Biogeochemistry (2017) 132:343–357
DOI 10.1007/s10533-017-0307-z

Soil Ca alters processes contributing to C and N retention in the Oa/A horizon of a northern hardwood forest

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Received: 26 July 2016 / Accepted: 1 February 2017 / Published online: 13 February 2017

Abstract Recent studies on the effects of calcium (Ca) additions on soil carbon (C) cycling in organic soil horizons present conflicting results, with some studies showing an increase in soil C storage and others a decrease. We tested the legacy effects of soil Ca additions on C and nitrogen (N) retention in a long-term incubation of soils from a plot-scale field experiment at the Hubbard Brook Experimental Forest, NH, USA. Two levels of Ca (850 and 4250 kg Ca/ha) were surface applied to field plots as the mineral wollastonite ($CaSiO_3$) in summer of 2006. Two years after field Ca additions, Oa/A horizon soils were collected from field plots and incubated in the laboratory for 343 days to test Ca effects on C mineralization, dissolved organic carbon (DOC) export, and net N transformations. To distinguish mineralization of soil organic C (SOC) from that of more recent C inputs to soil, we incubated soils with and without added ^{13}C-labeled sugar maple leaf litter. High Ca additions increased exchangeable Ca and pH compared to the control. While low Ca additions had little effect on mineralization of SOC or added litter C, high Ca additions reduced mineralization of SOC and enhanced mineralization of litter C. In litter-free incubations, $\delta^{13}C$ of respired C was enriched in the high Ca treatment compared to the control, indicating that Ca suppressed mineralization of ^{13}C-depleted SOC sources. Leaching of DOC and NH_4^+ were reduced by Ca additions in litter-free and litter-amended soils. Our results suggest that Ca availability in these organic soils influences mineralization of SOC and N primarily by stabilization processes and only secondarily through pH effects on organic matter solubility, and that SOC binding processes become important only with relatively large alterations of Ca status.

Responsible Editor: Christine V. Hawkes.

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Keywords Acid deposition · Calcium · ^{13}C · Isotope · Carbon mineralization · Microbial activity · Nitrogen

Introduction

Acid deposition has been linked to cation depletion and forest decline in some areas (Lawrence et al. 1995; DeHayes et al. 1999; Schaberg et al. 2001; Driscoll et al. 2003; Bailey et al. 2005). Effects of soil cation depletion, related to historical acid deposition in some regions, continue to be of interest as evidence reveals slow recovery of forested ecosystems despite improved air quality and reduced deposition. Forests growing on relatively young soils (ca 13000 BP) derived from base poor parent materials in the northeastern US appear to be especially sensitive (Likens et al. 1998). For example, substantial loss of forest floor calcium (Ca) has been reported at the Hubbard Brook Experimental Forest (HBEF) over the past 60 years (Lawrence et al. 1995; Likens et al. 1996, 1998), and Ca restoration was found to improve forest health at this (Hawley et al. 2006; Juice et al. 2006; Battles et al. 2013) and other northern hardwood forest sites (St. Clair and Lynch 2005; Moore and Ouimet 2010). As the acidity of precipitation has declined in recent decades, recovery of soil base status and pH has been observed in some northern hardwood sites (Lawrence et al. 2015). Changes in soil base status should influence soil carbon (C) and nitrogen (N) cycling (Clarholm and Skyllberg 2013), as well as forest productivity.

There has been recent interest in understanding the relative importance of biophysical accessibility and biochemical recalcitrance (e.g., Dungait et al. 2012) for soil C stabilization. Biophysical accessibility is thought to control soil organic matter (SOM) metabolism through mineral interactions, aggregation, and cation interactions, ultimately influencing the probability that organic molecules interact with decomposer organisms and enzymes (Kögel-Knabler et al. 2008; Dungait et al. 2012). The stabilizing effects of Ca on SOM have been recognized primarily in mineral soils where clay minerals are involved in cation bridging (Sollins et al. 1996; Six et al. 2002). In northern forests, organic horizons store substantial quantities of C and nutrients, yet the interactions of the heterogeneous organic matter forms in these horizons, and the effects of Ca on these interactions have received less attention. Litter-derived organic matter is gradually incorporated into the underlying organic horizons where it can persist as older soil organic C (SOC). Nutrient mineralization dynamics also change with depth in the profile (Fisk et al. 2010), especially in response to Ca addition (Minick et al. 2011).

To link changes in C metabolism to N mineralization requires better understanding of what forms of C are degraded by soil microorganisms. In the organic horizons that are common in northern hardwoods, mineralization of older SOC may provide microorganisms with less growth-promoting C and energy, fostering the net mineralization of N compared to metabolism of more recent inputs of organic C that can reduce C limitation and promote high N demand by decomposer microorganisms, potentially reducing net N mineralization (Hart et al. 1994; Schimel and Weintraub 2003; Fisk et al. 2015). Carbon isotope analysis can facilitate the study of soil C cycling, for example by separating different potential C sources to decomposer microorganisms (Bowling et al. 2008; Benner et al. 1987), and by tracing fates of added ^{13}C-labeled substrates into various pools [e.g., dissolved organic C (DOC), respired C, microbial biomass C, and soil C; Djikstra et al. 2011]. We employed ^{13}C natural abundance and tracing analysis to distinguish between microbial metabolism of litter-C versus SOC and thereby improve the mechanistic understanding of Ca effects on C and N transformations.

The Ca status of soils can influence microbial C and N processes through different and potentially opposing mechanisms that stabilize soil C via Ca interactions and that enhance microbial decomposition activity via increased pH. For example, Whittinghill and Hobbie (2012) found that soils with similar Ca concentrations exhibited higher C mineralization rates when incubated at high pH (6.5) compared to low pH (4.5), but that Ca additions (as CaOH) suppressed C mineralization rates in soils with high and low pH. Metal cations are known to associate with organic C in ways that reduce accessibility for enzymatic and microbial breakdown (Oades 1988; Clarholm and Skyllberg 2013). Calcium binding with organic matter has been invoked to explain patterns of increasing soil C stocks across Ca gradients (Paul et al. 2003; Hobbie et al. 2007; Morris et al. 2007) and accumulation of SOM in response to Ca addition (Melvin et al. 2013). In systems exposed to acidic deposition and extreme soil acidification, Ca loss from soils has potentially increased the availability of SOM for decomposition, with important implications for soil C storage. Alternatively, the higher pH that can be associated with higher base status increases the solubility of some organic molecules (Stevenson 1994). For example, higher pH has been found to increase the availability of DOC for leaching, possibly contributing to recent increases in DOC loss from some ecosystems as recovery from acidification proceeds (Evans et al. 2012). This may increase C availability to soil microorganisms, contributing to the stimulation of microbial activity that has been found in response to Ca addition (Bååth et al. 1980; Ste-Marie and Paré 1999; Andersson and Nilsson 2001; Melvin et al. 2013), buy may also facilitate enhanced binding of solubilized organic matter with metal ions as acidic functional groups on SOM deprotonate in response to higher pH (Nierop et al. 2002). Calcium binding processes are also expected to be relatively unresponsive in very low base status soils and become important only with substantial increases in Ca availability (Clarholm and Skyllberg 2013). The net outcome of Ca-C binding and pH effects on C and N cycling processes are therefore likely to be sensitive to initial base cation status and soil pH, as well as the extent of recovery from acidification that occurs either through ambient weathering processes or experimental Ca additions.

