New York State Energy Research and Development Authority

Investigating Interactions Between Carbon, Nitrogen, and Calcium Cycles in an Adirondack Forest

Final Report

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Investigating Interactions Between Carbon, Nitrogen, and Calcium Cycles in an Adirondack Forest

Final Report

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NOTICE

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ABSTRACT

Nutrient availability in New York forests has been dramatically altered by human activities. Acid deposition has increased the availability of nitrogen in soils, but has also been linked to soil acidification, calcium loss, and declines in forest health. These changes may have long-term implications for carbon and nitrogen cycling and retention in forests, yet have been understudied. The research presented here investigates how increasing soil calcium availability by liming has influenced carbon and nitrogen cycling in the Woods Lake Watershed, Adirondack Park, NY. Twenty years after the lime addition, elevated soil pH and calcium availability were observed. The forest floor in limed plots was significantly larger than that in controls, resulting in a doubling in carbon and nitrogen stored in the forest floor of limed plots relative to controls. This pattern was associated with a reduction in the rate of decomposition in limed forest floor. Neither tree stem growth or leaf litter production differed significantly between the limed and control areas, indicating that long-term effects of liming on aboveground tree biomass is minimal. These findings suggest that increased soil calcium availability and pH can alter forest floor nutrient cycling and increase carbon and nitrogen storage within forest soils. Continued reductions in acid deposition across this region will help to minimize future declines in soil pH and calcium concentrations, which could have implications for both carbon storage and nitrogen retention within New York forests.

KEY WORDS: forests, liming, carbon, nitrogen, calcium, soil, Woods Lake

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SUMMARY

Acid deposition has resulted in soil acidification and calcium depletion, and declines in tree health in New York forests. Implementation of the Clean Air Act has reduced the deposition of sulfate, a strong acid anion; however, nitrogen deposition remains high and it is uncertain whether current deposition rates are low enough to alleviate declines in forest health and allow recovery. While many studies have focused on how calcium availability affects soil pH and the acidification of freshwaters, fewer have investigated how altered soil pH and calcium content influence forest carbon sequestration and nitrogen retention. Calcium is an essential element for plant growth and carbon and nitrogen uptake, and also has important abiotic roles, including stabilizing organic matter and neutralizing acids in soils. This diverse set of functions suggests that declines in soil calcium availability associated with acid deposition may alter forest health, as well as carbon and nitrogen cycling.

Forests and freshwaters in the Adirondacks region of New York State have been strongly impacted by acid deposition. In 1989, calcium carbonate (lime) was added to ~100 hectares of the Woods Lake Watershed, located in the Adirondack Park, to assess whether forest liming could be an effective strategy to reduce acidification of surface waters. An additional 100 hectares were maintained as a control area. This unique site was utilized in this study to investigate the long-term effects of increased soil calcium availability on tree health and soil carbon and nitrogen stocks and fluxes.

Twenty years after lime addition, soil pH and exchangeable calcium concentrations were significantly higher in the limed plots relative to controls. Leaf litter produced by all trees species in limed plots had significantly higher calcium concentrations than in control plots, indicating that trees are utilizing the additional calcium. Despite differences in litter calcium however, no differences in tree growth were observed between measurements taken in 1989 and 2009. In addition, there was a net decline in live tree biomass across the entire watershed. This watershed is dominated by American beech and the biomass loss was attributed to beech bark disease. Both forest floor fine root biomass and leaf litter inputs were larger in limed plots, but this difference was only statistically significant for roots in the partially fragmented (Oe) layer of the forest floor.

Carbon and nitrogen stocks in the forest floor of limed plots were approximately double those in controls (68 versus 31 tons per hectare of carbon and 3.0 versus 1.5 tons per hectare of nitrogen). This pattern was driven primarily by greater accumulation of the very decomposed (Oa) layer of the forest floor. Basal soil respiration measurements were assessed to estimate relative differences in organic matter decomposition and revealed that liming reduced basal soil respiration rates by 17 and 43% in the Oe and Oa forest floor horizons, respectively. Net nitrogen mineralization, or the rate at which organic nitrogen is processed by soil microbes and converted to inorganic forms, was also suppressed in limed forest floor. In the Oe forest floor horizon the rate of nitrate production was significantly higher in limed plots. Soil carbon and nitrogen

stocks within the underlying mineral soils were more variable, but did not appear to be strongly affected by liming.

Liming has altered ecosystem-scale carbon and nitrogen balances in the Woods Lake Watershed, leading to a doubling of carbon and nitrogen stocks stored in the soil of limed plots. The observed suppression of soil basal respiration suggests that liming has altered the fundamental relationship between the microbial community and the organic matter it decomposes. These results highlight the importance of the coupled interactions among carbon, nitrogen, and calcium cycles and indicate that losses of soil Ca associated with acid deposition may have the potential to reduce carbon and nitrogen storage in forest soils. Additional research is needed to identify the primary drivers of altered decomposition rates in response to liming in mixed northern hardwood forests. Refining our understanding of the mechanisms driving changes in soil carbon and nitrogen accumulation and the specific role of calcium is essential to understanding carbon sequestration and nitrogen retention in the Adirondacks and other acid-impacted forests.

INTRODUCTION

Nutrient availability in northeastern U.S. forests has been dramatically altered by human activities. Acid deposition has increased nitrogen (N) availability and forest growth, but has also been linked to soil acidification, base cation losses, and declines in some temperate tree species (Driscoll et al. 2001; Likens et al. 1996; Siccama et al. 1982; Thomas et al. 2010; van Breemen et al. 1983). Amendments to the Clean Air Act have reduced the deposition of sulfate, a strong acid anion; however, N deposition remains high (NADP 2008) and declines in soil pH and exchangeable base cations, especially calcium (Ca), are continuing throughout the region (Bailey et al. 2005; Johnson et al. 2008; Warby et al. 2009). Calcium is typically the most abundant base cation on the soil exchange complex and is important in neutralizing acids in soil (Driscoll et al. 2001; Likens et al. 1998). As a result of this important function, studies of Ca cycling have focused largely on the links between Ca and acidification, including how Ca availability affects soil pH, mobilization of aluminum (Al), and the acid neutralizing capacity of freshwaters (Cronan and Schofield 1990; Driscoll et al. 2001). Far fewer studies have investigated how altered soil Ca content and changes in pH influence forest carbon (C) sequestration and N retention.

Calcium has many roles in forest ecosystems that can directly affect C and N stocks and fluxes. Trees utilize Ca for numerous biological functions that dictate C and N uptake and storage in tissues. These processes include growth, stomatal regulation, carbohydrate metabolism, cell wall synthesis and structure, and response to environmental stress (Lautner and Fromm 2010; McLaughlin and Wimmer 1999). Changes in pH and soil Ca content can also influence microbial and faunal communities, with higher Ca availability and soil pH often leading to increased microbial activity (Haimi and Huhta 1990), higher earthworm abundance, and higher rates of litter decomposition (Hobbie et al. 2006; Reich et al. 2005). In contrast, Ca can reduce the mobility and solubility of dissolved organic matter (OM) in mineral soils by forming cation bridges that stabilize OM and reduce decomposition, leading to greater OM retention (Chan and Heenan 1999; Mikutta et al. 2007; Muneer and Oades 1989; Oste et al. 2002; Romkens et al. 1996; Tipping and Ohnstad 1984). More recent work has also demonstrated that increased Ca availability can lead to greater N uptake by plants and reduced microbial N cycling, thereby reducing potential ecosystem N losses via leaching (Groffman and Fisk 2011).

Forest liming (with $CaCO_3$) has been used as a management strategy to reduce the effects of acidification and often leads to increased soil pH and exchangeable Ca concentrations. Liming studies provide an opportunity to explore interactions among C, N, and Ca cycles, as well as identify how this management technique affects ecosystem nutrient availability. Liming has been conducted extensively across Europe in conifer plantations and in some northeastern U.S. forests dominated by sugar maple (*Acer saccharum*), a species known to respond positively to increased soil Ca availability (Huggett et al. 2007; Juice et al. 2006; Long et al. 1997). It is unknown whether results of these studies can accurately represent the response of acid-impacted mixed hardwood forests. Further, many studies measure changes in vegetation and soil C

and N pools for just a few years immediately following Ca addition, or measure fluxes, such as soil respiration, N mineralization, nitrification, or dissolved organic C and N leaching, for weeks to months, which may be inadequate to assess long-term impacts of altered soil Ca and pH on ecosystem C and N dynamics.

This study investigates changes in C and N pools and fluxes approximately 20 years after an experimental Ca addition in the Woods Lake Watershed, a mixed northern hardwood forest located in New York State's Adirondack Park. In 1989, lime was added to roughly half of the catchment area to assess whether forest liming could be an effective strategy to reduce acidification of surface waters (Driscoll et al. 1996). It was hypothesized that the lime addition would improve forest health and that this improvement would be evident in increased tree biomass, leaf litter, and fine root production. Within the forest floor, it was anticipated that the increased pH associated with liming would stimulate microbial activity resulting in increased decomposition, basal soil respiration, and net N mineralization. Enhanced decomposition was also expected to occur, leading to reduced C and N stocks in limed forest floor horizons relative to controls. Conversely, it was hypothesized that increased Ca availability could enhance Ca-OM complexation in the upper mineral soils, leading to increased C and N stocks in these horizons.

METHODS

SITE DESCRIPTION

Research was conducted in the Woods Lake Watershed, the site of an Experimental Watershed Liming Study, located in Herkimer County NY, within the Adirondack Park (43^{o} 52' N, 74^{o} 57' W). In 1989, limestone was applied by helicopter to two ~50 ha subcatchments (L1 and L2) in a single application of 6.89 tons $CaCO_3$ ha^{-1} (2.76 t Ca ha^{-1}) (Driscoll et al. 1996). The lime pellet was 82% $CaCO_3$, 8% $MgCO_3$ and 4% organic binder (Driscoll et al. 1996). Two additional subcatchments were maintained as controls (C1 and C2). Mean annual precipitation at this site is 1230 mm and mean annual temperature is 5.2^{o}C (Yavitt et al. 1995).

This watershed has 98% forest cover (Staubitz and Zarriello 1989) and is dominated by American beech (*Fagus grandifolia*), red maple (*Acer rubrum*), and yellow birch (*Betula alleghaniensis*), with lesser amounts of red spruce (*Picea rubens*), sugar maple (*Acer saccharum*), and striped maple (*Acer pensylvanicum*) (Smallidge and Leopold 1994). The site is underlain by hornblende granitic gneiss bedrock covered by a sandy glacial till comprised of quartz and feldspar, with some interspersed hornblende, ilmenite, and magnetite (April and Newton 1985). The soils are classified as Orthod Spodosols (Smallidge and Leopold 1994) and mean mineral soil depth is 30 to 35 cm (Brocksen et al. 1988). Calcium is the dominant base cation in these soils (Blette and Newton 1996). Within 1-2 years after liming, the pH in the

forest floor rose from 3.7 to 4.9 in the Oe horizon and from 3.7 to 4.0 in the Oa (Simmons et al. 1996). Exchangeable Ca availability also increased during this period, from 8.5 to 35 $cmol_c\ kg^{-1}$ soil in the Oe and from 6 to 10 $cmol_c\ kg^{-1}$ soil in the Oa (Blette and Newton 1996). Following these early studies, very little research has been conducted within the forest at this site.

