

Long-term responses in soil solution and stream-water chemistry at Hubbard Brook after experimental addition of wollastonite

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Environmental context. Calcium silicate was added to a forest watershed in New Hampshire, USA, to accelerate its recovery from acid rain. The acid–base status of soil and stream quality improved over the 12-year study, with the most pronounced response in the upper elevation and the upper soil of the watershed. A total of 95 % of the added calcium and 87 % of the added silica were retained in the watershed over the study period.

Abstract. In October 1999, 3450 kg ha^{−1} of wollastonite (CaSiO₃) was applied to Watershed 1 at the Hubbard Brook Experimental Forest in New Hampshire, USA, with the objective of restoring calcium that had been depleted from soil-exchange sites by chronic inputs of acid deposition. After the treatment, the concentrations and fluxes of calcium and dissolved silica significantly increased in both soil solution and stream water throughout Watershed 1, as did the acid-neutralising capacity. The concentrations and fluxes of inorganic monomeric aluminium significantly decreased. The treatment improved the acid–base status and decreased the potential for aluminium toxicity in stream water, especially in the lower reaches of the watershed. Approximately 4.7 % of the added calcium and 17 % of the added silica from the wollastonite treatment was exported from Watershed 1 in stream water by the end of 2010. Meanwhile, ~1825 mmol m^{−2} of the added calcium and 2125 mmol m^{−2} of the added silica were either transported to lower mineral soil horizons – as particulate wollastonite, or as dissolved solutes (calcium 77.6 mmol m^{−2}; silica 592.2 mmol m^{−2}), thus contributing to increases in soil pools – or were taken up by vegetation and incorporated into internal calcium and silica cycles of the watershed ecosystem. This experimental wollastonite addition was an effective tool for mitigating the acidification of the ecosystem and restoring the calcium status and forest health of this base-poor watershed.

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Introduction

Decreases in atmospheric deposition^[1] associated with declines in sulfur dioxide (SO₂) and nitrogen oxide (NO_x) emissions have resulted in decreases in sulfate (SO₄^{2−}) and nitrate (NO₃[−]) concentrations in surface waters throughout the north-eastern USA.^[2–4] However, these reductions have failed to generate marked increases in pH and acid-neutralising capacity (ANC^[5]) in many acid-affected surface waters. This limited response has largely been attributed to the depletion of exchangeable calcium (Ca) and magnesium (Mg) in soil associated with historic atmospheric inputs of strong acid anions.^[5–7]

The biogeochemistry of Ca in forest ecosystems is complex and intricately linked with other element cycles. In many terrestrial ecosystems, high mineral weathering rates provide adequate Ca to support ecosystem structure and function. However, native Ca can be in short supply in regions with

parent materials that are resistant to weathering, and that have shallow surficial deposits or acidic soils. Although acidic forest soils are widely distributed, regions affected by acid deposition typically occur at high elevation, such as the Appalachian Mountains.^[8–11] At the Hubbard Brook Experimental Forest (HBEF) in New Hampshire, USA, soil materials derived from glacial till with low clay content support a cool-temperate forest representative of the Northern Forest region.^[12] The HBEF receives elevated acid deposition and has inherently low concentrations of available Ca in soil and drainage waters.^[9,13] As a result, the HBEF has experienced depletion of available soil Ca and the mobilisation of inorganic monomeric aluminium (Al_i) from soil to drainage waters in recent decades.^[5,9] These changes have affected the health of sensitive trees (e.g. red spruce, *Picea rubens*; sugar maple, *Acer saccharum*) and aquatic biota.^[5,14–16]

Watershed liming involves the addition of basic materials to surface soils to mitigate the acidification of soil and drainage waters.^[17–19] Studies have shown that base treatment can increase exchangeable Ca and cation-exchange capacity, and decrease exchangeable Al concentrations in forest soils, as well as increase Ca, pH and ANC in surface waters while decreasing Al.^[2,17,19–21]

