

Watershed-Level Responses to Calcium Silicate Treatment in a Northern Hardwood Forest

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ABSTRACT

Watershed 1 (W1) at the Hubbard Brook Experimental Forest in New Hampshire, with chronically low pH and acid neutralizing capacity (ANC) in surface water, was experimentally treated with calcium silicate (CaSiO₃; wollastonite) in October 1999 to assess the role of calcium (Ca) supply in the structure and function of base-poor forest ecosystems. Wollastonite addition significantly increased the concentrations and fluxes of Ca, dissolved silica (Si), and ANC and decreased the concentrations and fluxes of inorganic monomeric Al (Al_i) and hydrogen ion (H⁺) in both soil solution and stream water in all sub-watersheds of W1. Mass balances indicate that 54% of the added Ca remained undissolved or was retained by vegetation during the first 6 years after treatment. Of the remaining added Ca, 44% was retained on O horizon cation exchange sites. The Ca:Si ratio in the dissolution

products was greater than 2.0, more than twice the molar ratio in the applied wollastonite. This suggests that Ca was preferentially leached from the applied wollastonite and/or Si was immobilized by secondary mineral formation. Approximately 2% of the added Ca and 7% of the added Si were exported from W1 in streamwater in the first 6 years after treatment. Watershed-scale Ca amendment with wollastonite appears to be an effective approach to mitigating effects of acidic deposition. Not only does it appear to alleviate acidification stress to forest vegetation, but it also provides for the long-term supply of ANC to acid-impacted rivers and lakes downstream.

Key words: acidification; calcium amendment; Hubbard Brook; soil horizons; soil solution; stream water; wollastonite.

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INTRODUCTION

In spite of decreases in acidic atmospheric deposition, previous studies in acid-impacted watersheds in the northeastern US have observed limited increases in stream pH and acid neutralizing capacity (ANC) due to concomitant decreases in basic cation concentrations (C_B). This muted response has been attributed to the depletion of exchangeable calcium (Ex-Ca) from soils (Driscoll and others 1989; Likens

and others 1996; Driscoll and others 2001; Palmer and others 2004; Warby and others 2005), the result of historic, long-term elevated inputs of strong acids in atmospheric deposition, coupled with decreases in atmospheric deposition of basic cations (Gbondo-Tugbawa and Driscoll 2003) and, at some sites, the accumulation of Ca by biomass uptake (Markewitz and others 1998).

Ca is the major basic cation on the soil exchange complex and in drainage waters, and a critical controller of the acid–base status in soils and aquatic ecosystems (Driscoll and others 1989; Lawrence and others 1995). Acid-sensitive watersheds in the northeastern US are characterized by shallow deposits of surficial materials, soil minerals with slow rates of chemical weathering and associated Ca supply, and low concentrations and pools of exchangeable basic cations in soil (Landers and others 1988; April and Newton 1985; Driscoll 1991; Eilers and Selle 1991; Nezat and others 2004). A geochemical consequence of low Ca²⁺ supply and low ANC in forest watersheds receiving elevated acidic deposition is the mobilization of aluminum (Al) from soil to drainage waters (Cronan 1994; Cronan and Schofield 1990; Palmer and others 2004; Cho and others 2010). Due to these responses, the supply of Ca plays a critical role in regulating the acid–base status of forest soils and drainage waters and the associated structure and function of forest and aquatic ecosystems.

Forest liming (usually by the addition of calcium carbonate: CaCO₃) has been used to mitigate the acidification of soil and surface water. Previous forest liming studies have shown increases in exchangeable Ca, cation exchange capacity, and base saturation in soil accompanied by decreases in exchangeable acidity and exchangeable Al. Liming has also been demonstrated to induce increases in Ca, pH, and ANC and decreases in inorganic monomeric Al (Al_i) in surface waters (Blette and Newton 1996; Cirimo and Driscoll 1996; Driscoll and others 1996; Hindar 2005; Huber and others 2006; Löfgren and others 2009; Newton and others 1996).

In this study, 3,800 kg/ha of wollastonite (Ca-SiO₃) pellets (66 keq Ca/ha) with a pellet diameter of 1.5–4 mm and average 16- μ m particle size were added to a watershed at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire. We investigated the role of Ca supply in regulating the chemistry of soil, soil water, and stream water in the northern hardwood forest prior to and after the wollastonite treatment. We constructed whole-watershed and sub-watershed mass balances for Ca and silica (Si) to assess the fate of the added wollastonite.

We examined the responses of soils, soil solution, and stream water at three elevation/vegetation zones in the watershed in response to the experimental manipulation. We hypothesized that the Ca supplied in the wollastonite application would alter the acid–base status of the ecosystem by: (1) increasing soil pools of exchangeable Ca and decreasing soil pools of exchangeable Al; and (2) increasing fluxes of Ca and Si and decreasing fluxes of H⁺ and Al in soil solutions and stream water. We also hypothesized that (3) there would be distinct horizontal patterns in the acid–base response to the experimental treatment across sub-watersheds of the treated watershed. By calculating mass balances and mineral solubilities, we: (1) determined the likely sources and/or sinks of Ca and Si that occur within and between sub-watershed ecosystems; (2) examined the mechanisms of Ca and Si mobilization and immobilization; and (3) evaluated the overall changes in the biogeochemistry of the entire watershed.

STUDY SITE AND METHODS

Study Area and Wollastonite Application

The HBEF lies in the southern portion of the White Mountain National Forest in central New Hampshire, USA. (43°56'N, 71°45'W; Figure 1). The experimental watersheds at the HBEF exhibit a high degree of spatial variability in soils, vegetation, and biogeochemical processes across the landscape (Cho and others 2010; Johnson and others 2000). Soils at the HBEF are predominately Spodosols (Typic Haplorthods) derived from glacial till (Johnson and others 1991a, b). Generally shallow flow-paths of water occur at the highest elevations, whereas, at lower elevations deposits of glacial till are thicker and facilitate somewhat deeper hydrologic flow-paths (Johnson and others 2000). The watersheds of the HBEF generally exhibit a pattern common in mountainous forest landscapes throughout the Northeast, with low rates of Ca²⁺ supply by weathering and the diminution of the effects of acidic deposition with decreasing elevation (Johnson and others 1981; Driscoll 1991). The HBEF has a humid-continental climate, which is characterized by long and cold winter periods (average: –9°C in January), and short, cool summers (average: 10°C in July), having an average annual precipitation of 1,395 mm, 25–33% of which falls as snow (Federer and others 1990).

Watershed 1 (W1) has an area of 11.8 ha, a stream channel area of 0.18 ha, and an elevation range from 488 to 747 m. In October of 1999,

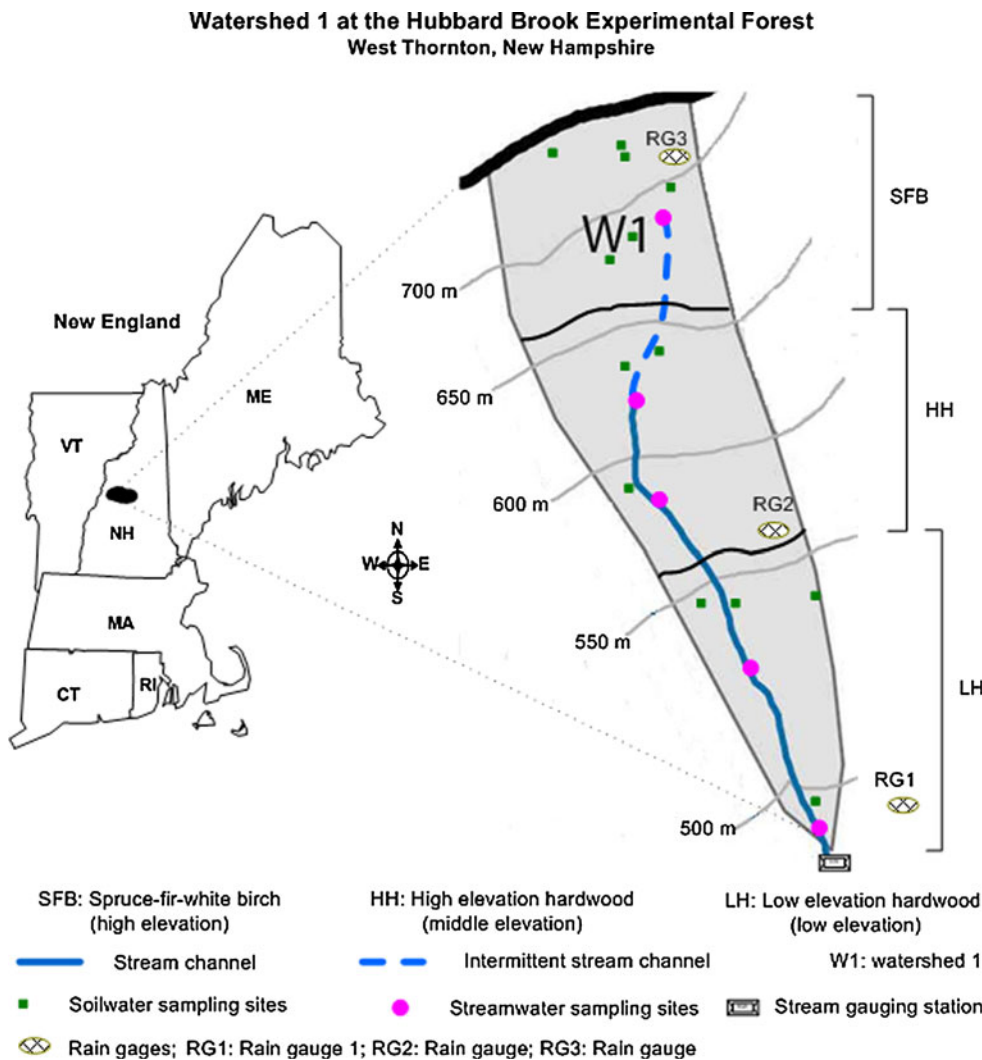


Figure 1. Map of W1 at the HBEF in New Hampshire, showing lysimeter locations and stream sample sites in spruce-fir-white birch (SFB), high-elevation hardwood (HH), and low-elevation hardwood (LH) sub-watersheds.