PLOT DESIGN

Vegetation and soil sampling was conducted in twenty 0.04 ha plots from across the watershed, distributed as five plots located along transects spanning each of the limed and control subcatchments. These plots were a subset of the 99 plots established during the original vegetation sampling in 1989 (Smallidge and Leopold 1994). All trees ≥ 10 cm diameter at breast height (dbh) were tagged in 1989 and dbh was recorded (P. Smallidge, personal communication). Plots for this study were chosen to span the spatial heterogeneity of the landscape and to minimize differences in tree species composition, slope, and aspect between control and limed subcatchments.

ABOVEGROUND VEGETATION MEASUREMENTS

In August 2009, dbh was measured on all trees ≥ 10 cm within each study plot. Aboveground tree biomass was calculated using allometric equations from Jenkins et al. (2003). To convert to units of C, it was assumed that woody biomass is 50% C (Fahey et al. 2005). Plot mortality and changes in aboveground live biomass were calculated using newly collected data from 2009 and prior measurements from 1989. Litterfall was collected from May 2009 to May 2010 using five 0.23 m^2 (40.6 cm x 55.9 cm) litter baskets distributed across each plot. Baskets were secured in place with stakes and lined with fiberglass window screen to prevent litter material from resting on the bottom of the basket.

Litter was air dried, then sorted into components including: foliage (sorted by species), seeds, branches and wood, and miscellaneous components (e.g. insects). Sorted samples were then dried at 50^{o}C for at least three days and weighed. Foliar litter from all baskets within a plot was combined by tree species into one composite sample per plot for analysis of C, N, Ca, and lignin. The composite foliage samples were ground to a fine powder using a Cyclone Sample Mill (Udy Corp., Fort Collins CO). Total C and N concentrations were measured via high temperature combustion using a Vario EL III elemental analyzer (Elementar, Hanau Germany) at Cornell University. Total Ca concentration was analyzed by nitric acid microwave digestion followed by analysis using a Varian Vista AX inductively coupled plasma atomic emission spectrometer at the U.S. Forest Service Laboratory, Durham NH. Foliar litter lignin content was determined at the Dairy One Forage Laboratory, Ithaca NY. Samples were digested in an ANKOM A200 fiber analyzer using the ANKOM A200 filter bag technique. First, samples were placed in filter bags and submerged in acid detergent fiber solution for 75 minutes in an ANKOM A200 Digestion Unit. Samples were then rinsed in boiling water, then in acetone, before being dried at 100^{o}C for two hours. The remaining residue was

combined with 72% sulfuric acid for three hours in an ANKOM A200 DaisyII Incubator. Lignin concentration was then determined using a FOSS NIRSystems Model 6500 VIS-NIR Spectrometer.

SOIL FIELD MEASUREMENTS

As detailed below, forest floor material was sampled on several occasions for various analyses. Forest floor mass was assessed twice on the 20 intensively studied plots, first in 2007 when both Oe and Oa were collected as a single sample, and again in 2008, when Oe and Oa were collected separately. All forest floor chemistry and mass data presented here is from the 2008 sample collection. During 2010, additional forest floor material was collected incrementally by horizon in the sample plots for measurement of soil basal respiration. Forest floor depth was also characterized at 100 additional locations within each subcatchment to assess watershed-wide forest floor depth patterns.

In the summer of 2007, forest floor and mineral soils were collected from five locations within each of the 20 study plots. The forest floor was collected by placing a 15 cm x 15 cm wood frame on the surface of the Oe and cutting out a block of OM using a knife. Roots within the block were clipped with pruners at the edges of the frame and all forest floor material was removed, either as an intact block, or by hand and with a spoon. After removal of the block, forest floor depth was recorded. The interface between the forest floor and mineral soil was usually easy to identify due to the presence of an E horizon immediately below the Oa. A spoon was used to collect as much OM as possible from this E-Oa boundary, with care taken to minimize mixing of mineral and organic horizons. Mineral soils were sampled incrementally for depths 0 - 10 cm, 10 - 20 cm, 20 - 30 cm, and 30 - 40 cm using a diamond-tipped rotary coring device with 9.5 cm internal diameter, which provides a quantitative sample of soil bulk density and OM stocks (Rau et al. 2011). Collected mineral soil samples were used to quantify current soil pH, exchangeable Ca availability, and C and N stocks.

In 2008, additional forest floor samples were collected from six locations within each plot to quantify forest floor pH, exchangeable Ca pools, C and N stocks, and net N mineralization. The 2007 sampling revealed differences in forest floor mass between limed and control plots. To further explore this pattern and improve the resolution of the forest floor analyses, Oe and Oa horizons were collected separately in 2008. Similar to the 2007 sampling, a knife was used to cut out 15 cm x 15 cm blocks. First, the Oe layer was removed. This layer consisted of partially fragmented litter, had a light brown color, and typically was removed as a solid block held together by hyphae and roots. The Oa horizon was dark brown to black in color, very moist, and often had to be removed with spoons and by hand.

An *in situ* net N mineralization study was conducted during the 2008 sampling and included the Oe and Oa samples described above, as well the top 10 cm of mineral soil. At each of the six sampling locations, two samples of Oe, Oa, and 0 - 10 cm mineral soil were taken side-by-side. Mineral soil was collected using a

tulip bulb corer (7 cm diameter). One set of samples (initial) was kept on ice packs and returned to the laboratory shortly after collection. These initial Oe and Oa samples were used to quantify forest floor pH, exchangeable Ca availability, C and N stocks, and pools of ammonium (NH_4^+) and nitrate (NO_3^-). The second set of soil samples (incubated) were sealed in polyethylene bags in the field and placed back in the soil from which they were removed. After a 30-day *in situ* incubation, samples were retrieved, placed on ice packs, and returned to the laboratory for analysis. In September 2010, additional Oe and Oa samples were collected from a 15 cm x 15 cm area using a square-edged shovel. Samples were kept on ice packs during transport and later used to assess basal soil respiration.

It was also recognized that the study plots may not adequately represent forest floor dynamics across the entire 200 ha watershed. To investigate this, additional forest floor depth measurements were taken in all subcatchments in 2010 (100 measurements across each subcatchment).

LABORATORY ANALYSES

The forest floor and mineral soil samples collected in 2007 were dried at 50^{o}C for approximately one week. These samples were then weighed, but no chemical analyses were performed. Mineral soils collected in 2007 were passed through a 2 mm sieve and rock and roots were removed and weighed. The Oe and Oa samples collected in 2008 were passed field moist through 5.6 mm and 4 mm sieves, respectively. All roots were removed from these samples while sieving. Large root pieces that slipped through the sieve were retrieved for quantification. Samples were then dried at 50^{o}C for at least three days. Forest floor fine root biomass was estimated later on Oe and Oa samples by sorting the dried samples into > 2 mm and < 2 mm size classes, then re-drying and weighing the < 2 mm roots. Two 10 g subsamples of moist Oe and Oa material were collected to determine moisture content and to measure net N mineralization (detailed below). The remaining sample was dried at 50^o C for at least five days, then three additional ~10 g subsamples were removed for analysis of total C, N, exchangeable Ca, and pH.

A subsample of forest floor (2008 collection) and mineral soil (2007 collection) samples were ground to a fine powder using a Retsch Mixer Mill, type MM200, and analyzed for total C and N on a Vario EL III elemental analyzer. Exchangeable cation concentrations were measured using a 1*M* ammonium chloride (NH_4Cl) extraction. Five grams of forest floor material were combined with 50 mL of NH_4Cl and 10 g of mineral soil were mixed with 100 mL of NH_4Cl. Each sample was placed on a shaker table for one hour. After shaking, solutions were vacuum filtered through Pall brand type A/E glass fiber filters. Extracts were frozen until analysis, using inductively coupled plasma emission spectroscopy at the State University of New York College of Environmental Science and Forestry, Syracuse NY. Soil pH analysis was performed using an Accumet basic AB15 pH meter with a flushable junction soil probe. For the mineral soils, a 10 g subsample of soil was mixed thoroughly with 20 mL of deionized water. For forest floor material, 5 g of

sample were mixed with 50 mL of water. After a 30-minute equilibration, samples were gently swirled and a reading was taken after pH stabilized.

To assess net N mineralization and nitrification of both initial and incubated Oe, Oa and 0 - 10 cm mineral soil samples, 10 g of field moist soil was mixed with 100 mL of 1*M* KCl and placed on a shaker table for one hour. After shaking, samples were passed through a Whatman Type GF/F glass fiber filter via vacuum filtration. Prior to sieving, soil samples were kept refrigerated. All extractions were performed on the same day the sample was sieved, and within one week of collection. Extracts were then frozen until analysis using the automated flow injection phenate method on a Lachat QuikChem 8000 automated ion analyzer at the Cary Institute of Ecosystem Studies, Millbrook NY. Net N mineralization was calculated as the difference between the incubated and initial sample concentrations of NH_4^+ and NO_3^- in the paired samples for each depth increment studied. Net nitrification was calculated as the accumulation of NO_3^- between the incubated and initial samples.

To measure soil basal respiration, the five samples collected within each plot in 2010 were composited by depth increment during sieving, creating one composite Oe and Oa sample for each plot. Samples were then kept at 4^{o}C until analysis, ~five months after collection. Approximately one week before measuring basal respiration, four subsamples weighing 20 g each (field moist), of each composite sample were placed in 355 mL Ball® glass jelly jars and left in the dark at 22^{o}C. A 10 g subsample of each composite was dried for at least 24 hours at 110^{o}C to calculate soil moisture content. Basal respiration was measured on two occasions approximately three weeks apart. Sample moisture was maintained by weighing samples weekly and adding deionized water as needed to return soils to field moisture. The last water addition occurred one week prior to the second respiration measurement. Soil basal respiration was measured by capping samples with an air-tight lid and allowing CO_2 to accumulate in the headspace. After 24 hours, 2 mL of headspace was removed using a syringe and immediately injected into an infrared gas analyzer (LI-6200, LI-COR, Lincoln NE). One replicate of each composite sample was incubated a third time and the collected headspace was analyzed for ^{13}C, to determine whether any undissolved lime pellets in the limed forest floor samples had contributed to the measured CO_2 accumulation during the incubation. Following the incubation, approximately 5 g of each sample were ground and analyzed for total C and N concentration using the same forest floor analytical methods described above.

STATISTICAL ANALYSES

Statistical analysis was performed using JMP 7.0 (SAS Institute). A mixed model was constructed, containing treatment (control vs. limed) and subcatchment (C1, C2, L1, L2) nested within treatment as fixed effects. Plot and samples obtained within plots were included as random effects. Main liming effects were confirmed using this model, then subcatchment mean comparisons were made using Tukey's test ($P < 0.05$).