We tested the legacy effects of Ca additions on C mineralization, DOC export, and leaching of inorganic N by incubating Oa/A horizon soils collected two years after a field Ca manipulation experiment in a northern hardwood forest at the HBEF, located in the White Mountains of central New Hampshire. We compared the effects of low level Ca additions, intended to restore soil base status to pre-acid deposition levels (Groffman et al. 2006), with those of high level Ca additions, similar to what has been used in traditional forest liming practices (Kreutzer et al. 1995), in soils collected from field plots amended with Ca. We tested whether the legacy of field Ca additions would increase retention of C and N by suppressing availability of organic C for microbial breakdown, or would reduce retention of C and N by enhancing microbial activity.

Methods

Study site and treatments

The HBEF is located in the White Mountain National Forest in New Hampshire, USA (43°56′N, 71°45′W) (http://www.hubbardbrook.org). The site and its biogeochemistry are described in detail in Likens and Bormann (1995). The climate is humid continental with short, cool summers with a mean July air temperature of 19 °C, and long cold winters with a mean January air temperature of −9 °C and a continuous winter snowpack of approximately 1.5 m (Federer et al. 1990). Annual precipitation averages approximately 139.5 cm (SD = 18.9). Overstory vegetation, dominated by American beech (*Fagus grandifolia* Ehrh.), sugar maple (*Acer saccharum* Marsh.), and yellow birch (*Betula alleghaniensis* Britt.), arose following selective cutting in the 1880s and 1910s, and some of the older stands were damaged by a hurricane in 1938. Soils at the HBEF are somewhat shallow (75–100 cm) typic and aquic Haplorthods developed from glacial till.

We tested Ca effects on C mineralization using soils from a plot-scale field Ca addition experiment that was established in 2006 (Minick et al. 2011; Groffman and Fisk 2011). Plots were established in four replicate blocks at ~500 m elevation in sugar maple dominated forest in the main Hubbard Brook valley, within an area of ~3 ha. Each plot was 5 m × 5 m and plots within each block were separated by at least 2 m. Each of three plots per block received one of the following treatments in August of 2006: control (nothing), low Ca addition (850 kg Ca ha^{-1}) and high Ca addition (4250 kg Ca ha^{-1}). Ca was added as wollastonite ($CaSiO_3$), a form intended to weather gradually over time. The amount added in the low Ca treatment was similar to that added in a watershed addition experiment at the HBEF (Peters et al. 2004) with the goal of restoring the quantity of Ca lost to acid deposition.

Sample collection and chemical analysis

Soils from the Oa/A horizon were collected from all plots in early fall (September 31st) 2008, approximately two years after soils were amended with Ca. Visual criteria were used to separate Oe and Oa/A horizons in the field. The surface organic matter of recognizable plant origin, fibrous, and generally reddish or dark brown was identified as Oe and the darker, more highly decomposed and amorphous organic material was identified as Oa. Due to the highly variable nature of these soils and the gradual transition between the Oa and A horizons, soils for this study were designated as Oa/A. Challenges in visually separating Oa and A horizons in the field were evident from SOC concentrations that were less than 200 g kg^{-1} (or 20%) (Table 2). Initial SOC concentrations in samples collected for this study ranged from 10 to 24% across all treatments. Previous work by Johnson et al. (2014) showed that SOC concentrations at the HBEF range from 23 to 29% in the Oa horizon and from 7 to 11% in the top 10 cm of mineral soil. Therefore, the C concentration of soils sampled from the current study fall in between those values of the Oa and mineral A soils as measured in Johnson et al. (2014), indicating a mixing of the organic Oa horizon and the underlying A horizon.

We collected 10 cores (5 cm diam.) from each plot and combined to produce one composite Oa/A sample per plot. Composite samples were gently homogenized by hand, removing roots and coarse fragments, within 12 h of sample collection. Soil samples were kept at 4 °C until the incubation began in mid-November (November 17th) 2008. Some of the more labile soil C compounds were likely mineralized over the time period between sample collection and incubation; however, this was unlikely to introduce bias in our interpretation of the long-term effects of soil Ca additions on decomposition of native SOC compared to that of more labile litter inputs.

Soil pH was measured in October 2008 with a glass electrode in a 1:2 mixture (by mass) of soil and water. We quantified soil extractable Ca for Oa/A soils collected in July and October 2008, by shaking soil subsamples ($\sim$5 dry mass) for ½ h with 100 mL of 1 M NH_4Cl. After sitting for 18 h, samples were shaken again for 45 min and filtered through Whatman #1 paper to retrieve the extract. Calcium concentration was analyzed using an air/acetylene flame on a Varian Spectra Atomic Absorption Spectrometer (Mulgrave, Victoria, Australia) with a 10,000 ppm (1%) lanthanum chloride solution as a releasing agent to eliminate chemical interferences.

Laboratory soil incubations

Oa/A horizon subsamples were placed on 2.5 cm Whatman glass fiber filters in bottletop filter units (Corning®) and incubated in 1 L canning jars for 343 d. Initial gravimetric soil moisture was measured by drying separate soil subsamples at 105 °C for 24 h. Approximately 15 g fresh mass (equivalent to 6–8 g dry mass) was placed in each unit on the filter paper. Two replicates were prepared for each sample. To the first replicate, nothing was added (litter-free) and the C mineralized over time is referred to as "basal respiration".

We mixed ground sugar maple leaf litter (0.05 g per g dry soil or approx. 0.4 g total) into the second replicate (litter-amended). Subtracting basal respiration from C mineralized from litter-amended subsamples provided "litter-associated respiration". Basal respiration represents mineralization of native SOC, and litter-associated respiration represents mineralization of recent C inputs. The sugar maple litter that we added was labeled with ^{13}C, so that we could more conclusively separate C derived from SOC or added litter. Litter was produced for the experiment by exposing sugar maple samplings to $^{13}CO_2$, as described in Fahey et al. (2011). The $\delta^{13}C$ value of litter measured before the start of the incubation was 161 ± 4.1‰. We analyzed the ^{13}C enrichment of litter and soils at the UC Davis Stable Isotope Facility using a PDZ Europa ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20–20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK).

Microbial respiration was measured by quantifying CO_2 evolved from soil incubations over the 343 d incubation period. Vials containing 10 mL 0.3 M NaOH were placed with incubating soils in sealed canning jars. Vials were replaced at regular intervals and the CO_2 absorbed was quantified by titrating with 0.3 N HCl in the presence of 0.75 mL 1.8 M $BaCl_2$ and phenolphthalein. Vials were replaced continuously (every 1–7 d) over the first 28 days. After this time period, CO_2 was quantified approximately once per month over a 4–10 d period, following each soil leaching event. We measured $\delta^{13}CO_2$ in the $BaCO_3$ precipitate that was produced by titration. We cleaned the $BaCO_3$ precipitate by washing three times in degassed dH_2O, centrifuging, and pouring off the supernatant. After cleaning, we dried the $BaCO_3$ at 60 °C and ^{13}C was analyzed at the UC Davis Stable Isotope Facility using a PDZ Europa ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20–20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK).