45×10^3 kg of wollastonite (CaSiO_3), a readily weatherable calcium silicate mineral, was applied to W1 by helicopter. The addition of wollastonite was relatively uniform across the catchment (Peters and others 2004).

W1 has 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 (*Picea rubens*), balsam fir (*Abies balsamea*) and white birch (*B. papyrifera*) at high-elevation (Juice and others 2006). For this analysis, W1 was divided into three distinct landscape zones, based on elevation. The high-elevation spruce-fir-white birch sub-watershed (SFB) is characterized by relatively flat topography, shallow soils and flow-paths, frequent bedrock outcrops, and a canopy dominated by spruce, fir, and white birch. The SFB sub-watershed accounts for approximately 2.95 ha of the catchment area and 451 m² of the

streambed area. The high-elevation hardwood sub-watershed (HH) has steep slopes, somewhat deeper soils, often lying on bedrock with no C horizon, and deciduous canopy vegetation. The HH sub-watershed occupies approximately 4.84 ha of the catchment area and 740 m² of the streambed area. Finally, the low-elevation hardwood sub-watershed (LH) is dominated by still deeper soils, dense glacial till, deciduous canopy trees, and accounts for approximately 4.01 ha of the sub-watershed area and 613 m² of the streambed area.

Collection and Analysis of Samples

The amount of precipitation has been measured daily at rain gauge 1, located 50 m from the W1 stream gauging station, from rain gauge 2 in the HH zone, and from rain gauge 3 in the SFB zone (Figure 1). The weekly precipitation concentrations of Ca^{2+} , H^+ , and SO_4^{2-} used in this study were obtained from the

National Atmospheric Deposition Program website [NADP, <http://nadp.sws.uiuc.edu>, NH02, Hubbard Brook, Grafton county, NH with elevation: 250 m (latitude: 43.9433, longitude: -71.7029)]. For the Si concentration in precipitation, data from samples collected and analyzed weekly by the Cary Institute of Ecosystem Studies in Millbrook, New York were used (www.hubbardbrook.org). Ratios of dry to wet deposition were used to estimate dry deposition fluxes. Dry deposition data from CASTNet site WST109, in Woodstock, New Hampshire (elevation 258 m; latitude: 43.945; longitude: -71.7008) were used to compute wet:dry ratios (Chen and Driscoll 2005). Stream flow is measured continuously at the stream gauging station at the base of W1, which has a sharp-crested V-notch weir. In this study, data for precipitation amount and stream flow were obtained from the HBES website (www.hubbardbrook.org).

Collection of soil samples and methods for the chemical analyses of soil are detailed in Cho and others (2010). Soil solution samples were collected at monthly intervals from zero-tension lysimeters, which were constructed of PVC troughs filled with acid-washed quartz sand and placed below the O, Bh, and Bs horizons. To assess spatial differences in biogeochemical cycles, soil solutions were sampled from 6 lysimeters in the SFB sub-watershed, 3 in the HH sub-watershed, and 4 in the LH sub-watershed, respectively (Figure 1). Stream water samples were also collected at monthly intervals longitudinally at five sites (1 site in the SFB, 2 in the HH, and 2 in the LH) as part of a long-term monitoring program (Figure 1). Details of the analytical methods used for soil solution and stream water are listed in Table 1. All water analyses were conducted using previously

described quality assurance and quality control (QA/QC) protocols (Cho and others 2009). We used a water year beginning on October 1 and ending on September 30 to calculate water and solute annual fluxes for all data sets between 1997 and 2005, since the addition of wollastonite to W1 was conducted in October of 1999. Although this definition of the water year coincides with the timing of the wollastonite addition, it differs from the definition commonly used at the HBEF (June 1–May 31; Likens and Bormann 1995; Likens and others 1998; Johnson and others 2000).

Calculation of Soil Pools and Fluxes

Soil pools of Ca and Al were calculated by multiplying exchangeable Ca and Al concentrations by their corresponding soil masses per unit area. Testing for significant changes between the pre- and post-treatment period in each of the three sub-watersheds was done using the two-sample *t* test for independent samples (MINITAB version 14; statistical software) to determine significant changes using an $\alpha = 0.05$.

Yearly solute fluxes in precipitation were determined by multiplying the solute concentrations for each month by the accumulated daily precipitation for the month of sample collection, and summing these values for each water year. In these calculations, we used the concentrations in wet deposition at the NADP collection site and precipitation quantity obtained from the rain gauges in each of the three sub-watersheds. For the estimation of yearly solute fluxes in soil water, the growing season (GS) and the non-growing season (NGS) were defined

Table 1. Analytical Methods for Soil Water and Stream Water Chemistry

Analyte	Method	Reference
Ca ²⁺	Atomic absorption spectroscopy with flame atomic emission	Slavin (1968)
Dissolved H ₄ SiO ₄	Molybdenum blue colorimetry with automated analysis	APHA (1992)
pH	Potentiometric measurement	APHA (1992)
Acid neutralizing capacity (ANC)	Strong acid titration, Gran plot analysis	Gran (1952)
Total monomeric Al (Al _m)	Colorimetric measurement following chelation with pyrocatechol violet	McAvoy and others (1992) Palmer and others (2004)
Organic monomeric Al (Al _o)	Same method as Al _m , after passing sample through an ion exchange column	McAvoy and others (1992) Palmer and others (2004)
Inorganic monomeric Al (Al _i)	Calculated: Al _m - Al _o	Driscoll (1984)
SO ₄ ²⁻	Ion chromatography (IC)	Tabatabai and Dick (1983)
Dissolved organic carbon (DOC)	Infrared (IR) CO ₂ detection with UV-enhanced persulfate oxidation	Dohrmann (1984)

from May 1 to September 30 and from October 1 to April 30th, respectively. Soil water fluxes were computed by subtracting evapotranspiration, which was partitioned by horizon using the distribution of fine root biomass (38, 41, and 21% at Oa, Bh, and Bs horizons in the SFB sub-watershed; 33, 47, 20% at Oa, Bh, and Bs horizons in the HH; 42, 36, 21% at Oa, Bh, and Bs horizons in the LH, respectively; Fahey and Hughes 1994), from precipitation (Dittman and others 2007). Total evapotranspiration was calculated as the difference between precipitation amount and stream flow. Evapotranspiration for the NGS was assumed to be zero. Yearly solute fluxes in soil water were determined by multiplying the calculated soil water flux for the GS and NGS by mean concentrations in each season and then summing the GS and the NGS. This approach is based on the assumption that water percolates vertically through the complete soil profile before emerging to the stream channel (that is, no short circuiting through shallow flow-paths). This simplified hydrologic model of soil water has been employed in previous studies at the HBEF (Dittman and others 2007). Solute fluxes in stream water were calculated by multiplying the measured solute concentrations for each month by the cumulative discharge for that month. Stream flow generated in each sub-watershed was estimated to be 25% in the SFB, 41% in the HH, and 34% in the LH sub-watershed, assuming that water yield in sub-watersheds was proportional to the area in each of the sub-watersheds (Johnson and others 2000; Dittman and others 2007).

Mass Balances

To determine whether the three elevational sub-watersheds in W1 were sinks or sources of Ca and Si, net outputs of Ca and dissolved Si were estimated for pre- (1997–1999) and post-treatment (2000–2005) periods. Net production (output–input) of Ca and H_4SiO_4 for each horizon in the three sub-watersheds was determined by mass-balance calculations, assuming that: (1) precipitation, dry deposition, and the addition of CaSiO_3 were the input fluxes to the forest floor and streambed in each sub-watershed; (2) solute transport through the soil profiles was vertical (Oa to Bh to Bs horizons) prior to discharge to the stream channel; (3) hydrologic losses and/or gains from underlying bedrock are negligible; and (4) the distribution of the added wollastonite was uniform across W1. Assumption (2), of vertical drainage of water through the soil profile prior to export to the stream channel, oversimplifies the soil hydrology, but has been invoked in previous mass-balance analyses at the HBEF (Dittman and others

2007; Johnson and others 2000). Through hydrologic modeling, Federer and others (1990) and Likens and Bormann (1995) suggested that assumption (3), of limited deep seepage from HBEF watersheds, is valid. Peters and others (2004) reported a relatively uniform application of wollastonite to W1, supporting assumption (4).

Mineral Saturation Indices

To evaluate the potential for Si precipitation in secondary minerals, we calculated the saturation index (SI) for five Si-bearing minerals [amorphous Si (ASi), quartz, kaolinite, allophane, and imogolite] using data from O horizon soil solutions (MINEQL+, chemical equilibrium modeling software, version 4.0). The SI values were used to assess the degree to which soil solutions were at or near equilibrium with the solubility of these mineral forms. The SI was calculated as:

$$\text{SI} = \log \frac{Q_p}{K_p} \quad (1)$$

where Q_p is the ion activity product and K_p is the thermodynamic solubility product ($\log K_{\text{amorphous silica}} = 2.710$, $\log K_{\text{quartz}} = 4.006$, $\log K_{\text{kaolinite}} = 5.726$, $\log K_{\text{allophane}} = 7.020$, $\log K_{\text{imogolite}} = 6.050$) of the mineral phase of interest. Negative SI values indicate undersaturation with respect to a given solid phase, whereas positive SI values indicate oversaturation, and a zero SI indicates chemical equilibrium (Cirimo and Driscoll 1996). Thus, a mineral phase would only be expected to form if its SI were positive. The SI values were computed assuming closed atmospheric CO_2 for soil solutions, and employing temperature and ionic strength corrections.