RESULTS

TREE RESPONSE TO LIMING

In 1989, live tree aboveground biomass averaged 123.4 t C ha^{-1} in study plots (TABLE 1). During the 20-year interval since lime application, there was a net decline in aboveground live tree biomass in all subcatchments, averaging 4.5 t C ha^{-1} yr^{-1} and resulting in a mean biomass of 82.3 t C ha^{-1} in 2009. There were no significant differences in biomass loss between limed and control subcatchments. Stand mortality rates, as well as mortality of individual species, did not differ significantly between limed and control areas (TABLE 2). Rates of mortality differed among species, however, with American beech showing significantly greater declines than all other species across the watershed ($P < 0.05$), accounting for 44% of all mortality.

Liming did not affect total annual aboveground litter inputs, nor did it influence any of the measured litter components (TABLE 3). There was a trend toward larger foliar litter inputs in the limed subcatchments (2.96 vs. 2.76 t OM ha^{-1} yr^{-1}), but this relationship was not statistically significant ($P = 0.36$). All tree species exhibited significantly larger Ca concentrations in foliar litter in limed plots relative to controls (TABLE 4). Total foliar Ca inputs (sum of all species) were also significantly higher in limed soils, while total foliar inputs of C and N did not differ between limed and control plots (TABLE 5). Significantly larger C concentrations were observed in the control plot foliar litter of all species except yellow birch (TABLE 4).

Fine root (< 2mm) biomass in the Oe horizon was significantly larger in the limed sites relative to controls ($P = 0.02$; TABLE 6). This pattern was driven by significantly greater root biomass in the L1 subcatchment relative to all other subcatchments. There was no effect of liming on fine root biomass in the Oa horizon; however, there was a trend toward greater biomass in limed soils.

SOIL RESPONSE TO LIMING

Nineteen years after the lime addition, ~48% of the added Ca was present in an exchangeable form within the forest floor and top 40 cm of mineral soil (TABLE 7). Total soil exchangeable Ca stocks were significantly higher in limed soils for all measured depths. The largest stocks occurred in the Oa horizon. Similarly, the largest concentrations of exchangeable Ca were in the forest floor, where both limed subcatchments showed significantly higher concentrations than controls ($P < 0.0001$ for both Oe and Oa; FIGURE 1A). Liming also resulted in significantly higher exchangeable Ca availability within mineral soils, to a depth of 30 cm ($P < 0.01$ for all depths). In response to the liming, the pH of the Oe layer increased significantly from 4.1 to 5.3 ($P < 0.0001$) and in the Oa layer from 3.9 to 4.7 ($P < 0.0001$; FIGURE 1B). In the mineral soils, significantly higher pH was only observed in the 0 - 10 cm increment ($P = 0.05$). Exchangeable magnesium pools did not differ significantly for any studied depth (data not shown).

TABLE 1. Live tree aboveground biomass (t C ha^{-1}) in 1989 and 2009 for all species in each subcatchment. Mean values are indicated ± SE (n = 5 plots).

	Subcatchment and year							
	C1		C2		L1		L2	
Tree species	1989	2009	1989	2009	1989	2009	1989	2009
Beech	25.8 ± 12.8	18.3 ± 5.7	75.7 ± 15.6	41.2 ± 13.4	36.2 ± 5.9	15.7 ± 3.1	62.8 ± 16.4	12.5 ± 3.0
Red maple	27.9 ± 16.3	26.9 ± 10.1	27.0 ± 6.4	19.7 ± 13.5	25.7 ± 12.3	18.3 ± 5.1	14.5 ±4.5	19.9 ± 7.5
Red spruce	6.9 ± 4.3	5.4 ± 3.0	5.9 ± 5.2	0.9 ± 0.5	10.7 ± 6.6	6.2 ± 2.5	14.6 ± 6.6	4.8 ± 3.3
Striped maple	2.0 ± 1.7	3.1 ± 2.0	0.0	3.9 ± 3.2	2.4 ± 1.5	1.9 ± 1.4	0.2 ± 0.2	1.9 ± 0.7
Sugar maple	17.0 ± 9.3	22.8 ± 14.3	0.8 ± 0.8	1.6 ± 1.6	0.9 ± 0.6	0.7 ± 0.7	2.2 ± 1.0	7.2 ± 3.1
Yellow birch	46.0 ± 32.2	14.9 ± 7.3	7.2 ± 3.1	2.0 ± 1.3	60.6 ± 26.8	64.8 ± 34.2	14.6 ± 7.9	14.5 ± 6.7
Other	5.6 ± 6.0	0.0	0.1 ± 0.1	0.0	0.0	0.0	0.0	0.0
Total	131.5 ± 34.2	91.3 ± 10.6	116.8 ± 12.6	69.3 ± 7.7	136.6 ± 22.5	107.6 ± 29.7	108.8 ± 14.3	60.8 ± 6.0

TABLE 2. Estimated aboveground C loss due to tree mortality between 1989-2009 (t C ha^{-1}) for each studied subcatchment. "-" indicates no mortality of that species (no measurable biomass loss or absence of species within subcatchment). Means values presented ± SE (n = 5 plots). Lime effect P values indicate a significant difference between limed and control subcatchments.

Tree species	Subcatchment C1	C2	L1	L2	Lime effect (P value)
Beech	27.9 13.3	66.5 12.5	33.0 5.8	60.9 16.7	0.99
Red maple	33.7 14.3	20.6 8.5	19.1 10.2	10.3 2.3	0.34
Red spruce	8.3 3.3	9.8 6.5	9.7 5.1	14.5 6.8	0.69
Striped maple	3.5 2.3	-	4.0 1.4	1.0	0.78
Sugar maple	16.7 7.9	-	2.9	15.2 0.5	0.37
Yellow birch	46.8 30.3	8.1 3.3	15.0 3.4	9.6 3.5	0.40

TABLE 3. Total annual aboveground litter inputs (t OM ha^{-1} yr^{-1}) for each studied subcatchment. Means indicated ± SE (n = 5 plots).

Litter component	Subcatchment C1		C2		L1		L2		Lime effect (P value)
Foliage	2.73	0.14	2.78	0.15	2.93	0.37	2.99	0.04	0.36
Bark and Branches	1.36	0.59	0.25	0.07	0.45	0.11	0.34	0.10	0.20
Cones	0.001	0.001	0	0	0.0002	0.0002	0.04	0.04	0.34
Seeds	0.01	0.01	0.02	0.01	0.005	0.004	0.002	0.001	0.18
Miscellaneous	0.001	0.001	0	0	0	0	0.0005	0.005	0.59
Total	4.52	0.71	3.52	0.22	3.84	0.45	3.80	0.16	0.65

TABLE 4. Individual tree species foliar litter chemistry. Row values with different letters indicate a significant difference among subcatchments (P < 0.05). Lime effect P values display overall effect of liming. Mean values are reported ± SE (n = 5 plots).

Tree species	Subcatchment C1	C2	L1	L2	Lime effect (P value)
Beech					
N (%)	1.02 0.03	1.03 0.05	1.03 0.02	1.02 0.04	0.98
C (%)	50.31 0.42 [a]	50.57 0.31 [a]	47.86 0.24 [b]	49.82 0.19 [a]	* < 0.0001
C:N ratio	49.54 1.50	49.74 2.21	46.65 0.90	49.12 1.60	0.29
Ca (%)	0.59 0.05 [a]	0.75 0.05 [ab]	1.06 0.03 [c]	0.87 0.06 [bc]	* < 0.0001
Lignin (%)	35.9 1.6	37.1 2.4	31.0 2.0	31.7 1.7	* 0.02
Red maple					
N (%)	0.76 0.03	0.87 0.06	0.78 0.02	0.86 0.06	0.90
C (%)	50.22 0.23a	50.01 0.32a	48.22 0.05b	49.71 0.23a	* 0.0001
C:N ratio	66.33 2.71	58.83 3.98	62.36 1.71	58.58 3.65	0.51
Ca (%)	0.73 0.03 [a]	1.01 0.09 [ab]	1.23 0.08 [b]	1.09 0.08 [b]	* 0.001
Lignin (%)	20.3 0.7	21.8 2.14	19.9 1.1	20.2 1.5	0.50
Striped maple					
N (%)	0.99 0.08	0.97 0.04	0.92 0.04	0.93 0.02	0.30
C (%)	49.24 0.28a	48.60 0.21a	46.53 0.71ab	48.10 0.39b	0.002
C:N ratio	50.97 4.12	50.65 2.35	51.12 1.86	51.60 1.24	0.84
Ca (%)	1.25 0.07 [a]	1.58 0.04 [ab]	2.50 0.29 [c]	2.21 0.19 [bc]	* 0.0001
Lignin (%)	39.7 2.1	39.9 1.4	31.8 0.3	37.3	* 0.04
Sugar maple					
N (%)	0.76 0.03	0.93 0.10	0.86 0.00	0.80 0.06	0.87
C (%)	49.91 0.28a	48.85 0.29ab	47.97 0.65b	47.83 0.20b	* 0.0005
C:N ratio	65.82 2.75	55.32 5.98	55.73 0.66	60.75 4.50	0.62
Ca (%)	0.52 0.03a	0.96 0.11b	1.53 0.22c	1.65 0.04c	* 0.0001
Lignin (%)	22.2 1.7	21.2	21.7	21.7 1.6	1.0
Yellow birch					
N (%)	1.41 0.06	1.37 0.10	1.25 0.07	1.38 0.06	0.29
C (%)	50.19 0.12 [a]	49.17 0.12 [c]	49.49 0.20 [bc]	49.89 0.12 [ab]	0.96
C:N ratio	35.80 1.53	36.66 2.74	40.26 2.37	36.52 1.47	0.32
Ca (%)	1.15 0.09 [a]	1.33 0.06 [a]	1.83 0.09 [b]	1.51 0.03 [c]	* 0.0001
Lignin (%)	39.5 1.1	32.3 2.1	34.6 0.3	34.1 2.5	0.40

TABLE 5. Total (species combined) annual foliar litter inputs of C, N, and Ca, and Ca and lignin concentrations. Row values with different letters indicate a significant difference among subcatchments (P < 0.05). Lime effect P value displays the overall effect of liming. Mean values are reported ± SE (n = 5 plots).

	Subcatchment				
Foliar chemistry	C1	C2	L1	L2	Lime effect (P value)
C (t ha^{-1} yr^{-1})	1.35 0.08	1.36 0.08	1.39 0.19	1.44 0.04	0.60
N (t ha^{-1} yr^{-1})	0.03 0.002	0.03 0.002	0.03 0.004	0.03 0.002	0.12
Ca (t ha^{-1} yr^{-1})	0.02 0.002 [a]	0.02 0.002 [a]	0.04 0.008 [b]	0.04 0.001 [ab]	* 0.001
Ca (%)	0.81 0.02 [a]	1.1 0.04 [b]	1.7 0.1 [c]	1.5 0.04 [c]	* < 0.0001
Lignin (%)	30.7 3.9 [ab]	34.6 4.3 [a]	28.1 3.0 [b]	28.6 3.2 [b]	* 0.01

TABLE 6. Fine root biomass < 2 mm diameter (t C ha^{-1}) in the Oe and Oa forest floor horizons. Row values with different letters indicate significant differences among subcatchments (P < 0.05) and lime effect P values indicate significant responses to liming.

