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# 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 ($CaSiO_3$; 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 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 six 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 six 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

# INTRODUCTION

In spite of decreases in acidic atmospheric deposition, previous studies in acid-impacted watersheds in the northeastern U.S. 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 (Ca) from soils (Driscoll et al. 1989, Likens et al. 1996, Driscoll et al. 2001, Palmer et al. 2004, Warby et al. 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 et al. 1998).

Calcium 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 et al. 1989, Lawrence et al. 1995). Acid-sensitive watersheds in the northeastern U.S. 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 et al. 1988, April and Newton 1985, Driscoll 1991, Eilers and Selle 1991, Nezat et al. 2004). A geochemical consequence of low $Ca^{2+}$ 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 et al. 2004, Cho et al. 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: $CaCO_3$) 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 Ali in stream water (Blette and Newton 1996, Cirmo and Driscoll 1996, Driscoll et al. 1996, Hindar 2005, Huber et al. 2006, Löfgren et al. 2009, Newton et al. 1996).

In this study, 3,800 kg/ha of wollastonite ($CaSiO_3$) pellets (66 keq Ca/ha) with a pellet diameter of 1.5 - 4 mm and average 16-µm particle size was 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 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 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 horizonal 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 Hubbard Brook Experimental Forest (HBEF) lies in the southern portion of the White Mountain National Forest in central New Hampshire, U.S.A. (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 et al. 2010, Johnson et al. 2000). Soils at the HBEF are predominately Spodosols (Typic Haplorthods) derived from glacial till (Johnson et al. 1991a, b). Generally shallow flow-paths of water occur at the highest elevations, while at lower elevations deposits of glacial till are thicker and facilitate somewhat deeper hydrologic flow-paths (Johnson et al. 2000). The watersheds of the HBEF generally exhibit a pattern common in mountainous forest landscapes throughout the Northeast, with low rates of $Ca^{2+}$ supply by weathering and the diminution of the effects of acidic deposition with decreasing elevation (Johnson et al. 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 et al. 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 m to 747 m. In October of 1999, 45 x $10^3$ 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 et al. 2004).

Watershed 1 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 (*Betula papyrifera*) at high elevation (Juice et al. 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 flowpaths, 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 $m^2$ 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 $m^2$ 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 $m^2$ of the streambed area.

## Collection and analysis of samples

The amount of precipitation has been measured daily at rain gauge 1 (RG1), located 50 m from the W1 stream gauging station, from rain gauge 2 (RG2) in the HH zone, and from rain gauge 3 (RG3) 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, NY 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, NH (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 Hubbard Brook Ecosystem Study website (www.hubbardbrook.org).

Collection of soil samples and methods for the chemical analyses of soil are detailed in Cho et al. (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 et al.

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. While 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 et al. 1998; Johnson et al. 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 from May 1st to September 30th and from October 1st 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 et al. 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 (i.e. no short circuiting through shallow flow paths). This simplified hydrologic model of soil water has been employed in previous studies at the HBEF (Dittmann et al. 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 et al. 2000, Dittman et al. 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 et al. 2007, Johnson et al. 2000). Through hydrologic modeling, Federer et al. (1990) and Likens and Bormann (1995) suggested that assumption (3), of limited deep seepage from HBEF watersheds, is valid. Peters et al. (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 silica, 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:

$$SI = \log \frac{Q_p}{K_p} \tag{1}$$

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 (Cirmo 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, 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 µmol/L in 1997 to 25 µmol/L in 2005) and $SO_4^{2-}$ (from 15 µmol/L in 1997 to 12 µmol/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±0.28 µmol/L) or Si (3.42±0.67 µmol/L) concentrations in precipitation. Annual stream flow in W1 fluctuated throughout the study period, decreasing from 970 mm in 1997 to 530 mm 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 exchangeable calcium (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.

While 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 et al. (2010).

## Soil water chemistry

The wollastonite treatment increased concentrations and fluxes of $Ca^{2+}$ and $H_4SiO_4$, and decreased $H^+$ and $Al_i$ in the soil solutions in all sub-watersheds (Figures 2, 3). Increases in $Ca^{2+}$ concentrations and fluxes were most evident in the first three years following treatment, and then decreased slightly after 2003. The magnitude of the increase in $Ca^{2+}$ 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 $H_4SiO_4$ 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 Ali 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 $Ca^{2+}$, $H_4SiO_4$, pH, and ANC, and decreases in $Al_i$ concentrations and fluxes in all sub-watersheds (Figures 4, 5). Average $Ca^{2+}$ 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 $Ca^{2+}$ 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 $H_4SiO_4$ 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 towards positive ANC and non-toxic concentrations ($< 2$ μmol/L) of $Al_i$ after treatment.

## 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 et al. 2004).

The inputs of Ca and Si from the wollastonite were applied approximately uniformly (Peters et al. 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. 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 et al. 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 naturally occurring organic acids that promote mineral dissolution (Johnson et al. 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 et al. (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, $Ca^{2+}$ 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 $Ca^{2+}$. Despite lower fluxes of $Ca^{2+}$ and dissolved Si in Oa soil solutions in the LH sub-watershed compared with other sub-watersheds, $Ca^{2+}$ 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 six years after the addition.

## Mechanisms of Ca and Si mobilization and immobilization

The amount of Ca and dissolved Si derived from the dissolution of the added wollastonite (i.e. 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 mol ha$^{-1}$ yr$^{-1}$ in the SFB sub-watershed; 76 mol ha$^{-1}$ yr$^{-1}$ in the HH; 69 mol ha$^{-1}$ yr$^{-1}$ in the LH, respectively, Lovett et al. 1996) from throughfall Ca fluxes in W1 after treatment (296 mol ha$^{-1}$ yr$^{-1}$ in the SFB sub-watershed; 350 mol ha$^{-1}$ yr$^{-1}$ in the HH; 311 mol ha$^{-1}$ yr$^{-1}$ 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 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 6th 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 in 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 et al. (2010) independently estimated that 2.6% of the wollastonite-Ca had been transported from W1 by October of 2008, nine 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 et al. 2004). Peters et al. (2004) suggested that Ca and Si from the added $CaSiO_3$ 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 $SiO_2$(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 et al. 2004, Weissbart and Rimstidt 2000, Xie and Walther 1994). Soil solutions in W1 O-horizons were undersaturated with respect to the solubility of amorphous Si (ASi) and allophane ($SiO_2 \cdot Al_2O_3 \cdot 2.5H_2O$) during both non-growing seasons (NGS) and growing seasons (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 ($Al_2Si_2O_5(OH)_4$) and imogoilite ($Al_2O_3 \cdot SiOH(OH)_3$) 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. Since 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 et al. 1987); (2) exhibits chronic acidification when ANC is below 0 μeq/L (Driscoll et al. 2001); and (3) is potentially toxic to aquatic biota when $Al_i$ is greater than 2 μmol/L (Driscoll et al. 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 ($r_{\text{pH-Ali}} = -0.620$, $p<0.001$) and post- treatment ($r_{\text{pH-Ali}} = -0.433$, $p<0.001$) 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 wollastonite 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 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 and 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 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 watershed 1 (*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 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).