RESULTS

Precipitation Quantity, Chemistry, and Stream Discharge

Annual precipitation was greatest in the HH zone and lowest in the SFB sub-watershed during the study period, although within-watershed variation was small (Table 2). Concentrations of both H^+ (from 35 $\mu\text{mol/l}$ in 1997 to 25 $\mu\text{mol/l}$ in 2005) and SO_4^{2-} (from 15 $\mu\text{mol/l}$ in 1997 to 12 $\mu\text{mol/l}$ in 2005) in precipitation decreased over the study period, as did the dry to wet deposition ratio of SO_4^{2-} (from 0.20 in 1997 to 0.14 in 2005; Table 2). We observed no trends in Ca^{2+} ($1.31 \pm 0.28 \mu\text{mol/l}$) or Si ($3.42 \pm 0.67 \mu\text{mol/l}$) concentrations in precipitation. Annual stream flow in W1 fluctuated throughout the study period, decreasing from 970 mm in 1997 to 530 mm

Table 2. Precipitation Amount, Solute Concentrations in Wet Deposition, Dry to Wet Deposition Ratios, and Streamflow at W1 of the HBEF—1997–2005 Water Years (October 1–September 30)

Water year	Sub-watershed ¹	Precip. (m)	Precipitation concentration ² (μmol/l) and dry to wet deposition ratio ³				Streamflow (m)
			Ca ²⁺	Si	H ⁺	SO ₄ ²⁻	
1997	LH	1.48	1.02 (0.30)	1.66	35.08	14.52 (0.20)	0.97
	HH	1.52					
	SFB	1.36					
1998	LH	1.38	1.57 (0.30)	3.56	32.21	13.40 (0.21)	0.91
	HH	1.41					
	SFB	1.38					
1999	LH	1.45	1.15 (0.30)	3.56	34.99	12.95 (0.19)	0.88
	HH	1.47					
	SFB	1.39					
2000	LH	1.32	1.80 (0.30)	3.86	39.17	14.95 (0.17)	0.83
	HH	1.35					
	SFB	1.31					
2001	LH	1.10	1.10 (0.30)	3.86	29.72	10.13 (0.16)	0.53
	HH	1.12					
	SFB	1.10					
2002	LH	1.21	1.57 (0.30)	3.56	33.50	13.16 (0.15)	0.58
	HH	1.24					
	SFB	1.19					
2003	LH	1.37	1.15 (0.30)	3.56	29.99	11.48 (0.15)	0.81
	HH	1.38					
	SFB	1.35					
2004	LH	1.57	1.40 (0.30)	3.56	29.65	11.89 (0.14)	1.14
	HH	1.58					
	SFB	1.49					
2005	LH	1.43	1.05 (0.30)	3.56	24.89	11.71 (0.14)	0.97
	HH	1.46					
	SFB	1.39					

¹Sub-watershed designations—LH = low-elevation hardwood; HH = high-elevation hardwood; SFB = spruce-fir-white birch.

²Precipitation chemistry obtained from the National Atmospheric Deposition Program (Ca, H, and SO₄²⁻) and the Hubbard Brook Ecosystem Study (Si). See “Study site and methods” for details.

³Numbers in parentheses are dry to wet deposition ratios obtained from Chen and Driscoll (2005).

in 2001, and then increasing to a maximum of 1,140 mm in 2004. These patterns in stream discharge corresponded with the patterns in precipitation amount (Table 2).

Soil Chemistry

Prior to the wollastonite application, soil pools of Ex-Ca in the Oie, Oa, and upper mineral horizons were generally lower in the SFB than in the HH and the LH sub-watersheds (Table 3). Exchangeable Ca pools increased significantly in O and mineral horizons in the SFB sub-watershed after the treatment. In other zones, the pool of exchangeable Ca in the Oie horizon increased significantly.

Although Ca dominated the cation exchange complex in the Oie horizons, Al was the dominant

exchangeable cation in the Oa horizon and upper mineral soil in all sub-watersheds (Table 3). Exchangeable Al (Ex-Al) in the upper mineral horizon decreased significantly ($P < 0.05$) in all sub-watersheds after the treatment. There were no significant differences in Ex-Al pools among sub-watersheds in Oie or mineral soil before or after treatment. In the Oa horizon, the largest pool of Ex-Al was found in the HH sub-watershed before and after the wollastonite addition. Detailed analysis of the soil chemistry response to the wollastonite treatment can be found in Cho and others (2010).

Soil Water Chemistry

The wollastonite treatment increased concentrations and fluxes of Ca²⁺ and H₄SiO₄, and decreased H⁺ and Al_i in the soil solutions in all sub-water-

Table 3. Soil Pools of Exchangeable Ca and Al Prior to (1998) and After (2000, 2002) Wollastonite Addition to W1 of the HBEF, New Hampshire

Horizon	Year	Exchangeable cation pool (mol _c m ⁻²)			Sub-watershed differences ¹
		SFB	HH	LH	
Exchangeable Ca					
Oie	1998	0.19	0.23	0.22	None
	2000	1.23***	1.04***	0.75***	SFB=HH > LH
	2002	1.35***	1.25***	1.44***	None
Oa	1998	0.15	0.54	0.52	SFB < HH=LH
	2000	0.30**	0.59	0.52	SFB < HH=LH
	2002	0.71***	0.77	0.66	None
Min. Soil	1998	0.11	0.29	0.42	SFB < HH < LH
	2000	0.15	0.15***	0.41	SFB=HH < LH
	2002	0.25***	0.27	0.43	SFB=HH < LH
Exchangeable Al					
Oie	1998	0.06	0.07	0.03	None
	2000	0.06	0.11	0.02	None
	2002	0.06	0.04	0.03	None
Oa	1998	0.89	1.33	0.47	None
	2000	0.84	1.52	0.74	HH > LH
	2002	0.72	0.85	0.51	None
Min. Soil	1998	2.83	2.97	2.85	None
	2000	1.88**	1.99***	2.08**	None
	2002	2.08*	2.30**	2.62	None

¹All contrasts tested at the $\alpha = 0.01$ level of significance.

*****Post-treatment mean (2000 or 2002) is significantly different than pre-treatment mean (1998), with $P < 0.05$, $P < 0.01$, and $P < 0.001$, respectively.

sheds (Figures 2, 3). Increases in Ca²⁺ concentrations and fluxes were most evident in the first 3 years following treatment, and then decreased slightly after 2003. The magnitude of the increase in Ca²⁺ after wollastonite addition diminished with increasing soil depth, with smaller post-treatment increases observed in Bh and Bs soil solutions. Relatively rapid increases in dissolved Si concentrations and fluxes were also observed in the Oa soil solutions in all sub-watersheds immediately after treatment (Figures 2, 3). Significant increases in H₄SiO₄ in the Bh and the Bs soil solutions occurred either in the second or in the third year following wollastonite treatment. Concentrations and fluxes of Al_i decreased throughout the soil profile in all sub-watersheds following treatment (Figures 2, 3). The magnitude of the decreases in Al_i was greater in the SFB sub-watershed than in other sub-watersheds.

Stream Water Chemistry

The wollastonite addition to W1 had a substantial influence on the stream chemistry, resulting in increases in Ca²⁺, H₄SiO₄, pH, and ANC, and decreases in Al_i concentrations and fluxes in all sub-watersheds (Figures 4, 5). Average Ca²⁺

concentrations increased by 244% in the SFB, 154% in the HH, and 174% in the LH zones immediately following treatment (2000 water year) compared to pre-treatment concentrations. Concentrations of Ca²⁺ then decreased somewhat through the end of the study period. Increases in dissolved Si concentrations and fluxes were particularly pronounced in the second year after treatment (2001) and these increases were followed by decreases in all sub-watersheds (Figures 4, 5). The magnitude of the initial increase and subsequent decrease in H₄SiO₄ was most evident at the SFB sub-watershed. The dissolution of the added wollastonite also resulted in increases in pH and ANC in all sub-watersheds, although stream water in the sub-watersheds remained acidic. Concentrations and fluxes of Al_i declined markedly in the SFB sub-watershed in 2003 and in both the HH and the LH sub-watersheds immediately following treatment. These distinct spatial patterns in Al_i inversely followed the patterns of pH in all sub-watersheds, suggesting that the immobilization of Al is a function of pH increase. Solution chemistry from all three sub-watersheds moved toward positive ANC and non-toxic concentrations (<2 µmol/l) of Al_i after treatment.

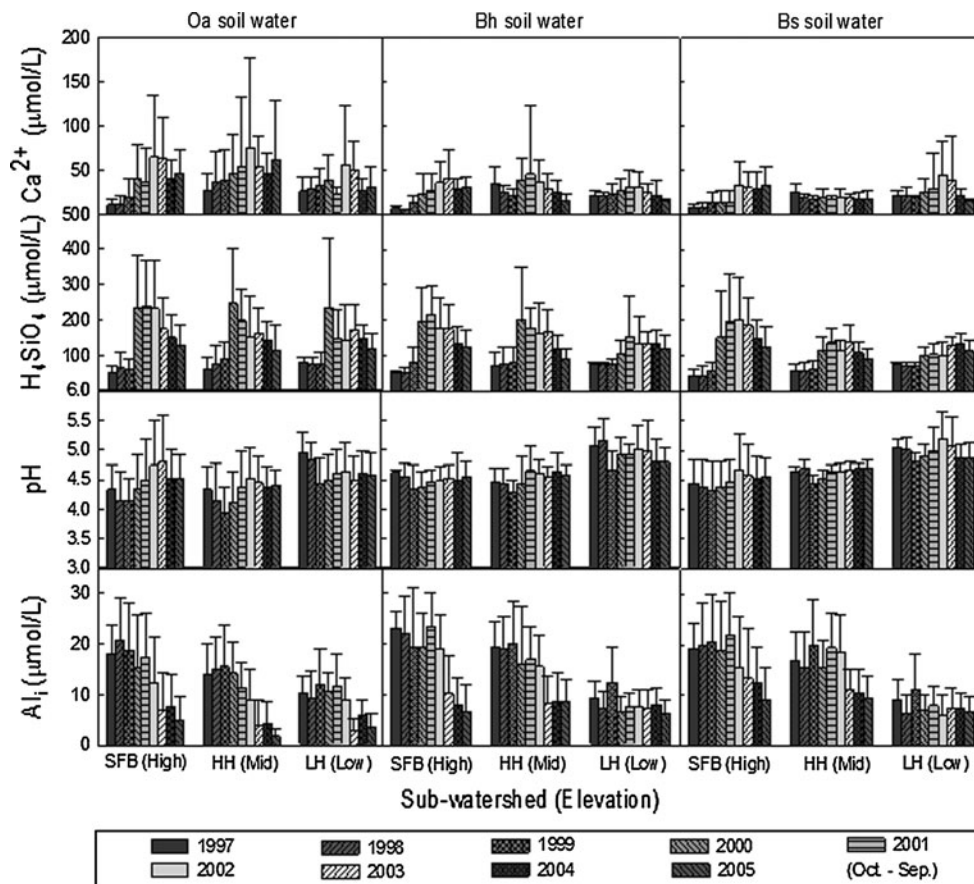


Figure 2. Spatial and temporal patterns in concentrations of Ca^{2+} , H_4SiO_4 , pH, and Al_i in soil water in W1 of the HBEF. The Ca manipulation was conducted in October of 1999. Annual average values are for water years (October 1st–September 30th). *SFB* spruce-fir-white birch sub-watershed; *HH* high-elevation hardwood sub-watershed; *LH* low-elevation hardwood sub-watershed. Error bars represent standard deviations for each water year.

