

## INFLUENCES OF A CALCIUM GRADIENT ON SOIL INORGANIC NITROGEN IN THE ADIRONDACK MOUNTAINS, NEW YORK

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**Abstract.** Studies of the long-term impacts of acidic deposition in Europe and North America have prompted growing interest in understanding the dynamics linking the nitrogen (N) and calcium (Ca) cycles in forested watersheds. While it has been shown that increasing concentrations of nitrate ( $\text{NO}_3^-$ ) through atmospheric deposition or through nitrification can increase Ca loss, the reciprocal effects of Ca on N transformation processes have received less attention. We studied the influence of soil Ca availability on extractable inorganic N ( $\text{NO}_3^- + \text{NH}_4^+$ ) across a Ca gradient in the Adirondack Mountains, New York, USA. Our results did not show the direct Ca–N interaction that we had expected, but instead showed that exchangeable Ca coupled with soil moisture, soil organic matter, and ambient temperature accounted for 61% of the variability in extractable inorganic N across 11 sites over two growing seasons. Soil Ca concentrations were, however, positively related to sugar maple (*Acer saccharum*) and American basswood (*Tilia americana*) basal areas and negatively related to American beech (*Fagus grandifolia*) basal area. Based on litter chemistry differences among these tree species and reported potential N mineralization values, we suggest that the influence of Ca on soil inorganic N is through a multistep pathway: reciprocal interactions between soil Ca concentrations and species composition, which in turn affect the quality of litter available for N mineralization. If chronic soil Ca depletion continues, as reported in some forested ecosystems, potential shifts in biotic communities could result in considerable alterations of N cycling processes.

**Key words:** *Acer saccharum*; Adirondack Mountains, New York, USA; American basswood; American beech; calcium; *Fagus grandifolia*; nitrogen; soil; sugar maple; *Tilia americana*.

### INTRODUCTION

Much of the research on calcium (Ca) in forested ecosystems has focused on its role in buffering soil and water pH (Schlesinger 1997, Likens et al. 1998) and as an essential nutrient for plants and animals (Berne and Levy 1996, Graveland and van der Wal 1996, McLaughlin and Wimmer 1999). However, Ca may also play an important role in affecting the nitrogen cycle. In this paper, we use existing literature and new data to consider the potential influences of soil Ca concentrations on vegetation and microbial communities, litter quality, and the substrate available for microbial N mineralization.

Soil Ca availability can be influenced by a number of variables, including atmospheric deposition, soil exchange pools, retention in biomass, soil leaching, timber harvesting, and mineral weathering. Potential mineral sources of Ca include plagioclase, calcite, dolomite, hornblende, pyroxene, and apatite. Blum et al. (2002) suggested that ectomycorrhizal fungi may be involved in the direct weathering of apatite and transport of Ca to

associated trees, bypassing the exchangeable Ca pool in the soil. A substantial amount of Ca is also made available by internal recycling among the soil exchangeable, forest vegetation, and organic matter pools (Likens et al. 1998). The rates of Ca mineralization from vegetation have been found to be correlated with litter decomposition rates and can vary significantly among species (Dijkstra 2003). Some of the internal Ca cycling pathways in forest ecosystems have recently been explored through the use of stable Ca isotopes (Wiegand et al. 2005, Perakis et al. 2006, Page et al. 2008).

The availability of Ca in the soil can influence plant species composition (Bigelow and Canham 2002, McGee et al. 2007), and species composition can in turn affect soil chemistry (Binkley and Giardina 1998, van Breemen and Finzi 1998). Sugar maple (*Acer saccharum*) tends to grow best on fertile, well-drained sites with relatively high Ca concentrations (Horsley et al. 2002, Kobe et al. 2002). In a study of old-growth forests in Upper Michigan, Fujinuma et al. (2005) indicated that both sugar maple and American basswood (*Tilia americana*) have relatively high demands for base cations including Ca and magnesium (Mg). Beech trees are generally regarded to be less sensitive than sugar maple to growth on sites with reduced soil Ca concentrations (Duchesne et al. 2005). Arii and Lechowicz (2002) found that the relative dominance of beech was inversely related to soil

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pH and Ca concentrations. Decreased vigor of species including sugar maple (Horsley et al. 2002, Bailey et al. 2004) and red spruce (*Picea rubens*; Shortle and Smith 1988) has been linked to low soil Ca concentrations.

Litter quality can vary substantially among plant taxa (Aber and Melillo 1982, Berg and McClaugherty 1987, Ollinger et al. 2002), influencing the chemical quality of substrate available for N mineralization and nitrification (Knoepp and Swank 1998, Lovett et al. 2004, Page and Mitchell 2008). For example, litter from beech (*Fagus*) and oak (*Quercus*) typically have lower mineralization and nitrification rates than maple (*Acer*) litter (Pastor and Post 1986, Finzi et al. 1998b). Studies that compared N mineralization rates among sites in New York and Ontario (Mitchell et al. 1992b) and within the northeastern United States (Lovett and Rueth 1999) found that soil  $\text{NO}_3^-$  and potential nitrification rates were higher in stands dominated by sugar maple as compared to those with greater American beech (*Fagus grandifolia*) dominance. The differences in litter quality between beech and sugar maple are often attributed to the relatively high lignin and phenolic content in beech leaves (Finzi et al. 1998b). Scott and Binkley (1997) found that lignin:N ratios were more important than other litter quality or quantity variables for explaining variation in N mineralization rates.

In addition to litter quality, soil N concentrations and the rates of organic matter mineralization are also affected by soil physical and chemical characteristics (Strong et al. 1999a, b, Sariyildiz and Anderson 2003) and climate (Meentemeyer 1978, Aerts 1997). Atmospheric deposition can also increase available soil N through input of nitrate ( $\text{NO}_3^-$ ) and ammonium ( $\text{NH}_4^+$ ) from sources including fossil fuel combustion, volatilized fertilizer, biomass burning, and lightning (Vitousek et al. 1997, Driscoll et al. 2003b).