All incubations were leached on the first day twice with 25 mL distilled (DI) H_2O under vacuum, to begin the incubation with a uniform water potential among samples. Filter units were incubated inside of closed canning jars to prevent moisture loss. Incubating soils were subsequently leached with 50 mL DI H_2O on days 32, 61, 91, 126, 157, 192, 229, and 288. Ammonium and NO_3^- concentrations in leachate were quantified for all leaching events and DOC concentration and ^{13}C isotopic composition were analyzed on the 1st (32 d), 3rd (91 d), 5th (157 d), and 6th (192 d) leaching events. We used a phenolate-hypochlorite method to quantify NH_4^+ (method 351.2, US EPA 1983) and a cadmium reduction method to quantify NO_3^- (method 353.2, US EPA 1983). For DOC concentration and ^{13}C analysis of DOC, leachate was kept frozen until samples were sent to the UC Davis Stable Isotope Facility for analysis on a O.I. Analytical Model 1030 TOC Analyzer (OI Analytical, College Station, TX) interfaced to a PDZ Europa 20–20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK) utilizing a GD-100 Gas Trap Interface (Graden Instruments).

We calculated the percent of C originating from the ^{13}C labeled leaf litter, utilizing a two source model outlined by Fry (2006), as follows:

$$\%\,\mathrm{C} = \left(\delta^{13}\mathrm{C}_{\text{litter-amended soil}} - \delta^{13}\mathrm{C}_{\text{litter-free soil}}\right) / \left(\delta^{13}\mathrm{C}_{\text{litter}} - \delta^{13}\mathrm{C}_{\text{litter-free soil}}\right) \times 100$$

where $\delta^{13}C_{\text{litter-amended soil}}$ is the $\delta^{13}C$ value of CO_2 or DOC from incubations in which ^{13}C-labeled leaf litter was added, $\delta^{13}C_{\text{litter-free soil}}$ is the $\delta^{13}C$ value of CO_2 or DOC from incubations without ^{13}C-labeled leaf litter additions, and $\delta^{13}C_{\text{litter}}$ was the average $\delta^{13}C$ value of ^{13}C-labeled leaf litter. These calculations were applied to $\delta^{13}C$ data at day 8, 12 and 112 for CO_2 and day 32, 91, 157, and 192 for DOC.

Statistical analyses

Carbon mineralization, DOC, percent of C originating from the ^{13}C labeled leaf litter, and inorganic N data were analyzed using repeated-measures analysis of variance (ANOVA) (PROC MIXED package) with time as the repeated measure. The spatial covariate structure used to analyze the data was power (sp(pow)). Raw data were natural log-transformed where necessary before analysis in order to establish homogeneity of variance. Data shown in figures are means of raw data, whereas treatment means comparisons were done using transformed data. We considered $P < 0.05$ as significant and $P < 0.1$ as marginally significant. When significant treatment or treatment × time interactions were detected in the repeated measures ANOVA data were analyzed for differences in treatment means on each individual sampling date using the LS means slice option in the PROC MIXED package.

Total soil C and N data were analyzed using one way ANOVA (PROC GLM package). Data were natural log-transformed before analysis where necessary in order to establish homogeneity of variance. Data were plotted as means of raw data and treatment comparisons done on transformed data. When a significant treatment effect was observed in the one-way ANOVA, treatment means were compared using Tukey's honestly significant difference (HSD) multiple comparison method. All analysis was performed using Statistical Analysis System (SAS) 9.4 software (SAS institute, Cary, NC).

Results

For Oa/A soils collected in July 2008, soil extractable Ca was higher in the high and low Ca treatment compared to the control ($F = 6.57$; $P = 0.03$; Table 1). In October 2008 treatment effects on extractable Ca were not detected ($F = 1.82$; $P = 0.27$; Table 1), although extractable Ca tended to be higher in both high Ca and low Ca treatments compared to control. In October 2008, soil pH was 4.1 ± 0.18, 4.6 ± 0.10 and 4.9 ± 0.14 in control, low Ca and high Ca treatments, respectively, and differed between control and high Ca soils (treatment: $F = 6.37$; $P = 0.03$; Table 1). No treatment

Table 1 Extractable soil Ca measured in July and October 2008 and soil pH measured in October 2008 in the Oa/A soil horizon collected from the Hubbard Brook Experimental Forest

Treatment	July 2008 Ca ($\mathrm{cmol_c/kg}$)	October 2008 Ca ($\mathrm{cmol_c/kg}$)	October 2008 pH
Control	1.6 (0.85)^a	2.1 (0.63)	4.1 (0.18)^a
Low Ca	3.8 (0.61)^b	4.8 (1.56)	4.6 (0.10)^{ab}
High Ca	6.7 (3.01)^b	5.5 (1.73)	4.9 (0.14)^b

Original $CaSiO_4$ treatments were applied in summer of 2006. Standard errors of the means are in parenthesis

Values with different superscript lowercase letters are significantly different at $P < 0.05$

Table 2 Carbon concentrations (g kg^{-1}) and soil $\delta^{13}C$ (‰) values pre- and post-incubation and total C mineralized (mg CO_2–C g^{-1}) over the course of the 343 d incubation of soils collected from field treatments with and without additions of ^{13}C-labeled sugar maple leaf litter

Treatment	Pre-C conc.	Post-C conc.	Pre-$\delta^{13}C$	Post-$\delta^{13}C$	$\Delta\delta^{13}C$	Total C mineralized*
Control	148 (29)	156 (19)	−26.1 (0.2)	−27.0 (0.2)	−0.9 $(0.14)^{ab}$	18.5 (1.4)
Low Ca	168 (26)	170 (22)	−25.7 (0.3)	−26.2 (0.4)	−0.5 $(0.07)^{a}$	19.7 (2.3)
High Ca	139 (17)	117 (19)	−25.9 (0.3)	−27.4 (0.4)	−1.4 $(0.10)^{b}$	14.3 (0.9)
Control + L	148 (29)	148 (19)	−26.1 (0.2)	−2.7 (3.4)	23 (3.6)	16.9 (1.0)
Low Ca + L	168 (26)	175 (30)	−25.7 (0.3)	−3.2 (1.4)	22 (1.8)	17.2 (3.4)
High Ca + L	139 (17)	157 (7)	−25.9 (0.3)	−2.5 (2.5)	23 (2.8)	18.1 (0.7)

Standard errors of the means are in parenthesis

Values with different superscript lowercase letters are significantly different at $P < 0.05$

* Total C mineralized for litter-amended incubations is subtracted from basal

differences were found for pre- (F = 0.41; $P = 0.7$) and post-incubation (F = 1.04; $P = 0.4$) bulk soil C concentrations or pre- (F = 0.44; $P = 0.7$) and post-incubation (F = 2.43; $P = 0.2$) $\delta^{13}C$ values (Table 2), but the change in $\delta^{13}C$ of SOC between initial and final values for litter-free incubations was more negative in the high Ca treatment compared to low Ca treatment (F = 8.9; $P = 0.02$; Table 2).