In October 1999, 3450 kg ha⁻¹ of a finely ground and rapidly weatherable calcium silicate mineral, wollastonite (CaSiO₃), was added to Watershed 1 (W1) at the HBEF by helicopter. Wollastonite was selected for use in this treatment because it is similar to the natural weathering source of Ca.^[22,23] The goal of the present study was to quantify the longer-term (>10 years) spatial and chemical responses of soil solutions and stream waters to the CaSiO₃ treatment on W1, and to compare watershed-level changes with measurements of changes in soil pools.^[24] Our approach included an evaluation of time-series observations, mass-balance calculations and an analysis of stoichiometric responses at three elevation zones in W1 before and after CaSiO₃ treatment. We investigated spatial and temporal patterns in concentrations of Ca, dissolved silica (H₄SiO₄), pH, ANC and Al_i in soil solutions and stream waters in W1 in response to the CaSiO₃ addition. We examined solute (Ca, H₄SiO₄, H⁺, Al_i) fluxes in soil water and stream water before and after CaSiO₃ addition and compared these values with results from a previous study of changes in soil Ca pools.^[24] We hypothesised that: (1) CaSiO₃ addition would alter the acid–base status of soil water and stream water over the longer term by increasing the concentration of Ca, pH and ANC, and decreasing the concentration of Al_i, alleviating chronic acidification stress; (2) further, CaSiO₃ addition would increase drainage water fluxes of Ca and dissolved Si and decrease fluxes of H⁺ and Al_i; and (3) the treatment effects would be most evident in the high-elevation zone of the watershed and least evident in lower-elevation reaches.^[25]

The present paper extends the period of analysis and observations of the wollastonite addition experiment at Hubbard Brook.^[26] Moreover, we integrate long-term solution chemistry measurements with studies of soil and vegetation response to the treatment.^[16,24]

Experimental

Study site

The HBEF is a 3160-ha basin located in the southern portion of the White Mountain National Forest in central New Hampshire, USA (43°56'N, 71°45'W). The region experiences humid continental climate with cold winters, with an average temperature of -9 °C in January, and short and cool summers, with an average temperature of 18 °C in July. The average annual precipitation is ~1400 mm, ~35 % occurring as snow, and estimated annual evapotranspiration (ET) is ~500 mm.^[27] Watershed 1 lies on a south-facing slope of the HBEF with an average slope between 20 and 30 %. It has total area of 11.8 ha, which contains a stream channel area of 1804 m² over its elevation range of 488 to 747 m.^[22] The predominant bedrock is the Silurian Rangeley Formation, which includes quartz mica schist and quartzite, interbedded with sulfidic schist and calc-silicate granulite.^[25] Soils at the HBEF are highly variable, predominantly Spodosols and Inceptisols derived from glacial till, with a sandy loam texture. The forest floor ranges in thickness from 2 to 20 cm, with an average depth of 6.9 cm. The thickness of the forest floor increases at high elevation.^[25] In contrast, the

mineral soil has an average depth of ~50 cm and although highly variable, its depth decreases with increasing elevation.^[25] This pattern suggests that mineral soil at lower elevation generally has a greater ability to neutralise acid deposition and organic acidity leached from litter and the forest floor.^[28–30]

Vegetation in W1 consists primarily of deciduous northern hardwood species: sugar maple (*Acer saccharum*), American beech (*Fagus grandifolia*) and yellow birch (*Betula alleghaniensis*) on the middle and lower parts of the watershed. Red spruce (*Picea rubens*), balsam fir (*Abies balsamea*) and white birch (*Betula papyrifera* var. *cordifolia*) are common at higher elevations and on rock outcrops.^[16,31] Watershed 1 has three distinct landscape zones based on elevation.^[26] (1) The spruce-fir–white birch sub-watershed (SFB) is the high-elevation zone, characterised by fairly flat topography, shallow soils and shallow flow-paths of water. The SFB sub-watershed represents 2.95 ha of the watershed area (25 %) and 451 m² of the stream channel area. (2) The high-elevation hardwood sub-watershed (HH) is the middle-elevation zone that is characterised by somewhat deeper soil, situated on thin till or bedrock with no C horizon, and has steep slopes and deciduous forest vegetation. The HH sub-watershed has a watershed area of 4.84 ha (41 %) and 740 m² of the stream channel area. (3) The low-elevation hardwood sub-watershed (LH) is the low-elevation zone, which has the deepest soil among the three sub-watersheds, deeper glacial till. The LH sub-watershed occupies ~4.01 ha (34 %) of the watershed area and 613 m² of the stream channel area.