Calcium may be involved in important physical and metabolic functions in bacterial cells (Norris et al. 1991, Dominguez 2004), which could affect N cycling. For example, low Ca concentrations could limit the growth of *Nitrosomonas* and *Nitrobacter* (nitrifying bacteria), either directly through affecting bacterial structural and regulatory functions (see Norris et al. 1991) or indirectly if reduced *Azotobacter* growth (Norris and Jensen 1957) resulted in lower N fixation and decreased availability of N for mineralization and nitrification (Williard et al. 2005).

Soil N is subject to nitrification, microbial immobilization, abiotic immobilization, vegetation uptake, and denitrification. If available soil N exceeds biotic demands, the system can become N "saturated" and result in N leaching (Aber et al. 1998). Leaching of soil N is most likely to occur during periods of vegetation dormancy and during large hydrological fluxes, such as snow melt and storm events (Mitchell et al. 1992a, 2003, McHale et al. 2002). Seasonal wet-dry and freeze-thaw cycles can also have a substantial influence on available N as drying and freezing can disrupt microbial cells and



FIG. 1. Map of study sites within Adirondack Park, New York State, USA.

soil organic matter, resulting in a build-up of soluble, N-rich substrates that can be rapidly mineralized with the onset of more favorable environmental conditions (Haynes 1986a). The leaching of  $\text{NO}_3^-$ -N is associated with a charge-equivalent loss of cations, frequently including Ca and Mg (Tomlinson 2003). In an analysis of 21 forested catchments across North America and Europe, Watmough et al. (2005) indicated that  $\text{NO}_3^-$  export was significantly correlated with Ca export and suggested that these links may be most evident at base-rich sites where rates of nitrification, an acidifying process, may be enhanced.

Our objective in this study was to determine the potential influence of soil Ca concentrations on the availability of extractable inorganic N ( $\text{NO}_3^- + \text{NH}_4^+$ ) within northern hardwood forests in the Adirondack Mountains of New York State.

## METHODS

### Site descriptions

We sampled 11 sites in the central Adirondack Mountains located between  $74^{\circ}00'$  and  $74^{\circ}35'$  W and between  $43^{\circ}30'$  and  $44^{\circ}15'$  N (Fig. 1). Elevation ranged from 475 to 603 m. Sites were selected according to the following criteria: (1) on property owned by New York State or the State University of New York College of Environmental Science and Forestry, (2) no evidence of recent timber harvesting, fire, or wind disturbance, (3) mixed hardwood stands dominated by sugar maple and American beech, (4) stands appearing to be of similar age by diameter at breast height (dbh) of dominant trees, and (5) stands with mature white ash (*Fraxinus*

*americana*), a non-climax and relatively shade-intolerant species (Merrens and Peart 1992), as an indicator of similar stand structure and age. In addition we sought information from other researchers working in the region who have previously identified both base-rich and base-poor sites as indicated by vegetation communities or soil chemistry data. It may be noteworthy that earthworms were found in the upper soil horizons at only two sites (Balfour and T3 and 30) and likely influenced organic matter mineralization, though their effects were not directly evaluated in our study.

#### Sampling

Forest floor and upper mineral soils were sampled six times: in May, June, and September 2004 and in May, July, and August 2005. The forest floor was sampled by removing the Oi horizon and cutting a small square  $\sim 20 \times 20$  cm into the Oe/Oa horizon with a knife. The forest floor–mineral soil boundary was estimated based on fine-root density, color contrast between darker organic matter and lighter mineral soil, and a qualitative texture assessment. Mean forest floor depth among sites was 2.8 cm (range 0.5–4.8 cm), with considerable intrasite variability. Each collected sample was homogenized in a bucket with a gloved hand; one subsample was placed in a cup containing 70 mL of 2 mol/L potassium chloride (KCl) solution for extraction of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  (modified from Mulvaney 1996). The remaining subsample was sealed in a polyethylene bag, and both subsamples were returned to the laboratory, where they were stored at 4°C prior to analysis. The upper mineral soil (0–10 cm) was sampled using a “bulb planter corer” under the location of the forest floor sample. Individual mineral soil samples were homogenized in a bucket and sealed in a polyethylene bag for later analysis. Field KCl extractions were only performed on mineral samples collected in 2005. Field KCl extractions were processed in the laboratory one to five days after collection based on the order in which sites were sampled. The sampling order of sites was alternated to reduce potential bias.

In 2004, a forest floor and upper mineral soil sample was collected from each of four plots at each site: a central plot and three plots radiating 30 m from the central plot at 120°, 240°, and 360°. In 2005, soil was not sampled from the central plot because forest floor compaction was becoming evident. Species composition and dbh of trees  $\geq 10$  cm were recorded at each site in July 2004 using a point-quarter method at the central plot and at one randomly selected outlying plot. Leaf litter samples were collected every two weeks during the 2004 litterfall period (13 September to 28 October) in nets  $\sim 2 \times 2$  m<sup>2</sup> and suspended  $\sim 2$  m above the ground at the center plot and at two randomly selected outlying plots at each site.

Due to preexisting plots and instrumentation at sites 14 and 15 (Christopher et al. 2006), these sites were sampled slightly differently than the other nine sites as outlined above. Both sites were set up as grids consisting of  $20 \times 20$  m plots. At each site, one plot without

instrumentation at lower, middle, and upper positions was randomly selected for sampling. The dates and method of sampling at sites 14 and 15 were the same as those outlined above for the other nine sites except for the vegetation assessments, which took place in July 2005. Forest floor, mineral soil, and leaf litter samples were collected from the center of each plot.