Forest floor horizon	Subcatchment C1		C2		L1		L2		Lime effect (P value)
Oe	0.26	0.04 [a]	0.31	0.06 [a]	0.59	0.05 [b]	0.27	0.04 [a]	* 0.01
Oa	0.22	0.05	0.44	0.05	0.40	0.08	0.45	0.05	0.11

TABLE 7. Soil exchangeable Ca stocks and estimated percent of added Ca still present in 2007-2008. Percentage calculations assume a Ca application rate of 68.87 kmol Ca ha^{-1} and that the excess exchangeable Ca observed in limed soils relative to controls originated from the lime addition. Row values with different letters indicate significant differences among subcatchments.

Soil depth	Subcatchment				Lime effect
	C1	C2	L1	L2	(P value)
Soil Ca stocks (kmol Ca ha^{-1})					
Oe	1.4 0.3 [a]	0.9 0.3 [a]	6.1 1.6 [b]	4.7 1.0 [b]	* < 0.0001
Oa	1.1 0.5 [a]	1.5 1.0 [a]	19.3 5.2 [b]	20.0 5.0 [b]	* < 0.0001
0 - 10 cm	1.4 0.4 [a]	1.9 0.9 [a]	6.7 2.3 [b]	7.5 3.2 [b]	* 0.0002
10 - 20 cm	0.8 0.2 [a]	1.3 0.6 [ab]	2.6 0.6 [bc]	3.2 0.8 [c]	* 0.0003
20 - 30 cm	0.6 0.2 [a]	0.9 0.3 [a]	1.7 0.4 [ab]	2.5 0.6 [b]	* 0.0002
30 - 40 cm	0.6 0.1 [a]	0.8 0.3 [ab]	1.5 0.4 [bc]	2.0 0.4 [c]	* 0.0002
Percent of added Ca residing in limed soils					
Oe	-	-	7	6	
Oa	-	-	26	27	
0 - 10 cm	-	-	8	8	
10 - 20 cm	-	-	3	3	
20 - 30 cm	-	-	2	2	
30 - 40 cm	-	-	1	2	

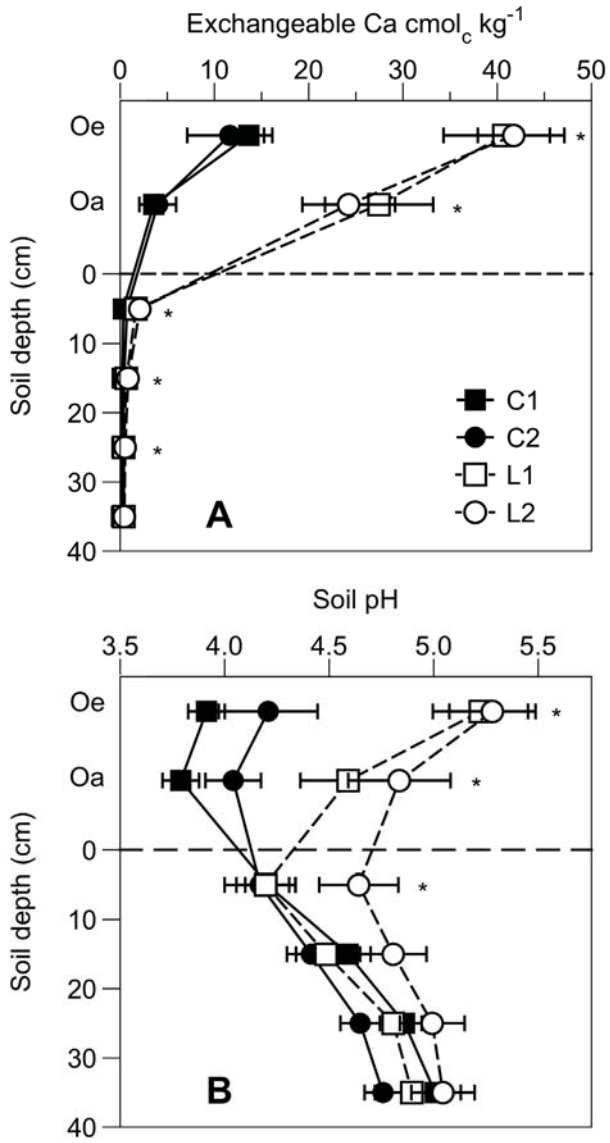

FIGURE 1. Exchangeable Ca concentration (A) and soil pH (B) for all measured forest floor and mineral soil depth increments (Oe, Oa, 0 - 10 cm 10 - 20 cm, 20 - 30 cm, 30 - 40 cm). Significant effects of liming are indicated by * ($P < 0.01$). Error bars indicate SE (n = 5 plots).

The forest floor mass was significantly larger in limed soils relative to controls (175 vs. 94 t OM ha^{-1}), resulting in larger forest floor C and N stocks in limed plots (FIGURE 2 A and B). This difference in C and N content was driven primarily by greater accumulation of Oa material in the limed subcatchments, which contained 57.5 t C ha^{-1} relative to 23.1 t C ha^{-1} ($P = 0.0002$) in controls and 2.5 vs. 1.1 t N ha^{-1} ($P = 0.0001$). The Oe also contained significantly larger C and N stocks in the limed subcatchments, but treatment differences were not as large as those in the Oa (10.4 vs. 8.0 t C ha^{-1}, $P = 0.01$ and 0.5 vs. 0.4 t N ha^{-1}, $P = 0.01$). A significantly higher C concentration in the limed Oa horizon was also observed (36 vs. 29%, in limed and control Oa, respectively, $P = 0.009$). No differences in C concentration were present in the Oe horizon ($P = 0.44$) or in N concentration for either forest floor horizon (Oe, $P = 0.47$ and Oa, $P = 0.09$). Mean forest floor depths from the watershed-wide measurements were 10 cm in control forest floor and 13 cm in limed. Estimated depths in the study plots were 11 cm for controls and 18 cm for limed. These results suggest a similar pattern of increased accumulation in limed soils; however, the relative difference in forest floor depth between limed and control soils was 57% lower with the more comprehensive watershed sampling.

In contrast to the forest floor, the effects of liming on mineral soil C and N were less clear. Significant differences among subcatchments were observed for both C and N concentrations and stocks, for all depth increments ($P < 0.05$). Overall liming effects indicate significantly larger cumulative C and N stocks in control soils for 0 - 40 cm depth ($P = 0.03$ and 0.0007 for C and N, respectively). This finding was driven primarily by significantly higher C and N concentrations in the mineral soils within the C2 subcatchment, relative to all other subcatchments. Therefore, it is unclear if this is a liming effect or due to inherent mineral soil heterogeneity. As a result of this difference in mineral soil C and N, the cumulative stocks of C and N in the forest floor and upper 40 cm of mineral soil did not differ significantly between limed and control soils ($P = 0.14$ and 0.46 for C and N, respectively). Instead, the total forest floor and mineral soil stocks of C and N in the C2 were more similar to the total stocks in the limed subcatchments while the C1 subcatchment values were lower (FIGURE 2 C and D). The soil C:N ratio increased with soil depth from a mean value of 21 in the Oe horizon to 27 in the 30 - 40 cm mineral soil depth increment (FIGURE 3). Liming resulted in a significantly larger C:N ratio in the Oa forest floor horizon and in the mineral soil depth increments 0 - 10 cm, 10 - 20 cm, and 20 - 30 cm ($P < 0.05$). These differences were driven primarily by a larger C:N ratio within the L1 limed subcatchment.

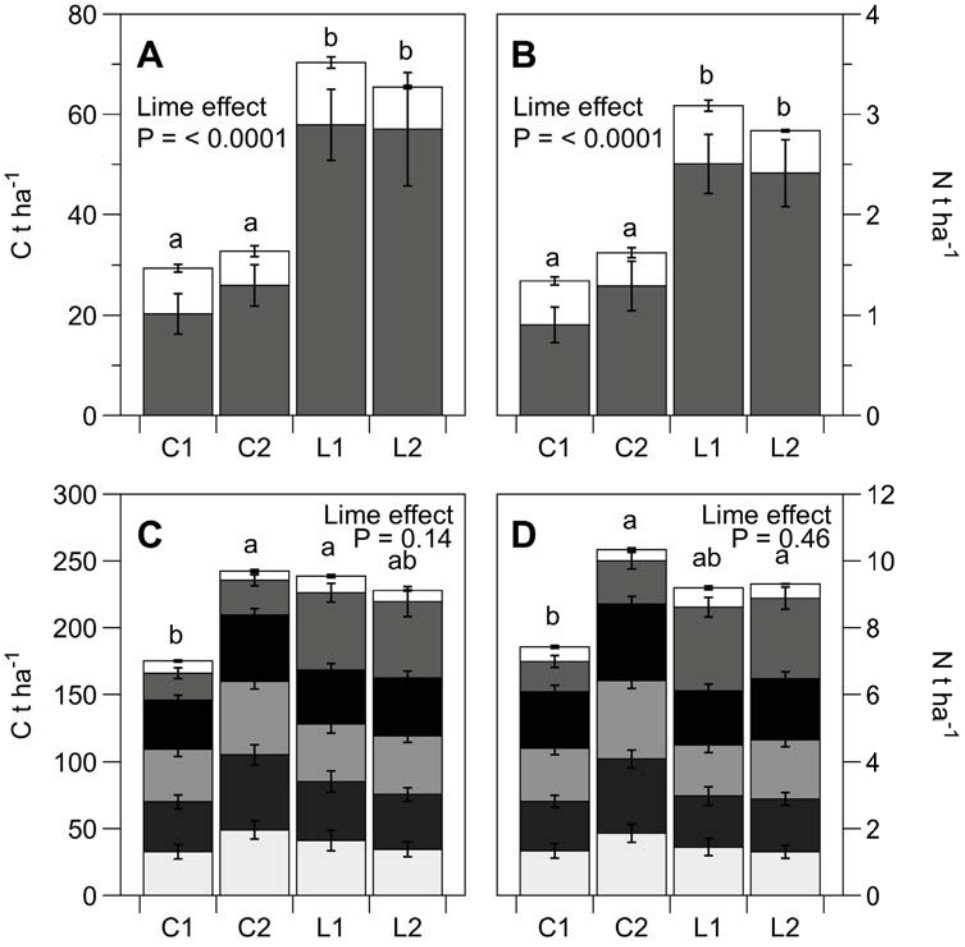

FIGURE 2. Cumulative soil C and N stocks for forest floor (A and B) and combined forest floor and top 40 cm of mineral soil (C and D) displayed with subcatchment mean values for each measured depth increment ± SE (n = 5 plots). Forest floor Oe horizon is displayed in white and Oa in gray in A and B. Mineral soil depth increments (0 - 10 cm 10 - 20 cm, 20 - 30 cm, 30 - 40 cm) are stacked below forest floor in C and D, with the 30 - 40 cm closest to the x-axis. Different letters indicate significant differences in cumulative C and N stocks among subcatchments. Lime effect indicates overall effect of liming on C and N stocks.