Wollastonite application

The application of CaSiO₃ was designed to enhance the supply of Ca and Si to W1 and to mitigate the acidification of soil and surface water. Dissolution of wollastonite in the soil environment can be described by the following reaction:



The elemental composition of the CaSiO₃ applied was 29.7 % Ca, 22.5 % Si and 1.1 % Mg by mass. The target dose of CaSiO₃ was determined by calculating the amount of Ca that would increase the base saturation of the entire soil profile from 10 % (the current value) to 19 % (the estimated value 70 years ago) plus a safety factor of 50 % in order to accommodate inefficiencies in CaSiO₃ dissolution.^[22] The CaSiO₃ was powdered (mean size of 16 μm) and pelletised (1.5–4 mm diameter) with a water-soluble lignin sulfonate binder. This approach facilitated effective aerial application to the watershed of pellets, which disaggregated to the original particle size in the presence of moisture.^[22] On 19 October 1999, 3550 kg ha⁻¹ of pellets, containing 3450 kg ha⁻¹ of wollastonite, and 2570 mmol m⁻² of Ca, was evenly applied across W1.^[22] The treatment was made by helicopter after leaf-fall to allow the immediate interaction of the CaSiO₃ with the forest floor.^[22]

Collection and analysis of samples

Soil solutions were collected at monthly intervals from tension-free lysimeters constructed from polyethylene funnels filled with acid-washed quartz sand installed in three soil horizons at 13 sites across the three sub-watersheds at W1. Soil solution sampling began in 1996, 3 years before the application of CaSiO₃. There are six lysimeter sites in the SFB sub-watershed, three lysimeter sites in the HH sub-watershed and four lysimeter sites in the LH sub-watershed.^[23] Lysimeters are

Table 1. Chemical methods used for analysis of soil solution and stream water samples

Analyte (units)	Method	Reference
Ca, Mg, Na, K ($\mu\text{mol L}^{-1}$)	Inductively coupled plasma mass spectrometry (ICP-MS)	Beauchemin ^[44]
SO_4^{2-} , F^- , Cl^- , NO_3^- ($\mu\text{mol L}^{-1}$)	Ion chromatography	Tabatabai et al. ^[45]
NH_4^+ ($\mu\text{mol L}^{-1}$)	Automated phenate method	APHA ^[46]
Dissolved silicate (H_4SiO_4 , $\mu\text{mol L}^{-1}$)	Molybdenum blue colorimetry	APHA ^[46]
pH	Potentiometric measurement	APHA ^[46]
Acid-neutralising capacity (ANC, $\mu\text{eq L}^{-1}$)	Strong acid titration, Gran plot analysis	Gran ^[47]
Dissolved organic carbon (DOC, $\mu\text{mol L}^{-1}$)	Infrared detection following persulfate oxidation	Dohrmann ^[48]
Total Al (Al_t)	ICP-MS	Beauchemin ^[44]
Total monomeric Al (Al_m , $\mu\text{mol L}^{-1}$)	Colorimetric measurement following chelation with pyrocatechol violet	McAvoy et al. ^[49]
Organic monomeric Al (Al_o , $\mu\text{mol L}^{-1}$)	Passing the sample through an ion-exchange column after Al_m measurement	Palmer et al. ^[30]
Inorganic monomeric Al (Al_i , $\mu\text{mol L}^{-1}$)	$\text{Al}_m - \text{Al}_o$	McAvoy et al. ^[49] Palmer et al. ^[30] Driscoll ^[32]

positioned at three depths: immediately beneath the Oa horizon, beneath the Bh horizon and within the Bs horizon. Soil solutions were extracted from each lysimeter using a vacuum hand-pump, then collected in acid-washed plastic bottles and transported to the laboratory.

Stream water samples were also collected at monthly intervals from five locations positioned longitudinally within the watershed. This sampling began in W1 in 1991. There was one stream site in the SFB sub-watershed, two sites in the HH sub-watershed and two sites in the LH sub-watershed.^[26] Stream samples were collected in acid-cleaned plastic bottles and transported to the laboratory.