#### ANALYSES

##### Field extractions

Field extractions were filtered through Whatman 42 ashless filter paper, rinsed three times with 10 mL of 2 mol/L KCl and the filtrate was raised to 100 mL with 2 mol/L KCl. A 20-mL subsample of the filtrate was decanted and mixed with three to four drops of chloroform for preservation. Nitrate and  $\text{NH}_4^+$  concentrations were determined using continuous flow colorimetry on a Bran-Luebbe AutoAnalyzer3 (SPX, Charlotte, North Carolina, USA).

To determine initial soil mass extracted, the wet, filtered soil in the original container along with the used filter paper were weighed for initial mass. The container and contents were then oven-dried at 65°C, and dry mass was determined. The mass of the residual KCl was determined as: moisture loss in grams  $\times 0.149$  g KCl/g water, assuming that all moisture remaining in the sample after extraction and filtration was 2 mol/L KCl. The estimated dry mass of the extracted soil was determined as: dry mass of container with contents – calculated residual KCl mass – mass of unused, oven-dried filter paper – mass of clean, dry container. To assess this method of estimating initial soil mass, the same extraction and drying procedure was also performed on 10–12 subsamples returned from the field with initial mass and moisture content previously determined. Using these samples of known initial mass, regression equations ( $R^2 = 0.99$ ,  $P < 0.0001$ ) were developed to predict the actual dry soil mass from the estimated mass. These regression-derived masses were then used to determine KCl-extractable N concentration in the soil.

##### Forest floor

Soil moisture was determined gravimetrically by oven-drying subsamples at 65°C. Soil pH was determined potentiometrically in a 2:1 slurry of 0.01 mol/L  $\text{CaCl}_2$ : fresh forest floor sample (modified from Thomas 1996). Forest floor samples were then oven-dried at 65°C and ground in a Wiley mill using a number 20 (0.85-mm) screen. Cation concentrations (Al, Ca, Fe, K, Mg, Mn, Na, P, S, and Zn) and percentage of organic matter were determined by ashing a 1-g homogenized sample at 470°C for 16 h and dissolving the ash in 10 mL of 6 mol/L HCl (modified from Jones and Case 1990). The acid solution was then evaporated to dryness on a hot plate and then the cations were redissolved in 10 mL of 6 mol/L HCl. The solution was filtered through Whatman 42 ashless filter paper, rinsed three times with deionized, distilled water ( $\text{ddH}_2\text{O}$ ), and raised to 100 mL with

ddH<sub>2</sub>O. Cations concentrations were determined with a Perkin-Elmer Optima DV 3300 inductively coupled plasma optical emission spectrometer (ICP-OES; Perkin-Elmer, Waltham, Massachusetts, USA). Percentage of carbon (C) and N were determined only for the 2004 samples on a Thermo Electron Flash EA 1112 elemental analyzer (Thermo Fisher Scientific, Waltham, Massachusetts, USA). Percentage of lignin was determined for September 2004 samples by the Dairy One Forage Laboratory in Ithaca, New York, USA, using an ANKOM A200 fiber analyzer (ANKOM Technology, Macedon, New York, USA).

#### *Mineral soil*

Upper mineral soil moisture content and pH were determined with the same method used for forest floor samples. Mineral soil samples were then air-dried and sieved to 2 mm to remove larger fragments. Exchangeable cations (Al, Ca, Fe, K, Mg, Mn, Na, P, S, and Zn) were isolated by extracting ~10 g dry soil in 50 mL of 1 mol/L ammonium chloride (NH<sub>4</sub>Cl; Blume et al. 1990), filtering through Whatman 42 ashless filter paper, rinsing three times with 10 mL of 1 mol/L NH<sub>4</sub>Cl, and raising volume to 100 mL with 1 mol/L NH<sub>4</sub>Cl. Samples were frozen until analyzed for cation concentrations using a Perkin-Elmer Optima DV 3300 ICP-OES. Percentage of organic matter was calculated as loss-on-ignition at 470°C for 16 h. Percentages of C and N for mineral soil were determined only for September 2004 samples as described for forest floor samples.

#### *Leaf litter*

Air-dried leaf litter collected over the litterfall period was pooled by plot (33 total) and sorted by species. Species analyzed were sugar maple, American beech, American basswood, and white ash. Subsamples of each plot–species combination were ground in a Wiley mill using a number 20 (0.85-mm) screen. Cations, organic matter, C, N, and lignin were determined as detailed above for forest floor samples. The leaflets and petioles of the compound leaf of white ash were analyzed separately because most petioles passed through the collection nets. From the complete ash leaves that were collected, we calculated that the petiole accounted for an average of 13.3% of the dry leaf mass. We used this mass calculation and the mean chemistry values from ash petioles to estimate mean mass-weighted chemistry values for whole-leaf ash litter. The whole-leaf data were used in all subsequent white-ash analyses.

#### *Climate data*

Climate data were obtained from the National Climate Data Center of the National Oceanic and Atmospheric Administration for the Newcomb, New York, station (elevation 494 m; data *available online*).<sup>2</sup>

<sup>2</sup> (<http://www.ncdc.noaa.gov>)

Temperature data were considered at five levels: mean temperature on the date of soil sampling, mean temperature from 3, 10, 20, and 30 d prior to sampling. Temperature values were adjusted for the elevation of each site using the adiabatic lapse rate of 0.6°C/100-m elevation change (Jobbágy and Jackson 2000). The same five time increments were used for precipitation data.

#### *Statistical analysis*

Vegetation data were analyzed as basal area means by site. Relationships comparing relative basal areas of sugar maple, beech, basswood, and white ash to exchangeable Ca in the mineral soils were analyzed using linear regression. Exchangeable Ca was transformed using the natural logarithm to normalize the data.

