.00	11.47	70.62	14.36	16.15	3.42	0.50	0.10	43.33	15.62
	B	Silicate	17	99.32	28.56	99.32	28.56	3.46	0.92	29.42	9.48	0.54	0.07	3.58	1.36
		Clastic	12	119.89	17.89	119.89	17.89	3.98	1.06	46.81	8.90	0.43	0.05	1.02	0.20
		Carbonate	27	46.27	10.44	46.27	10.44	94.00	41.37	15.47	2.92	0.39	0.08	36.91	18.37
	C	Silicate	4	40.94	8.63	40.94	8.63	3.83	1.29	13.97	4.61	0.59	0.06	3.77	3.10
		Clastic	4	37.72	4.95	37.72	4.95	11.85	3.14	11.27	2.19	0.41	0.08	1.64	0.62
		Carbonate	12	26.53	2.92	26.53	2.92	1069.36	255.94	14.86	1.57	0.79	0.15	464.77	114.13
Hot HNO$_3$	A	Silicate	4	402.30	131.05	402.30	131.05	1.91	0.75	330.35	106.18	8.70	4.99	150.98	54.33
		Clastic	8	87.26	24.18	87.26	24.18	1.40	1.06	97.30	22.44	2.13	0.47	14.27	4.73
		Carbonate	17	113.24	10.65	113.24	10.65	9.13	1.85	117.76	15.10	2.97	0.43	41.76	5.47
	B	Silicate	17	406.85	59.44	406.85	59.44	2.34	0.44	361.81	45.10	22.56	15.39	173.55	34.19
		Clastic	12	146.70	24.79	146.70	24.79	0.62	0.16	161.03	25.28	2.56	0.35	42.30	6.44
		Carbonate	27	104.78	13.77	104.78	13.77	8.76	3.25	131.32	16.22	3.03	0.56	43.04	9.08
	C	Silicate	4	401.95	124.68	401.95	124.68	1.81	0.39	371.79	107.27	24.80	20.83	214.85	68.77
		Clastic	4	110.78	46.51	110.78	46.51	1.38	0.52	138.17	59.56	3.09	0.87	46.58	15.09
		Carbonate	12	114.17	28.80	114.17	28.80	90.58	31.54	146.95	31.84	5.97	1.23	110.89	32.77

Note: Silicate means crystalline silicate and clastic, and carbonate is included sedimentary bedrock type. In A horizon, some Oa horizons were included. I assumed several B horizon in each pit as replicate, so n is different by horizon. Less than LOD is 0 here.

Table 3-2 (continued). Soil elemental concentrations by analysis method, bedrock type, and soil horizon.

