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Soil Chemical Dynamics after Calcium Silicate Addition to a Northern Hardwood Forest

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Acidic deposition has resulted in the loss of available soil Ca from base-poor soils in the northeastern United States. In 1999, wollastonite ($CaSiO_3$) was experimentally added to a watershed at the Hubbard Brook Experimental Forest in New Hampshire in an attempt to restore the base saturation of the soil to its estimated pre-acidification level. We measured the total Ca in the O horizon and the top 10 cm of mineral soil to track the fate of the added Ca. We also measured soil pH and exchangeable cations to assess the impact of the treatment on soil acidity. In the first 11 yr after treatment, Ca was transported downward through the forest floor and upper mineral soil in a progressive fashion. By Year 11, at least 650 kg ha^{-1} of the 1028 kg ha^{-1} of Ca that was added to the watershed was no longer in the O horizon or the top 10 cm of mineral soil. Soil pH and exchangeable Ca concentrations increased significantly in organic and mineral soils after treatment. Exchangeable H and Al concentrations decreased significantly. The pool of exchangeable Ca increased significantly after treatment, peaking in the O horizons 3 yr after treatment and in the upper mineral soil 7 yr after treatment. The pools of exchangeable Al and H steadily and significantly decreased through the study period. Only about 3% of the added Ca was exported from the watershed in stream water after 11 yr. Wollastonite treatment was thus an effective means of increasing available pools of Ca in this forest ecosystem.

Abbreviations: BS_e, effective base saturation; CEC_e, effective cation exchange capacity; HBEF, Hubbard Brook Experimental Forest; LOI, loss-on-ignition; pHw, pH in water.

Decades of acidic deposition in the northeastern United States has resulted in the acidification of soils and surface waters in acid-sensitive portions of the region (Skjelkvåle et al., 2001; Warby et al., 2005, 2009). In areas underlain by base-poor bedrock and glacial tills, mineral weathering has been unable to fully neutralize acid inputs to forest ecosystems, resulting in the net release of Ca and other basic cations from soil exchange sites. This depletion of available soil Ca is exacerbated by uptake of Ca in second-growth forests of the region, which have grown since wide-spread harvesting in the late 19th and early 20th centuries. As Markewitz et al. (1998) showed in a forest stand in South Carolina, soil acidification resulting from plant nutrient uptake can equal or exceed acidification caused by acidic deposition. The losses of available Ca from acidic soils in the northeastern United States have been substantial; Likens et al. (1996) estimated that 73% of the Ca exported in stream water from a watershed at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire between 1940 and 1993 was released from "labile" sources (defined as exchange sites and organic matter). Several researchers have documented large decreases in exchangeable Ca concen-

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trations in regional soils during the 20th century, in some cases as high as 77% (Johnson et al., 1994; Bailey et al., 2005; Warby et al., 2009).

The loss of available Ca from naturally base-poor soils has had deleterious effects on forest ecosystems of the northeastern United States. Several studies have concluded that losses of available soil base cations have delayed the recovery of acid neutralizing capacity (ANC) in streams and lakes draining forested watersheds following decreases in acid deposition (Lawrence et al., 1999; Driscoll et al., 2001; Warby et al., 2005). Low Ca stocks in forest soils are also a factor in the declining health and productivity of key tree species in the region, including red spruce (*Picea rubens* Sarg.) and sugar maple (*Acer saccharum* Marsh.) (Ouimet and Camiré, 1995; Shortle et al., 1997; DeHayes et al., 1999; Schaberg et al., 2006). Forest fauna that require Ca for shell formation, such as snails and birds, are also threatened by low soil Ca levels (Likens et al., 1998; Pabian and Brittingham, 2007; Skeldon et al., 2007).

One option for ameliorating the effects of Ca depletion is to amend forest soils with mineral forms of Ca. Forest liming has a long history in Europe but has been less widely used in the United States. Agricultural lime, normally calcium carbonate or dolomitic limestone, dissolves rapidly because it is carbonate-based and can result in large increases in solution pH and ANC. Wollastonite ($CaSiO_3$), a potential alternative to lime, dissolves more slowly, resulting in the release of Ca to the soil over a longer period (Peters et al., 2004). Increases in pH and ANC of soil solutions therefore occur at a more moderate rate, and the C balance of the soil system is not affected by the addition of inorganic C.

In 1999, wollastonite was applied to a watershed at the HBEF in an attempt to replace Ca that had been lost from the soils during the most intense period of acid deposition. The goals of the treatment experiment were to examine the biogeochemical and ecological effects of the addition and to evaluate the use of wollastonite as a forest Ca amendment. The wollastonite addition has produced a number of ecosystem-level impacts. Cold tolerance increased, winter injury was mitigated, and the chlorophyll content and crown mass increased in red spruce after the treatment (Hawley et al., 2006; Halman et al., 2008). The growth (Juice et al., 2006) and survival (Cleavitt et al., 2011) of sugar maple seedlings also increased significantly in response to wollastonite treatment. Battles et al. (2014) reported higher biomass accumulation in canopy trees in the treated watershed, compared with a reference watershed, with increases in foliar Ca documented for red spruce, sugar maple, and yellow birch (*Betula alleghanensis* Britt.) (Juice et al., 2006; Halman et al., 2008; Green et al., 2013). Increased tree growth and vigor resulted in increased transpiration and lower stream flow in the treated watershed (Green et al., 2013).

The response of forest vegetation to the treatment likely reflects dissolution of Ca from the added wollastonite, migration of Ca within the soil, and recycling via forest litter. We hypothesized that (i) wollastonite addition would result in sustained increases in total and exchangeable Ca in organic and surface mineral soils in the treated watershed, (ii) increases in exchangeable Ca after treatment would be accompanied by approximately equivalent decreases in exchangeable acidity, and (iii) soil chemical change would occur in a progressive pattern similar to a "breakthrough" curve, with Ca migrating downward over time since application.

Short-term (3-yr) changes in soil pH and exchangeable cations after the wollastonite treatment were reported by Cho et al. (2010, 2012). These included large increases in exchangeable Ca, pH, base saturation, and effective cation exchange capacity (CEC_e) in surface organic horizons (Oi and Oe), along with decreases in exchangeable acidity. Changes in the chemistry of the humus layer (Oa) and upper mineral soils were smaller and in many cases statistically insignificant after 3 yr. While these results were broadly consistent with our hypotheses, longer-term data are required to fully test them. This paper incorporates data from two additional soil sampling campaigns, extending the soil chemical record from 3 to 11 yr after the initial treatment. We use these data to examine our hypotheses and to discuss the soil chemical results in the context of observed changes in solution chemistry, vegetation patterns, and soil C and N cycling.

MATERIALS AND METHODS

Site Description and Treatment

Likens and Bormann (1994) provide a thorough description of the HBEF ecosystem. The HBEF is located in the southern part of the White Mountain National Forest in New Hampshire (43°56′ N, 71°45′ W). This study took place on Watershed 1 (W1), which ranges in elevation from 488 to 747 m and has an area of 11.8 ha. Watershed 1 has a southern aspect and an average slope of about 29%. The uppermost zone of W1 contains a mixture of red spruce, balsam fir [*Abies balsamea* (L.) Mill], and paper birch [*Betula papyrifera* var. *cordifolia* (Marsh.) Regel], while the rest of the watershed is dominated by a roughly equal mixture of sugar maple, yellow birch, and American beech (*Fagus grandifolia* Ehrh.).