Statistics for field-extracted inorganic N were calculated using the sum of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> (expressed as micromoles of N per gram of dry soil). The inorganic N variable was transformed using the natural logarithm. Soil variables (moisture, pH, organic matter, cation concentrations, and molar Ca:Al ratios for both forest floor and mineral soil) and climate variables (precipitation and temperature values from the sampling dates and means from 3, 10, 20, and 30 d prior to the sampling dates) were entered into a stepwise regression model to identify the most significant variables that predict extractable inorganic N from the forest floor samples. In the stepwise selection procedure, variables with *P* values ≤0.10 entered the regression model and remained in the model if *P* values remained ≤0.05 through the selection procedure. We used variance inflation factors (VIF) and correlation matrices to test for collinearity. The resulting multiple regression equation was plotted as predicted inorganic N against measured inorganic N with a 1:1 reference line as plotted by Venterea et al. (2003). Pearson correlation coefficients were determined for soil pH and Ca. Comparisons of litter chemistry means among species were conducted using ANOVA and Tukey's mean separation test (SAS Institute 1999).

#### RESULTS

There were no observed trends relating total basal area to mineral soil exchangeable Ca (Fig. 2; sites ranked from high to low Ca). However, the relative basal areas of sugar maple and basswood were positively related, and the basal area of beech was negatively related to mean soil exchangeable Ca concentrations (Fig. 3): sugar maple relative basal area =  $0.59 + 0.17 \times \ln(\text{Ca})$  ( $P = 0.08$ ,  $R^2 = 0.31$ ); American beech relative basal area =  $0.13 - 0.13 \times \ln(\text{Ca})$  ( $P = 0.04$ ,  $R^2 = 0.40$ ); American basswood relative basal area =  $0.04 + 0.05 \times \ln(\text{Ca})$  ( $P = 0.03$ ,  $R^2 = 0.42$ ); where  $\ln(\text{Ca})$  = natural logarithm of exchangeable Ca (in milligrams per gram) in the upper 0–10 cm mineral soil. The relationship between white-ash relative basal area and exchangeable Ca was not significant ( $P = 0.50$ ,  $R^2 = 0.05$ ). While basswood was only tallied during vegetation sampling in

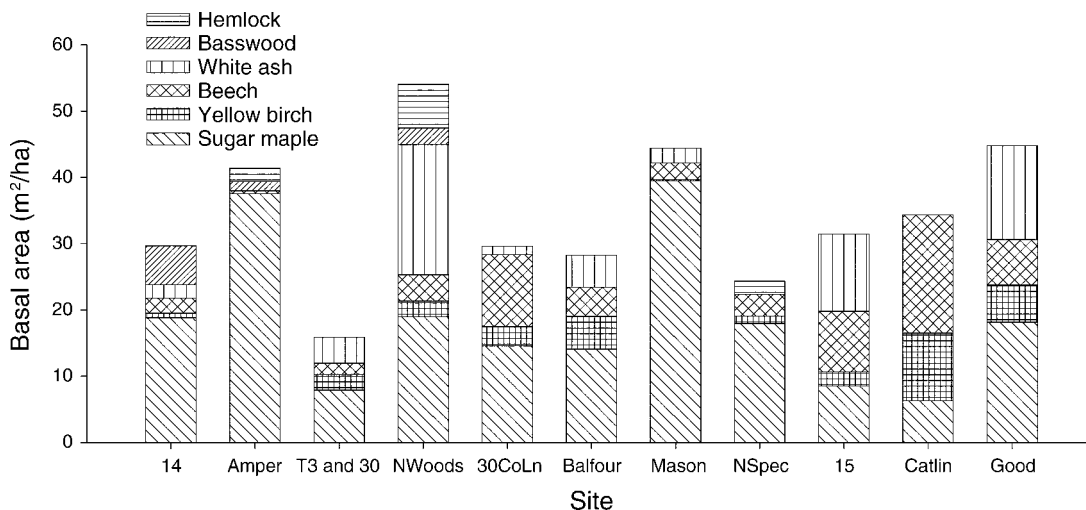


FIG. 2. Cumulative basal area of trees  $\geq 10$  cm dbh. Measurements were made during the 2004 and 2005 growing seasons in the central Adirondack Mountains, New York. Site order is from high to low exchangeable Ca in the upper (0–10 cm) mineral soil.

three sites (14, NWoods, and Amper), it also occurred at low densities in three additional sites (T3 and 30, 30CoLn, and Mason) and was represented in litter collections from each of these six sites.

In a comparison of litter chemistry from all sites, the lignin:N ratio was significantly greater for beech than that for sugar maple, which was greater than that for white ash and basswood. The difference in lignin:N was not significant between basswood and white ash. Basswood litter had the highest concentrations of base cations (Ca, K, and Mg) and N, while beech had the highest percentage of C and lignin by mass (Table 1). A comparison of two common litter quality indices, lignin:N and C:N ratios, showed that basswood had the greatest litter quality among the evaluated species (Fig. 4).

Mean forest floor and mineral soil chemistry data show the range of soil variables among sites (Table 2A, B, respectively). The sites in the table are ranked from high to low exchangeable Ca in the mineral soil. Multiple regression analysis indicates that 61% of the variability ( $P < 0.001$ ,  $R^2 = 0.61$ ) in field-extracted inorganic N (hereafter “field N”) from the forest floor can be explained by the following relationship:

$$\ln(\text{field N}) = 0.93 - (2.76 \times \text{Moist}) + (3.20 \times \text{OM}) + (0.14 \times \text{Ca}) - (0.07 \times \text{Temp})$$

where  $\ln(\text{field N})$  is the natural logarithm of forest floor inorganic N, Moist is the moisture proportion in the forest floor, OM is the proportion of organic matter in forest floor, Ca is the Ca in mineral soil (in milligrams