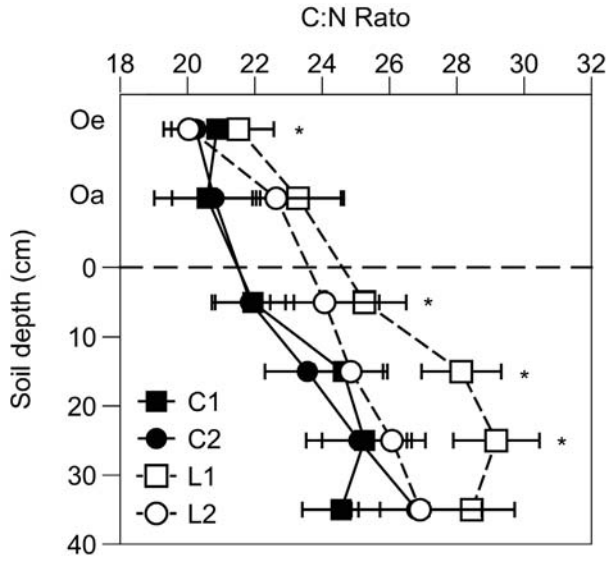

FIGURE 3. Mean forest floor and mineral soil C:N ratio for each subcatchment SE (n = 5 plots). * indicates significant differences among subcatchments (P < 0.05) and is detailed in the text.

Soil basal respiration was significantly lower in the forest floor of limed soils relative to controls, particularly for the Oa horizon (P = 0.04 and < 0.0001 for Oe and Oa, respectively; FIGURE 4 A and B). Soil basal respiration was 17% lower in the Oe horizon of limed soils and reduced by 43% in the Oa layer. The ^{13}C values of C respired as CO_2 did not differ significantly between limed and control forest floor material for either horizon ($\delta^{13}C$ = -25.6, P = 0.10 for Oe and $\delta^{13}C$ = -24.1, P = 0.30 for Oa), suggesting that abiotic CO_2 production caused by dissolution of any remaining lime pellets did not influence observed values.

Net N mineralization expressed on a mg N kg^{-1} soil basis indicated significantly lower rates in the limed soils for both forest floor horizons (P = 0.0003 and 0.0032 for Oe and Oa, respectively; Figure 5 A and C). No effect of liming on N mineralization in the top 0 - 10 cm of mineral soil was observed (P = 0.74; FIGURE 5E). Net nitrification was significantly higher in the limed soils in the Oe horizon (P < 0.0001; FIGURE 5B), while no differences were evident in the Oa (P = 0.95; FIGURE 5D) or upper mineral soils (P = 0.60; FIGURE 5F). Considering these N cycling measurements on an areal basis (kg N ha^{-1}) reveals a slightly different pattern. Limed Oa material showed significantly lower net N mineralization rates than controls (0.07 vs. 0.11 kg N ha^{-1} day^{-1}, P = 0.05) while no significant differences were observed in the Oe and 0 - 10 cm mineral soil depths (P = 0.06 and 0.81, respectively). Areal-based net nitrification rates were significantly higher in both Oe and Oa forest floor horizons in the limed soils (P = 0.0004 and 0.03, respectively).

DISCUSSION

LIMING EFFECTS ON FOREST FLOOR C AND N CYCLING AND STOCKS

Liming in the Woods Lake Watershed showed large and unexpected effects on C and N cycling 20 years after the lime addition. Perhaps most dramatically, the forest floor in the limed subcatchments was much larger than in the controls, resulting in almost twice the C and N storage in the organic horizons. It was hypothesized that the increase in pH associated with liming would stimulate decomposition and reduce OM accumulation in the forest floor of limed subcatchments, as has been shown in many other studies (Andersson and Nilsson 2001; Andersson and Valeur 1994; Baath and Arnebrant 1994; Priha and Smolander 1994; Shah et al. 1990; Smolander et al. 1994; Valeur and Nilsson 1993; Zelles et al. 1987). These C mineralization studies typically measured respiration immediately following Ca addition, however, which may only reveal a short-term response. Others have found a decline in respiration after the initial enhancement occurring days to weeks after addition (Groffman et al. 2006; Illmer and Schinner 1991; Neale et al. 1997; Persson et al. 1989; Persson et al. 1990). Previous *in situ* measurements of soil respiration at Woods Lake within the first year after liming showed a trend toward higher CO_2 efflux in control relative to limed soil in the peak of summer, but this pattern was not significant (Yavitt et al. 1995). Enhanced forest floor accumulation with liming has been observed previously in conifer forests in Finland and was attributed to increased OM inputs from ground vegetation, although they did not quantify these inputs (Derome 1990). Others report either no change (Lofgren et al. 2009) or large reductions in forest floor mass and C stocks in response to liming 7-40 years after lime application (Kreutzer 1995; Persson et al. 1995). The reasons for these differential responses remain unclear. At Woods Lake, it appears that a decrease in decomposition rate is the primary driver of forest floor accumulation, rather than an increase in litter or root inputs.

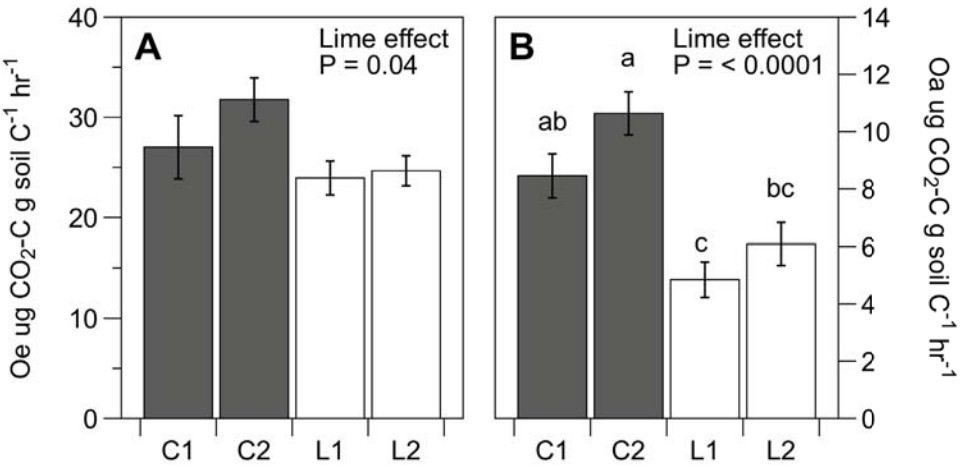

FIGURE 4. Soil basal respiration for Oe (A) and Oa (B) forest floor horizons. Mean values represent plot means within each subcatchment for the two sampling dates SE. Different letters indicate significant differences among subcatchments. Lime effect indicates overall effect of liming.

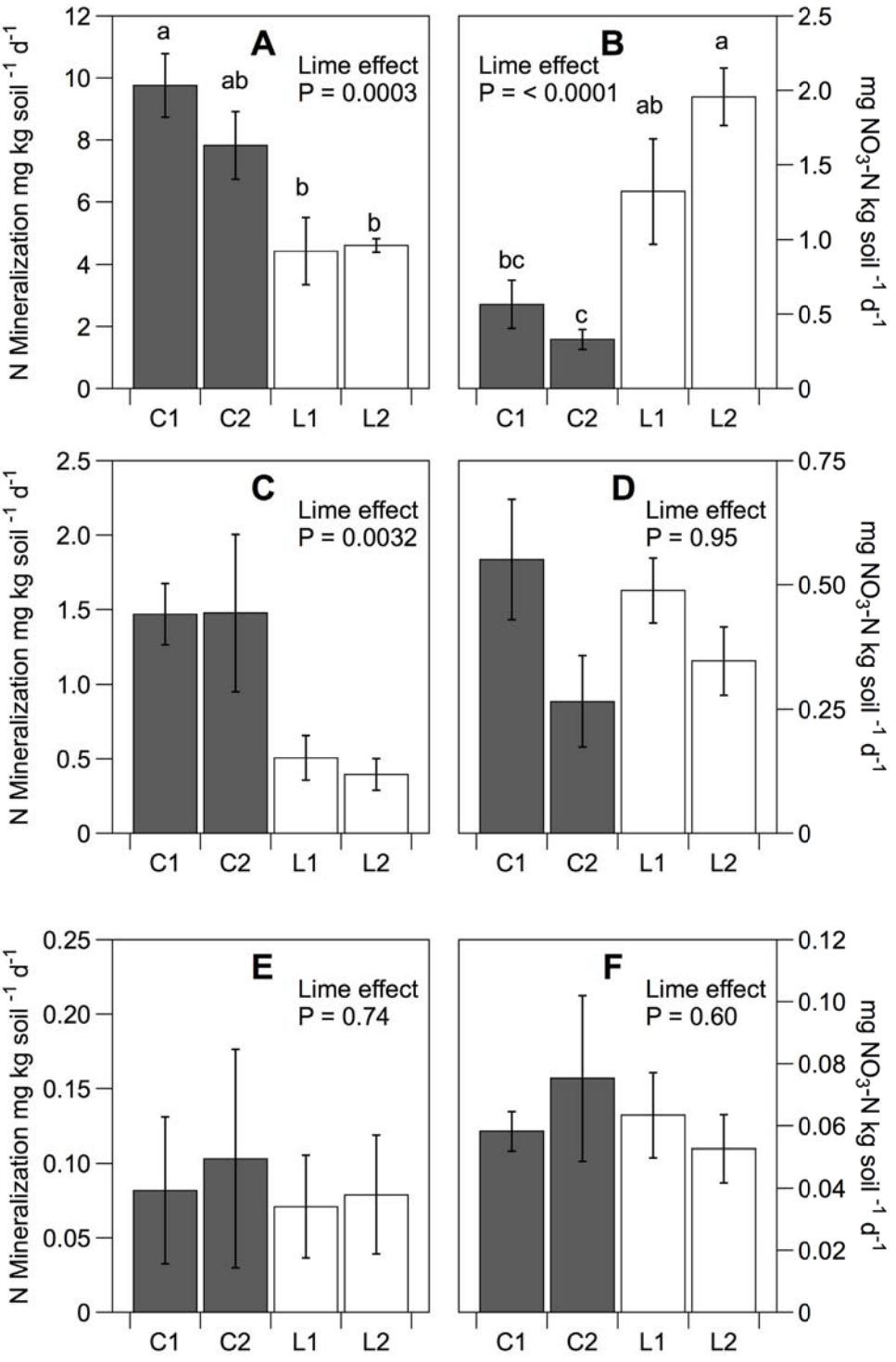

FIGURE 5. Net N mineralization for Oe (A), Oa (C), and 0 - 10 cm mineral soil (E) and nitrification for the same depths (B, D, F) displayed as mean SE for each subcatchment. Different letters indicate significant differences among studied subcatchments (P < 0.05). Lime effect indicates overall effect of liming.

The large observed reduction in soil basal respiration suggests that liming has altered the relationship between the microbial community and the organic matter it mineralizes. There are many ways in which liming could influence soil-microbe interactions, including: 1) changes in the microbial community, 2) altered recalcitrance of the OM produced, or 3) physical stabilization of OM. It is possible that the microbial community in the limed plots has shifted from being more fungal to bacterial dominated, as has been shown in other studies (Andersson and Nilsson 2001; Baath and Arnebrant 1994; Ivarson 1977). A new community may be unable to utilize the C substrate as effectively, either through a change in microbial population size, enzyme activity, or efficiency.