Watershed 1 is underlain by sillimanite-grade pelitic schist of the Rangeley formation. The most recent glaciation in the Wisconsin period left a mantle of till ranging in thickness from zero (scattered bedrock outcrops) to several meters in valley bottoms. Oxides of the basic cations (CaO, MgO, K_2O, and Na_2O) comprise 8.9% by weight of the schist and 7.1% of the till (Johnson et al., 1968). The soils that have formed are diverse, with Typic Haplorthods and Typic Dystrochrepts the most common. Depth to C horizon or bedrock in nearby Watershed 5 (W5) ranges from zero to 130 cm, averaging about 60 cm, with an O horizon averaging 7 cm in depth (Johnson et al., 1991).

The climate at the HBEF is humid-continental, with average monthly temperatures ranging from −8.5°C in January to 18.8°C in July (Bailey et al., 2003). Approximately 30% of the annual precipitation, which averages 1395 mm, falls as snow. The resulting spring snowmelt generates about half of the annual stream runoff, which averages 870 mm.

In October 1999, after leaf fall, pelletized wollastonite powder was applied to W1 by helicopter. Peters et al. (2004) provided a detailed description of the wollastonite material, its chemistry, preparation, and application. We estimated the amount of wollastonite needed to increase the base saturation of the soil from the then current average of 10% to the estimated preindustrial level of 19% and multiplied that amount by a safety factor of 1.5. The resulting application added 1028 kg Ca ha^{-1} to W1 in a uniform pattern (Peters et al., 2004). Based on laboratory dissolution experiments and literature-based assumptions regarding the difference between lab and field weathering rates, we estimated that the rate of wollastonite dissolution would peak at about 7 yr post-treatment (Peters et al., 2004).

Soil Sampling and Analysis

We collected soil samples in July 1998, before the wollastonite application, at 96 randomly located sites in W1. After the treatment we sampled at 100 randomly located sites in W1 in July 2000, 2002, 2006, and 2010. Not all horizons were present at all sites in all years, so sample sizes ranged from 76 to 100. Samples of the O horizons were collected by the pin block method (Federer et al., 1993) using 15- by 15-cm wooden or polyvinyl chloride templates. The Oi and Oe horizons were collected as a single sample (referred to hereafter as the Oie horizon), separate from the Oa horizon. After collecting the O horizons, the upper mineral soil was sampled using a 3.5-cm-diameter stainless steel corer. The target depth of the cores was 0 to 10 cm, but the actual sampled depth was often less due to rocks. The thicknesses of the Oie and Oa horizons were measured at eight places around the pin block, and the lengths of the mineral cores were also recorded.

Soil samples were air dried to constant weight. The Oie horizon samples were ground in a Wiley mill after removing sticks larger than 5-mm diameter. Samples of the Oa horizon and mineral cores were passed through 5- and 2-mm stainless steel screens, respectively, with gentle encouragement. Subsamples of the screened and ground material were oven dried (80°C) to determine moisture content and then combusted overnight (500°C) to determine loss-on-ignition (LOI), which is a good measure of organic matter content in these soils (Johnson et al., 1991). Another set of subsamples was ground to a fine powder using a mortar and pestle, oven dried, and analyzed for total C and N using a Costech ECS 4010 elemental analyzer (Costech Analytical).

Five milliliters of 6 mol L^{-1} HNO_3 was added to the ash from the LOI measurements and evaporated to dryness in a sand bath on a hot plate. The digested material was dissolved with another 5-mL aliquot of 6 mol L^{-1} HNO_3. The digestate was filtered through a Whatman no. 41 filter (GE Healthcare Bio-Sciences) and brought to 50 mL with deionized water. Total Ca (and other elements not discussed here) was determined by measuring the Ca concentration in the digests using inductively coupled plasma–optical emission spectroscopy (ICP-OES). Although this procedure may not result in complete digestion of all silicate minerals, our data suggest that it was capable of dissolving the added wollastonite, as discussed below.

Soil pH was determined in deionized water using a 5:1 (g water/g soil) suspension for O horizons and a 1:1 suspension for mineral soils. Exchangeable Ca, Mg, K, and Na were determined by extracting air-dried soil with 1 mol L^{-1} of NH_4Cl using a suspension ratio of 1 g of soil to 20 mL of extractant. Exchangeable acidity was determined on 1 mol L^{-1} of KCl extracts obtained with the same suspension ratio. All extractions were performed for 14 h using a mechanical vacuum extractor. The concentrations of Ca, Mg, K, and Na in the NH_4Cl extracts, and the concentration of Al in the KCl extracts, were determined by ICP-OES. Exchangeable acidity was determined by titration to the phenolphthalein endpoint using NaOH. Exchangeable H was estimated by subtracting exchangeable Al from exchangeable acidity and was assumed to be zero in the few cases where exchangeable Al was greater than exchangeable acidity. Effective cation exchange capacity was computed as the sum of exchangeable acidity and exchangeable basic cations (Ca, Mg, K, and Na). Effective base saturation (BS_e) was calculated as the percentage of CEC_e satisfied by the basic cations. For all analyses, procedural blanks and duplicate samples each comprised 10% of the sample load.

Cho et al. (2010) analyzed the concentration of Si in the NH_4Cl extracts of samples collected in 1998 (before treatment) and 2002. Although average Ca/Si ratios were somewhat lower in the post-treatment extracts, the high average molar Ca/Si ratios in the extracts, ranging from 193 to 525, suggested that dissolution of mineral wollastonite during the extraction was not an important source of Ca in the exchangeable Ca measurement. The soil samples are stored in glass jars. Soil pH was generally measured within 1 yr of sample collection, and exchangeable cations within 4 yr of collection. Storage effects under these conditions are likely to be small, though it is worth noting that soils tend to acidify during long-term storage (Falkengren-Grerup, 1995; Lawrence et al., 2012).

Statistical Analysis

Statistical analyses were performed using Minitab 16 (Minitab Inc.). For each horizon and analyte, we performed one-way analyses of variance (ANOVA) with sampling year as the treatment variable. We used Tukey's honestly significant difference test with a significance level of $\alpha = 0.05$ to identify significant differences among sampling years. Since the number of samples collected varied from year to year, ours was necessarily an unbalanced design. We acknowledge that this watershed-level study is not replicated. While we ascribe the differences among sampling years to the wollastonite treatment, we cannot entirely eliminate the possibility that the changes were the result of other factors.

Some of the results of this study differ slightly from corresponding results reported by Cho et al. (2010, 2012). In the intervening period we have analyzed several samples that had been thought to be lost and we reanalyzed a few samples that had suspicious results (e.g., C/N ratios <10). The changes do not affect the interpretations made by Cho et al. (2010, 2012). The data are available at the Hubbard Brook web page (www.hubbardbrook.org).