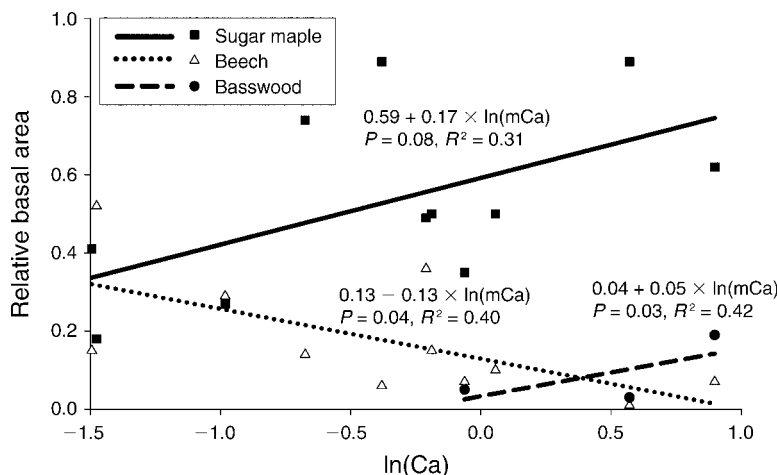


FIG. 3. Regressions of relative basal area of sugar maple (*Acer saccharum*), American beech (*Fagus grandifolia*), and American basswood (*Tilia americana*) against mean exchangeable Ca in the upper (0–10 cm) mineral soil;  $\ln(\text{mCa})$  is the natural logarithm of exchangeable Ca (originally measured in mg/g). Collections were made during the 2004 and 2005 growing seasons in the central Adirondack Mountains, New York.

TABLE 1. Chemistry data (means, with SD in parentheses) of senescent leaf litter collected during autumn 2004 at 11 sites in the Adirondack Mountains of New York, USA.

Species	OM (%)	Ca (mg/g)	K (mg/g)	Mg (mg/g)	N (%)	C (%)	Lignin (%)	C:N	Lignin:N
Sugar maple	94 <sup>c</sup> (1.1)	11.9 <sup>bc</sup> (3.1)	4.21 <sup>b</sup> (0.9)	1.37 <sup>c</sup> (0.32)	0.72 <sup>c</sup> (0.08)	46.9 <sup>bc</sup> (0.86)	17.8 <sup>c</sup> (2.3)	65.9 <sup>b</sup> (7.6)	24.9 <sup>c</sup> (3.4)
Beech	94 <sup>c</sup> (0.8)	8.7 <sup>c</sup> (1.2)	4.24 <sup>b</sup> (1.3)	1.75 <sup>c</sup> (0.36)	0.92 <sup>b</sup> (0.08)	48.3 <sup>a</sup> (1.00)	27.6 <sup>a</sup> (2.5)	53.0 <sup>cd</sup> (4.2)	30.2 <sup>b</sup> (3.3)
Basswood	91 <sup>d</sup> (1.8)	24.1 <sup>a</sup> (6.0)	8.22 <sup>a</sup> (2.4)	3.22 <sup>a</sup> (0.51)	1.41 <sup>a</sup> (0.31)	46.6 <sup>cd</sup> (0.49)	21.5 <sup>b</sup> (2.5)	35.3 <sup>c</sup> (11.3)	16.4 <sup>d</sup> (6.4)
White ash (whole-leaf†)	95 <sup>b</sup> (1.3)	13.9 <sup>b</sup> (4.3)	5.23 <sup>b</sup> (1.9)	2.54 <sup>b</sup> (0.72)	0.96 <sup>b</sup> (0.17)	47.5 <sup>ab</sup> (0.83)	16.1 <sup>c</sup> (2.8)	55.3 <sup>c</sup> (8.5)	19.1 <sup>d</sup> (4.7)
White ash (leaflet)	95 <sup>bc</sup> (1.3)	14.6 <sup>b</sup> (4.5)	5.22 <sup>b</sup> (1.7)	2.53 <sup>b</sup> (0.65)	1.03 <sup>b</sup> (0.20)	47.8 <sup>a</sup> (0.83)	16.0 <sup>c</sup> (2.9)	47.8 <sup>d</sup> (8.6)	16.2 <sup>d</sup> (4.5)
White ash (petiole‡)	97 <sup>a</sup> (1.2)	9.8 <sup>c</sup> (2.8)	5.33 <sup>b</sup> (3.0)	2.58 <sup>b</sup> (1.18)	0.44 <sup>d</sup> (0.03)	45.8 <sup>d</sup> (0.88)	16.6 <sup>c</sup> (2.4)	104 <sup>a</sup> (7.5)	37.9 <sup>a</sup> (6.2)

Note: Different lowercase letters indicate significant differences among litter types ( $P \leq 0.05$ ).

† Calculated from white-ash leaflet and petiole data.

‡ Represents only seven samples of ash petioles (60 petioles total).

per gram), and Temp is the mean temperature (in degrees Celsius) over 20 d prior to sampling (Fig. 5). The variable Temp largely reflected seasonal variability, with mean temperature values of 6.7°, 15.0°, 16.8°, 8.4°, 19.5°, and 19.8°C for the sampling periods of May, June, and September 2004 and May, July, and August 2005, respectively. The range of mean temperature values among sites within individual collection periods generally varied by <1°C, with the greatest range spanning 3°C during the May 2004 sample period. None of the variables in the regression equation showed high collinearity, with all VIF values  $\leq 1.5$ , and the only significant correlation was between OM and Moist ( $P = 0.002$ ,  $R = 0.38$ ). The values of pH and exchangeable Ca from the mineral soil were highly correlated ( $P < 0.001$ ,  $R = 0.71$ ) and resulted in similar coefficients of determination when pH was substituted for Ca in the above regression equation for predicting field N ( $R^2 = 0.60$  and 0.61, respectively).

Correlation analysis of litter lignin : N ratios indicated no significant relationship to exchangeable Ca in the mineral soil (0–10 cm). Field N from the forest floor was negatively related to initial lignin:N ratios of sugar maple litter, but not to lignin:N ratios of other species. Basswood was the only species for which relative basal area was related to forest floor inorganic N (Table 3).