Alternatively, decomposition rates might decrease if plants respond to liming by producing more recalcitrant litter. Plant physiological research has shown that higher Ca availability can increase the lignin concentration in cell walls of tree seedling shoots (Eklund and Eliasson 1990). It was hypothesized that increased Ca availability could enhance lignin production, leading to more recalcitrant litter inputs in limed plots. Findings here indicate the opposite however, that leaf litter lignin concentration was larger in controls than in limed plots, and that the lignin:N ratio in litter did not differ by liming treatment, suggesting that a shift in litter lignin concentration is not a driver of reduced decomposition rate. It is possible that liming could have increased quantities of other recalcitrant compounds that were not measured in this study.

Another possible explanation for the observed increase in Oa mass is that the OM has become physically stabilized via Ca-OM bridging. This mechanism is well studied in laboratory experiments using pure minerals and in agricultural soils (Mikutta et al. 2007; Muneer and Oades 1989; Oades 1988) and has been suggested as a factor influencing soil C and N accumulation in forest soils with neutral pH (5-8) (Morris et al. 2007; Paul et al. 2003) and in tundra ecosystems (pH 6-7) (Hobbie et al. 2002). Additionally, liming has been shown to enhance initial soil C losses, but over time lead to greater C accumulation in the limed soils relative to controls in an agricultural soil (Chan and Heenan 1999). Chan et al. suggested this was due to increased aggregate stability and greater Ca-OM bridging. This initial enhancement in C loss followed by improved OM stability could be the result of increased pH leading to solubilization of more labile C, which then leaves the remaining C pool relatively enriched in more recalcitrant C compounds. In acidic forest soils, Al is typically the dominant binding element (Oades 1988), and therefore little research has been done to explore Ca-OM bridging. In managed forests that are limed, however, this may be a plausible mechanism to enhance soil C and N stocks. There are studies indicating that Ca-OM complexation can occur in the forest floor (Kalbitz et al. 2000) and it may be possible that the increased pH and exchangeable Ca concentrations in the forest floor of limed plots provides an environment in which decadal-scale Ca-OM complexation could occur, thereby reducing microbial access to OM and reducing decomposition.

Forest floor net N mineralization rates were also reduced by liming in both the Oe and Oa horizons. Net nitrification was elevated in limed soils within these horizons, suggesting greater activity of nitrifying

microbes. These results are similar to those reported by Simmons et al. (1996), who found reduced N mineralization and enhanced nitrification in response to liming at Woods Lake two years after the lime addition. Studies at other forested sites have also shown suppression of N mineralization with added Ca (Groffman et al. 2006; Persson et al. 1995; Persson et al. 1990) and higher rates of nitrification (Andersson and Valeur 1994; Clough et al. 2004; De Boer et al. 1993; Groffman et al. 2006; Neale et al. 1997; Persson et al. 1995; Smolander et al. 1995; Ste-Marie and Pare 1999). The pH was most elevated in the Oe forest floor horizon and increased pH has often been linked with increased rates of nitrification (De Boer et al. 1993; Neale et al. 1997; Persson et al. 1995; Smolander et al. 1995; Ste-Marie and Pare 1999).

ESTIMATED FOREST FLOOR C BUDGET

The forest floor C stock in limed plots was approximately 37 t ha^{-1} greater than that in controls. To explore whether the observed treatment effects on C inputs and losses could quantitatively account for this large difference, a net C balance was constructed using empirical data collected in this study and literature values (TABLE 8). Inputs of foliar and non-foliar aboveground litter were calculated separately to reflect the higher input of foliar litter in limed plots and lower input of non-foliar litter (although neither showed a significant liming effect). It was assumed that all non-foliar litter contained 50% C (Fahey et al. 2005). Together, these aboveground inputs accounted for an increase of 0.12 t C ha^{-1} yr^{-1} in the limed forest floor relative to control, or 2.4 t C ha^{-1} in the 20-year period since liming.

Fine root C stocks were 0.24 t C ha^{-1} larger in limed soils. Using a turnover rate of 30% (Tierney and Fahey 2002) and an assumption that roots contained 50% C (Fahey et al. 2005), estimated enhanced root inputs were 0.07 t C ha^{-1} yr^{-1} due to liming, or 1.4 t C ha^{-1} since 1989. Soil basal respiration was significantly lower in limed plots relative to controls. A heterotrophic respiration rate of 2.5 t C ha^{-1} yr^{-1} was assumed for forest floor OM; a value calculated for a similar northern hardwood forest at Hubbard, NH by Fahey et al. (2005). Briefly, Fahey et al. inserted a plate between the forest floor and mineral soils and repeatedly measured *in situ* soil respiration. The annual heterotrophic respiration rate was estimated using this empirical data, measurements of fine root respiration, and a univariate exponential model that included soil temperature. A heterotrophic respiration rate of 2.5 t C ha^{-1} yr^{-1} was used to estimate the enhanced accumulation of C resulting from reduced respiration losses in limed forest floor. Reductions in C loss were estimated separately for the Oe and Oa forest floor horizons because of the large difference in their contribution to the forest floor C stocks. Across all studied plots (treatment and control), approximately 19% of forest floor C stock was in the Oe horizon and 81% was in the Oa. Assuming the heterotrophic respiration is proportional to C stocks in both horizons, approximately 0.47 t C ha^{-1} $yr^{-1}$was respired from the Oe and 2.01 t C ha^{-1} yr^{-1} from the Oa in control soils. Applying the measured 17% suppression of soil basal respiration by lime in the Oe resulted in additional accumulation of 0.08 t C ha^{-1} yr^{-1} in limed soils and the 43% reduction in the Oa resulted in 0.87 t C ha^{-1} greater C retention. Together, this suppression of

respiration might account for an increase of 0.95 t C ha^{-1} yr^{-1} in limed soils, or approximately 19 t C ha^{-1} since lime addition.

Table 8. Estimated annual and 20-year effects of liming on C accumulation in measured input and loss pathways.

Source of C flux	Increase in C stocks in limed soils (t C ha^{-1} yr^{-1})	20-year enhancement in C stocks due to liming (t C ha^{-1})
Foliar litter [nsd]	0.32	6.4
Non-foliar litter [nsd]	-.20	-4.0
< 2mm roots *	0.07	1.4
Heterotrophic respiration *	0.95	19
Observed increase in forest floor C stocks	1.85	37
Enhanced C retention in measured pools	1.14	22.8
C unaccounted for in measured pools		14.2

Combining all C inputs and losses, it was estimated that liming could have enhanced forest floor C stocks by ~22.8 t C ha^{-1}. This leaves 14.2 t C ha^{-1} of the observed difference unaccounted for, but all terms in this simple budget are uncertain. For instance, the respiration rate of Oa material is typically lower than that of Oe, indicating a likely overestimation in the increased accumulation of Oa material due to liming. Measurements taken across the entire watershed indicated that the relative difference in forest floor depth between limed and control soils was 57% smaller than plot observations. Reducing the 37 t C ha^{-1} measured stock difference by 57% yields an expected net enhanced forest floor accumulation due to liming of 15.9 t C ha^{-1}, which is greater than the estimated enhanced retention of 22.8 t C ha^{-1}.

Additional sources of uncertainty in the C budget include the possibility of a transient response to liming and inherent site differences. Liming may have stimulated aboveground and/or root C inputs or reduced basal respiration more strongly immediately following the liming. The small differences observed in inputs may be the residual effects of a much larger transient response. Pre-existing site heterogeneity could have also influenced observed patterns in forest floor. Unfortunately, there is limited pre-treatment data on forest floor nutrient stocks or mass from all studied subcatchments. In each of the limed subcatchments, six soil

pits were excavated prior to liming (Blette and Newton 1996). One control subcatchment had three pits, however this was a control subcatchment that was not used in this study because it was harvested in recent years. Blette et al. report data only on soil base cations and acidity and give no indication of differences in the forest floor. Simmons et al. (1996) utilized both limed subcatchment and the C2 control subcatchment for his forest floor N cycling research. He reports mean forest floor thickness data and gives no indication of differences among the subcatchments. Plot selection may have also influenced findings. As discussed above, forest floor depth measurements taken across the entire watershed indicate that there may be a smaller relative difference in forest floor depth between limed and control subcatchments than observed in the 20 study plots.

Although the plot C and N stock data for limed soils may overestimate watershed values, the pattern of enhanced C and N accumulation with liming is well supported by the data. Both limed subcatchments show similar relative increases in C and N accumulation compared to both control subcatchments. This is in contrast to the mineral soil C and N pools, which were more variable. Watershed-scale forest floor depth sampling also showed a pattern of deeper forest floor in limed subcatchments relative to controls. Finally, the basal soil respiration measurements showed a strong suppression of CO_2 efflux, indicating that mineralization of available C has been reduced in limed soils. The C balance estimates suggest that this can account for much of the observed enhanced C accumulation in limed forest floor.

FOREST FLOOR N

The additional 1.5 t N ha^{-1} observed in limed forest floor is also difficult to reconcile. Reducing the net difference in N accumulation to account for differences in forest floor depth results in an estimated addition 0.6 t N ha^{-1} in limed forest floor. Similar to C, this treatment difference must stem from either enhanced N inputs or reduced losses from limed forest floor. Total foliar N inputs did not differ between treatment and controls. Slightly higher fine root biomass observed in limed soils also seems unlikely to account for the observed difference. It is possible that the trees may have acquired N from deeper mineral soils and then deposited it as litter in the forest floor. No increases in foliar litter N concentrations were observed, but it is possible that the roots may have increased in N concentration, a soil pool not quantified in this study. It may also be possible that liming increased N fixation in the forest floor, but this process is not typically observed in temperate forests (Davidson 2008) and seems an unlikely cause of the large N stocks at the Woods Lake study site.

Smaller losses of N from limed forest floors could contribute to the observed pattern. Net N mineralization was reduced by 31% in Oe and 40% in Oa horizons in limed plots relative to controls. Using an annual net N mineralization rate of 40.1 kg N ha^{-1} yr^{-1} calculated for a nearby Adirondack forest (Ohrui et al. 1999), it was estimated that ~15.5 kg N ha^{-1} yr^{-1} of additional N could accumulate as a result of the observed

suppression in forest floor N mineralization. This accounts for 0.31 t N ha^{-1} over the 20-year period since liming and leaves approximately half of the estimated 0.6 t N ha^{-1} forest floor stocks unaccounted for.

TREE RESPONSE TO LIME ADDITION

A positive tree growth response to liming was expected, but no response was evident. Previous Ca addition studies have reported enhanced growth (Bakker et al. 1999b; Huggett et al. 2007; Kakei and Clifford 2002; Moore and Ouimet 2006), no response (Derome 1990; Huber et al. 2004), or declines (Derome et al. 1986). Long et al. (1997) found that American beech, a dominant species in the Woods Lake Watershed, did not respond to liming. Also, it has been ~100 years since this forest was harvested and therefore the annual woody biomass accumulation is likely low (Odum 1969), and could contribute to the lack of response to added Ca. The net decline in biomass since liming was driven by the high mortality rate of American beech, which is likely the result of beech bark disease in this region (Latty et al. 2003).