## 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, since 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 flowpaths, 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, since very little of the added Ca has left the ecosystem (Nezat et al. 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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**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 $H_4SiO_4$ | 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 et al. 1992<br>Palmer et al. 2004 |
| Organic monomeric Al ($Al_o$) | Same method as Alm, after passing sample through an ion exchange column | McAvoy et al. 1992<br>Palmer et al. 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 | Dohrman 1984 |

**Table 2**. Precipitation amount, solute concentrations in wet deposition, dry to wet deposition ratios, and streamflow at Watershed 1 of the Hubbard Brook Experimental Forest – 1997 to 2005 water years (October 1 – September 30).

| Water year | Sub-watershed[a] | Precip. (m) | Precipitation concentration[b] (μmol/L) and dry to wet deposition ratio[c] | | | | 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 | | | | | |

[a] Sub-watershed designations – LH: low-elevation hardwood; HH: high-elevation hardwood; SFB: spruce-fir-white birch.

[b] Precipitation chemistry obtained from the National Atmospheric Deposition Program (Ca, H, and $SO_4^{2-}$) and the Hubbard Brook Ecosystem Study (Si). See Methods for details.

[c] Numbers in parentheses are dry-to-wet deposition ratios obtained from Chen and Driscoll (2005).

**Table 3**. Soil pools of exchangeable Ca and Al prior to (1998) and after (2000, 2002) wollastonite addition to watershed 1 of the Hubbard Brook Experimental Forest, New Hampshire.

| | | Exchangeable Cation Pool ($mol_c\ m^{-2}$) | | | |
|---|---|---|---|---|---|
| Horizon | Year | SFB | HH | LH | Sub-watershed Differences[a] |
| | | **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 |

*, **, *** 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.

[a] All contrasts tested at the $\alpha = 0.01$ level of significance.

**Table 4**. Saturation index (SI) of Si-bearing minerals in O horizon soil solutions during the non-growing season (NGS) and the growing season (GS), prior to and after wollastonite addition. 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.

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

[a] ASi = amorphous Si,

[b] Sub-watershed designations – LH: low-elevation hardwood; HH: high-elevation hardwood; SFB: spruce-fir-white birch.

**Figure Captions**

**Figure 1**. Map of Watershed 1 at the Hubbard Brook Experimental Forest 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.

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

**Figure 3**. Solute fluxes ($Ca^{2+}$, $H_4SiO_4$, $H^+$, $Al_i$) in soil solutions of three sub-watersheds of Watershed 1 at the Hubbard Brook Experimental Forest 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.

**Figure 4**. Spatial and temporal patterns in concentrations of $Ca^{2+}$, $H_4SiO_4$, pH, ANC, and $Al_i$ in stream water from Watershed 1 of the Hubbard Brook Experimental Forest. Wollastonite ($CaSiO_3$) was added in October of 1999. Annual values are expressed on a water-year basis (from October 1st to September 30th). SFB is the spruce-fir-white birch sub-watershed, HH is the high-elevation hardwood sub-watershed, and LH is the low-

elevation hardwood sub-watershed. Error bars represent standard deviations for each water year.

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

**Figure 6**. Fluxes of Ca and Si in sub-watersheds of Watershed 1 at the Hubbard Brook Experimental Forest prior to wollastonite application. Values shown are averages for the 1997-1999 water years. Fluxes are given in moles $yr^{-1}$. 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 $yr^{-1}$) is the soil solution flux (472 mol $yr^{-1}$) minus precipitation input (84 mol $yr^{-1}$). 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 $yr^{-1}$) is the stream export from the HH sub-watershed (2,947 mol $yr^{-1}$) minus precipitation input (203+3 mol $yr^{-1}$) and input from the SFB sub-watershed (1,498 mol $yr^{-1}$).

**Figure 7**. Fluxes of Ca and Si in sub-watersheds of Watershed 1 at the Hubbard Brook Experimental Forest after wollastonite treatment. Values are averages for the 2000-2005

water years. Fluxes are given in moles yr$^{-1}$. Net production values were calculated as described in Figure 6.

**Figure 8**. Relationships between pH and acid neutralizing capacity (ANC) and inorganic monomeric Al ($Al_i$) in stream water of Watershed 1 at the Hubbard Brook Experimental Forest 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.

**Figure 9**. Relations between annual immobilization of inorganic monomeric Al ($Al_i$) and annual changes in Ca fluxes of soil solutions of sub-watersheds in response to wollastonite addition to Watershed 1 at the Hubbard Brook Experimental Forest in New Hampshire during the 2000-2005 water years: SFB: spruce-fir-white birch sub-watershed, HH = high-elevation hardwood sub-watershed, and LH = low-elevation hardwood sub-watershed.

**Figure 10**. Relations between annual production of acid neutralizing capacity (ANC) and annual immobilization of inorganic monomeric Al ($Al_i$), with annual changes in Ca fluxes of stream water of sub-watersheds in response to wollastonite addition to Watershed 1 at the Hubbard Brook Experimental Forest in New Hampshire during 2000-2005 water years: SFB: spruce-fir-white birch sub-watershed, HH: high-elevation hardwood sub-watershed, and LH: low-elevation hardwood sub-watershed.