Soil solution and stream water samples were analysed for pH, Ca, Mg, Na, K, SO_4^{2-} , NO_3^- , Cl^- , F^- , NH_4^+ , ANC, total Al, total monomeric Al, organic monomeric Al, dissolved Si, dissolved organic carbon, dissolved inorganic carbon and total nitrogen.^[26] Al_i ($\mu\text{mol L}^{-1}$) was calculated by subtracting organic monomeric Al from the measured total monomeric Al concentrations.^[32] The analytical methods used for soil solution and stream water are described in Table 1. Quality assurance and quality control (QA-QC) measures were used for all water sample analyses.^[33] The most distinct changes in solution chemistry over the study period were evident for Ca, dissolved Si, pH, ANC and Al_i . As a result, we focussed our analysis on these analytes.

To coincide with the timing of the CaSiO_3 addition, annual average values for each parameter were calculated on a water-year basis from 1 October to 30 September, which differs from the water-year basis (1 June to 30 May) typically used at the HBEF.^[9,25] The two-sample *t*-test was applied to evaluate the changes in soil solution and stream water chemical immediately in response to CaSiO_3 treatment (2000) and the changes in soil solution and stream water chemical between pretreatment (1999) and 12 years after the treatment (2011) at both the whole watershed scale and sub-watershed scale. Tests were carried out on a yearly basis with a significance level of $\alpha = 0.05$, 0.01 and 0.001 respectively (temporal and spatial statistical analyses are shown in Supplementary material Tables S1–S7).

Chemical equilibrium calculations for ANC and Al_i

We compared observations with a theoretical relationship between pH and ANC, which was derived by assuming that stream water is exposed to the atmosphere with a partial pressure

of carbon dioxide ($p\text{CO}_2$) = 32 Pa at 10 °C ($10^{-3.5}$ atm). Under these assumptions, ANC can be defined as:

$$\text{ANC} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad (2)$$

where the units for ion concentrations are micromoles per litre and the units of ANC are microequivalents per litre.

We also compared our Al_i measurements with the theoretical relationship between pH and Al_i , which assumes that Al_i is derived from the equilibrium dissolution of $\text{Al}(\text{OH})_3$ at 10 °C (logarithm of the mineral solubility constant (K_{s0}) = 8.99).

Calculation of solute fluxes

To compute yearly solute fluxes in soil solutions, we defined the growing season (GS) from 1 May to 30 September and the non-growing season (NGS) from 1 October to 30 April.^[26] Evapotranspiration for the GS was calculated by subtracting annual stream flow from annual precipitation and was assumed to be driven by plant root uptake. Plant root uptake for the NGS was assumed to be zero, and root uptake occurring from each soil horizon was assumed to be proportional to the fine root biomass in that horizon (SFB sub-watershed: 38 % at Oa, 41 % at Bh and 21 % at Bs; HH sub-watershed: 33 % at Oa, 47 % at Bh and 20 % at Bs; LH sub-watershed: 42 % at Oa, 36 % at Bh and 21 % at Bs).^[34] We assumed that water percolates vertically through the entire soil profile without lateral flowpaths before emerging to the stream channel.^[35] Finally, we assumed that the change in soil moisture between consecutive annual periods is low and can be neglected. Soil water fluxes from each horizon were thus calculated as the difference between precipitation and the cumulative root water uptake for the soil depth above the horizon of interest. Yearly solute fluxes were then computed by multiplying the average solute concentrations for GS and NGS by the soil water fluxes in each season and summing the values for the two periods.

Solute fluxes in stream water were computed by multiplying the measured solute concentrations for the stream sites at the outlet of each subwatershed for each month by the cumulative stream discharge in that month. Solute concentrations in each sub-watershed of W1 were measured at monthly intervals. For months in which data were missing or not measured, we used average concentrations, calculated from the adjacent months. Stream flow data were continuously measured at a stream

gauging station located at the base of W1, using a 90° sharp-crested V-notch weir.^[36] In order to estimate stream flow in each sub-watershed, we assumed that stream water generated in each sub-watershed was proportional to its area. As a result, stream flow yield in SFB, HH and LH sub-watersheds were estimated to be 25, 41 and 34% of total stream flow of W1 respectively.^[25,35] Note that routine monitoring did not include focussed measurements during hydrologic events. However, a previous study did not find significant relationships between stream Ca concentration and discharge, before or following CaSiO₃ application.^[37]