There was a trend toward greater annual foliar litter production in limed plots, but this difference was not significant. It is possible that litter inputs were more elevated after the lime addition and that inputs in 2009-2010 reflect the late stages of this enhancement. Very few Ca addition studies report litter responses. Huber et al. (2004) reported no response in a 77-year old, thinned Norway spruce plantation 2-5 and 9-15 years after liming. Although beyond the scope of this study, tree ring analysis might have revealed whether there was a growth enhancement immediately following the Ca addition that has diminished over time.

It was also expected that the enhanced Ca and forest floor pH might stimulate fine root growth or shift root allocation toward surface horizons. Although an overall increase in root biomass in the Oe was observed, this pattern was driven by much greater biomass in the L1 subcatchment relative to all other subcatchments. Some studies have shown increased root production and mycorrhizal infection (Bakker et al. 1999a; Hahn and Marschner 1998; Nowotny et al. 1998), but others have found little or mixed responses to liming (Andersson and Soderstrom 1995; Qian et al. 1998).

LIMING STUDIES AND RELEVANCE TO FOREST RECOVERY FROM ACIDIFICATION

Among published forest liming studies, the application rate of 2.76 t Ca ha^{-1} at Woods Lake is relatively high. This was well beyond a replenishment of Ca lost as a result of acid deposition (estimated to be ~0.85 t Ca ha^{-1} in NH; Groffman et al. 2006) and therefore may be viewed more as a Ca fertilization experiment than as assisted recovery to pre-acid deposition conditions. In regions where declines in acid deposition have been documented, similar C and N responses may not be expected without the addition of a large pulse of Ca and shift in pH generated by liming.

Forest C and N responses to natural de-acidification contrast with the results of this study. In the Czech Republic, Oulehle et al. (2011) measured significant declines in sulfur (S) deposition and soil water sulfate

concentrations in recent decades, with concurrent declines in C and N stocks in the forest floor Oa horizon averaging 1.16 t C ha^{-1} yr^{-1} and 0.04 t N ha^{-1} yr^{-1}. They attributed these changes to increased decomposition and loss of C as CO_2, greater N uptake by trees, and increased translocation of N into the mineral soil. Forest floor pH did not change over this time. This indicates that forest floor decomposition may be affected more strongly by soil S concentrations (or another factor directly related to soil S) than by an increase in soil pH. In the Woods Lake Watershed study, the large dose of lime may have pushed the pH too far in the opposite direction, thereby reducing microbial activity. Also, the large increase in exchangeable Ca concentration may have affected the microbes, or led to increased OM stabilization and reduced microbial access. Interestingly, rates of C and N loss in the Oa horizon observed by Oulehle et al. are similar in magnitude to the estimated rates of Oa accumulation (1.8 t C ha^{-1} yr^{-1} and 0.07 t N ha^{-1} yr^{-1}) observed in this study.

CONCLUSIONS AND POLICY IMPLICATIONS

Liming in the Woods Lake Watershed resulted in a profound increase in C and N storage within the forest floor. The results of this study are in concert with some Ca addition studies, but also show some dramatic differences, suggesting that liming can have differential effects on C and N driven by a suite of ecosystem processes. This work highlights the importance of the coupled interactions among C, N, and Ca cycles and indicates that declines in soil pH and Ca availability have the potential to influence soil C storage, which has direct implications for climate change. Further, the increased N storage suggests that liming may have reduced the export of nitrate, an ion that can be toxic to humans when found in high concentrations in drinking water. In situations where forest liming may be used as a management strategy, above- and belowground pools and fluxes of C and N should be monitored. This will enhance to our understanding of the effects of liming on New York Forests and provides additional insights into how alterations in pH and Ca affect C sequestration and storage, and N retention.

LITERATURE CITED

Andersson, S., and Nilsson, S.I. 2001. Influence of pH and temperature on microbial activity, substrate availability of soil-solution bacteria and leaching of dissolved organic carbon in a mor humus. Soil Biology and Biochemistry 33: 1181-1191.

Andersson, S., and Soderstrom, B. 1995. Efffects of lime ($CaCO_3$) on ectomycorrhizal colonization of *Picea abies* (L.) Karst. seedlings planted in a spruce forest. Scandinavian Journal of Forest Research 10: 149-154.

Andersson, S., and Valeur, I. 1994. Influence of lime on soil respiration, leaching of DOC, and C/S relationships in the mor humus of a haplic podsol. Environment International 20(1): 81-88.

April, R., and Newton, R. 1985. Influence of Geology on Lake Acidification in the ILWAS Watersheds. Water, Air, and Soil Pollution 26: 373-386.

Baath, E., and Arnebrant, K. 1994. Growth rate and response of bacterial communities to pH in limed and ash treated forest soils. Soil Biology and Biochemistry 26(8): 995-1001.

Bailey, S.W., Horsley, S.B., and Long, R.P. 2005. Thirty years of change in forest soils of the Allegheny Plateau, Pennsylvania. Soil Science Society of America Journal 69(3): 681-690.

Bakker, M.R., Kerisit, R., Verbist, K., and Nys, C. 1999a. Effects of Liming on Rhizosphere Chemistry and Growth of Fine Roots and of Shoots of Sessile Oak (*Quercus petraea*). Plant and Soil 217: 243-255.

Bakker, M.R., Nys, C., and Picard, J.F. 1999b. The effects of liming and gypsum applications on a sessile oak (Quercus petraea (M.)Liebl.) stand at La Croix-Scaille (French Ardennes) I. Site characteristics, soil chemistry and aerial biomass. Plant and Soil 206: 99-108.

Blette, V.L., and Newton, R.M. 1996. Effects of watershed liming on the soil chemistry of Woods Lake, New York. Biogeochemistry 32: 175-194.

Brocksen, R.W., Zoettl, H.Z., Porcella, D.B., Huettl, R.F., Feger, K.-H., and Wisniewski, J. 1988. Experimental Liming of Watersheds: an International Cooperative Effort Between the United States and West Germany. Water, Air, and Soil Pollution 41: 455-471.

Chan, K.Y., and Heenan, D.P. 1999. Lime-induced loss of soil organic carbon and effect on aggregate stability. Soil Science Society of America Journal 63: 1841-1844.

Clough, T.J., Kelliher, F.M., Sherlock, R.R., and Ford, C.D. 2004. Lime and soil moisture effects on nitrous oxide emissions from a urine patch. Soil Science Society of America Journal 68(5): 1600-1609.

Cronan, C.S., and Schofield, C.L. 1990. Relationships between aqueous aluminum and acidic deposition in forested watersheds of North-America and northern Europe. Environmental Science & Technology 24(7): 1100-1105.

Davidson, E.A. 2008. Biogeochemistry: Fixing forests. Nature Geoscience 1(7): 421-422.

De Boer, W., Hundscheid, M.P.J., Schotman, J.M.T., Troelstra, S.R., and Laanbroek, H.J. 1993. In situ net N transformations in pine, fir, and oak stands of different ages on acid sandy soil, 3 years after liming. Biology and Fertility of Soils 15(2): 120-126.

Derome, J. 1990. Effects of forest liming on the nutrient status of podzolic soils in Finland. Water Air and Soil Pollution 54: 337-350.

Derome, J., Kukkola, M., and Malkonen, E. 1986. Forest liming on mineral soils results of Finnish experiments. The Finnish Forest Research Institute.

Driscoll, C.T., Cirmo, C.P., Fahey, T.J., Blette, V.L., Bukaveckas, P.A., Burns, D.A., Gubala, C.P., Leopold, D.J., Newton, R.M., Raynal, D.J., Schofield, C.L., Yavitt, J.B., and Porcella, D.B. 1996. The experimental watershed liming study: comparison of lake and watershed neutralization strategies. Biogeochemistry 32: 143-174.

Driscoll, C.T., Lawrence, G.B., Bulger, A.J., Butler, T.J., Cronan, C.S., Eagar, C., Lambert, K.F., Likens, G.E., Stoddard, J.L., and Weathers, K.C. 2001. Acidic deposition in the Northeastern United States: sources and inputs, ecosystem effects, and management strategies. BioScience 51(3): 180-198.

Eklund, L., and Eliasson, L. 1990. Effects of calcium ion concentration on cell wall synthesis. Journal of Experimental Botany 41(228): 863-867.

Fahey, T.J., Tierney, G.L., Fitzhugh, R.D., Wilson, G.F., and Siccama, T.G. 2005. Soil respiration and soil carbon balance in a northern hardwood forest ecosystem. Canadian Journal of Forest Research 35: 244-253.

Fahey, T.J., Siccama, T.G., Driscoll, C.T., Likens, G.E., Campbell, J., Johnson, C.E., Battles, J.J., Aber, J.D., Cole, J.J., Fisk, M.C., Groffman, P.M., Hamburg, S.P., Holmes, R.T., Schwarz, P.A., and Yanai, R.D. 2005. The Biogeochemistry of Carbon at Hubbard Brook. Biogeochemistry **75**: 109-176.

Groffman, P.M., and Fisk, M.C. 2011. Calcium constrains plant control over forest ecosystem nitrogen cycling. Ecology 92(11): 2035-2042.

Groffman, P.M., Fisk, M.C., Driscoll, C.T., Likens, G.E., Fahey, T.J., Eagar, C., and Pardo, L.H. 2006. Calcium additions and microbial nitrogen cycle processes in a northern hardwood forest. Ecosystems 9: 1289-1305.

Hahn, G., and Marschner, H. 1998. Effect of acid irrigation and liming on root growth of Norway spruce. Plant and Soil 199: 11-22.

Haimi, J., and Huhta, V. 1990. Effects of earthworms on decomposition processes in raw humus forest soil - a microcosm study. Biology and Fertility of Soils 10(3): 178-183.

Hobbie, S.E., Miley, T.A., and Weiss, M.S. 2002. Carbon and Nitrogen Cycling in Soils from Acidic and Nonacidic Tundra with Different Glacial Histories in Northern Alaska. Ecosystems 5: 761-774.

Hobbie, S.E., Reich, P.B., Oleksyn, J., Ogdahl, M., Zytkowiak, R., Hale, C., and Karolewski, P. 2006. Tree Species Effects on Decomposition and Forest Floor Dynamics in a Common Garden. Ecology 87(9): 2288-2297.

Huber, C., Kreutzer, K., Rohle, H., and Rothe, A. 2004. Response of artificial acid irrigation, liming, and N-fertilisation on elemental concentrations in needles, litter fluxes, volume increment, and crown transparency of a N saturated Norway spruce stand. Forest Ecology and Management 200: 3-21.

Huggett, B.A., Schaberg, P.G., Hawley, G.J., and Eagar, C. 2007. Long-Term Calcium Addition Increases Growth Release, Wound Closure, and Health of Sugar Maple (*Acer saccharum*) Trees at the Hubbard Brook Experimental Forest. Canadian Journal of Forest Research 37: 1692-1700.

Illmer, P., and Schinner, F. 1991. Effects of lime and nutrient salts on the microbiological activities of forest soils. Biology and Fertility of Soils 11(4): 261-266.

Ivarson, K.C. 1977. Changes in decomposition rate, microbial-population and carbohydrate content of an acid peat bog after liming and reclamation. Canadian Journal of Soil Science 57(2): 129-137.