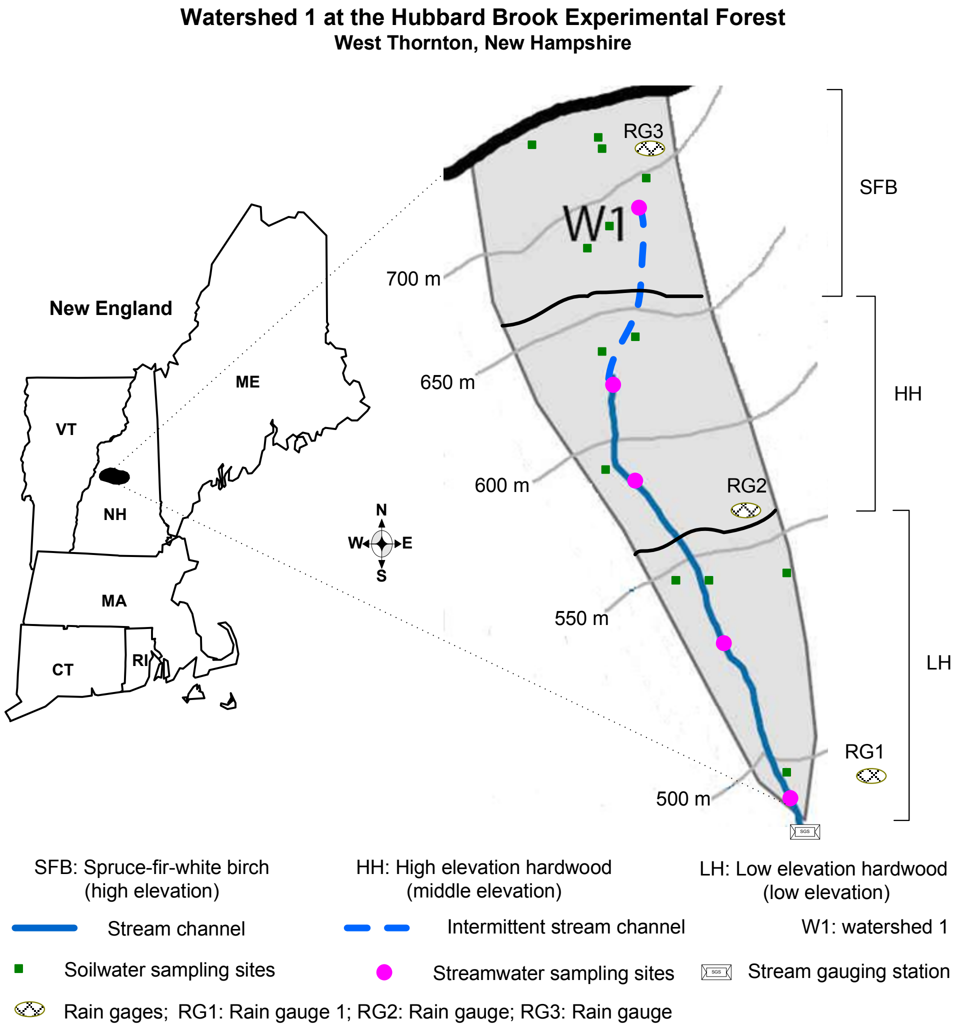

Watershed 1 at the Hubbard Brook Experimental Forest
West Thornton, New Hampshire
New England
ME
VT
NH
MA
CT
RI
N
W
E
S
W1
RG3
RG2
RG1
700 m
650 m
600 m
550 m
500 m
SFB
HH
LH
SFB: Spruce-fir-white birch (high elevation)
HH: High elevation hardwood (middle elevation)
LH: Low elevation hardwood (low elevation)
Stream channel
Intermittent stream channel
W1: watershed 1
Soilwater sampling sites
Streamwater sampling sites
Stream gauging station
Rain gages; RG1: Rain gauge 1; RG2: Rain gauge; RG3: Rain gauge

Figure 1.

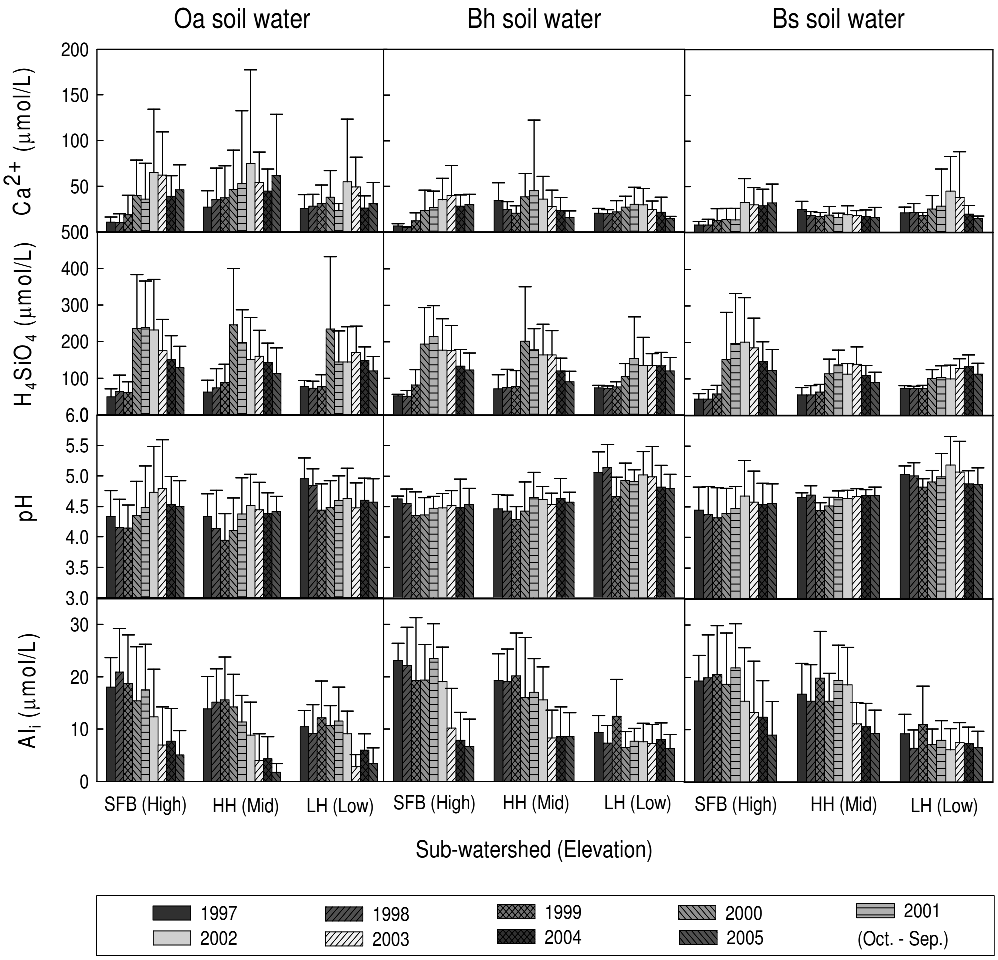

Oa soil water
Bh soil water
Bs soil water
Ca2+ (μmol/L)
H4SiO4 (μmol/L)
pH
Ali (μmol/L)
200
150
100
50
500
400
300
200
100
6.0
5.5
5.0
4.5
4.0
3.5
3.0
30
20
10
0
SFB (High)
HH (Mid)
LH (Low)
Sub-watershed (Elevation)
1997
1998
1999
2000
2001
2002
2003
2004
2005
(Oct. - Sep.)

Figure 2.