Sub-Watershed Input–Outputs Budgets

Mass-balance calculations for Ca and dissolved Si in the three sub-watersheds were made for the pre-treatment (1997–1999 water years) and the post-treatment (2000–2005 water years) periods to quantify the sources and sinks of Ca and Si within the experimental watershed (Figures 6, 7). Average annual atmospheric inputs of Ca and Si, precipitation combined with estimated dry deposition, to each sub-watershed were considerably smaller than mean Ca and Si outputs in stream water from each sub-watershed prior to treatment. Deposition inputs directly to the stream channel were much smaller than to the terrestrial system because the stream bed occupies only 1.53% of total area in each sub-watershed (Peters and others 2004).

The inputs of Ca and Si from the wollastonite were applied approximately uniformly (Peters and others 2004) to the area of the whole-watershed (118,000 m^2). These total Ca and Si input values were converted into average annual fluxes for each sub-watershed based on the terrestrial areas (SFB: 29,049 m^2 , HH: 47,640 m^2 , LH: 39,506 m^2), and stream channel areas (SFB: 451 m^2 , HH: 740 m^2 , LH: 614 m^2) in each sub-watershed, and by then

dividing by the 6-year study period. Although the wollastonite was added in a single pulse, this computation allowed us to properly compare the fluxes of Ca and Si added in the wollastonite to the average annual fluxes of Ca and Si in precipitation and drainage water (Figure 7).

Net production or immobilization of Ca and Si in the Oa, Bh, and Bs horizons in the three sub-watersheds was calculated by subtracting the influxes to each horizon from the effluxes from that horizon. All values of net production in the Oa horizon in the three sub-watersheds were positive prior to treatment (Figure 6), indicating that the Oa horizon in all sub-watersheds was a major source of Ca and dissolved Si. The decline in soil solution Ca and dissolved Si fluxes downward in the soil profile in all sub-watersheds, except the Bs horizon in the SFB sub-watershed, implies that Ca and dissolved Si were generally retained in mineral soils, and suggests that the Bh and the Bs horizons were net sinks of Ca and dissolved Si prior to wollastonite treatment.

Values of net Ca and Si production were uniformly negative in the forest floor and mineral soil following the wollastonite treatment, indicating that both elements were retained in the soil.

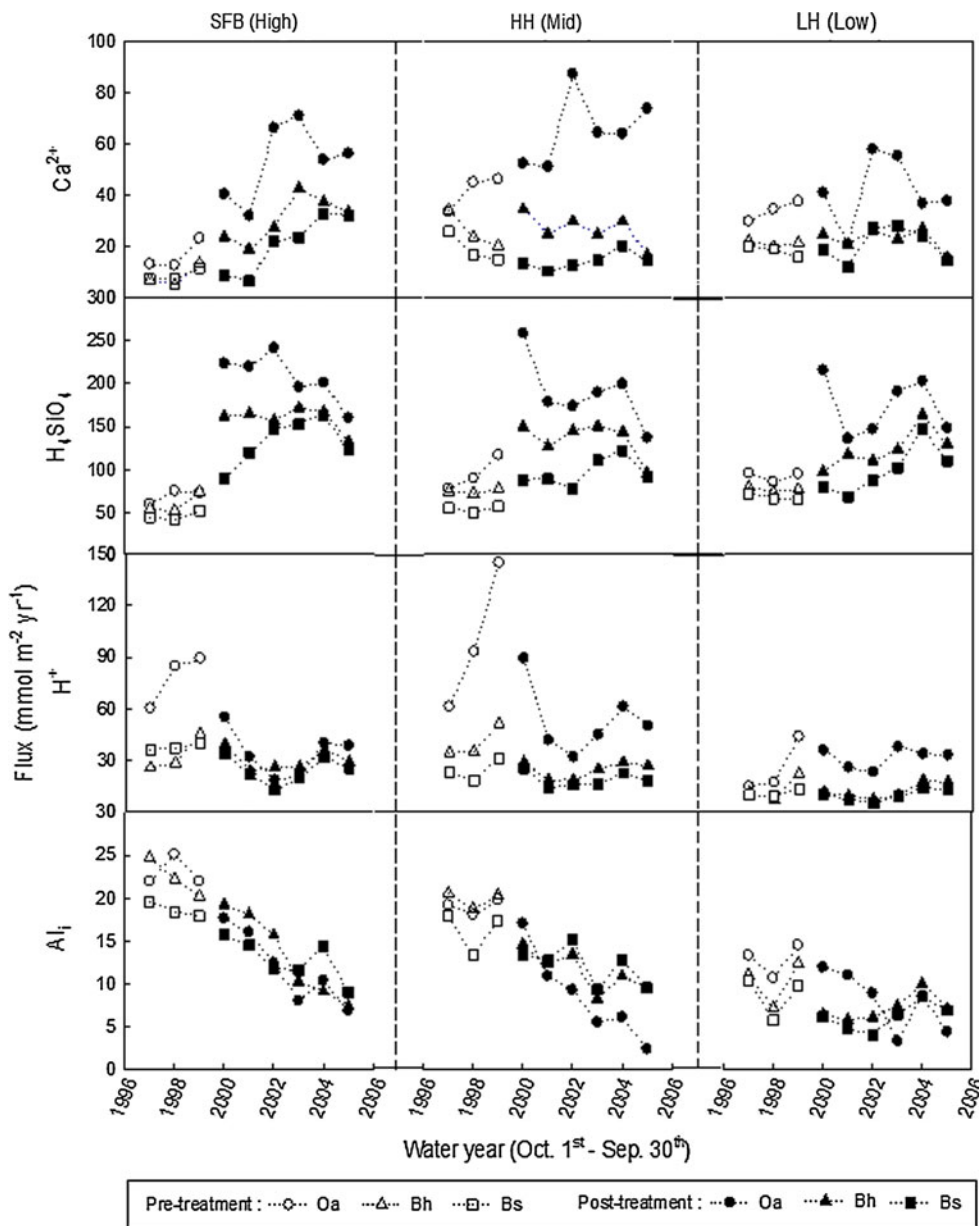


Figure 3. Solute fluxes (Ca^{2+} , H_4SiO_4 , H^+ , Al_i) in soil solutions of three sub-watersheds of W1 at the HBEF in New Hampshire prior to (open symbols) and following (filled symbols) the wollastonite treatment. Data are shown for water years beginning October 1st and ending September 30th.

Immobilization of Ca and Si in the O horizon was much greater than in the mineral horizons in all three sub-watersheds (Figure 7). These high net immobilization values indicate that the forest floor was a large net sink for the added Ca and dissolved Si. Net production of Ca and Si in Bh and Bs1 horizons continued to be negative after the wollastonite addition, indicating that mineral soils remained sinks for Ca and Si.

DISCUSSION

Elevational Patterns

Annual Ca fluxes in Oa soil solutions exhibited large changes in response to the wollastonite treatment

compared with mineral soil solutions (Figure 3). This pattern was due to retention of much of the Ca derived from the dissolution of the added wollastonite in the O horizon, in part associated with deprotonation of soil organic functional groups and increases in cation exchange capacity (Cho and others 2010). Mineral soil solution during the study period showed minimal changes in Ca^{2+} , H^+ fluxes and significant changes in dissolved Si and Al_i fluxes compared with pre-treatment values (Figure 3). Treatment effects were most prominent in the SFB sub-watershed, suggesting that wollastonite dissolution was greatest in the high-elevation SFB zone. This condition is undoubtedly due to the relatively flat topography, saturated soils, and elevated concentrations of