RESULTS

Calcium Dynamics

As expected, wollastonite addition resulted in an immediate increase in the pool of total Ca in W1 soils. In July 2000, 9 mo after the treatment, total Ca in the O horizons and the upper mineral soil had increased by 900 kg ha^{-1} compared with pretreatment values (Table 1), slightly less (12%) than the 1028 kg ha^{-1} added to the watershed. Initially, much of the added wollastonite remained in the Oie horizon, which experienced a sevenfold increase in total Ca immediately after treatment, then significant decreases in each sampling interval thereafter. Eleven years after the addition, total Ca in the Oie horizon remained significantly greater than before treatment. Total Ca in the Oa horizon and upper mineral soil also increased after treatment, though the response was delayed (Table 1). In the Oa horizon, a statistically significant increase in total Ca was not observed until 2002, 3 yr after the addition. Total Ca remained elevated through the remainder of the study period, though the difference between the pool after 11 yr and the pretreatment pool was not significant. In the top 10 cm of mineral soil, a statistically significant increase in the pool of total Ca was not observed until 7 yr after treatment. By Year 11 the pool of Ca in the upper mineral soil had returned to the pretreatment level. Eleven years after treatment, the total pool of Ca in O horizons and the upper mineral soil remained significantly greater (577 ± 28 kg ha^{-1}; mean ± SE) than the pretreatment value (327 ± 16 kg ha^{-1}) but had declined to less than half of the post-treatment peak (1227 ± 65 kg ha^{-1}) (Table 1).

Soil Acid–Base Chemistry

As with total Ca, exchangeable Ca significantly increased after the wollastonite addition (Fig. 1). In the Oie horizon, the exchangeable Ca concentration more than tripled after treatment and remained significantly greater than the pretreatment concentration after 11 yr. Similar to total Ca, the timing of exchangeable Ca increases in Oa horizons and the upper mineral soil was delayed. In the Oa horizon, the exchangeable Ca concentration did not increase significantly until 3 yr after treatment and remained significantly elevated through 11 yr. The upper mineral soil had significantly elevated exchangeable Ca 7 yr after treatment.

Exchangeable acidity decreased significantly in response to the wollastonite addition (Fig. 1). As with exchangeable Ca, the response was immediate and persistent in the Oie horizon, where the mean exchangeable acidity concentration was more than 30% lower the year after treatment than before treatment. Exchangeable acidity in the Oa horizon did not decline significantly until 3 yr after treatment and continued to decline through 11 yr. The upper mineral soil experienced a modest but significant decrease in exchangeable acidity seven and 11 yr after the addition, relative to the pretreatment concentration.

In contrast to our second hypothesis, the changes in exchangeable Ca did not result in equivalent changes in exchangeable acidity. In the Oie horizon, increases in exchangeable Ca after wollastonite addition far exceeded the decreases in exchangeable acidity (Fig. 2), resulting in significant increases in CEC$_e$. Exchangeable Al was very low in the Oie horizons, where the decrease in exchangeable acidity after treatment was entirely due to decreases in exchangeable H. In Oa horizons, decreases in exchangeable acidity after treatment were the result of decreases in both exchangeable H and Al (Fig. 2). The increases in exchangeable Ca in Oa horizons 3 and 7 yr after treatment were greater than the decreases in acidity, resulting in an increase in CEC$_e$. Exchangeable Ca, Al, and H in the Oa horizon all decreased between post-treatment Years 7 and 11, resulting in CEC$_e$ that was significantly lower than before treatment. The CEC$_e$ in the upper mineral soil fluctuated throughout the study (Fig. 2). The significant increase in exchangeable Ca observed 7 yr after treatment was accompanied by a significant decrease in exchangeable H. No significant changes in exchangeable Al were observed in the mineral soil.

As a result of the observed changes in exchangeable Ca and acidity, W1 soils experienced significant increases in pH and base saturation after wollastonite addition (Table 2). In both the Oie and Oa horizons, the pH in water (pH$_w$) increased steadily after treatment. By Year 11, the mean pH$_w$ in the Oie horizon had increased nearly a full pH unit, from 3.88 to 4.71. The magnitude of the pH$_w$ increases in the Oa and mineral soils was more modest, though still significant. Effective base saturation in the Oie horizon increased from an average of 49% before treatment to a high of 86% 3 yr after treatment, and remained near that level through Year 11 (Table 2). In the Oa horizon, BS$_e$ nearly

Table 1. Pools of total Ca (6 mol L^{-1} HNO_3 digest) in soils before and after the addition of 1028 kg ha^{-1} of wollastonite ($CaSiO_3$) to Watershed 1 at the Hubbard Brook Experimental Forest, New Hampshire. Wollastonite was added in October 1999.

Horizon	Total Ca content				
	1998	2000	2002	2006	2010
	kg ha^{-1}				
Oi + Oe	142 ± 10 A†	989 ± 62 E	825 ± 52 D	620 ± 38 C	367 ± 24 B
Oa	88 ± 12 A	108 ± 10 AB	159 ± 17 C	156 ± 15 BC	120 ± 14 ABC
0–10-cm mineral soil	97 ± 6 A	130 ± 19 A	127 ± 10 A	239 ± 25 B	90 ± 6 A
Total	327 ± 16 A	1227 ± 65 C	1111 ± 56 C	1015 ± 50 C	577 ± 28 B
Change from previous sampling year		+900	−116	−96	−438

† Means ± standard errors. Means followed by different letters in a row are significantly different ($P < 0.05$).

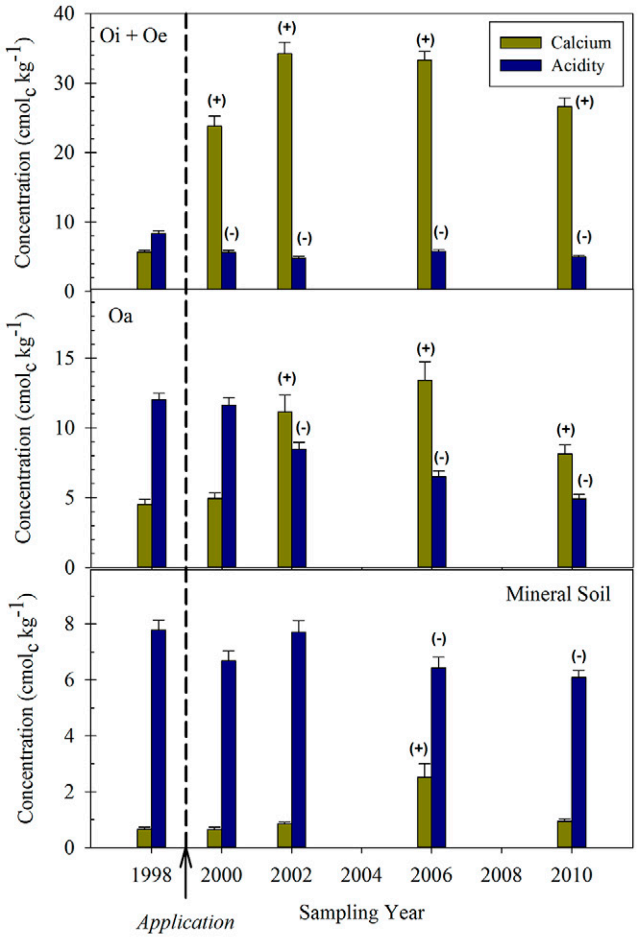

Fig. 1. Changes in the concentrations of exchangeable Ca and exchangeable acidity after wollastonite ($CaSiO_3$) treatment. Error bars indicate one standard error. A plus (+) or minus (–) symbol above or adjacent to any bar indicates a significant increase or decrease, respectively, relative to the pretreatment mean (P < 0.05). All concentrations are based on oven-dry mass.