Jenkins, J.C., Chojnacky, D.C., Heath, L.S., and Birdsey, R.A. 2003. National-Scale Biomass Estimators for United States Tree Species. Forest Science 49(1): 12-35.

Johnson, A.H., Moyer, A., Bedison, J.E., Richter, S.L., and Willig, S.A. 2008. Seven decades of calcium depletion in organic horizons of Adirondack forest soils. Soil Science Society of America Journal 72(6): 1824-1830.

Juice, S.M., Fahey, T.J., Siccama, T.G., Driscoll, C.T., Denny, E.G., Eagar, C., Cleavitt, N.L., Minocha, R., and Richardson, A.D. 2006. Response of Sugar Maple to Calcium Addition to Northern Hardwood Forest. Ecology 87(5): 1267-1280.

Kakei, M., and Clifford, P.E. 2002. Long-term effects of liming on needles, soil properties, and soil water in a sitka spruce stand on deep peat. Forestry 75: 553-567.

Kalbitz, K., Solinger, S., Park, J.-H., Michalzik, B., and Matzner, E. 2000. Controls on the Dynamics of Dissolved Organic Matter in Soils: A Review. Soil Science 164(4): 277-304.

Kreutzer, K. 1995. Effects of Forest Liming on Soil Processes. Plant and Soil 168-169: 447-470.

Latty, E.F., Canham, C.D., and Marks, P.L. 2003. Beech bark disease in northern hardwood forests: the importance of nitrogen dynamics and forest history for disease severity. Canadian Journal of Forest Research-Revue Canadienne De Recherche Forestiere 33(2): 257-268.

Lautner, S., and Fromm, J. 2010. Calcium-dependent physiological processes in trees. Plant Biology 12(2): 268-274.

Likens, G.E., Driscoll, C.T., and Buso, D.C. 1996. Long-term effects of acid rain: response and recovery of a forest ecosystem. Science 272(5259): 244-246.

Likens, G.E., Driscoll, C.T., Buso, D.C., Siccama, T.G., Johnson, C.E., Lovett, G.M., Fahey, T.J., Reiners, W.A., Ryan, D.F., Martin, C.W., and Bailey, S.W. 1998. The biogeochemistry of calcium at Hubbard Brook. Biogeochemistry 41: 89-173.

Lofgren, S., Cory, N., Zetterberg, T., Larsson, P.-E., and Kronnas, V. 2009. The long-term effects of catchment liming and reduced sulphur deposition on forest soils and runoff chemistry in southwest Sweden. Forest Ecology and Management 258(5): 567-578.

Long, R.P., Horsley, S.B., and Lilja, P.R. 1997. Impact of Forest Liming on Growth and Crown Vigor of Sugar Maple and Associated Hardwoods. Canadian Journal of Forest Research 27: 1560-1573.

McLaughlin, S.B., and Wimmer, R. 1999. Tansley review No. 104 calcium physiology and terrestrial ecosystem processes. New Phytologist 142(3): 373-417.

Mikutta, R., Mikutta, C., Kalbitz, K., Scheel, T., Kaiser, K., and Jahn, R. 2007. Biodegradation of Forest Floor Organic Matter Bound to Minerals via Different Binding Mechanisms. Geochimica et Cosmochimica Acta 71: 2569-2590.

Moore, J.-D., and Ouimet, R. 2006. Ten-Year Effect of Dolomitic Lime on the Nutrition, Crown Vigor, and Growth of Sugar Maple. Canadian Journal of Forest Research 36: 1834-1841.

Morris, S.J., Bohm, S., Haile-Mariam, S., and Paul, E.A. 2007. Evaluation of carbon accural in afforested agricultural soils. Global Change Biology 13: 1145-1156.

Muneer, M., and Oades, J.M. 1989. The role of Ca-organic interactions in soil agregate stability. III. Mechanisms and models. Australian Journal of Soil Research 27: 411-423.

NADP. 2008. National Atmospheric Deposition Program. Available from http://nadp.isws.illinois.edu/data/ [accessed July 28, 2011 2011].

Neale, S.P., Shah, Z., and Adams, W.A. 1997. Changes in Microbial Biomass and Nitrogen Turnover in Acidic Organic Soils Following Liming. Soil Biology and Biochemistry 29(9/10): 1463-1474.

Nowotny, I., Dahne, J., Klingelhofer, D., and Rothe, G.M. 1998. Effect of Artificial Soil Acidification and Liming on Growth and Nutrient Status of Mycorrhizal Roots of Norway Spruce (*Picea abies* [L.] Karst.). Plant and Soil 199: 29-40.

Oades, J.M. 1988. The retention of organic matter in soils. Biogeochemistry 5: 35-70.

Odum, E.P. 1969. The Strategy of Ecosystem Development. Science 164(3877): 262-270.

Ohrui, K., Mitchell, M.J., and Bischoff, J.M. 1999. Effect of landscape position on N mineralization and nitrification in a forested watershed in the Adirondack Mountains of New York. Canadian Journal of Forest Research-Revue Canadienne De Recherche Forestiere 29(4): 497-508.

Oste, L.A., Temminghoff, E.J.M., and van Riemsdijk, W.H. 2002. Solid-solution Partitioning of Organic Matter in Soils as Influenced by an Increase in pH or Ca Concentration. Environmental Science and Technology 36: 208-214.

Oulehle, F., Evans, C.D., Hofmeister, J., Krejci, R., Tahovska, K., Persson, T., Cudlin, P., and Hruska, J. 2011. Major changes in forest carbon and nitrogen cycling caused by declining sulphur deposition. Global Change Biology 17(10): 3115-3129.

Paul, E.A., Morris, S.J., Six, J., Paustian, K., and Gregorich, E.G. 2003. Interpretation of Soil Carbon and Nitrogen Dynamics in Agricultural and Afforested Soils. Soil Science Society of America Journal 67: 1620-1628.

Persson, T., Lundkvist, H., Wiren, A., Hyvonen, R., and Wessen, B. 1989. Effects of Acidification and Liming on Carbon and Nitrogen Mineralization and Soil Organisms in Mor Humus. Water, Air, and Soil Pollution 45: 77-96.

Persson, T., Rudebeck, A., and Wiren, A. 1995. Pools and fluxes of carbon and nitrogen in 40-year-old forest liming experiments in Southern Sweden. Water, Air, and Soil Pollution 85: 901-906.

Persson, T., Wiren, A., and Andersson, S. 1990. Effects of Liming on Carbon and Nitrogen Mineralization in Coniferous Forests. Water, Air, and Soil Pollution 54(1): 351-364.

Priha, O., and Smolander, A. 1994. Fumigation-extraction and substrate-induced respiration derived microbial biomass C, and respiration rate in limed soil of Scots pine sapling stands. Biology and Fertility of Soils 17: 301-308.

Qian, X.M., Kottke, I., and Oberwinkler, F. 1998. Influence of Liming and Acidification on the Activity of the Mycorrhizal Communities in a *Picea abies* (L.) Karst. Stand. Plant and Soil 199: 99-109.

Rau, B.M., Melvin, A.M., Johnson, D.W., Goodale, C.L., Blank, R.R., Fredriksen, G., Miller, W.W., Murphy, J.D., Todd, D.E., and Walker, R.F. 2011. Revisiting Soil Carbon and Nitrogen Sampling: Quantitative Pits Versus Rotary Cores. Soil Science 176(6): 273-279.

Reich, P.B., Oleksyn, J., Modrzynski, J., Mrozinski, P., Hobbie, S.E., Eissenstat, D.M., Chorover, J., Chadwick, O.A., Hale, C.M., and Tjoekler, M.G. 2005. Linking Litter Calcium, Earthworms and Soil Properties: a Common Garden Test with 14 Tree Species. Ecology Letters 8: 811-818.

Romkens, P.F., Bril, J., and Salomons, W. 1996. Interaction Between Ca2+ and Dissolved Organic Carbon: Implications for Metal Mobilization. Applied Geochemistry 11: 109-115.

Shah, Z., Adams, W.A., and Haven, C.D.V. 1990. Composition and activity of the microbial population in an acidic upland soil and effects of liming. Soil Biology and Biochemistry 22: 257-263.

Siccama, T.G., Bliss, M., and Vogelmann, H.W. 1982. Decline of red spruce in the Green Mountains of Vermont. Bulletin of the Torrey Botanical Club 109(2): 162-168.

Simmons, J.A., Yavitt, J.B., and Fahey, T.J. 1996. Watershed liming effects on the forest floor N cycle. Biogeochemistry 32: 221-244.

Smallidge, P.J., and Leopold, D.J. 1994. Forest community composition and juvenile red spruce (*Picea rubens*) age-structure and growth patterns in an Adirondack watershed. Bulletin of the Torrey Botanical Club 121(4): 345-356.

Smolander, A., Kitunen, V., Priha, O., and Malkonen, E. 1995. Nitrogen Transformations in Limed and Nitrogen Fertilized Soil in Norway Spruce Stands. Plant and Soil 172: 107-115.

Smolander, A., Kurka, A., Kitunen, V., and Malkonen, E. 1994. Microbial Biomass C and N, and Respiratory Activity in Soil of Repeatedly Limed and N- and P-Fertilized Norway Spruce Stands. Soil Biology and Biochemistry 26(8): 957-962.

Staubitz, W.W., and Zarriello, P.J. 1989. Hydrology of two headwater lakes in the Adirondack Mountains of New York. Canadian Journal of Fisheries and Aquatic Sciences 46(2): 268-276.

Ste-Marie, C., and Pare, D. 1999. Soil, pH and N availability effects on net nitrification in the forest floors of a range of boreal forest stands. Soil Biology & Biochemistry 31(11): 1579-1589.

Thomas, R.Q., Canham, C.D., Weathers, K.C., and Goodale, C.L. 2010. Increased tree carbon storage in response to nitrogen deposition in the US. Nature Geoscience 3: 13-17.

Tierney, G.L., and Fahey, T.J. 2002. Fine root turnover in a northern hardwood forest: a direct comparison of the radiocarbon and minirhizotron methods. Canadian Journal of Forest Research-Revue Canadienne De Recherche Forestiere 32(9): 1692-1697.

Tipping, E., and Ohnstad, M. 1984. Aggregation of Aquatic Humic Substances. Chemical Geology 44: 349-357.

Valeur, I., and Nilsson, I. 1993. Effects of lime and two incubation techniques on sulfur mineralization in a forest soil. Soil Biology & Biochemistry 25(10): 1343-1350.

van Breemen, N., Mulder, J., and Driscoll, C.T. 1983. Acidification and alkalinization of soils. Plant and Soil 75: 283-308.

Warby, R.A.F., Johnson, C.E., and Driscoll, C.T. 2009. Continuing acidification of organic soils across the Northeastern USA: 1984-2001. Soil Science Society of America Journal 73(1): 274-284.

Yavitt, J.B., Fahey, T.J., and Simmons, J.A. 1995. Methane and carbon dioxide dynamics in a northern hardwood ecosystem. Soil Science Society of America Journal 59: 796-804.

Zelles, L., Scheunert, I., and Kreutzer, K. 1987. Bioactivity in Limed Soil of a Spruce Forest. Biology and Fertility of Soils 3(4): 211-216.

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