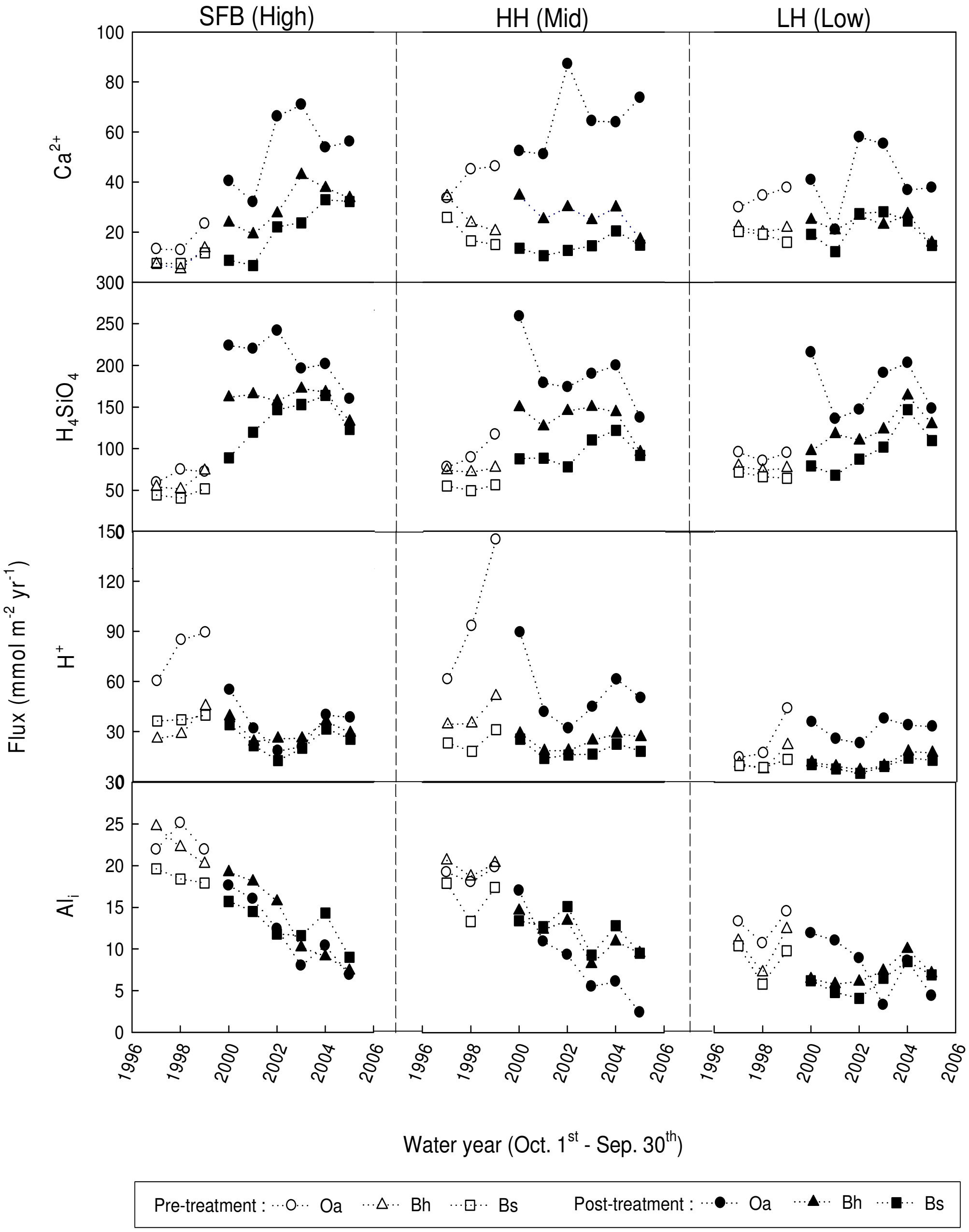

SFB (High)
HH (Mid)
LH (Low)
$Ca^{2+}$
$H_4SiO_4$
$H^+$
$Al_i$
Flux (mmol m-2 yr-1)
100
80
60
40
20
300
250
200
150
100
50
150
120
90
60
30
30
25
20
15
10
5
0
1996
1998
2000
2002
2004
2006
Water year (Oct. 1st - Sep. 30th)
Pre-treatment : Oa Bh Bs
Post-treatment : Oa Bh Bs

Figure 3.

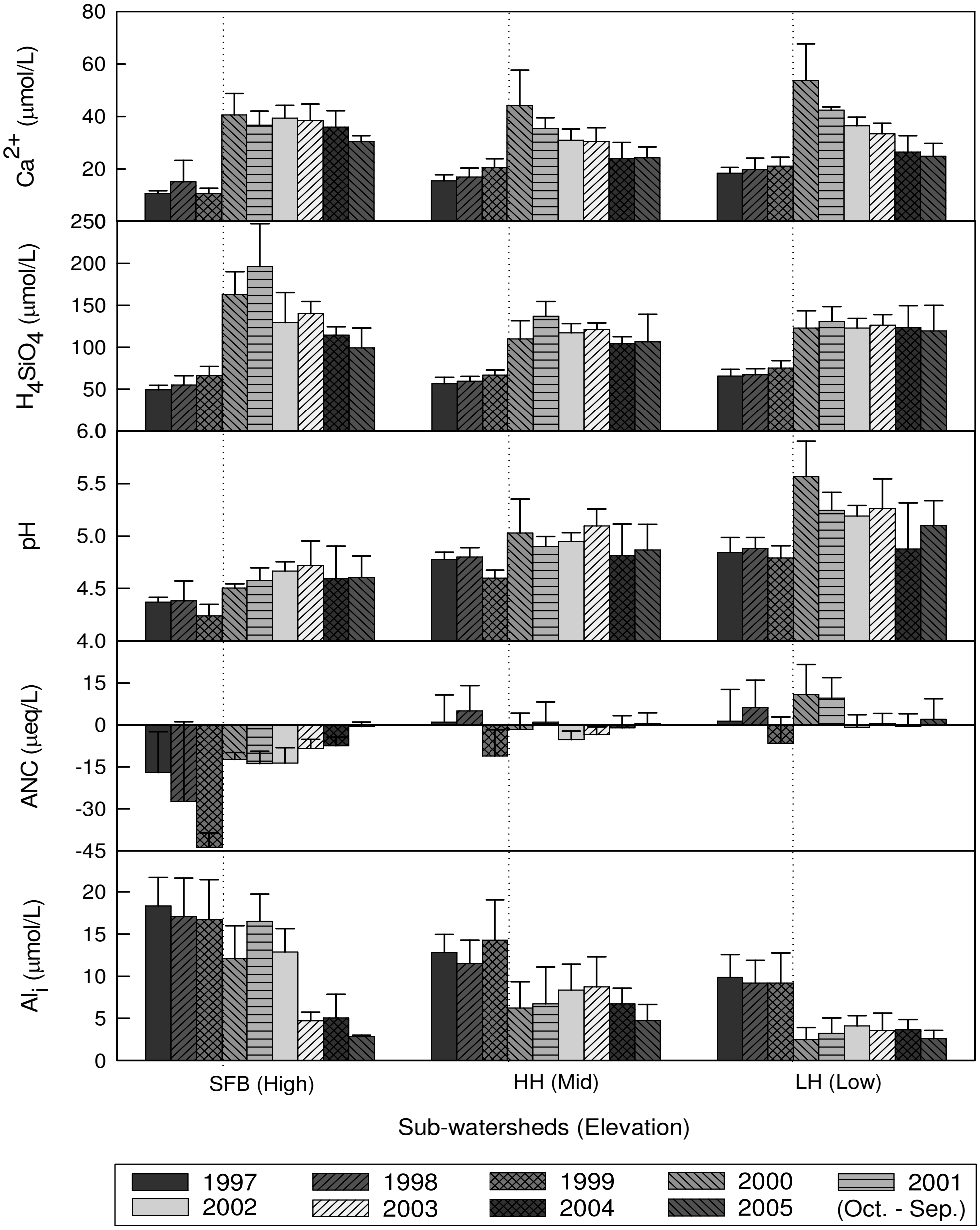

$Ca^{2+}$ (µmol/L)
80
60
40
20
$H_4SiO_4$ (µmol/L)
250
200
150
100
50
pH
6.0
5.5
5.0
4.5
4.0
ANC (µeq/L)
15
0
-15
-30
-45
$Al_i$ (µmol/L)
20
15
10
5
0
SFB (High)
HH (Mid)
LH (Low)
Sub-watersheds (Elevation)
1997
1998
1999
2000
2001
2002
2003
2004
2005
(Oct. - Sep.)

Figure 4.