Results

Soil water chemistry

The CaSiO₃ addition altered soil water chemistry by increasing concentrations of Ca and dissolved Si, increasing pH and ANC, and decreasing the concentrations of Al_i in Oa (forest floor), Bh and Bs (mineral horizon) horizons in all three sub-watersheds based on comparisons between the pretreatment (1998–99) and post-treatment (2000–11) periods (Fig. 1). Prior to CaSiO₃ treatment, Ca and dissolved Si concentrations in soil solutions decreased with soil depth as water drained through Bh and Bs horizon in all sub-watersheds. This horizon pattern continued during the post-treatment period (Fig. 1). After CaSiO₃ addition, concentrations of Ca and dissolved Si increased significantly in Oa, Bh and Bs horizons in all sub-watersheds, but Ca and dissolved Si showed different patterns in response to the addition (Fig. 1). In general, Ca concentrations gradually increased in soil solutions during the first 3 years after the treatment in all three sub-watersheds, followed by a slight decrease in concentrations through the end of the study period. In contrast, dissolved Si exhibited a rapid increase in response to the CaSiO₃ addition and then decreased markedly following the third year after treatment. Twelve years after CaSiO₃ addition (2011), the concentrations of dissolved Si in soil solutions in W1 remained significantly higher than pretreatment concentrations (1999). The concentrations of Ca in all soil solutions draining the SFB sub-watershed remained significantly higher than pretreatment concentrations. In the HH zone, Ca concentrations were significantly higher than pretreatment values in Oa and Bh horizons. Significant differences for Ca were not evident in the LH sub-watershed. The initial increases in Ca and dissolved Si concentrations and subsequent decreases were most evident in the SFB sub-watershed (Fig. 1).

The molar Ca : Si ratio in soil solutions of all horizons in all sub-watersheds decreased immediately after the CaSiO₃ addition. These initial decreases were generally followed by increases for the rest of the study period after the treatment (Fig. 1). The magnitude of the initial decrease in Ca : Si ratio was most evident in the Oa horizon, where the ratio decreased from 0.54 (LH: 1999) to 0.21 (LH: 2000). The magnitude of increases in Ca : Si following this initial decrease was most pronounced in Oa horizon solutions. Prior to the treatment, the Oa horizon had a higher Ca : Si ratio than mineral soil solutions and this pattern persisted through the study period (i.e. 2011; Fig. 1).

Concentrations of Al_i decreased significantly in soil solutions of Oa and Bh horizons in SFB and HH sub-watersheds following CaSiO₃ treatment (Fig. 1). Concentrations of Al_i in soil solutions from Oa and Bh horizons decreased immediately after CaSiO₃ addition, whereas the decreases in Al_i in Bs horizons were not observed until 2001. Concentrations of Al_i in soil water increased with increasing soil depth before and

after treatment; soil water draining the Oa horizon had the lowest Al_i and concentrations increased in mineral soil solutions (Fig. 1). As with Ca, dissolved Si and pH, the decreases in Al_i were most evident in the high-elevation SFB zone and also the HH zone (Table S7). Twelve years after CaSiO₃ treatment (2011), the concentrations of Al_i throughout the soil profile in the SFB and HH sub-watersheds remained significantly lower than pretreatment (1999) values. Soil solutions in the W1 showed no pattern of reacidification after the treatment (i.e. increases in Al concentration).

Prior to the treatment (1998 to 1999), the mean molar Ca : Al_i ratios of solution draining all horizons in the SFB sub-watershed were less than 1.0 (Oa: 0.9, Bh: 0.6, Bs: 0.5). In contrast, the average Ca : Al_i ratios in the HH and LH sub-watersheds were greater than 1.0 (Oa: 4.2 and 5.3, Bh: 1.9 and 3.7, Bs: 1.5 and 3.5 respectively). After the treatment, the Ca : Al_i ratio of soil solutions in Oa and Bh horizons increased significantly (Fig. 1). The magnitude of the increases in the Ca : Al_i ratio was much greater in the Oa horizon than in mineral soils. There were marked increases in Ca to Al_i ratio of Oa horizon leachate in the HH sub-watershed (e.g. 2008: 219, 2009: 311, 2010: 109) resulting from very low Al_i concentrations (e.g. 2008: 0.3 µmol L⁻¹, 2009: 0.2 µmol L⁻¹, 2010: 0.5 µmol L⁻¹).