In litter-free incubations, C mineralization rates declined over time, from rates of about 50–100 µg C g^{-1} d^{-1} up to day 175 to 25–40 µg C g^{-1} d^{-1} for the remainder of the incubation (Fig. 1). Adding ^{13}C-labeled leaf litter substantially increased C mineralization rates relative to those of SOC for the first 120 d (Fig. 2). Mineralization rates of litter C declined rapidly over the first 10 days of incubation, suggesting depletion of a small and very labile C pool. Rates continued to decline more gradually to about 175 d, after which they remained stable (Fig. 2).

In litter-free incubations, mineralization of SOC differed among Ca treatments (F = 32.37; $P < 0.0001$) and over time (F = 27.08; $P < 0.0001$). Carbon mineralization rates were lower in the high Ca compared to low Ca treatment and controls at multiple sampling dates spanning the entire 343 d incubation period (Fig. 1). High Ca treatment suppressed C mineralization rates most frequently in the first 28 d before the first leaching but also following several of the subsequent leaching events (Fig. 1). A marginally significant treatment effect was found for total C mineralized in litter-free incubations (F = 3.81; $P = 0.1$), with total C mineralized in the high Ca treatment ~23% lower than the control and ~27% lower than the low Ca treatment (Table 2). Over the course of the 1st 28 days, when litter-derived labile C was the highest, litter-amended incubations exhibited the opposite treatment pattern as that of the litter-free incubations. A treatment × time interaction was found (F = 2.06; $P = 0.0007$), with elevated rates of C mineralization in the high Ca + L treatment primarily during the first 28 d before leaching and at approximately 175 d, following the 6th leaching event (Fig. 2). Total litter-derived C mineralized throughout the incubation period did not differ among treatments (F = 0.21; $P = 0.8$) (Table 2), suggesting that the initial positive effect of high Ca additions on litter mineralization was small relative to longer-term decomposition dynamics.

In litter-free incubations, C mineralized from SOC was enriched in ^{13}C in the high Ca treatment compared to controls (treatment × time: F = 3.37; $P = 0.002$; Fig. 3a), suggesting that mineralization of more ^{13}C-enriched SOC drove the depletion of the remaining SOC pool found at the end of the incubation (Table 2). Carbon mineralized from incubations with ^{13}C-labeled leaf litter was highly enriched in ^{13}C, especially during the first 28 d, and became less enriched over time (Fig. 3b). Overall, the high Ca treatment affected mineralization of ^{13}C from litter-amended soils (F = 11.12; $P = 0.0001$), with $\delta^{13}C$ of mineralized C being greater in the high Ca treatment (108 ± 10.7‰) compared to controls (87 ± 9.8‰). A treatment × time interaction was found for the proportion of C originating from the ^{13}C labeled leaf litter (F = 5.58; $P = 0.004$). At 28 d, before the 1st leaching, 81 ± 4.5% of C mineralized from high Ca

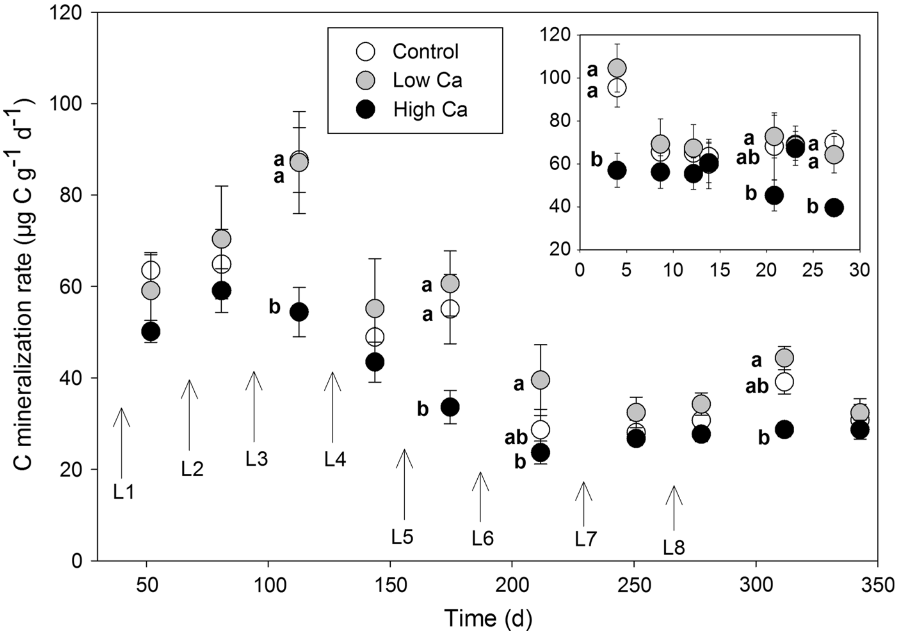

Fig. 1 Carbon mineralization rates over a 343 d laboratory incubation of soils collected from control plots or plots amended with low Ca (850 kg Ca/ha) or high Ca (4250 kg Ca/ha). The main figure shows CO_2 data collected after the first leaching at day 32, while the *inset* represents continuous C mineralization rates measured during the first 28 days of the incubation. Leaching occurred between all CO_2 measurements occurring after day 28 and up to day 275. Values are means (n = 4 for control and low Ca, n = 3 for high Ca) with standard *error bars*. Significant differences are indicated by different lowercase *letters* ($P < 0.05$)

soils came from added litter with the rest coming from native SOC, whereas 51 ± 3.2 and 57 ± 0.9% of C mineralized came from added litter in the control and low Ca treatments, respectively ($F = 24.16$; $P < 0.0001$). No treatment differences at days 8 or 112 (the only other comparable results between litter-free and litter-amended incubations) were found for the proportion of C mineralization arising from added leaf litter.

Rates of DOC export ranged from 0.3 to 1.4 µg DOC g^{-1} d^{-1} in the absence of added litter (Fig. 4a) and differed marginally among treatments at 91 d ($F = 2.67$; $P = 0.09$) and with time ($F = 2.49$; $P = 0.08$). Cumulative DOC export from litter-free incubations was 369 ± 83 µg g^{-1} (control), 290 ± 87 µg g^{-1} (low Ca), and 190 ± 30 µg g^{-1} (high Ca), but Ca effects were not detected ($F = 1.29$; $P = 0.3$). Adding leaf litter increased DOC export relative to litter-free incubations, especially at the first time point (28 days; Fig. 4a, b). In litter-amended soils, treatment ($F = 4.39$; $P = 0.02$) and time ($F = 25.78$; $P < 0.001$) effects were stronger compared to litter-free soils. DOC export from the low Ca + L treatment was lower than control + L treatment at 91 d and the high Ca + L treatment was lower than the control + L treatment at 157 d (Fig. 4b). Cumulative DOC originating from litter was 110 ± 21 µg g^{-1} (control), 119 ± 63 µg g^{-1} (low Ca), and 159 ± 90 µg g^{-1} (high Ca), but treatment differences were not significant ($F = 0.16$; $P = 0.9$).

