Changes in soil chemistry following a watershed-scale application of wollastonite ($CaSiO_3$) at Hubbard Brook, New Hampshire, USA

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Abstract

Decades of acidic deposition in the northeastern United States is believed to have caused the loss of substantial amounts of calcium from forest soils. This process of ‘calcium depletion’ affected the chemistry of drainage waters in the region and may have impacted forest health. To study this phenomenon, we applied 45 Mg of wollastonite (1316 kg Ca ha^{-1}) to watershed 1 (W1) at the Hubbard Brook Experimental Forest, in New Hampshire, USA in October, 1999. Exchangeable Ca (1 M NH_4Cl) and soil pH increased significantly in the Oie and Oa horizons, and in the top 10 cm of the mineral soil, in samples collected 1, 3, and 7 years after treatment. Exchangeable acidity (1 M KCl) decreased significantly in the Oie and Oa horizons after treatment, but the effect in the upper mineral soil was not clear. Base saturation and effective cation exchange capacity (CEC_e) increased significantly after wollastonite application in all layers studied, primarily on the strength of the increased exchangeable Ca. We did not observe compensatory decreases in exchangeable Al, or other exchangeable cations, as initially hypothesized. Therefore, while wollastonite addition has improved the base status of W1 soils, it has not resulted in decreases in exchangeable Al.

Key Words

Soil acidity, acid rain, base saturation, calcium, cation exchange, liming.

Introduction

Acidic deposition, primarily in the form of sulfuric and nitric acid, has resulted in the acidification of soils and surface waters of the northeastern United States, and many other regions of the world. There is a growing consensus that this acidification has resulted in the depletion of available calcium from many base-poor soils (Likens *et al.* 1996; Driscoll *et al.* 2001). Soil calcium depletion may partly explain the sluggish response of surface waters in the northeastern United States to recent decreases in acidic deposition, and may also be related to declining forest health in the region (Warby *et al.* 2005; Hawley *et al.* 2006). To study these relationships, we initiated a watershed-level experiment in which calcium was added to the soil in the form of wollastonite ($CaSiO_3$), to replace the calcium believed to have been lost from the soil during the period of chronic acid rain. Unlike liming studies, we used calcium silicate because silicate weathering is the dominant weathering process in the base poor soils at our study site. The use of silicates also avoids the introduction of large amounts of alkalinity that accompanies the use of calcium carbonate lime.

This study is an ecosystem-level investigation of the response of vegetation, soils, fauna, and drainage waters to the addition of wollastonite. The objective of this presentation is to report the effects of the treatment on soil chemistry, particularly the acid-base status of the soils, as indexed by exchangeable Ca, Al, cation exchange capacity, base saturation, and pH. The results presented here extend the work of Cho *et al.* (In Press), which may be consulted for details of experimental design, sampling, and analysis.

Methods

Site Description

This work was done at the Hubbard Brook Experimental Forest, in the southern portion of the White Mountain National Forest in central New Hampshire, USA. The treated watershed – watershed 1 (W1) has an area of 11.8 ha and an elevation range from 488 m to 747 m. The soils at the HBEF are predominately Spodosols (Typic Haplorthods) derived from glacial till, and the average depths of the organic and the mineral soils are 7 cm and 50 cm, respectively. The dominant vegetation type on W1 consists of northern hardwood species (sugar maple (*Acer saccharum*), American beech (*Fagus grandifolia*) and yellow birch (*Betula alleghaniensis*)) on the lower 90 % of the watershed, and a montane boreal transition forest of red spruce (*Ricea rubens*), balsam fir (*Abies balsamea*) and white birch (*Betula papyrifera*) at high elevation. The climate at the HBEF is humid-continental, characterized by long, cold winters (average temperature for January is –9°C) and short cool summers (average for July is 10°C) with 1,400 mm of average annual

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precipitation, approximately 30% of which falls as snow.
The experimental addition of wollastonite to W1 was designed to restore the base saturation of the soil to a level estimated to have existed at the advent of acidic deposition. Theoretically, the amount of Ca required to restore the overall base saturation of W1 soils from 10% to 19% was approximately 850 kg Ca/ha, equivalent to 30.2 tons of wollastonite over the area of W1. To account for potential losses or inefficiencies in wollastonite dissolution, a "safety factor" of 50% was added to the dose, resulting in an application of 45 tons of wollastonite, or 1,316 kg Ca/ha. The wollastonite was pelletized into 1.5 – 4 mm diameter pellets with a water-soluble binder, which allowed the pellets to disintegrate to individual particles (mean diameter 16 ㎛) in the presence of moisture after the manipulation (Peters *et al.* 2004). The application was made in October of 1999, after leaf fall, by helicopter, and was determined to be remarkably uniform across the watershed (Peters *et al.* 2004).