#### DISCUSSION

Exchangeable Ca concentrations in the upper 10 cm of the mineral soil were positively correlated with the relative basal areas of sugar maple and basswood, but negatively correlated with that of beech. These trends likely reflect the interaction of soil fertility, species nutrient requirements, litter mineralization, and species competition for available resources. American beech has been reported to be less sensitive than sugar maple to reduced Ca concentrations and can become more dominant in stands with lower base status (Arii and Lechowicz 2002, Duchesne et al. 2005). The relatively poor quality of beech litter may contribute to soil acidification and decreasing Ca availability to an extent that sugar maple saplings may experience increased mortality on marginal sites and thereby further increase

the dominance of beech (Arii and Lechowicz 2002). The poorer litter quality of beech could therefore lead to greater production of organic acids during the decomposition process which, in association with relatively high lignin and phenolic concentrations, could increase Ca leaching (Finzi et al. 1998a, Arii and Lechowicz 2002). In a liming study on the Allegheny Plateau, the vigor and growth of sugar maple were improved in the lime-treated plots, while beech showed no significant response to treatment (Long et al. 1997). In addition to tree species interactions, forest composition and dominance can also be influenced by other factors, including disease, disturbance, and herbivory (Lovett and Rueth 1999, Rooney and Waller 2003).

The six sites in which basswood was observed in this study all had mean Ca in the mineral soil >0.9 mg/g and mean molar Ca:Al ratios >15. Site 14 exhibited the highest exchangeable mineral Ca concentrations, the greatest relative basal area of basswood, and the highest concentration of KCl extractable inorganic N in the forest floor. While basswood is not considered a climax species in the Adirondack region, the high litter quality as expressed by low lignin:N ratios and high base cation concentrations suggest the potential for rapid mineral-

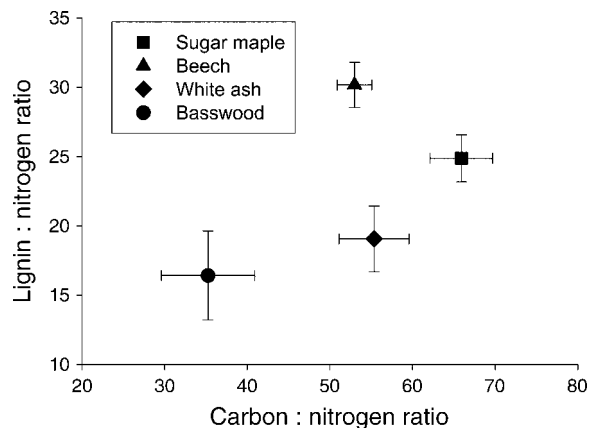


FIG. 4. Lignin : nitrogen ratios and carbon : nitrogen ratios (mean  $\pm$  SD) of senescent foliage collected during autumn 2004 in the central Adirondack Mountains, New York.

TABLE 2. Chemistry (means, with SD in parentheses) of the forest floor and the upper 0–10 cm layer analyzed by site.

Site	Ca (mg/g)	Ca:Al (molar ratio)	pH	Field NH <sub>4</sub> <sup>+</sup> (μmol N/g)	Field NO <sub>3</sub> <sup>-</sup> (μmol N/g)	Total C (%)	Total N (%)	Moisture (%)
A) Forest floor chemistry								
14	21.6 (1.6)	8.6 (3.5)	5.32 (0.11)	5.2 (2.2)	0.293 (0.501)	44.8 (1.9)	2.22 (0.05)	62.4 (10.3)
Amper	13.8 (0.4)	4.7 (1.7)	4.73 (0.16)	2.4 (1.3)	0.110 (0.209)	42.7 (0.5)	2.05 (0.15)	65.9 (5.0)
T3 and 30	8.8 (1.5)	2.6 (1.0)	4.41 (0.31)	2.3 (1.3)	0.084 (0.113)	42.2 (2.8)	1.76 (0.08)	68.7 (5.4)
NWoods	15.7 (1.0)	9.2 (3.7)	5.02 (0.21)	4.2 (1.7)	0.042 (0.061)	46.7 (2.5)	2.09 (0.18)	54.0 (7.9)
30CoLn	8.8 (1.5)	7.0 (5.4)	4.15 (0.19)	1.9 (1.1)	0.049 (0.096)	44.0 (2.0)	2.06 (0.02)	73.4 (5.5)
Balfour	10.4 (2.6)	1.6 (1.0)	4.59 (0.19)	2.7 (3.3)	0.006 (0.009)	38.7 (2.7)	1.32 (0.04)	54.3 (6.8)
Mason	10.0 (1.3)	3.9 (0.8)	4.19 (0.26)	2.9 (1.3)	0.029 (0.031)	41.4 (2.1)	1.99 (0.15)	63.5 (7.1)
NSpec	7.5 (2.2)	4.9 (3.8)	3.88 (0.25)	3.8 (1.9)	0.010 (0.018)	47.8 (0.3)	2.19 (0.09)	65.0 (7.4)
15	6.5 (1.2)	3.0 (1.1)	3.97 (0.14)	3.4 (0.9)	0.041 (0.069)	47.4 (1.3)	2.18 (0.25)	68.4 (5.2)
Catlin	7.7 (1.8)	4.0 (2.6)	4.15 (0.22)	2.9 (1.9)	0.015 (0.015)	40.7 (3.4)	1.88 (0.07)	64.0 (6.2)
Good	6.9 (0.6)	2.1 (0.6)	4.01 (0.12)	2.1 (0.6)	0.014 (0.018)	42.8 (2.0)	2.16 (0.15)	67.7 (3.2)
B) Upper (0–10 cm) mineral soil chemistry								
14	3.1 (0.55)	1410 (752)	5.04 (0.10)	0.49 (0.29)	0.118 (0.126)	10.0	0.76	41.5 (4.8)
Amper	2.3 (0.65)	146 (95.7)	4.27 (0.17)	0.42 (0.34)	0.014 (0.022)	12.4	0.74	46.1 (5.2)
T3 and 30	1.2 (0.42)	15.1 (14.3)	4.09 (0.26)	0.35 (0.21)	0.126 (0.115)	15.5	0.83	56.1 (5.1)
NWoods	1.1 (0.34)	66.9 (82.4)	4.12 (0.18)	0.42 (0.43)	0.006 (0.010)	7.5	0.46	27.8 (5.0)
30CoLn	1.1 (0.31)	15.5 (23.0)	3.74 (0.34)	0.35 (0.32)	0.004 (0.008)	8.7	0.55	52.1 (8.3)
Balfour	1.0 (0.16)	8.0 (5.9)	4.42 (0.16)	0.36 (0.23)	0.014 (0.013)	12.9	0.73	51.8 (4.8)
Mason	0.9 (0.23)	29.8 (34.4)	3.86 (0.27)	0.22 (0.14)	0.018 (0.031)	11.0	0.71	40.4 (2.7)
NSpec	0.8 (0.78)	25.3 (59.5)	3.63 (0.36)	0.46 (0.52)	0.008 (0.014)	14.6	0.75	40.9 (9.2)
15	0.4 (0.13)	1.3 (0.8)	3.62 (0.14)	0.21 (0.09)	0.001 (0.002)	12.1	0.70	42.6 (4.1)
Catlin	0.4 (0.25)	2.0 (1.6)	3.76 (0.23)	0.21 (0.08)	0.018 (0.031)	8.2	0.46	36.3 (2.4)
Good	0.2 (0.06)	0.5 (0.1)	3.93 (0.12)	0.21 (0.03)	0.001 (0.002)	13.2	0.71	45.2 (2.0)