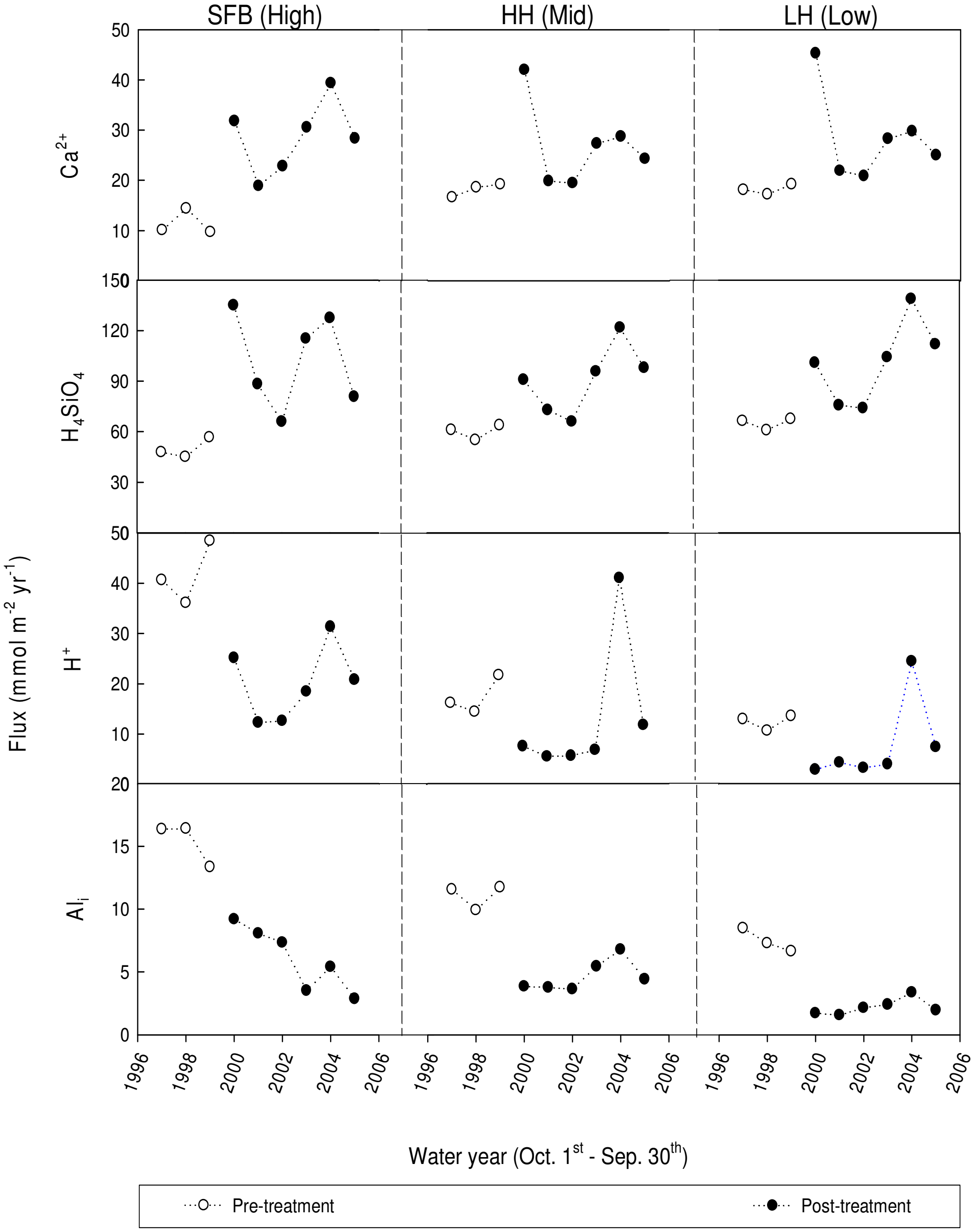

SFB (High)
HH (Mid)
LH (Low)
$Ca^{2+}$
$H_4SiO_4$
$H^+$
$Al_i$
Flux (mmol m$^{-2}$ yr$^{-1}$)
50
40
30
20
10
150
120
90
60
30
50
40
30
20
10
20
15
10
5
0
1996
1998
2000
2002
2004
2006
Water year (Oct. 1$^{st}$ - Sep. 30$^{th}$)
Pre-treatment
Post-treatment

Figure 5.