Sequential extracts	Horizon	Bedrock	n	Mn (*u*mol g^{-1})		Na (*u*mol g^{-1})		P (*u*mol g^{-1})		Si (*u*mol g^{-1})		Sr (*u*mol g^{-1})		Ti (*u*mol g^{-1})	
				Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
Exchangeable	A	Silicate	4	0.14	0.10	0.33	0.04	0.01	0.01	0.03	0.03	0.00	0.00	0.00	0.00
		Clastic	8	1.60	1.01	0.97	0.25	0.35	0.15	0.25	0.19	0.02	0.01	0.00	0.00
		Carbonate	17	0.04	0.01	2.88	1.01	0.00	0.00	0.13	0.02	0.07	0.02	0.00	0.00
	B	Silicate	17	0.03	0.01	0.38	0.08	0.00	0.00	0.05	0.02	0.00	0.00	0.00	0.00
		Clastic	12	0.04	0.02	0.62	0.12	0.00	0.00	0.07	0.02	0.00	0.00	0.00	0.00
		Carbonate	27	0.04	0.03	0.99	0.23	0.07	0.07	0.31	0.13	0.05	0.01	0.00	0.00
	C	Silicate	4	0.02	0.01	0.25	0.01	0.00	0.00	0.02	0.02	0.01	0.00	0.00	0.00
		Clastic	4	0.02	0.01	0.41	0.06	0.01	0.01	0.16	0.08	0.00	0.00	0.00	0.00
		Carbonate	12	0.05	0.04	1.54	0.61	0.00	0.00	0.43	0.08	0.04	0.02	0.00	0.00
Cold HNO_3	A	Silicate	4	3.38	1.30	0.47	0.03	3.73	3.15	3.66	1.91	0.00	0.00	0.11	0.04
		Clastic	8	5.77	2.98	0.52	0.04	4.04	1.20	6.01	1.96	0.01	0.00	0.36	0.10
		Carbonate	17	2.06	0.52	0.89	0.12	4.84	2.08	9.49	1.50	0.07	0.01	0.11	0.05
	B	Silicate	17	1.86	0.50	0.47	0.01	4.03	1.14	12.26	1.90	0.01	0.00	0.33	0.16
		Clastic	12	0.89	0.29	0.46	0.02	3.86	0.78	8.92	2.10	0.00	0.00	0.47	0.09
		Carbonate	27	1.48	0.30	0.71	0.09	9.87	4.86	8.91	2.34	0.07	0.03	0.12	0.04
	C	Silicate	4	1.22	0.42	0.45	0.02	3.26	0.93	12.37	3.75	0.01	0.00	0.12	0.08
		Clastic	4	0.41	0.08	0.43	0.03	8.79	2.10	9.25	1.92	0.01	0.00	0.14	0.06
		Carbonate	12	3.59	0.40	2.36	0.38	14.07	2.33	13.18	3.75	0.34	0.13	0.09	0.05
Hot HNO_3	A	Silicate	4	6.43	2.28	0.76	0.11	11.34	4.13	1.56	0.56	0.02	0.01	1.36	1.00
		Clastic	8	6.37	2.78	0.61	0.03	9.39	2.08	1.00	0.24	0.00	0.00	0.58	0.19
		Carbonate	17	1.20	0.29	0.90	0.06	6.97	1.02	1.99	0.08	0.02	0.00	0.27	0.12
	B	Silicate	17	6.62	1.44	0.86	0.12	7.35	1.51	2.13	0.40	0.02	0.00	3.12	1.60
		Clastic	12	1.69	0.33	0.66	0.03	4.76	0.81	0.88	0.19	0.00	0.00	0.58	0.14
		Carbonate	27	1.72	0.27	0.82	0.06	3.92	0.51	1.96	0.20	0.01	0.00	0.35	0.10
	C	Silicate	4	9.23	3.47	0.91	0.18	3.80	1.01	2.17	0.96	0.01	0.00	2.32	2.10
		Clastic	4	2.26	0.83	0.69	0.04	3.17	1.04	0.85	0.44	0.00	0.00	0.53	0.18
		Carbonate	12	1.68	0.40	1.16	0.21	3.32	0.78	1.93	0.34	0.05	0.02	1.17	0.65

Table 3-3. Leaf litter nutrient concentrations by species and bedrock type.

Species	Bedrock type	n	Al (mg g^{-1})		Ca (mg g^{-1})		Fe (mg g^{-1})		K (mg g^{-1})		Mg (mg g^{-1})	
			Mean	SE	Mean		Mean	SE	Mean	SE	SE	Mean
Beech	Silicate	1	0.085	.	7.23	.	0.120	.	4.74	.	1.52	.
	Clastic	2	0.215	0.001	8.76	0.64	0.251	0.015	1.08	0.13	0.45	0.00
	Carbonate	5	0.210	0.098	9.99	1.16	0.206	0.082	3.68	1.54	1.21	0.11
Birch	Silicate	3	0.058	0.006	11.40	1.61	0.081	0.009	7.04	2.33	2.58	0.38
	Carbonate	3	0.121	0.040	20.80	5.60	0.125	0.045	8.81	2.61	4.08	0.85
Oak	Silicate	3	0.117	0.023	9.28	2.05	0.100	0.014	3.64	1.85	1.30	0.12
	Clastic	3	0.149	0.017	10.24	1.59	0.123	0.008	0.91	0.08	0.53	0.11
	Carbonate	2	0.145	0.066	8.62	0.59	0.087	0.027	2.85	1.67	1.09	0.38
Red maple	Silicate	3	0.024	0.006	7.69	0.14	0.051	0.006	4.63	0.30	1.43	0.05
	Clastic	2	0.045	0.019	7.87	1.11	0.065	0.013	2.53	0.16	1.42	0.39
	Carbonate	5	0.448	0.378	16.37	6.69	1.824	1.731	4.30	0.99	2.30	0.42
Sugar maple	Silicate	2	0.044	0.004	9.15	0.12	0.076	0.005	8.01	1.12	1.50	0.33
	Clastic	1	0.201	.	12.36	.	0.249	.	1.65	.	0.72	.
	Carbonate	2	0.849	0.818	14.74	9.71	0.825	0.761	3.87	2.77	1.89	0.91
Others	Silicate	4	0.045	0.009	9.85	1.82	0.060	0.005	8.29	1.19	2.09	0.28
	Clastic	1	0.028	.	8.46	.	0.065	.	6.62	.	4.05	.
	Carbonate	12	1.019	0.340	19.09	2.76	1.759	0.788	3.39	0.84	3.02	0.50
Spruce-fir	Silicate	1	0.276	.	7.34	.	0.104	.	3.09	.	0.99	.
	Clastic	1	0.241	.	5.37	.	0.047	.	5.72	.	1.47	.
	Carbonate	4	0.400	0.085	8.06	4.19	0.291	0.106	4.21	1.48	1.54	0.22
Pine	Clastic	1	0.360	.	9.82	.	0.117	.	1.28	.	0.90	.
	Carbonate	4	0.445	0.032	4.17	0.62	0.053	0.006	1.71	0.47	0.69	0.31

Birch includes gray birch, white birch, and yellow birch. Oak includes red oak and white oak. Others include American basswood, bigtooth aspen, black cherry, black walnut, quaking aspen, and white ash.