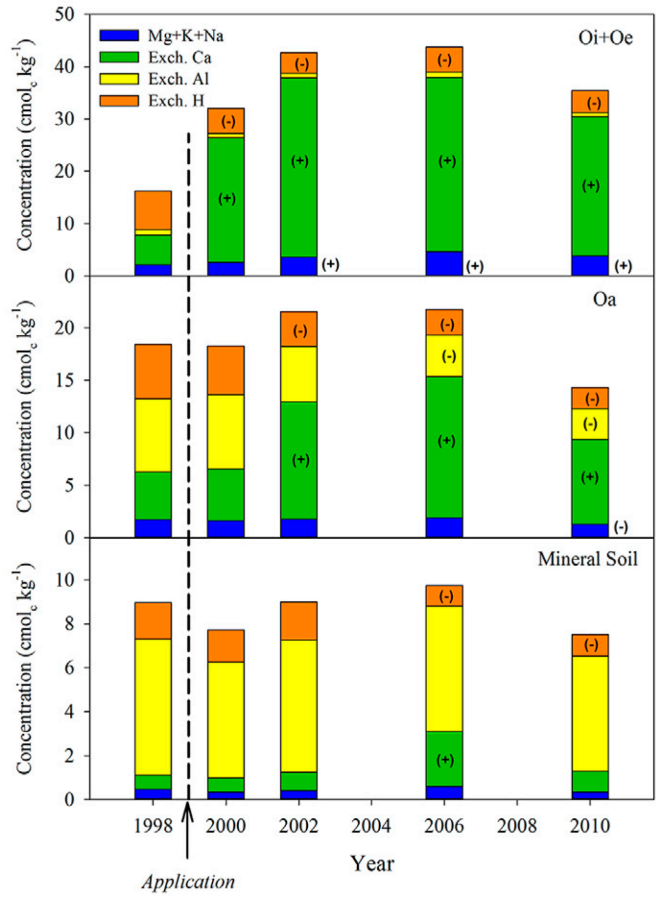

Fig. 2. Effective cation exchange capacity (CEC_e) in soils before and after wollastonite ($CaSiO_3$) treatment at the Hubbard Brook Experimental Forest, New Hampshire. The CEC_e, represented by the total bar height, is broken into sections corresponding to various exchangeable components. A plus (+) or minus (–) symbol inside or adjacent to a bar segment indicates a significant increase or decrease, respectively, in that component relative to the pretreatment mean (P < 0.05). All concentrations are based on oven-dry mass.

doubled, from 33% before the addition to 61% after 11 yr. In the upper mineral soil, BS_e increased from an average of 12% to a high of 28% 7 yr after treatment and remained significantly elevated through Year 11.

Organic Matter, Carbon, and Nitrogen

Wollastonite treatment had no significant effect on the mass of the Oie horizon (Table 3). However, we observed a significant decrease in the mass of the Oa horizon in the first 7 yr after the addition; in 2006, the Oa horizon mass was 47% lower than before treatment. After 11 yr, the mean Oa horizon mass was still 27% lower than the pretreatment value, but this difference was not significant. No significant differences were observed in organic matter concentration, based on LOI, for either the Oie or Oa horizons. Thus, the mass of organic matter in Oie horizon soils was not significantly affected by the wollastonite treatment, while the organic matter mass decreased in the Oa horizon, significantly in the later years of the study.

The concentration of C in the Oie horizon declined significantly after wollastonite treatment and remained significantly lower than the pretreatment value 11 yr later (Table 3). Nitrogen concentration in the Oie horizon also decreased significantly in the first 3 yr after wollastonite treatment, but it returned to pretreatment levels by Year 7. The C/N ratio was significantly lower in the Oie horizon 7 and 11 yr after treatment. The magnitudes of the observed decreases in C and N concentrations were small, 13% or less. Consequently, there were no significant treatment effects observed in C or N pools in the Oie horizon. In the Oa horizon, there were no significant changes in C or N concentrations. However, because of the decrease in Oa horizon mass, the pools of C and N were significantly lower 7 and 11 (C only) yr after treatment than they were before the treatment (Table 3).

The mass of mineral soil collected in the cores was significantly greater 1 yr after treatment and significantly lower 11 yr after treatment than the mass collected before treatment (Table 3). We attribute this change to sampling variation since there is no reason to believe that the wollastonite addition should affect the mass or bulk density of mineral soil. The LOI in the mineral soils was significantly lower 1 yr after treatment and significantly greater in Year 11 than before treatment. Since LOI decreases with depth in the mineral soil (Johnson et al., 1991), this pattern

Table 2. Soil pH in water (pH_w), base saturation, pools of exchangeable cations, and effective cation exchange capacity (CEC_e) before and after wollastonite ($CaSiO_3$) treatment in soils from Watershed 1 at the Hubbard Brook Experimental Forest, New Hampshire. Wollastonite was added in October 1999.