Note: There is no standard deviation for total C and total N for upper mineral soil chemistry because analysis was conducted for only one sample period.

ization of organically bound N of basswood litter (Melillo et al. 1982, Scott and Binkley 1997, Preston et al. 1999). At a plot-level scale, clusters of basswood trees may result in localized nitrification hotspots related to the relatively Ca-rich soils and the high litter quality associated with basswood (Page and Mitchell 2008).

Leaf litter lignin:N ratios in this study decreased with beech > sugar maple > ash ≈ basswood, similar to results reported by others (Melillo et al. 1982, Ferrari 1999, Preston et al. 1999).

While field N did have a significant and inverse relationship with initial lignin:N ratios of sugar maple

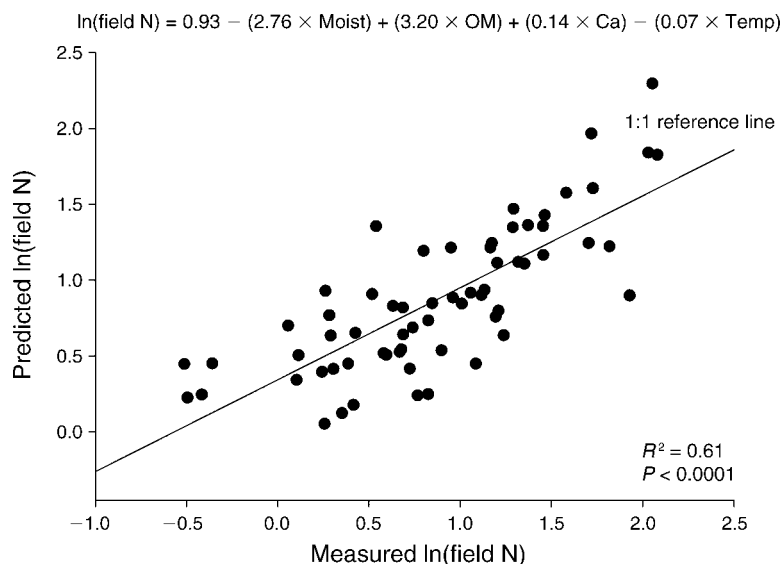


FIG. 5. Regression plot showing actual vs. predicted field-extracted inorganic N from the forest floor. Regression variables are: (1) field-extracted inorganic N from the forest floor expressed as a natural logarithm ( $\ln$  [field N]); measured as  $\mu\text{mol N/g}$ , (2) forest floor moisture (Moist), (3) forest floor organic matter (OM), (4) upper mineral soil exchangeable Ca in mg/g (Ca), and (5) mean temperature from 20 days prior to sampling (Temp). The line is a 1:1 reference line to indicate  $R^2 = 1.0$  and residual values. Samples were collected during the 2004 and 2005 growing seasons in the central Adirondack Mountains, New York.

litter (Table 3), no such relationship was detected for other species. It is possible that litter of ash and basswood, with relatively low lignin:N ratios, were largely mineralized between litterfall and initial soil collections the following May. Conversely, beech litter may be of sufficiently low quality as to not be a major source for N mineralization, especially where other more labile litter sources are present. Variations in litter quality among species and substrate chemical changes throughout the growing season can affect the temporal and spatial distribution of soil microbial communities involved in organic matter mineralization (Myers et al. 2001).

The relative basal areas of species other than basswood showed no significant relationship with field N (Table 3). This was an unexpected result as others, including Mitchell et al. (1992b) and Lovett and Rueth (1999), found greater soil  $\text{NO}_3^-$  and potential nitrification rates in stands dominated by sugar maple as compared to American beech. The lack of a strong correlation between field N and other species suggests that other site variables, such as those presented in our regression equation, may have had greater influence on soil N than tree species alone. Nitrogen deposition rates have also been shown to have a substantial influence on N cycling processes through influencing both inorganic N and dissolved organic N (DON) leaching (Pregitzer et al. 2004). However, annual wet N deposition ( $\text{NO}_3^- + \text{NH}_4^+$ ) estimates in this region occupy a fairly narrow range of  $\sim 300\text{--}360 \text{ mol N}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$  (Ito et al. 2005).