For litter-free incubations, $\delta^{13}C$ natural abundance of DOC exhibited a marginally significant treatment × time interaction ($F = 2.26$; $P = 0.07$; Fig. 5a). Initially, $\delta^{13}C$ of DOC from the high Ca treatment was more enriched but over time this trend reversed with $\delta^{13}C$ of DOC from the high Ca treatment becoming more depleted in ^{13}C compared to low Ca and control treatments (Fig. 5a). Calcium treatments did not affect $\delta^{13}C$ of DOC from incubations amended with litter (Treatment: $F = 0.9$; $P = 0.4$; Treatment × Time: $F = 0.14$; $P = 1.0$; Fig. 5b), and the relative importance of leaf litter as a source of DOC declined over time ($F = 17.55$; $P < 0.0001$) as indicated by decreasing $\delta^{13}C$ values with each subsequent measurement. Overall, ~20% of DOC export over the course of the incubation originated from added litter,

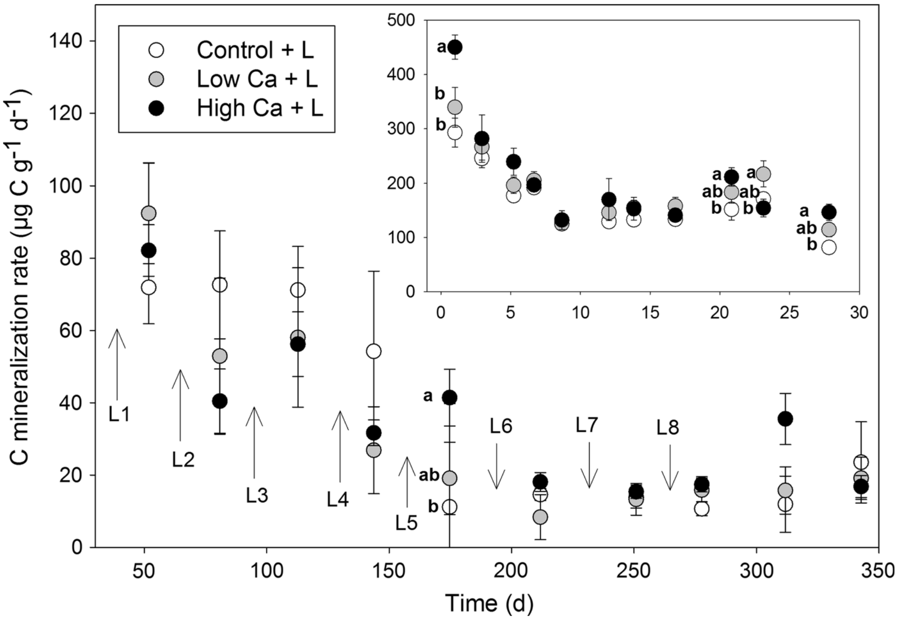

Fig. 2 Leaf litter associated C mineralization rates for a 343 d laboratory incubation of soils amended with Ca and ^{13}C-labeled sugar maple leaf litter. The main figure shows CO_2 data collected after the first leaching at day 32, while the *inset* represents continuous C mineralization rates measured during the first 28 days of the incubation. Leaching of incubations occurred between all CO_2 measurements occurring after day 28 and up to day 275. Mineralization rates are expressed as the difference between incubations with and without addition of leaf litter. Values are means (n = 4) with standard *error bars*. Significant differences are indicated by different lowercase *letters* ($P < 0.05$)

varying from ~25% at 28 d (1st leach) to ~17% at 192 d (6th leach) but with no treatment (F = 0.94; $P = 0.4$) or treatment × time effects (F = 0.34; $P = 0.9$).

Overall, distinct patterns in ^{13}C natural abundance of soil, DOC, and respired C were evident regardless of Ca treatment (Treatment: F = 39.79; $P < 0.0001$; Fig. 6). Over the course of the incubation and across all treatments, litter-free soil δ^{13}C decreased from −25.9 ± 0.19‰ to −26.8 ± 0.18‰, indicating that SOC pool became depleted in ^{13}C over the duration of the incubation. In contrast, respired C was enriched in ^{13}C (−23.9 ± 0.25‰) compared to that of SOC, likely leading to the observed depletion in ^{13}C of the SOC pool by the end of the incubation. Finally, the ^{13}C signature of DOC (−26.8 ± 0.08‰) was similar to the SOC pool, but depleted compared to respired C.

Ammonium concentration in leachate was lower overall in the litter-free high Ca (0.01 ± 0.002 µg NH_4-N g^{-1} d^{-1}) and low Ca treatments (0.50 ± 0.112 µg NH_4-N g^{-1} d^{-1}) compared to the control (1.03 ± 0.196 µg NH_4-N g^{-1} d^{-1}) (Treatment: F = 23.86; $P < 0.0001$; Fig. 7a). Cumulative NH_4^+ leached from litter-free soils was also lower in the high Ca treatment compared to control and low Ca treatment (F = 11.15; $P = 0.01$) (data not shown). In litter-amended soils, NH_4^+ concentration in leachate was also lower in high and low Ca treatments compared to controls (Fig. 7c). The differences were most evident between 120–160 d, giving rise to a treatment × time interaction (F = 3.52; $P < 0.001$). In litter-amended incubations, high Ca suppressed cumulative NH_4^+ leaching (F = 5.97; $P = 0.04$), but did not significantly affect cumulative NH_4^+ leaching attributable to litter (F = 0.72; $P = 0.5$) (data not shown). For litter-free soils, NO_3^- concentration in leachate increased up to day 200 (Fig. 7b) but treatments had no effect (Treatment: F = 2.31; $P = 0.11$; Treatment × Time: F = 0.64; $P = 0.8$). For litter-amended soils, a significant treatment effect was found for leached NO_3^- (F = 3.45; $P = 0.04$) with overall higher NO_3^- concentrations in the control + L incubations (7.8 ± 1.4 µg NO_3-N g^{-1} d^{-1}) and low Ca + L incubations (8.0 ± 1.4 µg NO_3-N g^{-1} d^{-1}) compared to high Ca + L incubations (6.1 ± 1.2 µg NO_3-N g^{-1} d^{-1}) (Fig. 7d). No treatment effects were detected in cumulative NO_3^- leached from litter-free