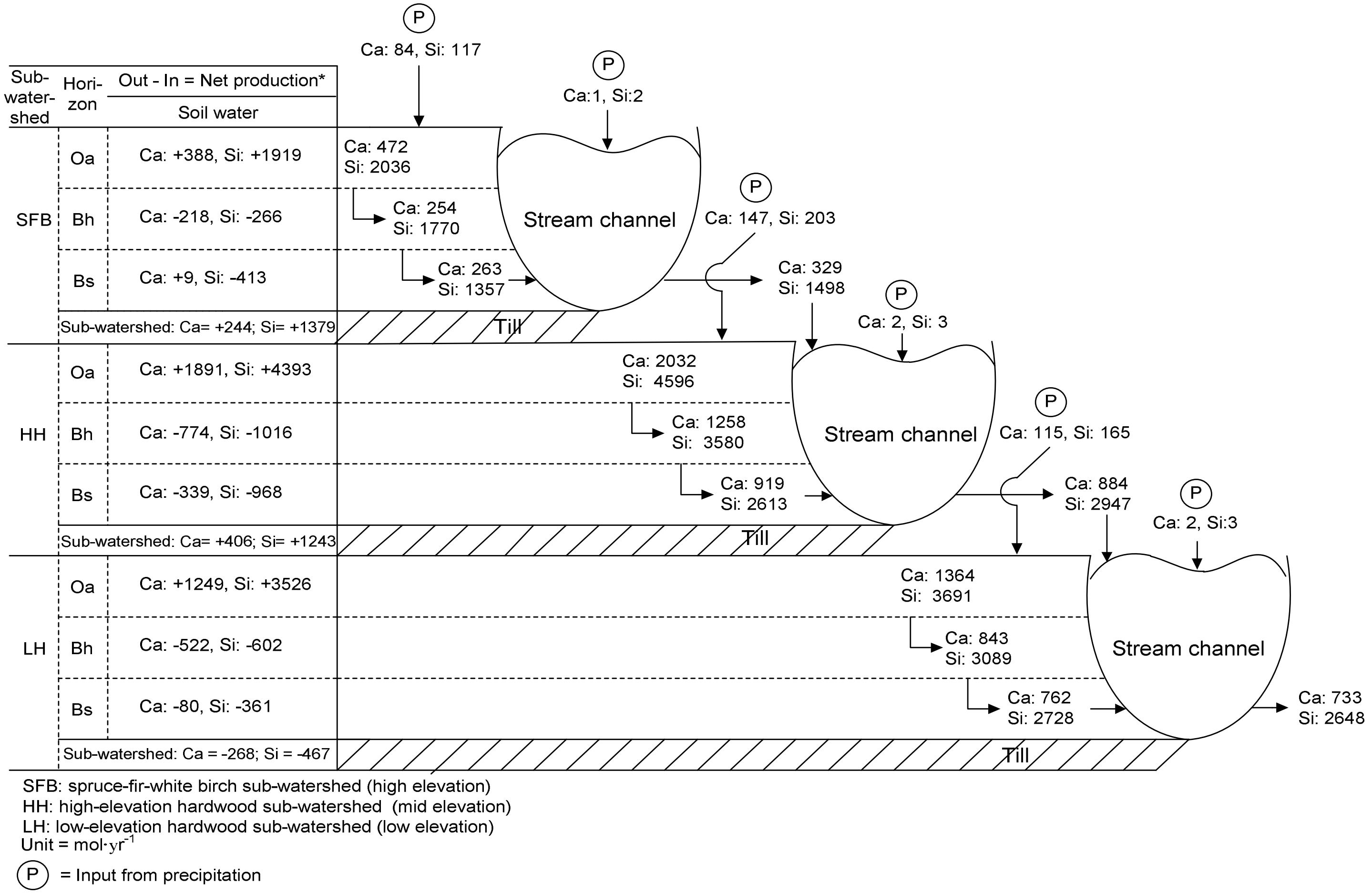

Sub-watershed
Horizon
Out - In = Net production*
Soil water
SFB
Oa
Ca: +388, Si: +1919
Bh
Ca: -218, Si: -266
Bs
Ca: +9, Si: -413
Sub-watershed: Ca= +244; Si= +1379
HH
Oa
Ca: +1891, Si: +4393
Bh
Ca: -774, Si: -1016
Bs
Ca: -339, Si: -968
Sub-watershed: Ca= +406; Si= +1243
LH
Oa
Ca: +1249, Si: +3526
Bh
Ca: -522, Si: -602
Bs
Ca: -80, Si: -361
Sub-watershed: Ca = -268; Si = -467
P
Ca: 84, Si: 117
P
Ca:1, Si:2
Ca: 472
Si: 2036
Ca: 254
Si: 1770
Ca: 263
Si: 1357
Stream channel
Till
P
Ca: 147, Si: 203
Ca: 329
Si: 1498
P
Ca: 2, Si: 3
Ca: 2032
Si: 4596
Ca: 1258
Si: 3580
Ca: 919
Si: 2613
Stream channel
Till
P
Ca: 115, Si: 165
Ca: 884
Si: 2947
P
Ca: 2, Si:3
Ca: 1364
Si: 3691
Ca: 843
Si: 3089
Ca: 762
Si: 2728
Stream channel
Ca: 733
Si: 2648
Till
SFB: spruce-fir-white birch sub-watershed (high elevation)
HH: high-elevation hardwood sub-watershed (mid elevation)
LH: low-elevation hardwood sub-watershed (low elevation)
Unit = mol·yr⁻¹
P = Input from precipitation

Figure 6.