Nitrogen cycling can also be affected by forest health. Tree decline, as evidenced in part by crown dieback among the sugar maples, has been associated with sites having reduced Ca availability (Driscoll et al. 2003a, Bailey et al. 2004, Lovett and Mitchell 2004). Only one of the 11 sites in our study (Good), had a mean exchangeable Ca:Al ratio in the mineral soil  $<1.0$ , a value below which Ca can be limiting to tree growth (Cronan and Grigal 1995). The otherwise relatively high soil Ca concentrations at the remaining sites suggest that Ca likely was not limiting to tree health.

In the regression analysis of field N, we included variables accounting for moisture and temperature, which are known to be important in affecting microbial mineralization rates (McClougherty et al. 1985, Aerts 1997). Given the temporal and spatial variability of sampling 11 sites over two years, our regression analysis accounted for 61% of the variation in field N by including moisture, temperature, forest floor organic matter, and mineral soil Ca. Soil moisture and ambient temperature were both negatively related to soil inorganic N concentrations. Increased soil moisture can increase N uptake by plants (Pastor and Post 1986), microbial N immobilization (Stark and Firestone 1995), and N leaching losses (Perakis 2002). Increased moisture can also increase the potential for denitrification (Groffman and Tiedje 1989), though the degree to which denitrification occurs in upland forests is not well

TABLE 3. Pearson correlation coefficients (with *P* values in parentheses; boldface type indicates significant values) of mineral soil exchangeable Ca ( $\ln[\text{Ca}]$ ) and forest floor field-extracted inorganic N ( $\ln[\text{field N}]$ ) with initial tree litter lignin:N ratios and relative basal area.

Species	$\ln(\text{Ca})$	$\ln(\text{field N})$
Lignin:N		
Sugar maple	-0.03 (0.93)	<b>-0.61 (0.04)</b>
Beech	-0.37 (0.27)	-0.03 (0.93)
White ash	0.53 (0.11)	0.14 (0.69)
Basswood	-0.19 (0.72)	-0.57 (0.23)
Relative basal area		
Sugar maple	<b>0.55 (0.08)</b>	0.02 (0.95)
Beech	<b>-0.63 (0.04)</b>	-0.21 (0.54)
White ash	-0.23 (0.50)	0.02 (0.95)
Basswood	<b>0.65 (0.03)</b>	<b>0.72 (0.01)</b>

understood. The negative relationship between temperature and field N is likely a seasonal effect associated with higher temperatures in the summer when N availability is generally reduced due to increased biotic demand. The positive relationships between field N with forest floor organic matter and exchangeable Ca in the mineral soil is likely associated with the quality and availability of substrate for N mineralization. As noted previously, tree species such as sugar maple and basswood that produce litter with higher N mineralization and nitrification rates were more dominant on sites with greater Ca availability. Myers et al. (2001) similarly reported that sugar maple/basswood-dominated sites had higher N mineralization and nitrification rates relative to sites where oak species were dominant.

Soil pH is frequently cited as an important variable influencing N transformation rates (Boerner and Koslowsky 1989, Venterea et al. 2003). Generally low pH is thought to inhibit microbial nitrification, but nitrification has been reported in relatively acidic soils (Ohri et al. 1999). Haynes (1986b) suggested that pH at the microsite level may be within a suitable range for nitrification as a possible explanation for sites with low pH and measurable nitrification rates. While we used Ca in the regression equations instead of pH, it is clear that these two variables are closely linked and additional evaluations would be required to ascertain their relative effects.

Acidic deposition along with elevated N mineralization rates associated with improved litter quality (low lignin:N ratios; Scott and Binkley 1997) and higher soil pH (Mladenoff 1987) at sites with greater soil Ca availability could lead to greater mobility and potential leaching of  $\text{NO}_3^-$  and Ca from soils. If Ca export through leaching and biomass removal exceeds inputs and soil Ca concentrations decline, this may result in a decrease in the relative growth rate of sugar maple compared to less Ca-demanding species such as beech. Duchesne et al. (2005) found that decreased health and growth rates of sugar maple were correlated with increased density of beech in southeastern Canada.

The declining health of sugar maple in the Allegheny Plateau has been attributed to stresses including decreased availability of soil Ca and Mg, along with the effects of topographic and physiographic position (Horsley et al. 2000, Bailey et al. 2004). Bailey et al. (2005) indicated that soil Ca, Mg, and pH in the Allegheny Plateau have decreased significantly over a 30-year period. In support of the importance of Ca to sugar maple nutrition, Juice et al. (2006) reported that since the 1999 addition of wollastonite ( $\text{CaSiO}_3$ ) to Watershed 1 at the Hubbard Brook Experimental Forest, crown health and sugar maple seedling density have increased markedly compared to the untreated reference watershed. In unglaciated soils in the south-eastern United States, Huntington et al. (2000) suggested that soil Ca may be depleted below the requirements for a merchantable forest stand in as little as 80 years given current trends.

#### CONCLUSIONS

With continued acidic deposition and recent reports of declining Ca concentrations in European and North American forested ecosystems, the role of Ca in ecosystem functioning has been gaining attention. In this study we evaluated the influence of soil Ca concentrations on extractable inorganic N in the forest floor. While our data did not indicate a direct relationship between soil Ca and N, our results do support a multistep linkage whereby soil Ca concentrations were positively related to the basal areas of tree species, such as sugar maple and basswood, that have relatively high litter quality, favorable for N mineralization. Given these relationships, if chronic soil Ca depletion continues, as reported in some forested ecosystems, potential shifts in biotic communities could result in considerable alterations of N cycling. Additional laboratory experimentation on the interactions between Ca and N cycling could help clarify these links by reducing the variables that are inherent in field-based studies.

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