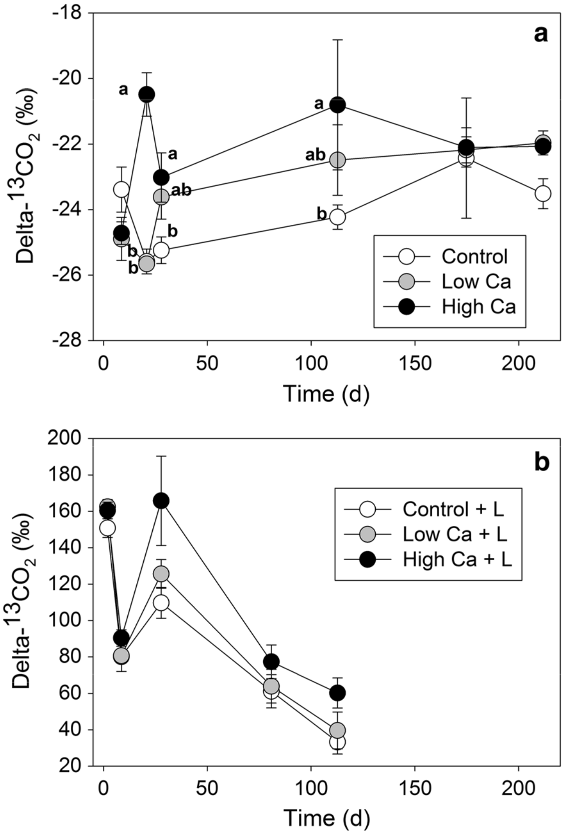

Fig. 3 Delta-^{13}C values (‰) for CO_2 captured in NaOH base traps at various times throughout the laboratory incubations of **a** soils amended with Ca only, **b** soils amended with Ca and ^{13}C-labeled sugar maple leaf litter. Significant differences are indicated by lowercase different *letters* ($P < 0.05$)

(F = 0.88; $P = 0.5$) or litter-amended (F = 1.17; $P = 0.4$) incubations data not shown).

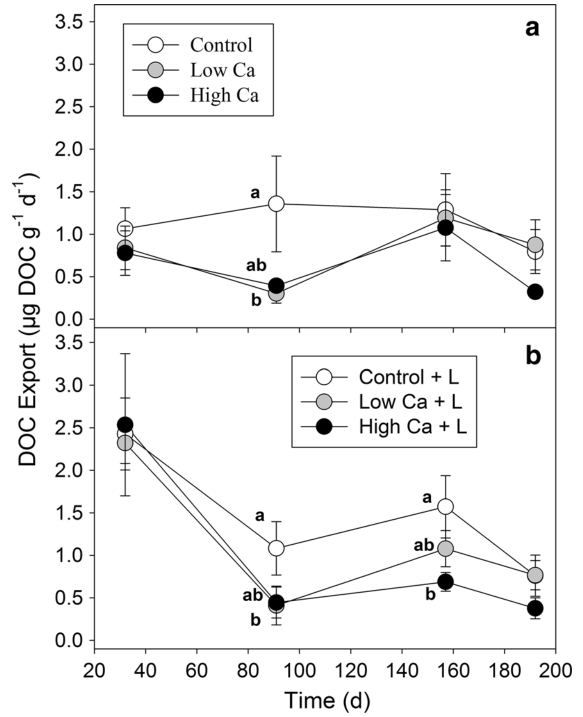

Fig. 4 Dissolved organic C (DOC) measured at four leaching events in laboratory incubations of, **a** soils amended with Ca only, **b** soils amended with Ca and ^{13}C-labeled sugar maple leaf litter. Significant differences are indicated by different lowercase *letters* ($P < 0.1$)

Discussion

We found support for the general hypothesis that elevated soil Ca suppresses mineralization of C and N from SOC. In these base-poor soils, mineralization of C was suppressed only at high levels of Ca. In litter-free incubations, δ^{13}C of CO_2 and post-incubation SOC suggest that Ca additions have reduced availability of ^{13}C-depleted SOC for microbial utilization. In contrast, mineralization of litter-derived C was not suppressed by high Ca, but instead was enhanced, particularly in the initial phases of decomposition. However, the positive effects of Ca on litter-C mineralization were small relative to the negative effects on SOC mineralization. Over the course of the incubation, total mineralization of litter-derived C was approximately 1.2 mg CO_2–C g^{-1} greater in high Ca than control soils, compared to that of SOC, which was approximately 4.2 mg CO_2–C g^{-1} lower in high Ca than control soils (Table 2). Considered together with trends toward Ca suppression of DOC export, our results show the overall potential for higher soil Ca status to contribute to greater net C retention in soils of these base-poor northern hardwood forests. This finding is consistent with the reduction in soil respiration and the long-term (19 year) increase in organic horizon C stocks at the Woods Lake Watershed, New York, USA, following liming with 2.76 Mg Ca ha^{-1} (Melvin et al. 2013). In comparison, we added 0.85 Mg Ca ha^{-1} and 4.25 Mg Ca ha^{-1} for the low and high Ca treatments, respectively. Natural Ca inputs are low at the HBEF because weathering of plagioclase, the principal Ca-bearing mineral, is slow and atmospheric Ca deposition has decreased over the

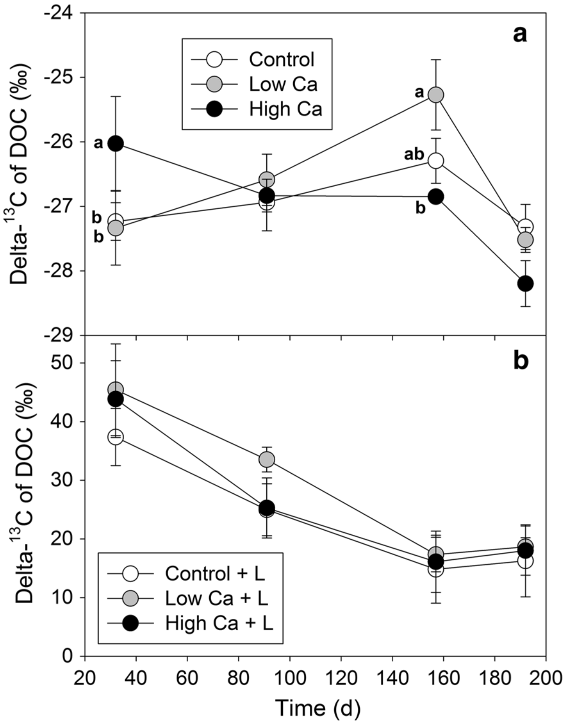

Fig. 5 Delta-^{13}C values (‰) of dissolved organic carbon (DOC) from four leaching events of laboratory incubations of, **a** soils amended with Ca in the field, **b** field soils amended with ^{13}C-labeled sugar maple leaf litter. Significant differences are indicated by different lowercase *letters* ($P < 0.1$)

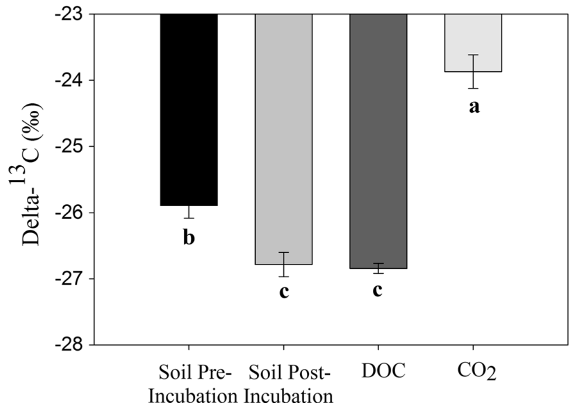

Fig. 6 Delta-^{13}C values (‰) of soil prior to (soil pre-incubation) and at the end (soil post-incubation) of the 343 d incubation and of average dissolved organic C (DOC) and respired C (CO_2) over the course of the incubation period. Bars represent means of all treatments and sampling dates with standard error (n = 4). Significant differences are indicated by different lowercase *letters* ($P < 0.05$)

last 50 years as a consequence of air quality controls in the U.S. and Canada (Likens et al. 1998). As forested ecosystems in the northeastern USA recover from decades of acidification either naturally or through Ca additions, impacts on soil C and N retention appear sensitive to the magnitude of change in exchangeable Ca and pH.