Table 3-3 (continued). Leaf litter nutrient concentrations by species and bedrock type.

Species	Bedrock type	n	Mn (mg g^{-1})		P (mg g^{-1})		Si (mg g^{-1})		Sr (mg g^{-1})		Ti (mg g^{-1})	
			Mean	SE	Mean	SE	Mean	SE	Mean	SE	SE	Mean
Beech	Silicate	1	1.275	.	0.868	.	0.364	.	0.030	.	0.001	.
	Clastic	2	0.670	0.018	0.794	0.101	0.431	0.035	0.021	0.002	0.005	0.001
	Carbonate	5	0.777	0.321	1.009	0.172	0.415	0.016	0.021	0.003	0.005	0.003
Birch	Silicate	3	3.689	0.527	1.507	0.157	0.408	0.058	0.051	0.008	0.000	0.000
	Carbonate	3	0.534	0.421	1.013	0.324	0.265	0.129	0.040	0.008	0.003	0.002
Oak	Silicate	3	2.971	0.556	1.122	0.340	0.400	0.134	0.025	0.004	0.001	0.001
	Clastic	3	0.989	0.172	0.585	0.061	0.392	0.193	0.017	0.003	0.002	0.000
	Carbonate	2	1.744	0.792	1.165	0.437	0.467	0.145	0.018	0.006	0.002	0.002
Red maple	Silicate	3	1.272	0.459	0.720	0.202	0.468	0.026	0.031	0.001	0.000	0.000
	Clastic	2	1.249	0.272	0.649	0.043	0.418	0.090	0.023	0.006	0.000	0.000
	Carbonate	5	0.756	0.342	0.946	0.213	0.375	0.089	0.017	0.004	0.012	0.010
Sugar maple	Silicate	2	1.833	0.232	2.146	0.408	0.434	0.005	0.053	0.010	0.000	0.000
	Clastic	1	1.114	.	1.157	.	0.388	.	0.034	.	0.004	.
	Carbonate	2	0.426	0.301	0.723	0.391	0.227	0.193	0.078	0.057	0.025	0.025
Others	Silicate	4	0.509	0.099	1.412	0.406	0.392	0.099	0.046	0.013	0.000	0.000
	Clastic	1	1.171	.	0.971	.	0.099	.	0.036	.	0.000	.
	Carbonate	12	0.157	0.063	0.742	0.137	0.227	0.071	0.056	0.020	0.040	0.014
Spruce-fir	Silicate	1	0.393	.	1.163	.	0.179	.	0.025	.	0.001	.
	Clastic	1	0.581	.	1.204	.	0.178	.	0.004	.	0.000	.
	Carbonate	4	0.534	0.483	1.036	0.343	0.130	0.063	0.026	0.011	0.008	0.004
Pine	Clastic	1	0.716	.	0.917	.	0.051	.	0.018	.	0.002	.
	Carbonate	4	1.034	0.298	0.592	0.234	0.292	0.024	0.011	0.003	0.000	0.000

Spruce-fir includes balsam fir, hemlock, white spruce, and northern white cedar. Pine includes scotch pine, red pine, white pine, and pitch pine