Stream water chemistry

The CaSiO₃ manipulation of W1 influenced stream water chemistry, changing the acid–base status in all three sub-watersheds in similar ways as for soil solutions. The CaSiO₃ addition resulted in increases in Ca, dissolved Si, pH (data are not shown) and ANC, and a decrease in Al_i in stream water (Figs 2, 3). These increases were maintained through 2011. After CaSiO₃ addition, stream Ca concentrations increased significantly in all sub-watersheds. In 2000, the year after the treatment, Ca concentrations had increased by 237% in the SFB zone, 162% in the HH zone and 160% in the LH zone compared with average pretreatment Ca concentrations (1992 to 1999). Stream Ca concentrations peaked in 2000 (SFB: 40.6 ± 8.1 µmol L⁻¹, HH: 43.9 ± 11.2 µmol L⁻¹, LH: 53.9 ± 2.1 µmol L⁻¹; mean ± standard deviation), then decreased through 2011 in all three sub-watersheds at different rates (SFB: -1.88 µmol L⁻¹ year⁻¹, HH: -2.28 µmol L⁻¹ year⁻¹, LH: -3.17 µmol L⁻¹ year⁻¹). By the end of 2011, Ca concentrations in all three sub-watersheds were similar (SFB: 21.7 ± 2.8 µmol L⁻¹, HH: 18.9 ± 2.5 µmol L⁻¹, LH: 19.1 ± 2.1 µmol L⁻¹). Only Ca concentrations in the SFB sub-watershed remained significantly higher than pretreatment values (SFB: 11.9 ± 2.3 µmol L⁻¹). Ca concentrations in the HH and LH sub-watersheds were close to pretreatment levels (HH: 17.3 ± 1.3 µmol L⁻¹, LH: 18.2 ± 1.9 µmol L⁻¹).

Dissolved Si concentrations also increased significantly in stream water in all sub-watersheds after treatment. In contrast to Ca, the peak of dissolved Si concentrations (SFB: 199.4 ± 51.6 µmol L⁻¹, HH: 134.5 ± 19.8 µmol L⁻¹, LH: 127.7 ± 21.3 µmol L⁻¹) occurred in the second year after CaSiO₃ addition (2001) in all three sub-watersheds. These increases were followed by decreases through 2011 in all sub-watersheds. By the end of 2011, the concentrations of dissolved Si in all three sub-watersheds (SFB: 65.7 ± 11.6 µmol L⁻¹, HH: 73.6 ± 7.0 µmol L⁻¹, LH: 82.7 ± 9.7 µmol L⁻¹) remained significantly higher than average pretreatment concentrations (SFB: 58.9 ± 11.3 µmol L⁻¹, HH: 58.5 ± 5.2 µmol L⁻¹, LH: 68.5 ± 4.7 µmol L⁻¹).

The Ca : Si ratio increased significantly in HH and LH sub-watersheds in response to the treatment (Fig. 2). These initial