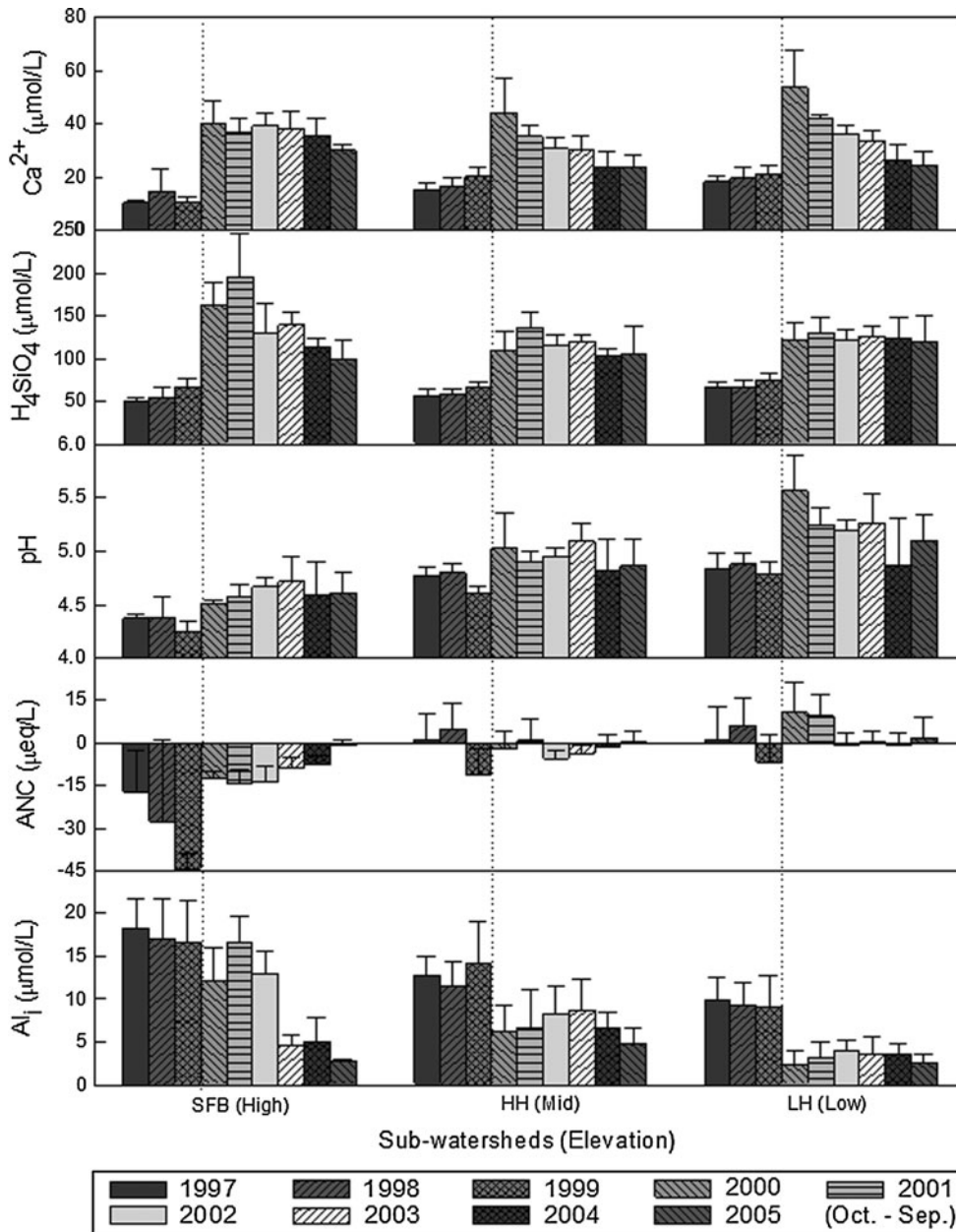


Figure 4. Spatial and temporal patterns in concentrations of Ca²⁺, H₄SiO₄, pH, ANC, and Al_i in stream water from W1 of the HBEF. Wollastonite (CaSiO₃) was added in October of 1999. Annual values are expressed on a water year basis (from October 1st to September 30th). *SFB* spruce-fir-white birch sub-watershed; *HH* high-elevation hardwood sub-watershed; *LH* the low-elevation hardwood sub-watershed. Error bars represent standard deviations for each water year.

naturally occurring organic acids that promote mineral dissolution (Johnson and others 2000). Enhanced wollastonite dissolution in the SFB sub-watershed has allowed for some penetration of Ex-Ca into the mineral soil. Using Ca/Sr and Sr isotope ratios, Nezat and others (2010) inferred that some wollastonite-derived Ca has penetrated to deeper horizons.

In all sub-watersheds, the average annual fluxes of H⁺ and Al_i in stream water were lower than those in the Bs horizon soil solution during the post-treatment period (Figures 3, 5). Conversely, Ca²⁺ fluxes in stream water were greater than in Bs soil solutions (Figure 7). These patterns indicate that seepage of soil water through the deeper

mineral soil horizons results in additional neutralization of H⁺, immobilization of Al_i, and release of Ca²⁺. Despite lower fluxes of Ca²⁺ and dissolved Si in Oa soil solutions in the LH sub-watershed compared with other sub-watersheds, Ca²⁺ and dissolved Si fluxes in stream water draining the LH sub-watershed were greater than those from other sub-watersheds, suggesting that extended contact between percolating water and mineral soils was especially important in this sub-watershed (Figures 3, 5). These observations indicate that the biogeochemical effects of wollastonite treatment extended throughout the soil profile in the first 6 years after the addition.

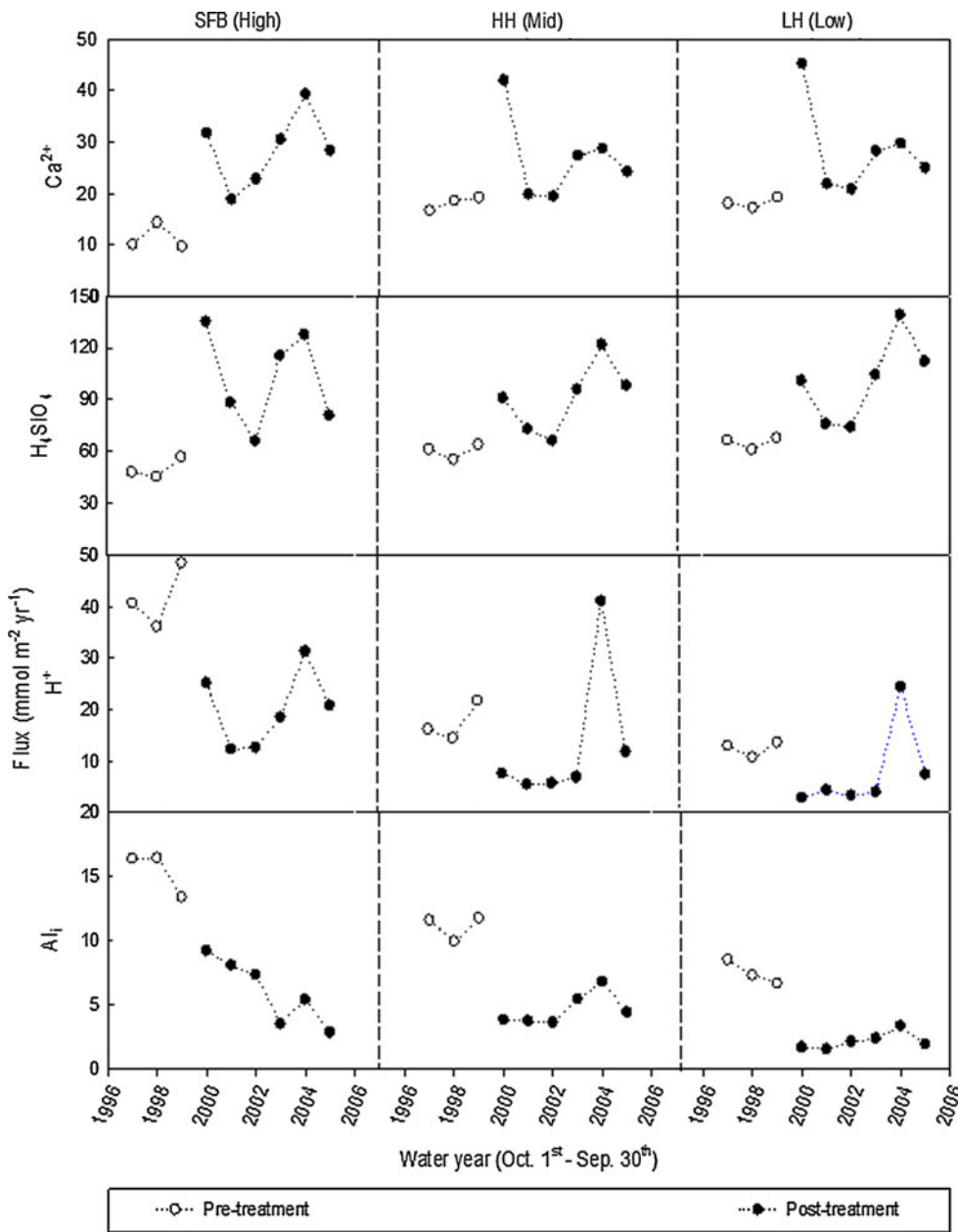


Figure 5. Solute fluxes (Ca^{2+} , H_4SiO_4 , H^+ , Al_i) of stream water in three sub-watersheds of W1 at the HBEF in New Hampshire prior to (open symbols) and following (filled symbols) the wollastonite treatment. Data are shown for water years beginning October 1st and ending September 30th.

Mechanisms of Ca and Si Mobilization and Immobilization

The amount of Ca and dissolved Si derived from the dissolution of the added wollastonite (that is, the “excess” Ca flux) was estimated by subtracting pre-treatment fluxes from post-treatment values. Changes in throughfall Ca in response to the wollastonite manipulation were estimated by subtracting throughfall Ca fluxes at the untreated reference watershed ($61 \text{ mol ha}^{-1} \text{ y}^{-1}$ in the SFB sub-watershed; $76 \text{ mol ha}^{-1} \text{ y}^{-1}$ in the HH; $69 \text{ mol ha}^{-1} \text{ y}^{-1}$ in the LH, respectively, Lovett and others 1996) from throughfall Ca fluxes in W1 after

treatment ($296 \text{ mol ha}^{-1} \text{ y}^{-1}$ in the SFB sub-watershed; $350 \text{ mol ha}^{-1} \text{ y}^{-1}$ in the HH; $311 \text{ mol ha}^{-1} \text{ y}^{-1}$ in the LH, respectively). These increases in throughfall fluxes were likely the result of dissolution of wollastonite caught in the canopy and uptake of wollastonite-derived Ca into foliage by trees.