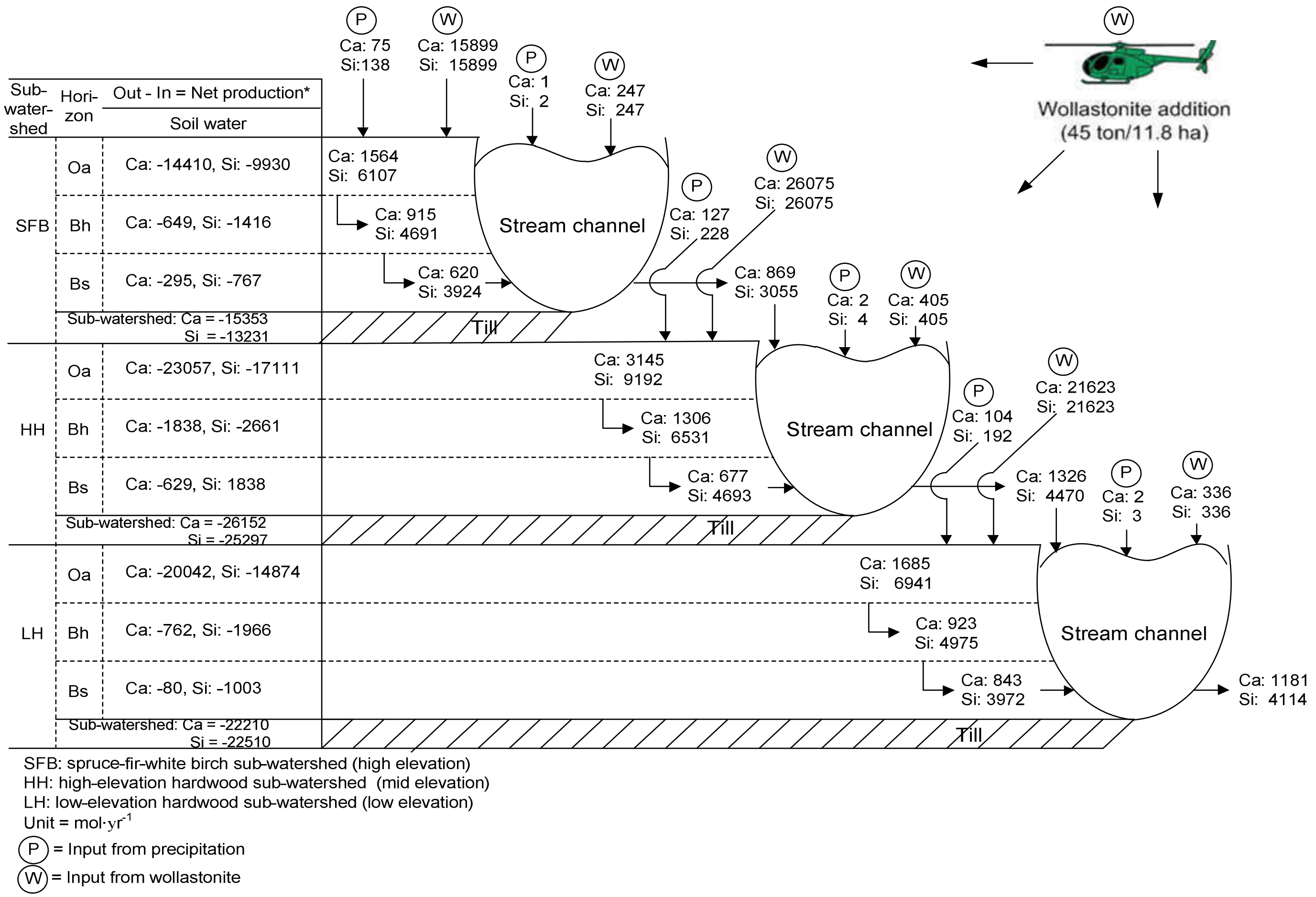

P
Ca: 75
Si:138
W
Ca: 15899
Si: 15899
P
Ca: 1
Si: 2
W
Ca: 247
Si: 247
W
Wollastonite addition
(45 ton/11.8 ha)
Sub-watershed
Horizon
Out - In = Net production*
Soil water
SFB
Oa
Ca: -14410, Si: -9930
Bh
Ca: -649, Si: -1416
Bs
Ca: -295, Si: -767
Sub-watershed: Ca = -15353
Si = -13231
Ca: 1564
Si: 6107
Ca: 915
Si: 4691
Ca: 620
Si: 3924
Stream channel
Till
P
Ca: 127
Si: 228
W
Ca: 26075
Si: 26075
Ca: 869
Si: 3055
P
Ca: 2
Si: 4
W
Ca: 405
Si: 405
HH
Oa
Ca: -23057, Si: -17111
Bh
Ca: -1838, Si: -2661
Bs
Ca: -629, Si: 1838
Sub-watershed: Ca = -26152
Si = -25297
Ca: 3145
Si: 9192
Ca: 1306
Si: 6531
Ca: 677
Si: 4693
Stream channel
Till
P
Ca: 104
Si: 192
W
Ca: 21623
Si: 21623
Ca: 1326
Si: 4470
P
Ca: 2
Si: 3
W
Ca: 336
Si: 336
LH
Oa
Ca: -20042, Si: -14874
Bh
Ca: -762, Si: -1966
Bs
Ca: -80, Si: -1003
Sub-watershed: Ca = -22210
Si = -22510
Ca: 1685
Si: 6941
Ca: 923
Si: 4975
Ca: 843
Si: 3972
Stream channel
Ca: 1181
Si: 4114
Till
SFB: spruce-fir-white birch sub-watershed (high elevation)
HH: high-elevation hardwood sub-watershed (mid elevation)
LH: low-elevation hardwood sub-watershed (low elevation)
Unit = mol·yr⁻¹
P = Input from precipitation
W = Input from wollastonite

Figure 7.

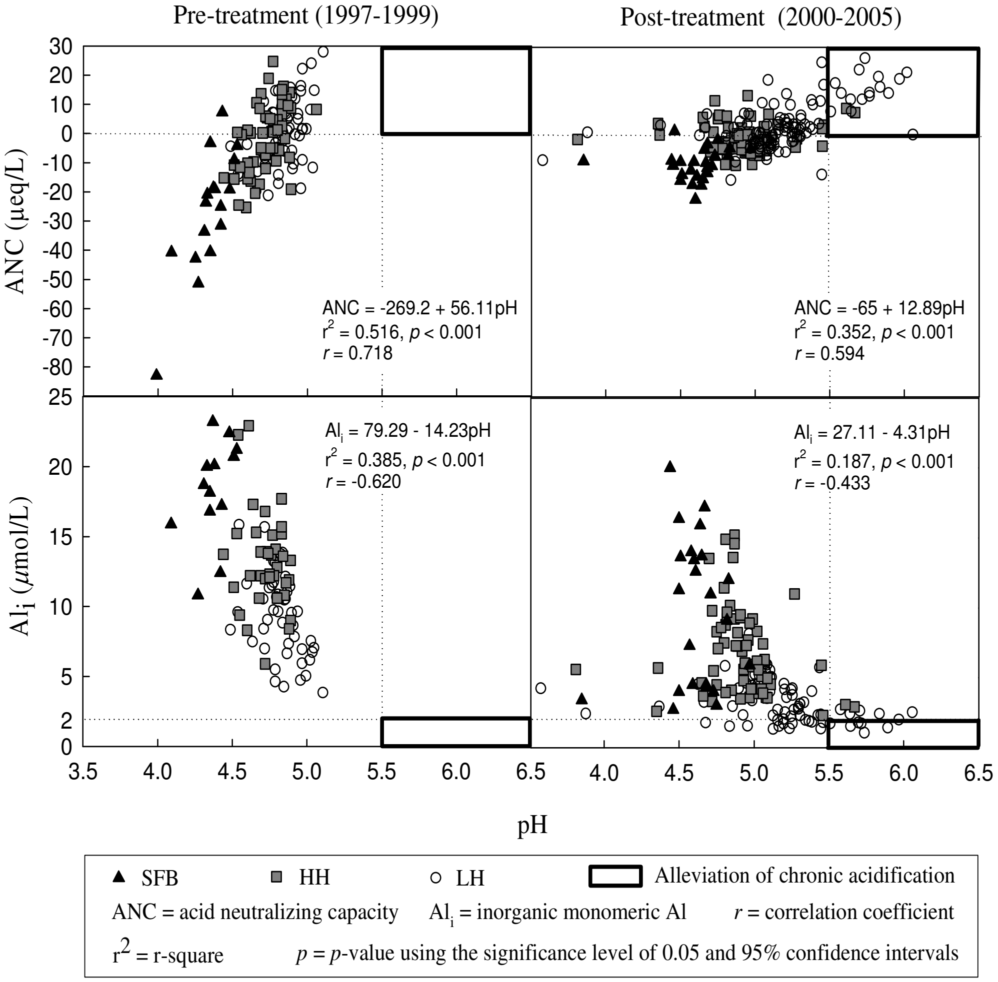
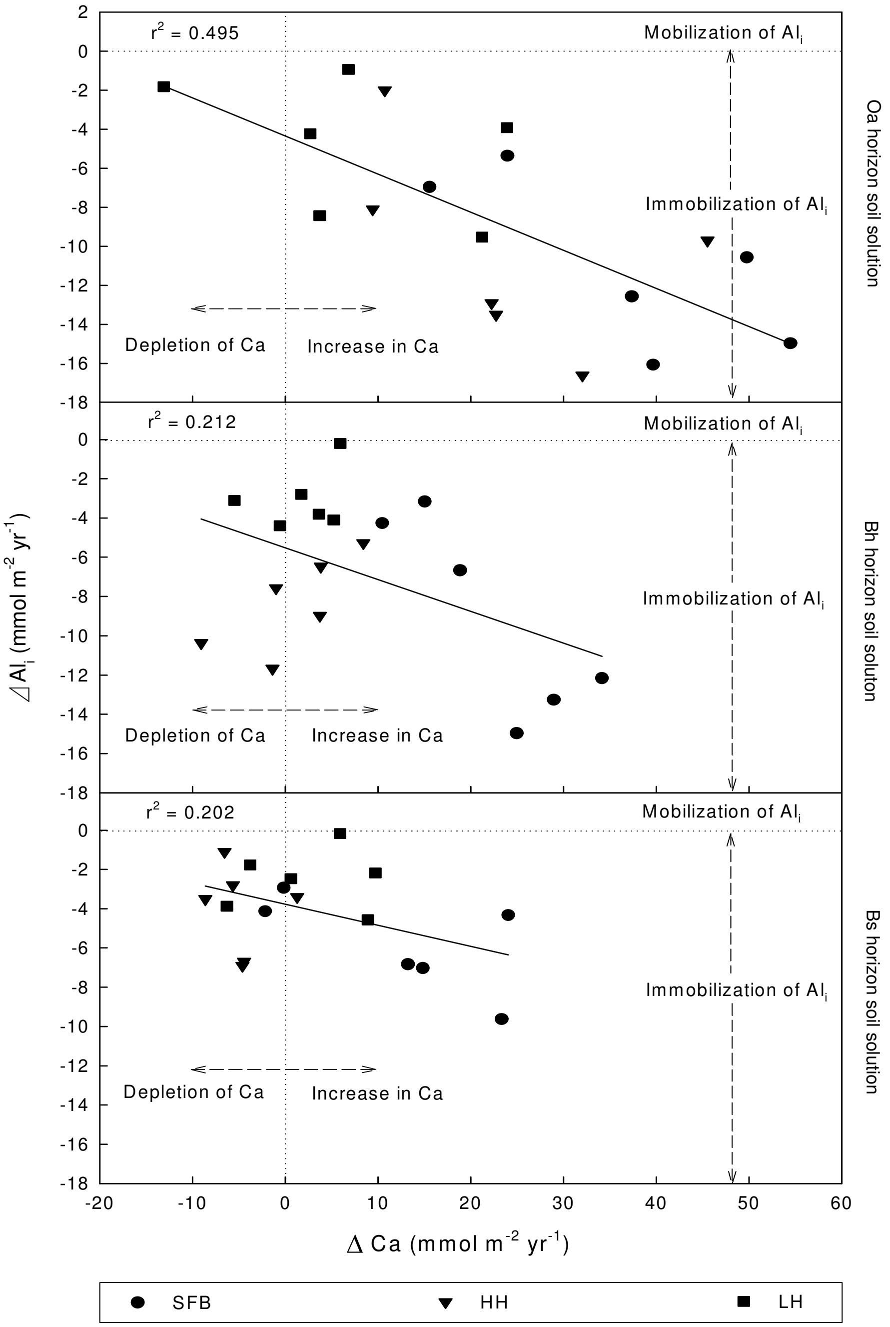
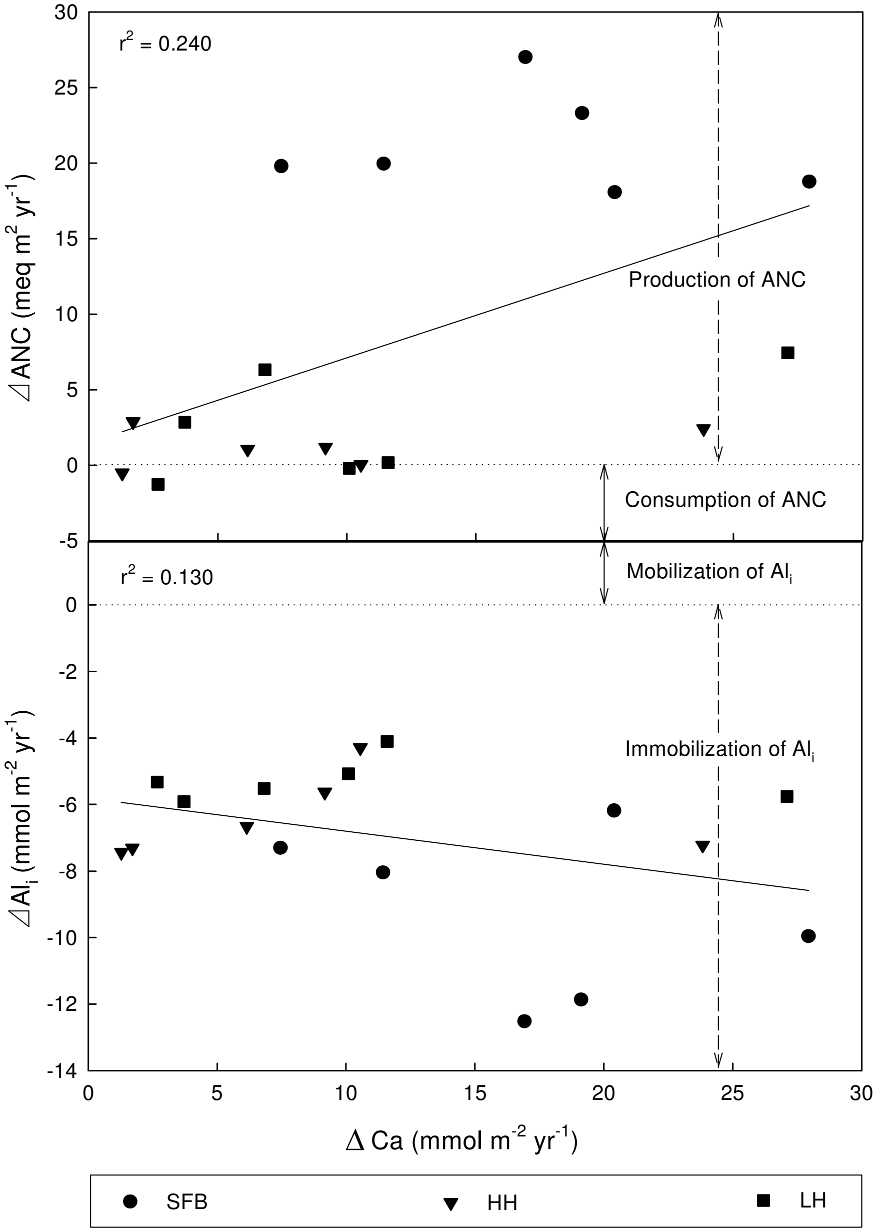