Ca effects on C retention

The net response of C and N following soil Ca additions in this study supports the importance of soil Ca for C and N processes in base-poor northern hardwood forest soils. Soil C stocks have been found to increase in relation to soil Ca status (Oades 1988; Morris et al. 2007), supporting the notion that increasing soil Ca availability will reduce microbial access to organic C and increase soil C retention. Extractable soil Ca was higher in our treatment plots two growing seasons following application. Although the trend persisted into the third autumn season in the soils that we incubated, high spatial variation precluded detection of significant treatment effects on extractable Ca, likely owing to heterogeneity in uptake, recycling, and soil stabilization processes that move added Ca into non-exchangeable pools over time (Johnson et al. 2014). The formation of insoluble compounds through cation–C binding (Sokoloff 1938; Muneer and Oades 1989; Baldock and Skjemstad 2000) may have contributed to this redistribution of added Ca. This binding of cations to organic matter is also a likely mechanism suppressing the availability of SOC for microbial utilization. Calcium is thought to associate only weakly with organic matter at the pH range of our acidic soils, in which other cations such as Al and Fe may dominate SOM associations (Clarholm and Skyllberg 2013). Nevertheless, large amounts of added Ca may increase Ca–SOM binding, or, alternatively, the increase in pH following Ca addition could alter the chemistry of Al or Fe to increase their binding with organic matter (Li and Johnson 2016). While the specifics of these interactions deserve further attention in our soils, some form of stabilization mechanism appears to dominate the Ca effect on mineralization of SOC.

In the litter-free high Ca treatment, respired C was enriched in ^{13}C compared to controls, leading to the depletion of ^{13}C of the SOC pool by the end of the incubation. This indicates that additions of Ca at the

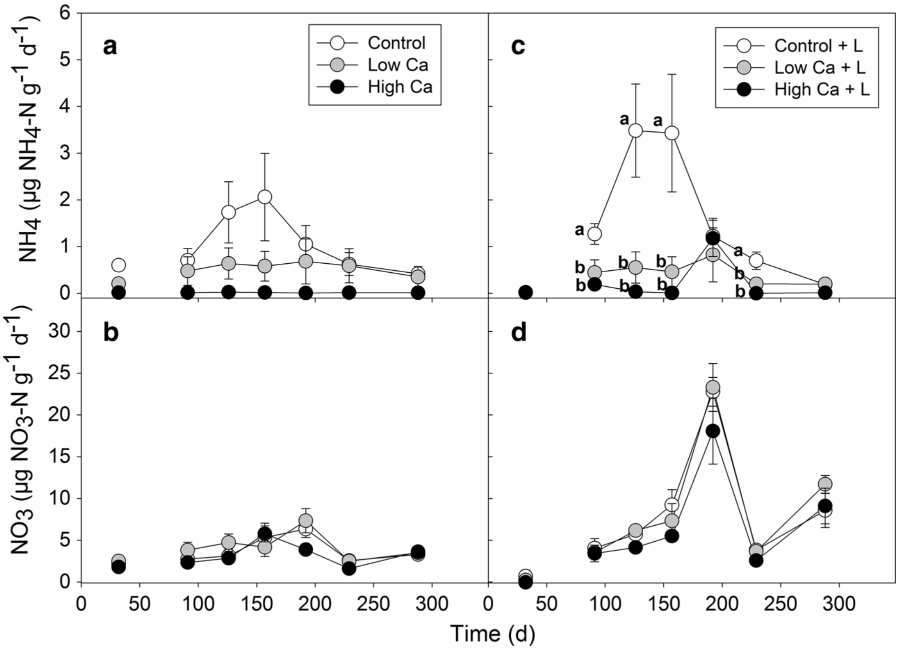

Fig. 7 Soil NH_4^+ (**a**, **c**) and NO_3^- (**b**, **d**) concentrations recovered at seven leaching events of soils amended with Ca in the field (**a**, **b**) and soils amended with Ca in the field and ^{13}C-labeled sugar maple leaf litter (**c**, **d**). Significant differences are indicated by different lowercase *letters* ($P < 0.05$)

high level altered the form of C being mineralized by reducing mineralization of ^{13}C-depleted C compounds. In our study, differences in the ^{13}C signature of respired C and SOC were also present regardless of treatment, but this difference was exacerbated in the high Ca treatment, and likely reflects the molecular nature of C compounds which microbes preferentially decompose. More rapid loss of ^{13}C compared to ^{12}C from the SOC pool has been found (Benner et al. 1987; Ågren et al. 1996; Šantrůčková et al. 2000; Werth and Kuzyakov 2010) as a result of more energetically favorable C sources being enriched in ^{13}C (such as cellulose, −22.1 to −27.2‰ for various C3 tree species) (Benner et al. 1987) compared to the bulk SOC pool (Melillo et al. 1989; Wedin et al. 1995; Cotrufo et al. 2005; Bowling et al. 2008) and more recalcitrant compounds such as lignin (−26.5 to −30.8‰ for various C3 tree species) (Benner et al. 1987). Over time though, ^{13}C enrichment of bulk soils has been shown to occur due to discrimination against ^{13}C by biological processes (Natelhoffer and Fry 1988; Balesdent et al. 1993; Wedin et al. 1995). However, the effects of this biological discrimination can be overcome by microbial utilization of more labile compounds that are enriched in ^{13}C (Wedin et al. 1995; Cotrufo et al. 2005; Bowling et al. 2008), as indicated by ^{13}C enrichment of microbial biomass C compared to bulk soils and respired C (Šantrůčková et al. 2000; Bowling et al. 2008; Werth and Kuzyakov 2010). In the field with intact litter and soil profiles, where plant-derived C inputs replenish soil C pools and as microbial C pools turnover, interactions between ^{13}C enriched microbially-derived C with clay and mineral surfaces may help explain observations of ^{13}C enriched bulk soil C over the long-term (Schmidt et al. 2011). In our laboratory study, Ca effects on C mineralization were performed in a closed system, which lack plant-derived C inputs and other biotic and abiotic factors present in the field. Therefore, the effect of incubating soils in the laboratory likely contributed to the observed depletion in ^{13}C of SOC over the course of the incubation. Regardless, our study provides new insights into the effects of Ca additions on the form of C which microbes utilize.