Soil sampling and analyses
Soil samples were collected at 100 randomly selected sites in W1 prior to (1998) and after (2000, 2002, and 2006) the treatment. Soil samples were collected from the Oi+Oe (Oie) and Oa layers, using 15 cm x 15 cm forest floor blocks. After the O horizon sampling, the upper mineral soil was sampled using a 5-cm diameter stainless steel corer. The depth of the cores was a maximum of 10 cm, but often less due to refusal of the corer by rocks.

The soil samples from the Oie horizons were oven dried at 80 °C to a constant weight, and ground in a Wiley mill. Samples from the Oa and upper mineral horizon were air dried, weighed, and sieved through 5-mm and 2-mm stainless steel screens, respectively. All soil samples were analyzed for pH_s (0.01 M CaCl_2). Exchangeable cations (Ca, Mg, K, Na, Al) were extracted with 1 M NH_4Cl. Exchangeable acidity was determined by titration of 1 M KCl extracts to a phenolphthalein end-point. Effective cation exchange capacity (CEC_e) was calculated as the sum of exchangeable acidity and exchangeable Ca, K, and Mg (Na was negligible in the extracts). Effective base saturation (BS_e) was computed as the sum of exchangeable bases, divided by the CEC_e and multiplied by 100.

Table 1. Changes in soil chemistry after wollastonite (CaSiO_3) addition to watershed 1 at the Hubbard Brook Experimental Forest, New Hampshire, USA.

Property	Horizon	Pre-Treatment	Post-Treatment		
		1998	2000	2002	2006
	Oie	5.62	24.4	34.7	33.9
Exch. Ca (cmol_c /kg)	Oa	4.44	4.94	11.1	14.2
	Mineral	0.58	0.65	0.85	1.74
	Oie	1.13	0.84	0.87	0.86
Exch. Al (cmol_c /kg)	Oa	6.90	7.07	5.29	3.89
	Mineral	6.19	5.26	6.02	5.22
	Oie	8.41	5.69	5.11	5.83
Exch. Acidity (cmol_c /kg)	Oa	11.9	11.6	8.48	6.58
	Mineral	7.79	6.68	7.71	6.43
	Oie	16.2	32.7	43.6	44.4
CEC_e (cmol_c /kg)	Oa	18.0	18.2	21.4	22.7
	Mineral	8.80	7.68	8.96	8.67
	Oie	48.7	78.6	86.1	86.9
BS_e (%)	Oa	32.9	35.8	56.0	71.0
	Mineral	12.1	13.1	14.3	25.8
	Oie	3.26	4.21	4.34	4.23
pH_s	Oa	3.03	3.24	3.48	3.62
	Mineral	3.35	3.47	3.44	3.50

Results

After wollastonite addition to W1, the pH and exchangeable Ca concentration in the soils increased significantly (Table 1). Exchangeable acidity and exchangeable Al decreased significantly, though the magnitudes of these decreases were less than the increase in exchangeable Ca. Consequently, wollastonite addition resulted in significant increases in both CEC_e and BS_e. Soil pH increased by nearly a whole pH unit in the Oie horizon, and 0.6 pH units in the Oa horizon.

The magnitude and timing of the changes in soil chemistry were strongly related to soil horizon. For example, seven years after treatment, exchangeable Ca had increased by a factor of 6 in the Oie horizon, compared to a factor of 3 in the Oa and mineral horizons. Most of the increase in exchangeable Ca in the Oie horizon occurred in the first year after treatment, whereas in the Oa and mineral horizons, it took 3 and 7 years, respectively, for the changes to be apparent (Table 1).

Discussion

The soil chemistry data suggest that the dissolution of the wollastonite added to W1 has resulted in an increase in the base status of soils which is progressive in time and space. Large increases in exchangeable Ca and base saturation occurred almost immediately in the Oie horizon, whereas increases in the Oa and mineral horizons occurred progressively later. These results are consistent with continuing dissolution of the added wollastonite and downward migration of the weathering products.

We had initially hypothesized that Ca released by the weathering of the wollastonite would displace Al and H from soil exchange sites. Our data indicate that this did occur to an extent. Exchangeable Al and acidity both decreased significantly after wollastonite addition. However, the magnitude of these decreases was much smaller than increases in exchangeable Ca. For example, in the Oa horizon, exchangeable Ca increased from 4.44 $cmol_c$ /kg prior to wollastonite, to 14.2 $cmol_c$ /kg seven years later (Table 1). In contrast, exchangeable acidity decreased by only half that amount, from 11.9 to 6.58 $cmol_c$ /kg. Because of this non-stoichiometric exchange, wollastonite addition resulted in a significant increase in the effective CEC in the soil.

The increase in CEC_e that we observed is consistent with increase in pH observed in W1 soils. Organic matter provides nearly all of the cation exchange capacity in soils at Hubbard Brook, and elsewhere in the region (Johnson 2002).

Conclusions

Wollastonite addition resulted in persistent increases in the base status of soils at Hubbard Brook. Our results suggest that wollastonite may be a good alternative to traditional lime as a potential amendment for acidified soils in the northeastern United States. Wollastonite appears to offer a long-lasting release of Ca without the alkalinity 'shock' produced by lime.

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