Property	1998	2000	2002	2006	2010
			Oi + Oe horizon		
pH_w	3.88 ± 0.02 A†	4.39 ± 0.05 B	4.48 ± 0.05 B	4.50 ± 0.04 B	4.71 ± 0.04 C
Base saturation, %	49 ± 2 A	78 ± 2 B	86 ± 1 C	85 ± 1 C	83 ± 1 BC
Exchangeable Ca, $kmol_c\ ha^{-1}$	2.1 ± 0.2 A	10.0 ± 0.7 BC	13.8 ± 0.9 D	12.3 ± 0.6 CD	9.8 ± 0.6 B
Exchangeable Al, $kmol_c\ ha^{-1}$	0.50 ± 0.12 A	0.61 ± 0.28 A	0.51 ± 0.10 A	0.43 ± 0.07 A	0.51 ± 0.19 A
Exchangeable H, $kmol_c\ ha^{-1}$	2.86 ± 0.23 A	2.34 ± 0.19 AB	1.71 ± 0.15 BC	1.92 ± 0.14 BC	1.58 ± 0.14 C
CEC_e, $kmol_c\ ha^{-1}$	6.3 ± 0.4 A	14.0 ± 0.9 B	17.4 ± 1.0 C	16.4 ± 0.7 BC	13.0 ± 0.8 B
			Oa horizon		
pH_w	3.82 ± 0.04 A	3.62 ± 0.03 B	3.86 ± 0.06 A	4.20 ± 0.05 C	4.42 ± 0.03 D
Base saturation, %	33 ± 2 A	36 ± 2 A	56 ± 2 B	63 ± 3 B	61 ± 2 B
Exchangeable Ca, $kmol_c\ ha^{-1}$	4.4 ± 0.7 A	4.7 ± 0.4 A	7.1 ± 0.6 B	4.9 ± 0.5 A	4.8 ± 0.5 A
Exchangeable Al, $kmol_c\ ha^{-1}$	9.6 ± 1.67 A	10.4 ± 1.3 A	6.9 ± 1.2 AB	3.2 ± 0.6 B	3.4 ± 0.6 B
Exchangeable H, $kmol_c\ ha^{-1}$	5.39 ± 0.81 A	4.95 ± 0.45 A	2.61 ± 0.33 B	1.20 ± 0.18 B	1.11 ± 0.14 B
CEC_e, $kmol_c\ ha^{-1}$	21.0 ± 2.5 A	21.6 ± 1.9 A	17.9 ± 1.6 A	10.5 ± 0.9 B	10.1 ± 0.9 B
			0–10 cm mineral soil		
pH_w	3.96 ± 0.04 A	3.79 ± 0.03 C	3.73 ± 0.04 C	4.04 ± 0.04 AB	4.16 ± 0.03 B
Base saturation, %	12 ± 1 A	14 ± 1 AB	15 ± 1 AB	28 ± 2 C	19 ± 1 B
Exchangeable Ca, $kmol_c\ ha^{-1}$	3.2 ± 0.3 A	3.8 ± 0.4 A	4.4 ± 0.3 A	8.6 ± 0.7 B	3.7 ± 0.3 A
Exchangeable Al, $kmol_c\ ha^{-1}$	30.5 ± 1.0 A	29.9 ± 1.2 AB	29.5 ± 1.2 AB	25.9 ± 1.4 BC	22.2 ± 1.3 C
Exchangeable H, $kmol_c\ ha^{-1}$	9.1 ± 0.8 A	9.4 ± 0.8 A	9.0 ± 0.7 A	4.7 ± 0.1 B	4.0 ± 0.1 B
CEC_e, $kmol_c\ ha^{-1}$	44.8 ± 0.9 A	44.9 ± 13.2 A	44.6 ± 1.3 A	40.5 ± 1.1 A	30.6 ± 1.5 B

† Means ± standard errors. Means followed by different letters in a row are significantly different ($P < 0.05$).

suggests that field personnel may have unintentionally collected mineral soils slightly deeper on average in 2000, causing a lower average LOI, and slightly shallower in 2010 than in 1998. The concentrations of C and N in mineral soils, and the C/N ratio, were not significantly affected by the wollastonite addition.

DISCUSSION

Release of Wollastonite-Derived Calcium

The 1028 kg ha^{-1} of Ca added to W1 in the wollastonite application in October 1999 represented a substantial amount of Ca in comparison with existing ecosystem pools. It was more than three times the amount of total Ca that we measured in the O horizon and cores of surface mineral soils before the treatment (Table 1). The added Ca was approximately equivalent to the sum of the Ca in living biomass in the forest (751 kg ha^{-1} [Likens et al., 1998]) and the exchangeable Ca in the entire soil profile (264 kg ha^{-1} [Johnson et al., 1997]). The dissolution of the added wollastonite therefore has the potential to alter substantially both the soil chemical environment and ecosystem cycling of Ca.

Much of the added wollastonite dissolved in the first 11 yr after the application, and the Ca released in this process passed through the O horizon and upper mineral soil in a progressive "breakthrough" pattern (Fig. 3). Total Ca increased by 900 kg ha^{-1} between the pretreatment sampling and 9 mo after the application. Some of the discrepancy between the added Ca (1028 kg ha^{-1}) and the measured increase in total Ca may be attributed to Ca that dissolved during the winter and spring of 1999 to 2000 and either passed through the upper soil horizons during snowmelt and early summer or was taken up by roots before our sampling in July.

The 6 mol L^{-1} HNO_3 digestion used to estimate "total" Ca probably did not completely dissolve all of the mineral Ca in our samples. Boiling 1 mol L^{-1} HNO_3 extracted approximately 24% of the total Ca in C horizon samples from W5 (Blum et al., 2002). It is likely that our boiling 6 mol L^{-1} HNO_3 extraction procedure extracted a greater percentage of total Ca than 1 mol L^{-1} HNO_3, although probably not 100%. Nevertheless, the close correspondence between the change in total Ca and the applied amount strongly suggests that the digestion was effective for the dissolution of the added wollastonite powder.

The increase in total Ca 1 yr after treatment was only significant in the Oie horizon (Table 1). Afterward, the total Ca in the Oie horizon decreased significantly in every subsequent sampling interval. Total Ca in the Oa horizon was not significantly elevated until 3 yr after the addition of wollastonite, and the total Ca in the mineral soil was not significantly elevated until 7 yr after treatment. This pattern demonstrates the progressive downward migration of Ca, first through the Oie horizon, then the Oa, and finally through the upper mineral soil (Fig. 3). After 11 yr, the pool of total Ca remained significantly elevated in the Oie horizon. In the Oa horizon, the total Ca pool was 36% higher 11 yr after treatment than before the addition, but the difference was not significant, partly due to lower soil mass in the Oa horizon after treatment (Table 3).

After the initial increase following wollastonite application, the total pool of Ca in the O horizon and upper mineral soil declined steadily, decreasing by 116 kg ha^{-1} between post-

Table 3. Soil mass and organic matter, C, and N concentrations and pools in soils before and after wollastonite ($CaSiO_3$) treatment at the Hubbard Brook Experimental Forest, New Hampshire. Wollastonite was added in October 1999. All concentrations are expressed on the basis of oven-dry mass.