The percent of the added Ca that has become labile was estimated by adding the measured increase in the pools of Ex-Ca [mean Ex-Ca pools in Oie and Oa horizons after treatment (2000, 2002) minus mean Ex-Ca pools in Oie and Oa horizons prior to treatment (1998)] in O horizons and the excess Ca in the O horizon soil water (mean Ca flux in the Oa

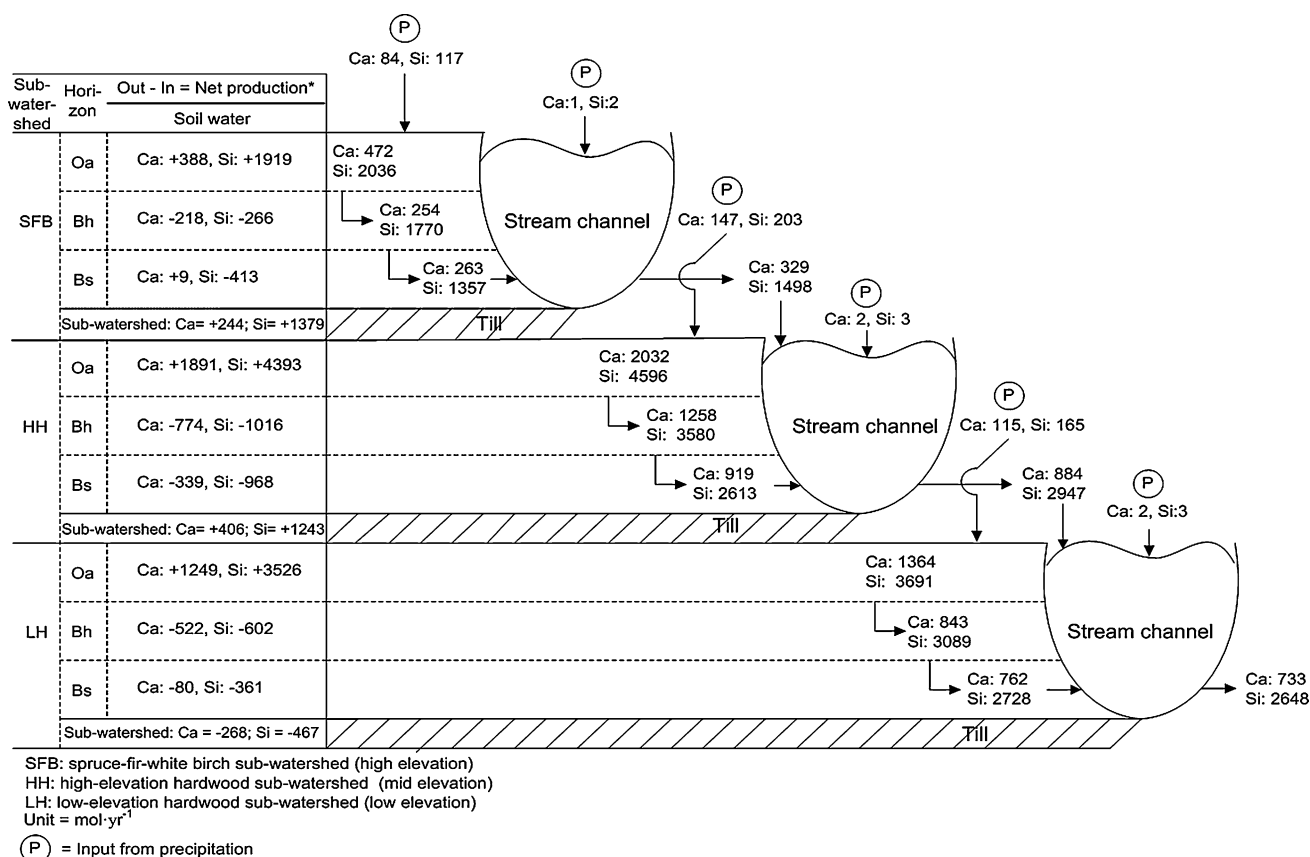


Figure 6. Fluxes of Ca and Si in sub-watersheds of W1 at the HBEF prior to wollastonite application. Values shown are averages for the 1997–1999 water years. Fluxes are given in mole y^{-1} . Net production of Ca and Si in three soil layers is estimated as the difference between efflux in soil water and input to that layer from above. For example, net Ca production in the SFB O horizon (+388 mol y^{-1}) is the soil solution flux (472 mol y^{-1}) minus precipitation input (84 mol y^{-1}). Net production of Ca and Si in each sub-watershed is calculated as the difference between loss from the watershed (export in streamwater) and inputs to the watershed (precipitation and streamwater entering from the preceding sub-watershed). For example, net production of Si in the HH sub-watershed (1,243 mol y^{-1}) is the stream export from the HH sub-watershed (2,947 mol y^{-1}) minus precipitation input (203 + 3 mol y^{-1}) and input from the SFB sub-watershed (1,498 mol y^{-1}).

soil solution after treatment (2000–2005) minus mean Ca flux in the Oa soil solution prior to treatment (1997–1999), and dividing by the amount of Ca added in the wollastonite. We estimated that 59% of the Ca added from the wollastonite treatment was either dissolved and exported in soil water (7%) or added to O horizon soil exchange sites (52%) in the SFB sub-watershed by the sixth year following treatment. In the HH sub-watershed, 42% of the added Ca was either dissolved and exported in soil solution (5%) or immobilized in the O horizon by soil exchange (37%). Similarly, 43% of the Ca added in wollastonite was either dissolved and transported in soil water (1%) or retained in the O horizon exchange complex (42%) in the LH sub-watersheds. Approximately 3.1% of the Ca added as

wollastonite in the SFB, 1.6% in the HH, and 1.9% in the LH sub-watersheds was ultimately exported via the stream outlets in each sub-watershed over the 6-year study period. This analysis suggests that 41% of the applied Ca in the SFB, 58% in the HH, and 57% in the LH sub-watersheds, respectively, remained undissolved or had been sequestered by vegetation by 2005. For the entire watershed, we estimate that approximately 54% of the added Ca remained undissolved or was retained by vegetation during the first 6 years after the wollastonite treatment. Of the remaining added Ca, 44% was retained on O horizon cation exchange sites and 2% was exported in stream water on a whole-watershed basis (by 2005). Nezat and others (2010) independently estimated that 2.6% of the

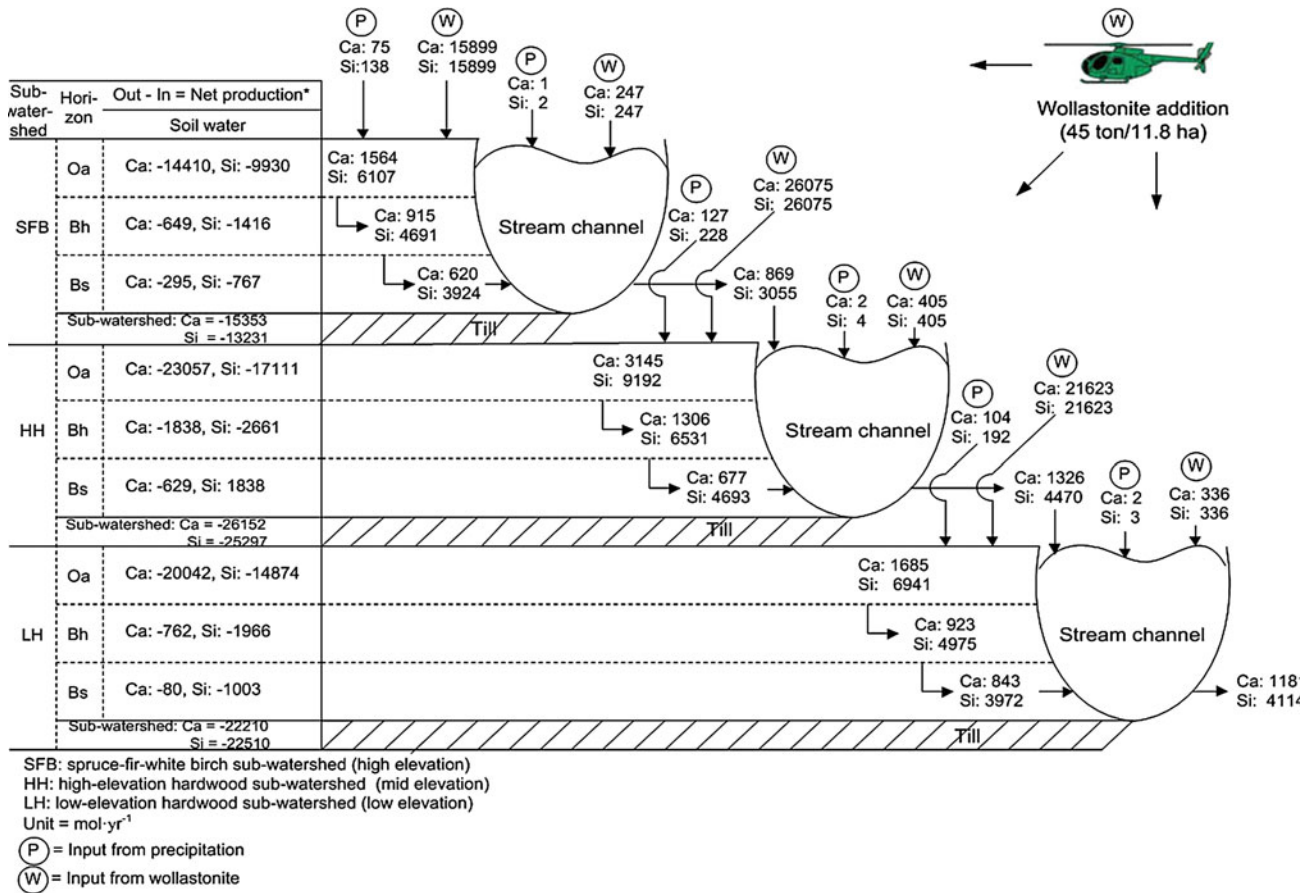


Figure 7. Fluxes of Ca and Si in sub-watersheds of W1 at the HBEF after wollastonite treatment. Values are averages for the 2000–2005 water years. Fluxes are given in mol y⁻¹. Net production values were calculated as described in Figure 6.

wollastonite-Ca had been transported from W1 by October of 2008, 9 years following treatment.

The Ca/Si ratios for the wollastonite dissolved in the three sub-watersheds were estimated by adding the excess Ca fluxes in O horizon soil water to the average annual increase in soil pools of exchangeable Ca in the O horizon, subtracting the increase in the net throughfall fluxes of Ca (throughfall flux in response to wollastonite treatment minus bulk precipitation flux), then dividing by the excess Si fluxes in the O soil solutions. The Ca:Si ratios for dissolving wollastonite were estimated to be 2.2 in the SFB, 2.2 in the HH, and 2.6 in the LH sub-watersheds, respectively. These ratios are much higher than the theoretical Ca:Si ratio of wollastonite (1.0) and the measured ratio for the material applied to W1 (0.923; Peters and others 2004). Peters and others (2004) suggested that Ca and Si from the added CaSiO₃ minerals did not dissolve congruently, with Ca released preferentially over dissolved Si. Alternatively, dissolution may be approximately congruent, but dissolved Si released

from wollastonite dissolution could be subsequently immobilized through precipitation of SiO₂(s) or other secondary aluminosilicate minerals in the O horizon.