When Ca treatments increase soil pH, this can also increase the solubility of organic matter and contribute to enhanced microbial activity (Bååth et al. 1980; Anderson 1998; Andersson and Nilsson 2001; Whittinghill and Hobbie 2012). An effect of pH on microbial activity probably contributed to the greater mineralization of litter-derived C in our high Ca treatment. This result agrees with findings in agricultural soils, in which increasing pH enhanced mineralization of added wheat straw (Pietri and Brookes 2009). At the same time, if mineralization of SOC was enhanced in our litter-free incubations by the pH response to high Ca, this effect was small relative to the opposing mechanisms that caused net suppression of SOC mineralization. Johnson et al. (2014) found that wollastonite additions (1.03 Mg Ca ha^{-1}) at the HBEF increased pH, increased exchangeable Ca pools and led to a long-term (11 year) decline in SOC stocks in the Oa horizon, potentially owing to positive effects of Ca on litter-C mineralization compared to negative effects on SOC mineralization in field soils with intact litter and soil profiles. Interactive effects of Ca and pH were demonstrated in a laboratory experiment by Whittinghill and Hobbie (2012), who found that elevated Ca in soils from Alaskan tundra ecosystems suppressed C mineralization, at both low and high pH, whereas at constant Ca levels, higher pH enhanced C mineralization rates. In our forest system these opposing effects of Ca and pH on C mineralization also interact with the form of C, adding further complexity to the nature of Ca status controls of soil C retention. Together, our findings suggest that soil Ca status of hardwood forested ecosystems influences microbial activity and C cycling by decreasing mineralization of existing SOC sources and increasing mineralization of new litter C.

Carbon retention in soils depends on C exports via leaching of DOC, in addition to controls of loss as CO_2. While recent work has suggested that deacidification of some ecosystems leads to increased solubility and leaching of DOC (Evans et al. 2012; SanClements et al. 2012), the lack of increase in DOC export in our study and others at HBEF do not support this idea (Fuss et al. 2015). Alternatively, if this process occurs in our soils, it appears to be offset by cation binding effects on solubility of DOC (Kaiser and Guggenberger 2000; Balaria et al. 2014) or by lower production of DOC by microbial decomposition activities. The low Ca treatment suppressed DOC leaching more strongly than would be expected if regulated by microbial activity, suggesting a stronger role of solubility effects. Isotopic analysis of DOC in litter-free incubations also argues against microbial controls of the DOC response to Ca. The DOC ^{13}C signature from the high Ca treatment was similar to that of SOC but was depleted compared to respired C, suggesting that DOC is originating from SOC pools more depleted in ^{13}C than the SOC pools that microbes are mineralizing. After the initial flush of DOC in litter incubations (during which time there were no Ca effects), DOC leaching in incubations with litter was similar to that in litter-free incubations, indicating that litter did not have a lasting effect on DOC export and that responses to Ca were driven by SOC processes similar to those in the litter-free incubations. This is similar to the findings by Hagedorn et al. (2004) which suggested that the major source of DOC from beech and spruce soils was humified SOM and not recent litter inputs. Net effects in intact soil profiles in the field will likely depend on sorption processes in underlying mineral soil (Kaiser and Guggenberger 2000; Guggenberger and Kaiser 2003; Kalbitz et al. 2005).

Ca effects on NH_4^+ and NO_3^- leaching

The suppression of NH_4^+ leaching in our incubations indicates lasting effects of Ca treatments on soil N retention. Nitrate leaching exceeded that of NH_4^+, but was less responsive to the Ca treatments. Hence, Ca did not influence NH_4^+ leaching by increasing its transformation to NO_3^-. Instead, Ca effects appear to be a consequence of lower NH_4^+ supply from N mineralization (Minick et al. 2011; Simmons et al. 1996). In the high Ca treatment, but not the low Ca, this is consistent with lower microbial activity indicated by C mineralization. Lower NH_4^+ leaching may also arise from microbial immobilization of a higher proportion of mineralized N, shown in these sites by Minick et al. (2011), along with a strong negative relationship between soil pH and net N mineralization. The suppression of NH_4^+ leaching but not C mineralization in the high Ca treatment in litter-amended incubations further suggests the importance of immobilization. While Ca effects on NH_4^+ are consistent with past work at the HBEF (Groffman et al. 2006; Groffman and Fisk 2011; Minick et al. 2011) and in other northern hardwood forests (Simmons et al. 1996), the lack of NO_3^- response is not. Groffman and Fisk (2011) found a substantial increase in NO_3^- concentrations and nitrification in response to Ca addition to plant-free incubations. They suggested that reductions in NH_4^+ in field soils (with plants) resulted from plant uptake which masked positive effects of Ca additions on pH and nitrifying microorganisms in plant-free mesocosms. Direct addition of Ca to mesocosms, as opposed to legacy effects in our study, and higher pH response to Ca (6.9–7.2) in Groffman and Fisk (2011) compared to this study (4.9) likely contribute to these contrasting findings. Nitrification has been shown to be sensitive to pH with higher pH typically supporting higher nitrification rates (Bäckman and Klemedtsson 2003; De Boer and Kowalchuck 2001; Simmons et al. 1996; Ste-Marie and Paré 1999), although nitrification in acidic forest soils is not uncommon (Booth et al. 2005; De Boer and Kowalchuck 2001; Ross et al. 2009; Stark and Hart 1997; Minick et al. 2016). Therefore, it seems likely that only modest pH effects played an important role in the lack of Ca effect on NO_3^- availability in our study. In Groffman and Fisk (2011), mesocosms also received no moisture additions over the two-year study and were likely drier than soils from our study. Therefore, we cannot rule out that periodic leaching of soils in our study led to soils being wet enough that denitrification of extra NO_3^- occurred, although we did not measure N_2O or N_2 concentrations and therefore cannot confirm this.

Conclusion

Loss of Ca in these northern hardwood forest soils owing to acid deposition has altered some mechanisms of soil C and N retention capacity of these ecosystems. Our study provides evidence of the importance of cation-organic matter binding processes in response to relatively high levels of Ca addition. However, the general lack of C mineralization response to our low Ca treatment, which was intended to restore the amount of Ca lost to acid deposition, suggests that the magnitude of previous Ca loss was not enough to substantially alter cation-SOM binding processes. Our results are consistent with a study showing a 19 year increase in SOC stocks with liming at levels comparable to our high Ca treatment (Melvin et al. 2013), but not with the decline in SOC stocks 11 years following wollastonite addition at levels comparable to our low Ca treatment (Johnson et al. 2014), suggesting that the relative importance of opposing effects of pH and cation binding in undisturbed soil profiles differ from what we found in our laboratory incubations. Transformations of N that contribute to soil N retention appear to be less dependent on the amount of Ca added, indicating a lack of direct coupling in the response of C and N transformations. As deacidification processes continue to improve soil base status and pH of these northern hardwood forests, our mechanistic studies suggest that recovery to pre-deposition Ca status will enhance N but not C retention, and that changes in soil C retention will likely depend on the relative importance of the processing of the various forms of C as litter-derived C is transformed to SOC with depth in the profile of the organic horizon.

Acknowledgements We thank Lisa Martel, Tera Ratliff, and many other members of the Fisk Lab for their assistance in the field and laboratory. We also thank the insightful comments of two anonymous reviewers. This study was supported by the USDA National Research Initiative Competitive Grants Program Grant #: 2005-35107-16200, by a Grant from the National Science Foundation, and by the Miami University Department of Zoology Field Study and Research program. This project is a contribution to the Hubbard Brook Ecosystem Study. The Hubbard Brook Experimental Forest is operated and maintained by the Northeastern Research Station, USDA Forest Service, Newtown Square, PA.

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