Pre-treatment (1997-1999)
Post-treatment (2000-2005)
ANC (μeq/L)
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
ANC = -269.2 + 56.11pH
$r^2$ = 0.516, $p$ < 0.001
$r$ = 0.718
ANC = -65 + 12.89pH
$r^2$ = 0.352, $p$ < 0.001
$r$ = 0.594
$Al_i$ (μmol/L)
25
20
15
10
5
2
0
$Al_i$ = 79.29 - 14.23pH
$r^2$ = 0.385, $p$ < 0.001
$r$ = -0.620
$Al_i$ = 27.11 - 4.31pH
$r^2$ = 0.187, $p$ < 0.001
$r$ = -0.433
3.5
4.0
4.5
5.0
5.5
6.0
6.5
4.0
4.5
5.0
5.5
6.0
6.5
pH
▲ SFB
■ HH
○ LH
Alleviation of chronic acidification
ANC = acid neutralizing capacity
$Al_i$ = inorganic monomeric Al
$r$ = correlation coefficient
$r^2$ = r-square
$p$ = $p$-value using the significance level of 0.05 and 95% confidence intervals

Figure 8.



r² = 0.495
Mobilization of Al_i
Immobilization of Al_i
Depletion of Ca
Increase in Ca
Oa horizon soil solution
r² = 0.212
Mobilization of Al_i
Immobilization of Al_i
Depletion of Ca
Increase in Ca
Bh horizon soil soluton
r² = 0.202
Mobilization of Al_i
Immobilization of Al_i
Depletion of Ca
Increase in Ca
Bs horizon soil solution
2
0
-2
-4
-6
-8
-10
-12
-14
-16
-18
-20
-10
0
10
20
30
40
50
60
ΔAl_i (mmol m⁻² yr⁻¹)
Δ Ca (mmol m⁻² yr⁻¹)
● SFB
▼ HH
■ LH

Figure 9.



r² = 0.240
Production of ANC
Consumption of ANC
Mobilization of Al_i
r² = 0.130
Immobilization of Al_i
∆ANC (meq m² yr⁻¹)
∆Al_i (mmol m⁻² yr⁻¹)
∆ Ca (mmol m⁻² yr⁻¹)
30
25
20
15
10
5
0
-5
-2
-4
-6
-8
-10
-12
-14
0
5
10
15
20
25
30
● SFB
▼ HH
■ LH

Figure 10.