Property	1998	2000	2002	2006	2010
			Oi + Oe horizon		
Soil mass, kg m^{-2}	3.85 ± 0.26 A†	4.61 ± 0.22 A	4.48 ± 0.29 A	3.94 ± 0.20 A	4.25 ± 0.38 A
Loss-on-ignition, g kg^{-1}	826 ± 13 A	731 ± 13 A	756 ± 14 A	756 ± 14 A	714 ± 17 A
C conc., g kg^{-1}	445 ± 7 A	388 ± 7 C	411 ± 8 BC	415 ± 8 ABC	404 ± 10 C
N conc., g kg^{-1}	19.7 ± 0.3 A	17.3 ± 0.3 B	17.6 ± 0.3 B	19.5 ± 0.4 A	19.1 ± 0.5 A
C/N ratio	22.8 ± 0.3 A	22.5 ± 0.3 AB	23.4 ± 0.3 A	21.3 ± 0.2 C	21.1 ± 0.2 C
Organic matter, kg m^{-2}	3.22 ± 0.24 A	3.40 ± 0.18 A	3.31 ± 0.21 A	2.93 ± 0.16 A	2.81 ± 0.18 A
C, kg m^{-2}	1.72 ± 0.13 A	1.81 ± 0.10 A	1.81 ± 0.12 A	1.63 ± 0.09 A	1.61 ± 0.12 A
N, g m^{-2}	74.0 ± 4.9 A	79.5 ± 3.8 A	76.5 ± 4.6 A	75.3 ± 3.6 A	75.6 ± 5.0 A
			Oa horizon		
Soil mass, kg m^{-2}	11.0 ± 1.5 A	10.8 ± 0.9 A	7.1 ± 0.9 AB	5.81 ± 0.6 B	8.05 ± 0.9 AB
Loss-on-ignition, g kg^{-1}	515 ± 18 A	480 ± 20 A	513 ± 19 A	512 ± 23 A	437 ± 21 A
C conc., g kg^{-1}	266 ± 11 A	239 ± 12 A	276 ± 11 A	290 ± 13 A	231 ± 13 A
N conc., g kg^{-1}	12.5 ± 0.5 A	11.2 ± 0.5 A	13.1 ± 0.5 A	14.2 ± 0.6 A	11.4 ± 0.6 A
C/N ratio	21.1 ± 0.4 A	21.1 ± 0.3 A	21.0 ± 0.4 A	20.5 ± 0.4 A	20.0 ± 0.3 A
Organic matter, kg m^{-2}	5.45 ± 0.72 A	4.91 ± 0.44 AB	3.57 ± 0.41 BC	2.49 ± 0.29 C	3.13 ± 0.30 BC
C, kg m^{-2}	2.76 ± 0.36 A	2.41 ± 0.22 A	1.93 ± 0.23 AB	1.46 ± 0.17 B	1.63 ± 0.15 B
N, g m^{-2}	125 ± 15 A	114 ± 10 A	92 ± 11 AB	69 ± 7 B	83 ± 8 AB
			0–10 cm mineral soil		
Soil mass, kg m^{-2}	57.8 ± 2.1 A	67.0 ± 2.4 B	56.7 ± 2.0 A	53.5 ± 2.5 A	44.7 ± 2.4 C
Loss-on-ignition, g kg^{-1}	164 ± 10 A	125 ± 8 A	168 ± 12 AB	214 ± 18 B	148 ± 10 A
C conc., g kg^{-1}	97 ± 6 AB	76 ± 4 B	90 ± 6 AB	114 ± 9 A	74 ± 5 B
N conc., g kg^{-1}	4.9 ± 0.3 AB	3.9 ± 0.2 B	4.6 ± 0.3 AB	5.8 ± 0.5 A	3.8 ± 0.3 B
C/N ratio	20.0 ± 0.2 A	19.4 ± 0.3 A	20.0 ± 0.4 A	20.0 ± 0.3 A	19.4 ± 0.3 A
Organic matter, kg m^{-2}	7.75 ± 0.14 A	6.99 ± 0.21 B	7.84 ± 0.13 A	7.85 ± 0.17 A	5.33 ± 0.22 C
C, kg m^{-2}	4.63 ± 0.11 A	4.27 ± 0.15 A	4.22 ± 0.09 A	4.35 ± 0.12 A	2.68 ± 0.11 B
N, g m^{-2}	234 ± 6 A	221 ± 8 A	216 ± 6 A	220 ± 6 A	140 ± 6 B

† Means ± standard errors. Means followed by different letters in a row are significantly different ($P < 0.05$).

treatment Years 1 and 3, 96 kg ha^{-1} between Years 3 and 7, and 438 kg ha^{-1} between Years 7 and 11 (Table 1). Thus, at least 650 kg ha^{-1} of Ca, representing 63% of the added Ca from the wollastonite, passed out of the forest floor and the top 10 cm of the mineral soil in the first 11 yr after treatment. While it is possible that some of this migration occurred by the transport of particulate wollastonite, it is likely that most was transported as dissolved Ca, based on observed increases in Ca concentrations of soil solutions draining Oa and Bh horizons on W1 (Cho et al., 2010). A substantial portion of the dissolved Ca was likely removed from soil by root uptake. Green et al. (2013) observed that foliar Ca concentration in the dominant tree species on W1 increased by 40 to 50% in response to the wollastonite addition.

The total pool of Ca in the O horizon and upper mineral soil 11 yr after the application was 250 kg ha^{-1} greater than the pretreatment pool (Table 1), a statistically significant increase. Most of this difference can be accounted for by increased exchangeable Ca, particularly in the Oie horizon. Eleven years after the treatment, the exchangeable Ca pool in the Oie horizon remained nearly five times greater than the pretreatment pool (Table 2). The increase of 7.7 $kmol_c$ ha^{-1} in Oie horizon exchangeable Ca represents 154 kg ha^{-1} of Ca. Adding in the small increases in the Oa horizon and mineral soil, the increase in the pool of exchangeable Ca (172 kg ha^{-1}) represents 69% of the increase in the total Ca pool in the surface soils. Some of the increase in total and exchangeable Ca in the Oie was probably associated with detrital recycling. Likens et al. (1998) estimated the annual litter fall Ca flux at Hubbard Brook to be 40.7 kg ha^{-1} yr^{-1}. Assuming that the post-treatment increases in foliar Ca observed by Green et al. (2013) were due to uptake of wollastonite-derived Ca, litter fall may have returned approximately 10 to 20 kg ha^{-1} yr^{-1} of wollastonite-derived Ca to the soil.

If we assume that the increase in exchangeable Ca in the O horizon and mineral soil is due to the binding of Ca dissolved from wollastonite, then at most 78 kg ha^{-1} of Ca remained undissolved in surface soils 11 yr after the application (250 kg ha^{-1} minus 172 kg ha^{-1}). This 78 kg ha^{-1} represents 7.6% of the 1028 kg ha^{-1} of Ca originally added in 1999. If we further assume that the net loss of Ca from the O horizon and upper mineral soil layers after the treatment was also Ca dissolved from wollastonite, then 92.4% or more of the Ca added in the wollastonite treatment has dissolved and entered the ecosystem as labile Ca.

Effects of Wollastonite Addition on Soil Acidity

As expected, the application of wollastonite to W1 increased soil pH and base status. Significant increases in both pH_w and BS_e were observed in all horizons, and both remained significantly elevated after 11 yr (Table 2). The magnitude of the

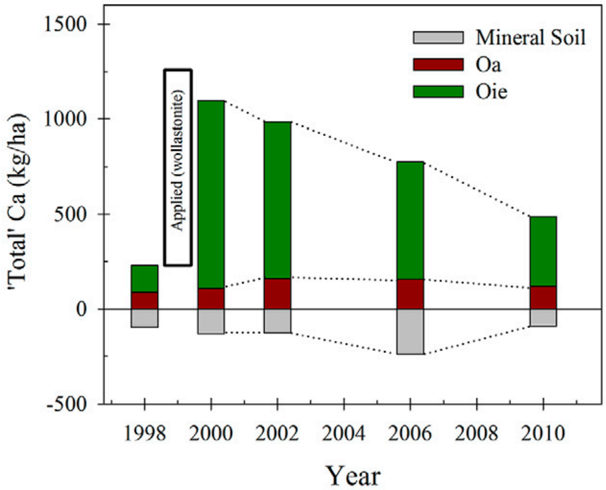

Fig. 3. Changes in total Ca in soils following watershed-scale amendment with wollastonite ($CaSiO_3$) in 1999 at the Hubbard Brook Experimental Forest, New Hampshire. The Ca dose was 1028 kg ha^{-1}. Calcium released from the dissolution of the added wollastonite moved downward through the upper soil profile in a progressive manner. See Table 1 for estimates of uncertainty.