Wollastonite has been observed to dissolve incongruently in laboratory experiments, with Ca released preferentially relative to Si, leading to the development of a leached layer, a layer of altered or secondary minerals whose components are derived from the dissolution of the parent phase (Peters and others 2004; Weissbart and Rimstidt 2000; Xie and Walther 1994). Soil solutions in W1 O horizons were undersaturated with respect to the solubility of AlSi and allophane (SiO₂·Al₂O₃·2.5H₂O) during both NGS and GS, before and after wollastonite treatment, except for allophane in the LH zone during the GS prior to treatment. The SI of quartz was near equilibrium or slightly oversaturated in all sub-watersheds during both the NGS and the GS prior to wollastonite addition, and became more oversaturated after treatment (Table 4). Solutions were undersaturated or near equilibrium with respect to the solubility of kaolinite (Al₂Si₂O₅(OH)₄) and imogolite (Al₂O₃·SiOH(OH)₃)

in the SFB and the HH sub-watersheds during both the NGS and the GS before the treatment, except in the LH sub-watershed (Table 4). Following the wollastonite manipulation, O horizon soil solutions became oversaturated with respect to the solubility of both kaolinite and imogolite in all three sub-watersheds throughout the year (Table 4). The observed conditions of oversaturation with respect to the solubility of quartz, kaolinite, and imogolite suggest that the experimental treatment may have facilitated some immobilization of dissolved Si. However, it is unlikely that Si is precipitating as crystalline quartz. Because soil solutions were undersaturated with respect to amorphous Si and allophane following treatment, precipitation of these forms cannot explain the high Ca:Si ratios of dissolving wollastonite. Thus, the most likely mechanisms are incongruent dissolution of the wollastonite and/or formation of kaolinite or imogolite.

Acidification Indicators

There are several critical chemical indicators of acid-base status in surface waters. Stream water: (1) is acidic when pH is less than 5.5 (Reuss and others 1987); (2) exhibits chronic acidification when ANC is below 0 µeq/l (Driscoll and others 2001); and (3) is potentially toxic to aquatic biota when Al_i is greater than 2 µmol/l (Driscoll and others 2001). Based on these acidification indicators, stream water in W1 was chronically acidic and had potentially toxic concentrations of Al_i prior to the wollastonite treatment (Figure 8). Prior to wollastonite treatment, stream ANC throughout W1 was generally below 0

µeq/l with a minimum value of -83 µeq/l. Every stream water sample collected from W1 prior to treatment had an Al_i concentration above the 2 µmol/l threshold (Figure 8). After treatment, stream water in the low-elevation hardwood sub-watershed showed some alleviation of conditions of chronic acidification and Al toxicity (Figure 8). The general pattern of decreasing acidity and Al_i from SFB to HH to LH sub-watersheds persisted after wollastonite treatment, indicating that both dissolution of the added material and natural acid neutralization mechanisms contributed to the post-treatment patterns. The patterns of Al_i fluxes in soil solutions (Figure 3) also suggest that decreases in Al_i by the precipitation of Al(OH)₃ or Al-Si minerals may partially contribute to these decreasing patterns of Al_i concentrations in stream water.

The ANC was positively correlated with pH in W1 prior to ($r_{\text{pH-ANC}} = 0.718, P < 0.001$) and after treatment ($r_{\text{pH-ANC}} = 0.594, P < 0.001$). The concentration of Al_i was negatively correlated with pH during both pre-treatment ($r_{\text{pH-Al}_i} = -0.620, P < 0.001$) and post-treatment ($r_{\text{pH-Al}_i} = -0.433, P < 0.001$) periods, respectively (Figure 8). The gradients in the relationships between ANC and pH, and ANC and Al_i became significantly less steep after the wollastonite application than before (ANCOVA using Levene's test; $P < 0.05$ in all cases). The steeper slopes during the pre-treatment period (56.1 for ANC vs. pH and -14.2 for Al_i vs. pH), compared with the lower slopes during the post-treatment period (12.9 for ANC vs. pH and -4.31 for Al_i vs. pH), indicates that the control over ANC and Al_i by pH is less profound after wollas-

Table 4. SI of Si-Bearing Minerals in O Horizon Soil Solutions During the NGS and the GS, Prior to and After Wollastonite Addition

Season	Treatment	Sub-watershed	ASi	Quartz	Kaolinite	Allophane	Imogolite
NGS	Pre-treatment	SFB	-1.31 ± 0.075	0.12 ± 0.074	-0.34 ± 0.132	-1.23 ± 0.056	-0.26 ± 0.056
		HH	-1.28 ± 0.076	0.14 ± 0.075	-0.77 ± 1.027	-1.46 ± 0.551	-0.49 ± 0.551
		LH	-1.24 ± 0.026	0.19 ± 0.025	2.06 ± 1.523	-0.07 ± 0.751	0.90 ± 0.751
	Post-treatment	SFB	-0.76 ± 0.154	0.66 ± 0.154	2.07 ± 1.439	-0.30 ± 0.652	0.67 ± 0.652
		HH	-0.82 ± 0.033	0.61 ± 0.032	0.84 ± 1.086	-0.88 ± 0.528	0.09 ± 0.528
		LH	-0.91 ± 0.060	0.51 ± 0.060	1.94 ± 0.374	-0.29 ± 0.158	0.68 ± 0.158
GS	Pre-treatment	SFB	-1.42 ± 0.053	-0.05 ± 0.053	0.08 ± 1.075	-1.40 ± 0.560	-0.43 ± 0.560
		HH	-1.21 ± 0.099	0.17 ± 0.098	-0.29 ± 0.925	-1.69 ± 0.507	-0.72 ± 0.507
		LH	-1.22 ± 0.046	0.19 ± 0.025	3.10 ± 1.058	0.01 ± 0.546	0.98 ± 0.546
	Post-treatment	SFB	-0.76 ± 0.153	0.61 ± 0.153	3.37 ± 1.395	-0.08 ± 0.723	0.89 ± 0.723
		HH	-0.88 ± 0.259	0.49 ± 0.259	1.83 ± 1.708	-0.79 ± 0.894	0.18 ± 0.894
		LH	-0.89 ± 0.262	0.48 ± 0.261	2.56 ± 0.245	-0.42 ± 0.153	0.55 ± 0.153

A negative value indicates that solutions are undersaturated with respect to mineral solubility. A positive value indicates conditions of oversaturation. Shown are mean values and standard deviations.

ASi = amorphous Si; Sub-watershed designations = LH = low-elevation hardwood; HH = high-elevation hardwood; SFB = spruce-fir-white birch.

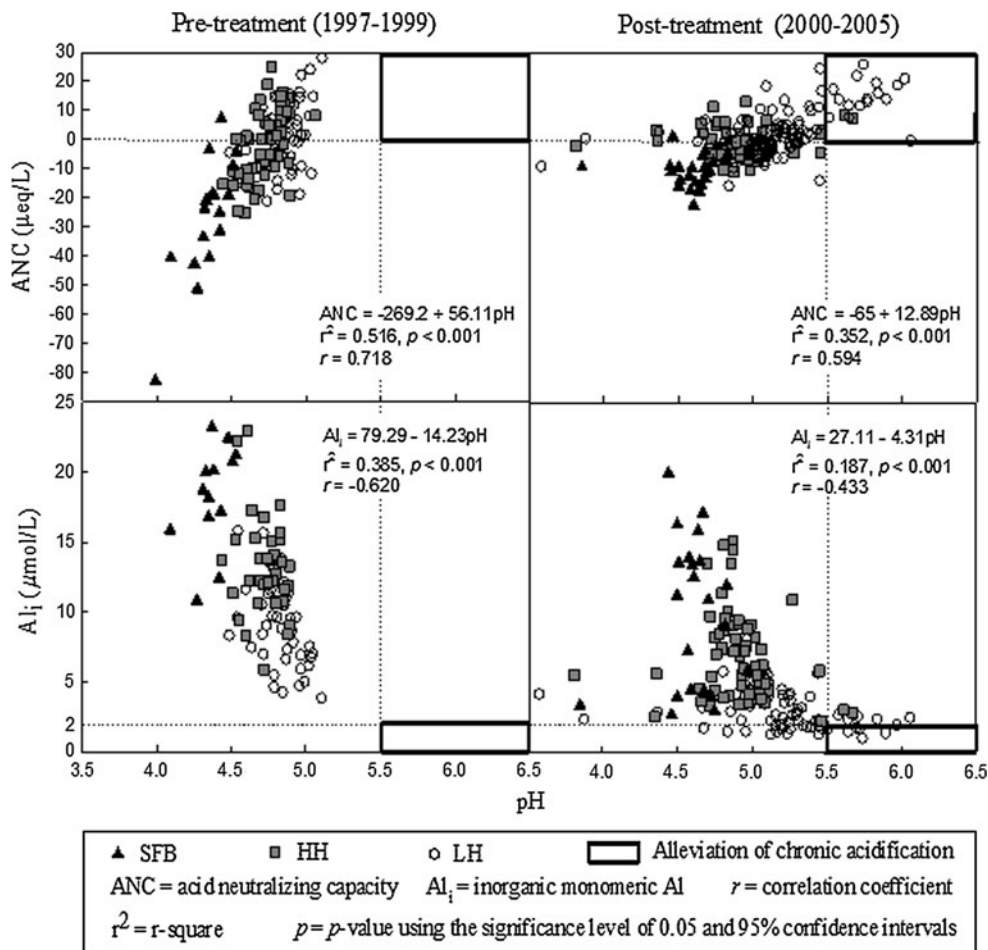


Figure 8. Relationships between pH and ANC and Al_i in stream water of W1 at the HBEF in New Hampshire prior to and after the wollastonite treatment. The outlined area represents conditions in which neither pH, ANC, nor Al_i indicate conditions of chronic acidification.

tonite addition. This interesting observation suggests that there has been a change in acid neutralization mechanisms in W1. The increase in Ca from both the direct input of wollastonite to the stream bed and/or changes in soil processes likely contributed to increase ANC production and Al immobilization following treatment, respectively. Taken as a whole, these patterns indicate that increased Ca supply from the added wollastonite has greatly lessened acidification stress in W1 stream water during the post-treatment period.