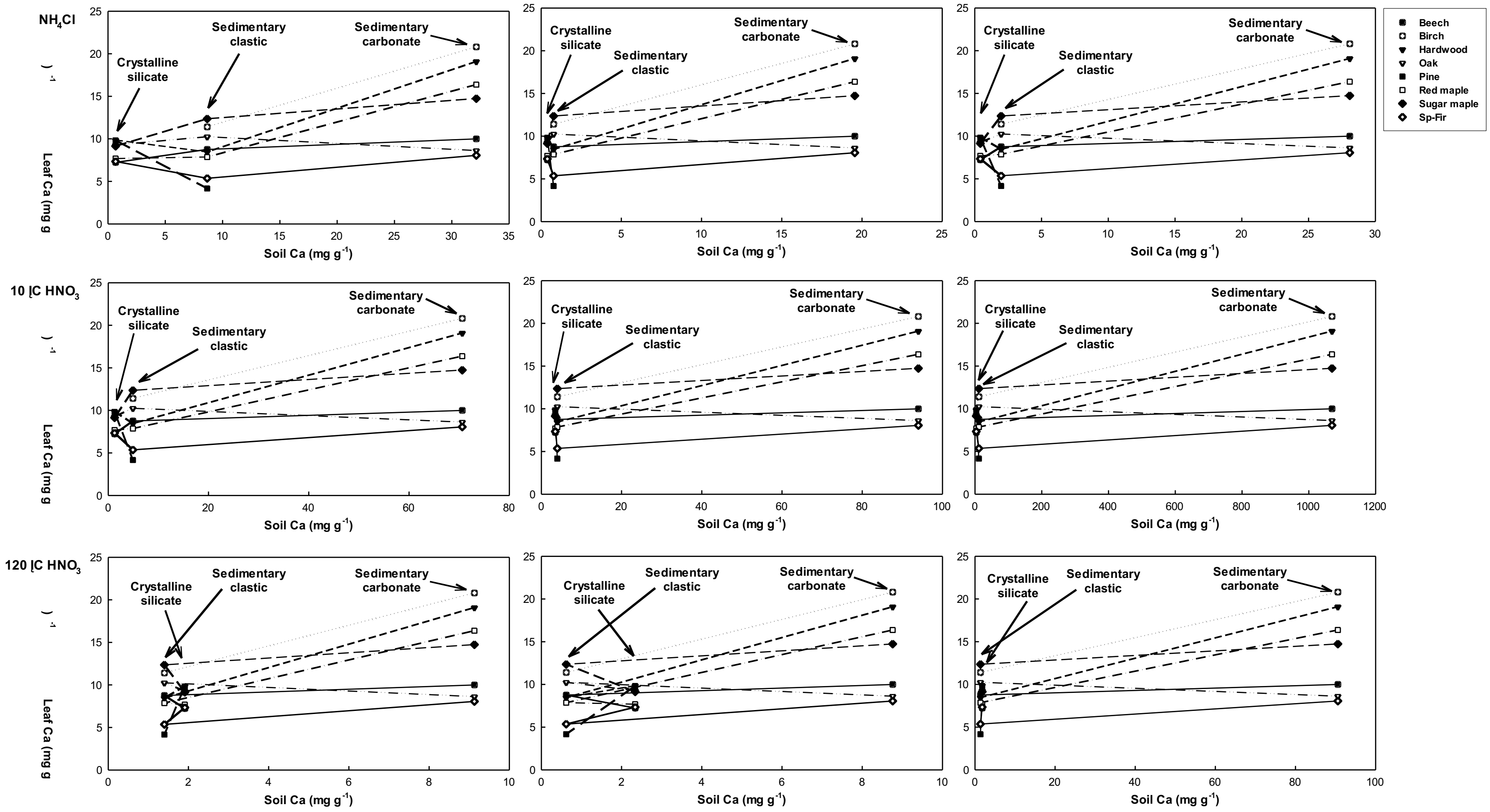


Figure 3-2. Leaf Calcium versus Calcium in the A horizon (left), B horizon (center), and C horizon (right) by extraction method.

5. Usefulness and Value of Project Results

There has long been concern that base cations are being depleted from forest soils in the northeastern United States as a result of acid rain (Shortle and Bondietti, 1992; Likens et al., 1998). These losses from soil were predicted to be compounded by timber harvesting and the associated loss of nutrients, with Ca the element most likely to become limiting (Federer et al., 1989). Retrospective studies have reported dramatic declines in pools of exchangeable base cations (Johnson et al., 1994; Knoepp and Swank, 1994; Huntington et al., 2000). The loss of cations in general and Ca in particular over past decades is thought to have adversely affected forest productivity and health in eastern North America (Shortle and Bondietti, 1992) and Europe (Ulrich et al., 1980; Graveland et al., 1994). Clearly, assessing the importance of regulating pollutants associated with the generation of electricity depends on accurate assessments of the threat posed to ecosystems by cation depletion.

We addressed one aspect of soil acidification by comparing forest soils that have been undisturbed but receiving ambient acidic deposition with soils that had been treated with lime to reverse the acidification process. We found more organic matter and nitrogen in soils that were not treated. This comparison suggests that soils may be storing more C and N in organic matter over time as they acidify.

Our examination of parent materials in forest soils across New York State demonstrates that the pool of readily weathered Ca can be substantial. In non-carbonate rocks, this pool has not traditionally been included in assessment of Ca availability to plants, and the threat of Ca depletion is probably not as great as previously supposed. More research is needed to interpret the degree to which forest management could be used to improve Ca availability to forests via weathering of native soil minerals.

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ASSESSING THE SENSITIVITY OF NEW YORK FORESTS TO CATION DEPLETION FROM ACID RAIN

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