increase in pH_w was greatest in the Oie horizon and less in the Oa and upper mineral soil, suggesting that much of the dissolution of wollastonite, which neutralizes 2 moles of H^+ per mole of wollastonite, occurred in the Oie horizon. Interestingly, the pH_w in the Oie horizon increased immediately after the treatment, whereas the pH_w in the Oa horizon and upper mineral soil decreased significantly in the first year after the treatment. In the Oa horizon, pH_w returned to the pretreatment level by post-treatment Year 3, and exceeded the pretreatment value by Year 7. The response was slower in the upper mineral soil, where pH_w did not return to the pretreatment level until 7 yr after treatment and only exceeded the pretreatment mean in Year 11. Although base saturation did not decline significantly in the Oa and upper mineral soil, its response to the treatment was also delayed in those horizons. These patterns suggest that Ca released from dissolving wollastonite in the Oie horizon displaced exchangeable acidity from exchange sites. Transport of this acidity to the Oa horizon and upper mineral soil resulted in temporary decreases in pH_w and delayed increases in BS_e in those horizons.

This progressive downward migration of Ca and acidity is consistent with the changes we observed in exchangeable cations. In the Oie horizon, the concentration of exchangeable Ca increased more than 400% immediately after the addition, while the concentration of exchangeable acidity decreased significantly (Fig. 1). Increases in exchangeable Ca and decreases in exchangeable acidity were delayed until 3 yr and 7 yr after treatment in the Oa and upper mineral horizons, respectively. Blette and Newton (1996) also observed progressive increases in exchangeable Ca downward in the forest floor and upper mineral horizons in the first 2 yr after $CaCO_3$ addition to the watershed of Woods Lake in the Adirondack region of New York.

Contrary to our original hypothesis, the changes in exchangeable Ca and acidity were not well-balanced. In the Oie horizon, for example, exchangeable Ca increased by almost 30 cmol$_c$ kg^{-1} between 1998 and 2006, while the decrease in exchangeable acidity was only 3 cmol$_c$ kg^{-1} (Fig. 1). Consequently, the CEC_e in the Oie horizon increased significantly, more than doubling after the wollastonite addition (Fig. 2). The differences were less dramatic in the Oa horizon, where CEC_e was significantly greater after 7 yr than before treatment, but only by 20%. The exchange capacity of Hubbard Brook soils is largely supplied by organic matter (Johnson et al., 1997; Johnson, 2002). The net negative charge of these carboxylic and phenolic functional groups (i.e., the CEC) increases with increasing pH (Stevenson, 1994). The pH dependence of organic matter charge may partly explain the increased CEC_e in Oie and Oa horizons, which experienced significant pH increases after wollastonite addition (Table 2). However, CEC_e decreased significantly between post-treatment Years 7 and 11, a period in which pH_w increased significantly in both horizons (Table 2), suggesting a more complex explanation. Previous research has shown that O horizon soils at the HBEF exhibit a significant negative correlation between pH and CEC_e, perhaps due to decreased solubility of Al–organic matter complexes at higher pH (Johnson, 2002). More detailed analyses of W1 soils, including measurements of organically bound Al and H, may shed light on this relationship.

The decreases we observed in exchangeable acidity were the result of decreases in both exchangeable H and Al (Fig. 2). In the Oie horizon, where the concentration of exchangeable Al was very low, even before treatment, exchangeable H dominated the decrease in exchangeable acidity. In the Oa and mineral horizons, both exchangeable Al and H decreased proportionally, though in the mineral soil cores only the decrease in exchangeable H was significant. Lawrence et al. (1995), using data from Hubbard Brook and elsewhere, proposed that transport of reactive Al from mineral soils into the O horizon was an important factor in the depletion of exchangeable Ca from forest floor soils in the northeastern United States. They also suggested that the high Al saturation in Oa horizons would prevent the soil from adsorbing naturally supplied Ca as the region recovers from chronic acid deposition. The Oa horizon on W1 before wollastonite treatment had an average exchangeable Al/Ca ratio of 1.54, higher than all but three of the sites studied by Lawrence et al. (1995). Despite this high degree of Al saturation, W1 soils were able to adsorb and retain a considerable amount of Ca (Fig. 2). Seven years after the treatment the exchangeable Al/Ca ratio in the Oa horizon had declined to 0.30, similar to the value reported for Sleepers River in Vermont, a Ca-rich site. While our results do not refute the mechanism Lawrence et al. (1995) proposed, they do show that the application of Ca to highly acidified soils can result in the displacement of Al and the retention of Ca on exchange sites in the forest floor.

The decreases we observed in exchangeable H in all horizons are particularly important because of their direct relationship to soil pH. Johnson (2002) found that the pH of Oa and mineral horizons in acid forest soils in the northeastern United States, including the HBEF, was significantly correlated with the fraction of CEC_e accounted for by H. The Oa horizons from this study show a similar pattern (Fig. 4). Furthermore, the pretreatment and post-treatment samples appear to follow a common relationship, suggesting that the increases in pH_w after wollastonite addition were largely explained by the exchange of H for Ca on organic matter exchange sites.

Implications for Ecosystem Biogeochemistry

In forest ecosystems the soil serves as a biogeochemical regulator, in which the chemistry of drainage waters is buffered, nutrient demands of vegetation are met, and organic matter decomposition and sequestration determine long-term C balance. Manipulation of the soil chemical environment through Ca addition has the potential to significantly impact all of these processes.

Numerous researchers have documented that liming of forest soils can stimulate microbial activity and decomposition, especially in O horizons (Illmer and Schinner, 1991; Ingvar Nilsson et al., 2001). In some cases, these amendments have led to decreases in organic matter and C stocks (Persson et al., 1990; Kreutzer, 1995). We observed significant decreases of more than 40% in the stock of organic matter and C in the Oa horizon 11 yr after wollastonite addition on W1 (Table 3). The N pool in the Oa horizon was significantly lower 7 yr after the treatment and remained low after 11 yr, though the 11-yr mean was not significantly different from the pretreatment mean. There were no significant changes in LOI, C, or N concentrations after wollastonite treatment, so the decreases in standing stocks were the result of decreased humus mass. Our results contrast sharply with those of Melvin et al. (2013), who observed much greater organic matter, C and N stocks, and reduced microbial basal respiration in limed O horizons compared with unlimed soils in the Woods Lake study. The Ca addition at Woods Lake was almost three times greater per unit area than the Ca added as wollastonite to W1, and the increases in exchangeable Ca in the Oa horizon at Woods Lake greatly exceeded the increases we observed.