ANC Production and Immobilization of Al_i

To further assess the effects of $CaSiO_3$ treatment on ANC production and Al mobility, the relationships between the changes in annual Al_i and ANC fluxes with changes in annual Ca fluxes in soil solutions and stream water were examined (Figures 9, 10). The changes in annual fluxes of Al_i , ANC, and Ca in the three sub-watersheds were calculated individually for each water year following treatment

(2000–2005) by subtracting the average flux in the pre-treatment period (1997–1999 water years).

The changes in annual Al_i fluxes after the treatment were negatively correlated with changes in annual Ca fluxes in the Oa horizon soil solutions in W1 ($r = -0.703, P = 0.001$, Figure 9). In the Bh and Bs horizon soil solutions, negative relationships were also evident between annual changes in Al_i fluxes and Ca fluxes ($r = -0.461$ and $P = 0.054$ in the Bh soil solution, $r = -0.449$ and $P = 0.062$ in the Bs soil solution, Figure 9) but were not statistically significant. These patterns indicate that decreases in Al_i fluxes after treatment are likely due to increasing pH, caused by the enhanced supply of Ca in drainage waters. The decreases in Al_i fluxes were most evident in Oa horizon soil solutions, which showed the largest increases in annual Ca fluxes, compared with the Bh and Bs horizons (Figure 9).

In stream water, there was a significant positive correlation ($r = 0.490, P = 0.039$) between changes in annual ANC and Ca fluxes (Figure 10). Increases in ANC production were most evident in the SFB sub-watershed due to the greater increases in Ca

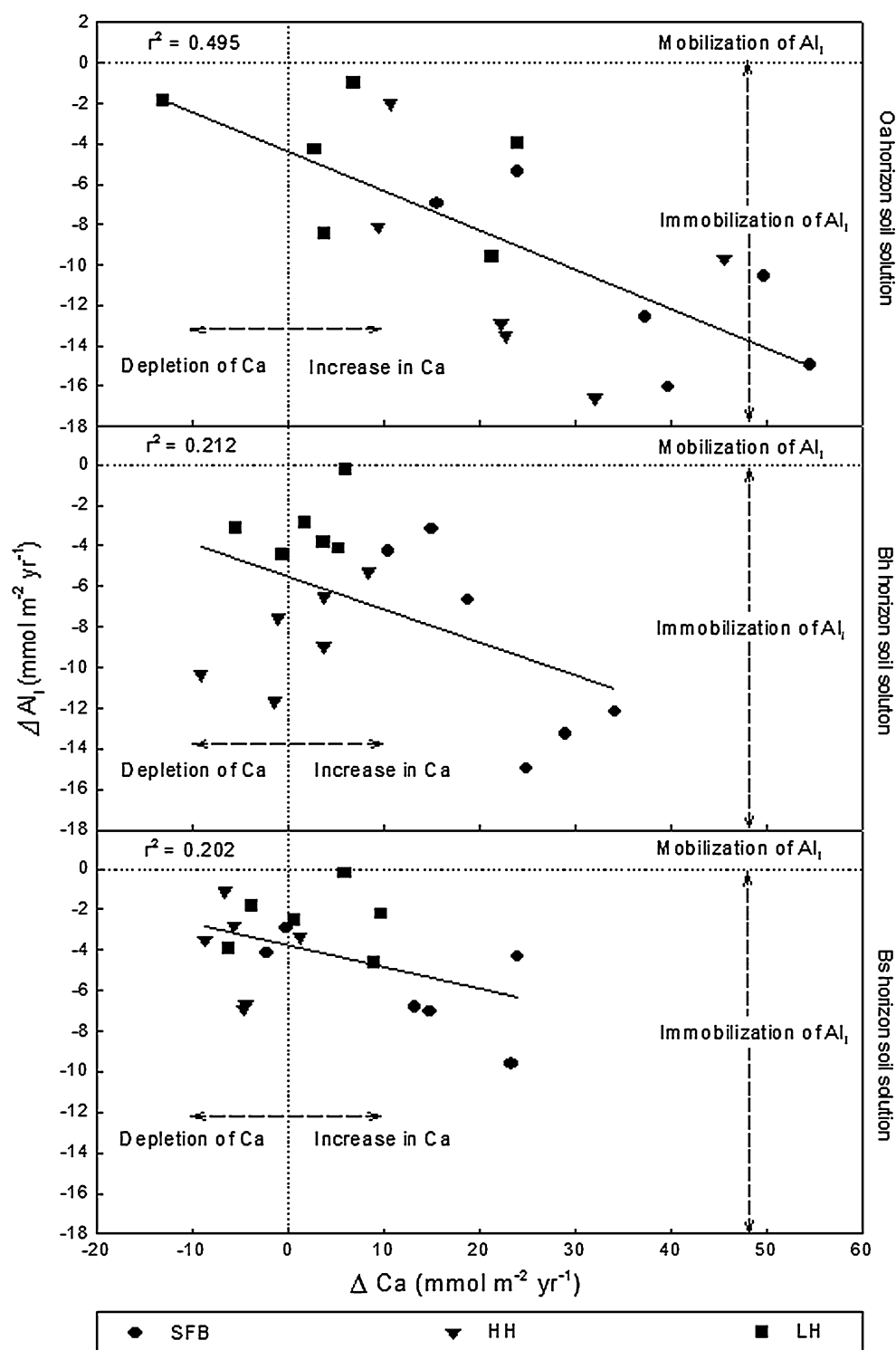


Figure 9. Relations between annual immobilization of Al_i and annual changes in Ca fluxes of soil solutions of sub-watersheds in response to wollastonite addition to W1 at the HBEF in New Hampshire during the 2000–2005 water years. *SFB* spruce-fir-white birch sub-watershed; *HH* high-elevation hardwood sub-watershed; *LH* low-elevation hardwood sub-watershed.

flux in that sub-watershed compared with the hardwood sub-watersheds. Increases in annual ANC fluxes in the hardwood sub-watersheds were limited due to modest increases in annual Ca fluxes during the 2002–2003 water years (Figure 5).

Immobilization of Al_i in stream water was observed in all three sub-watersheds, corresponding to increases in annual Ca fluxes associated with enhanced Ca supply by wollastonite addition (Figure 10).

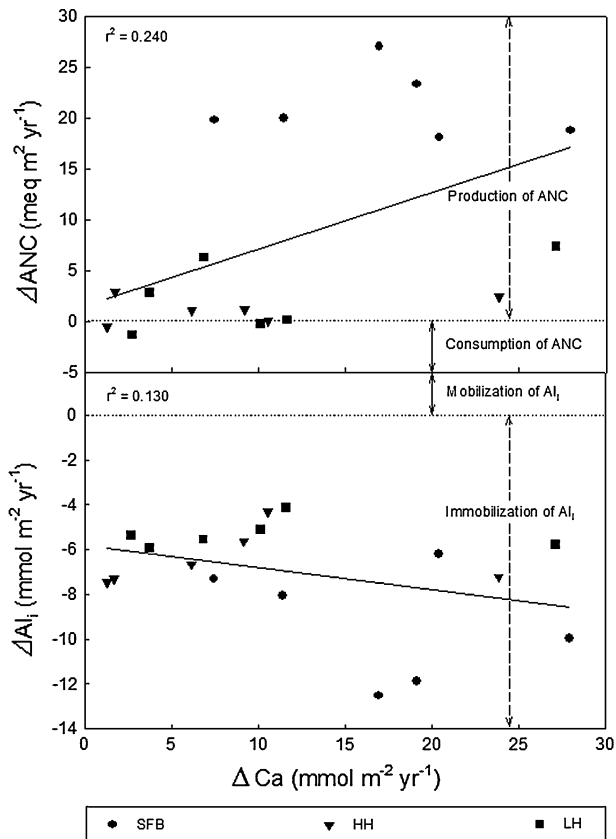


Figure 10. Relations between annual production of ANC and annual immobilization of Al_i , with annual changes in Ca fluxes of stream water of sub-watersheds in response to wollastonite addition to W1 at the HBEF in New Hampshire during 2000–2005 water years. *SFB* spruce-fir-white birch sub-watershed; *HH* high-elevation hardwood sub-watershed; *LH* low-elevation hardwood sub-watershed.

CONCLUSIONS

We observed increases in concentrations and fluxes of Ca, H_4SiO_4 , and pH, and decreases in Al_i in soil solutions and stream water, as well as increases in stream ANC, in all three sub-watersheds after treatment. The impact of the wollastonite treatment was most evident in the forest floor, because most of the added Ca remained in the organic horizon. However, we found that post-treatment effects of the dissolution of the added wollastonite on Si and Al_i in soil solution were also substantial in B horizon soil solutions and streamwater, indicating that wollastonite addition affected biogeochemical processes throughout the soil profile. Ca:Si ratios for the dissolving wollastonite suggests that the mineral is not dissolving congruently and/or Si is immobilized by precipitation of secondary minerals after dissolution.

Elevation and topography were important factors influencing the response of W1 to wollastonite addition. The high-elevation SFB sub-watershed has relatively shallow soil depth and flow-paths, exhibiting a high water table and often saturated soil conditions. As a result, the responses of soil solutions and stream water in the SFB sub-watershed to the wollastonite application were relatively pronounced compared with the lower elevation hardwood sub-watersheds.

The addition of wollastonite to W1 as a Ca amendment showed improvements of acid-base status in soil, soil solution, and stream chemistry during the study period. We anticipate that W1 will continue to respond to wollastonite treatment for the next few decades, because very little of the added Ca has left the ecosystem (Nezat and others 2010) and approximately 44% of exchangeable Ca from the added wollastonite remains in exchange sites of the forest floor. The penetration of the added Ca to organic and mineral soils should continue to help regulate acid-base chemistry and mitigate the mobilization of Al to soil solutions and stream water. So far, wollastonite has proven to be an effective amendment in this acidic, base-poor ecosystem, producing significant, but not overwhelming changes in drainage water chemistry.

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