Groffman et al. (2006) found evidence for possible suppression of N cycling processes in W1 in the first 4 yr after the wollastonite treatment, including decreases in microbial biomass N, potential net nitrification, and soil inorganic N concentrations. They also reported no treatment effect on soil–atmosphere CO_2 flux, and increased microbial C respiration in only 1 of the 4 yr. Similarly, Fisk et al. (2006) reported a significant decrease in microarthropod abundance 3 yr after the wollastonite addition. These results suggest that the decrease in the mass and C stock in the Oa horizon may be the result of chemical rather than biological processes. Humic substances become more soluble with increased pH due to the deprotonation of carboxylic functional groups (Stevenson, 1994), and leaching of dissolved organic carbon (DOC) might contribute to the decreased Oa horizon mass. In addition, dissolved Ca^{2+} derived from the dissolution of wollastonite can bind with these negatively charged humic substances and facilitate DOC transport to lower soil horizons.

There are several lines of evidence that the increased Ca content in W1 soils has positively affected tree growth and health. Two species that are especially sensitive to soil Ca are red spruce and sugar maple. Hawley et al. (2006) observed significantly lower winter injury in red spruce needles on W1 than on a reference site during a severe event in 2003. Juice et al. (2006) observed significant increases in foliar Ca of sugar maple as early as 2 yr after the wollastonite treatment. They also reported increased seedling density, lower seedling mortality over the winter, and higher seedling foliar chlorophyll concentrations in W1 compared with a reference watershed. In a paired watershed study, 3-yr survivorship (2007–2009) of sugar maple seedlings planted in the lower elevation of W1 was 1.5 times higher ($P < 0.001$) than seedlings planted in comparable microsites in an adjacent reference watershed (Cleavitt et al., 2011). The relatively rapid responses of red spruce and sugar maple suggest that these acid-sensitive species were able to quickly access Ca in Oie horizons, since total and exchangeable Ca concentrations and pools in lower horizons did not immediately increase after the treatment (Tables 1 and 2; Fig. 1). This is not surprising, since 43% of fine-root biomass at the HBEF is found in O horizons (Fahey, 1994). Fahey and Blum (2011) confirmed this in a study in which they reciprocally transplanted Oie soil from W1 and a reference watershed. Based on differences in Ca/Sr ratios, resulting from the wollastonite addition, they found evidence for uptake of wollastonite-derived Ca from the Oie horizon by sugar maple seedlings in the reference watershed.

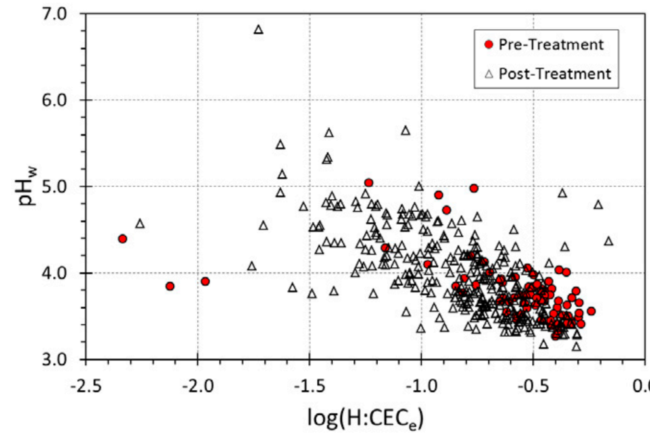

Fig. 4. Relationship between soil pH in water (pH_w) and the base-10 logarithm of the fraction of effective CEC explained by exchangeable H (H/CEC_e) for Oa horizon soils at the Hubbard Brook Experimental Forest. Post-treatment data include all samples collected after wollastonite addition.

The total aboveground biomass of trees has taken longer to respond to the Ca addition. Through 2001 to 2002, the total aboveground biomass of trees greater than 2-cm in diameter on W1 was nearly identical to the biomass of trees on reference W6. For the 10-yr period beginning in 2001 to 2002, wood production and aboveground net primary production were significantly higher on W1 than W6 (Battles et al., 2014). The higher production values have persisted through the period in which Ca has moved through the upper soil horizons. Together with the increases observed in foliar Ca (Dasch et al., 2006; Juice et al., 2006, Green et al., 2013), this suggests that wollastonite-derived Ca is now being recycled to the forest floor in the form of litter.

As expected, the concentrations and fluxes of Ca in drainage waters increased significantly after the wollastonite addition. Significant increases in soil solution Ca concentrations and pH were consistent with the downward migration of wollastonite-derived Ca we observed. Solutions draining O horizons responded sooner and exhibited greater increases in Ca and pH than solutions draining Bs horizon mineral soils (Dasch et al., 2006; Cho et al., 2010). In contrast, stream water Ca and pH increased dramatically immediately after the treatment (Peters et al., 2004) and have gradually decreased in the years afterward (Nezat et al., 2010). Using Ca/Sr ratios and Sr-isotope analyses, Nezat et al. (2010) estimated that more than 60% of the Ca in stream water leaving W1 immediately after the addition was derived from the added wollastonite. That percentage declined steadily to about 30% after 3 yr, where it remained through 9 yr. They hypothesized three phases of wollastonite dissolution to explain the stream Ca dynamics. In the first year after treatment, wollastonite directly deposited in the stream channel could account for the pulse in the Ca concentration. Years 2 and 3 were proposed to be a period of “hyporheic exchange” in which elevated Ca concentrations were largely the result of wollastonite dissolution in the near-stream zone. After 3 yr, stream Ca concentrations stabilized, marking the beginning of the “infiltration” period, characterized by the transport of wollastonite-derived Ca from the entire watershed. Our soils data support these proposed mechanisms explaining Ca transport. In 2000, 1 yr after the treatment, most of the added wollastonite was still in the Oie horizon, with no significant increase in either total or exchangeable Ca in the Oa or upper mineral horizons, and unlikely to be transported to the stream (Table 1; Fig. 1). In the next 2 yr, the hyporheic exchange period, total and exchangeable Ca increased significantly in the Oa horizon and remained significantly elevated in the Oie horizon (Table 1; Fig. 1). During snowmelt and storm events, shallow flow paths contribute much of the water to the stream (Cho et al., 2009). Thus, the wollastonite-derived Ca that leached into these horizons was available for transport to the stream. After 2002, Ca continued to be transported into the Oa horizon and mineral soils, making transport via both shallow and deep flow paths possible.

Nezat et al. (2010) estimated that approximately 30 kg ha^{-1} of the added Ca in W1 was exported in stream water in the first 9 yr after the treatment. They also calculated that the loss of wollastonite-derived Ca in stream water had stabilized at approximately 0.9 kg ha^{-1} yr^{-1}. Thus, approximately 32 kg ha^{-1} of the Ca added in the wollastonite treatment was exported from the system in the first 11 yr after treatment. The remaining 996 kg Ca ha^{-1}, 97% of the amount added, remained in the ecosystem. Of this amount, approximately 250 kg Ca ha^{-1} remained in the forest floor and upper mineral soil (Table 1). Therefore, we estimate that about 750 kg ha^{-1}, or 73%, of the wollastonite-derived Ca was either taken into forest vegetation or has passed into mineral soil horizons below 10 cm in the first 11 yr after the treatment. We do not yet have quantitative estimates of Ca uptake by vegetation or measurements of deep mineral soils. Nevertheless, with such small losses of Ca in stream water, it is clear that the wollastonite addition on W1 was an effective means of increasing the amount of internal Ca cycling in an ecosystem that had experienced substantial Ca depletion due to acid deposition.

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