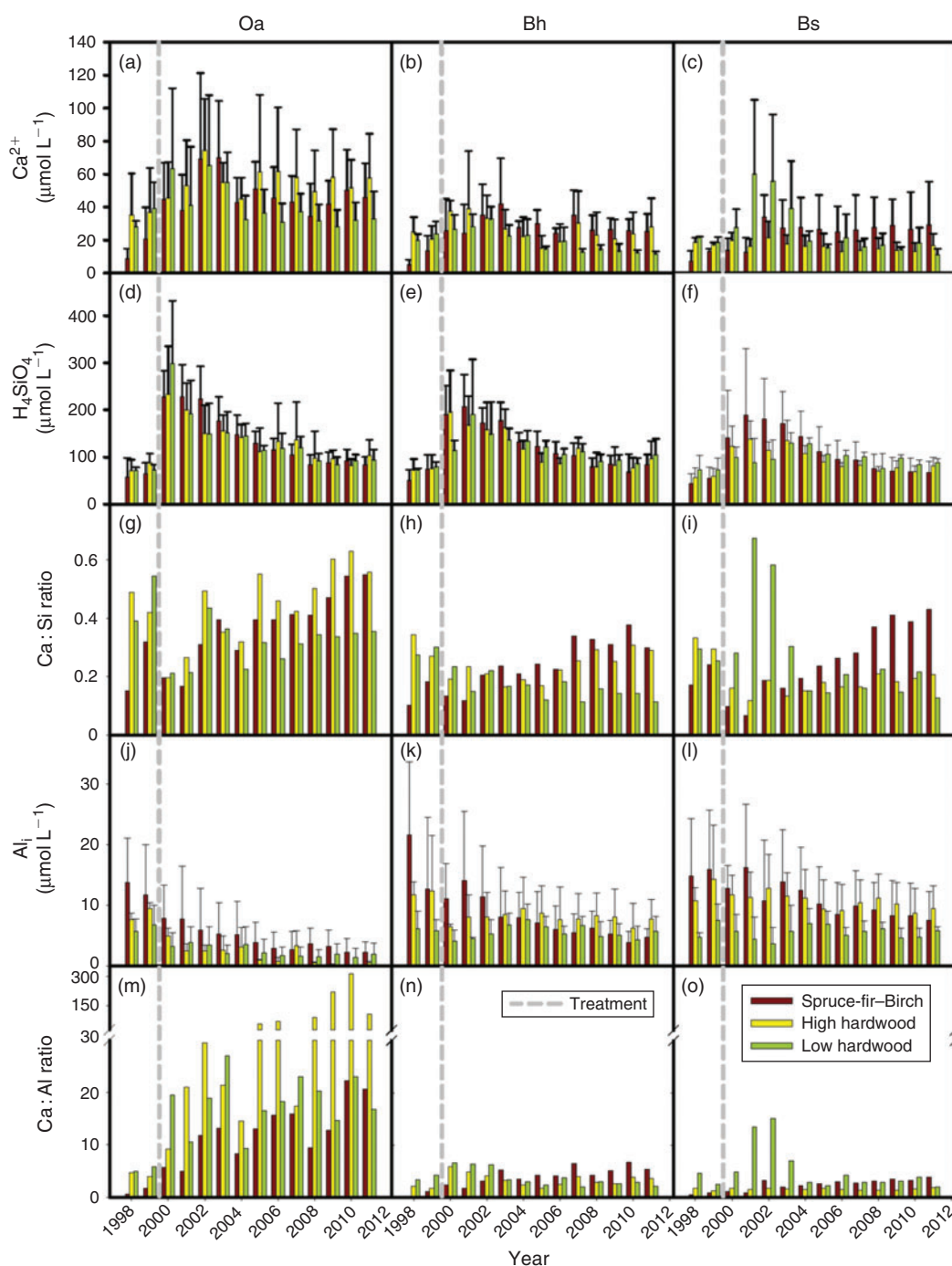


Fig. 1. Spatial and temporal patterns in concentrations of Ca, H_4SiO_4 , Ca : Si, Al and Ca : Al in soil solutions in Watershed 1 (W1) of the Hubbard Brook Experimental Forest (HBEF), including Oa, Bh and Bs horizons leachate. Data are shown for three elevation zones: the spruce-fir-white birch zone (SFB), the high-elevation hardwood zone (HH) and the low-elevation hardwood zone (LH). Wollastonite was added in October 1999. Annual mean values are expressed on a water year basis (from 1 October to 30 September). Error bars represent standard deviations for each water year. The vertical line separates the pretreatment and post-treatment periods.

increases were followed by decreases in the HH and LH sub-watersheds in the next few years, whereas the Ca : Si ratio in the SFB sub-watershed continued to increase through the entire study period (Fig. 2). At the end of study period (2011), the Ca : Si ratio in the SFB sub-watershed remained significantly higher than pretreatment values (pretreatment: 0.17 ± 0.04 , 2011: 0.34 ± 0.07). The Ca : Si ratios in the HH

and LH sub-watersheds were lower than pretreatment values (pretreatment: 0.29 ± 0.06 and 0.29 ± 0.06 , 2011: 0.26 ± 0.05 and 0.23 ± 0.05 respectively).

The CaSiO_3 addition also resulted in significant increases in ANC in all three sub-watersheds (Figs 2, 3). Nevertheless, ANC values in the three sub-watersheds were low, with many observations below $0 \mu\text{eq L}^{-1}$, suggesting chemical conditions that

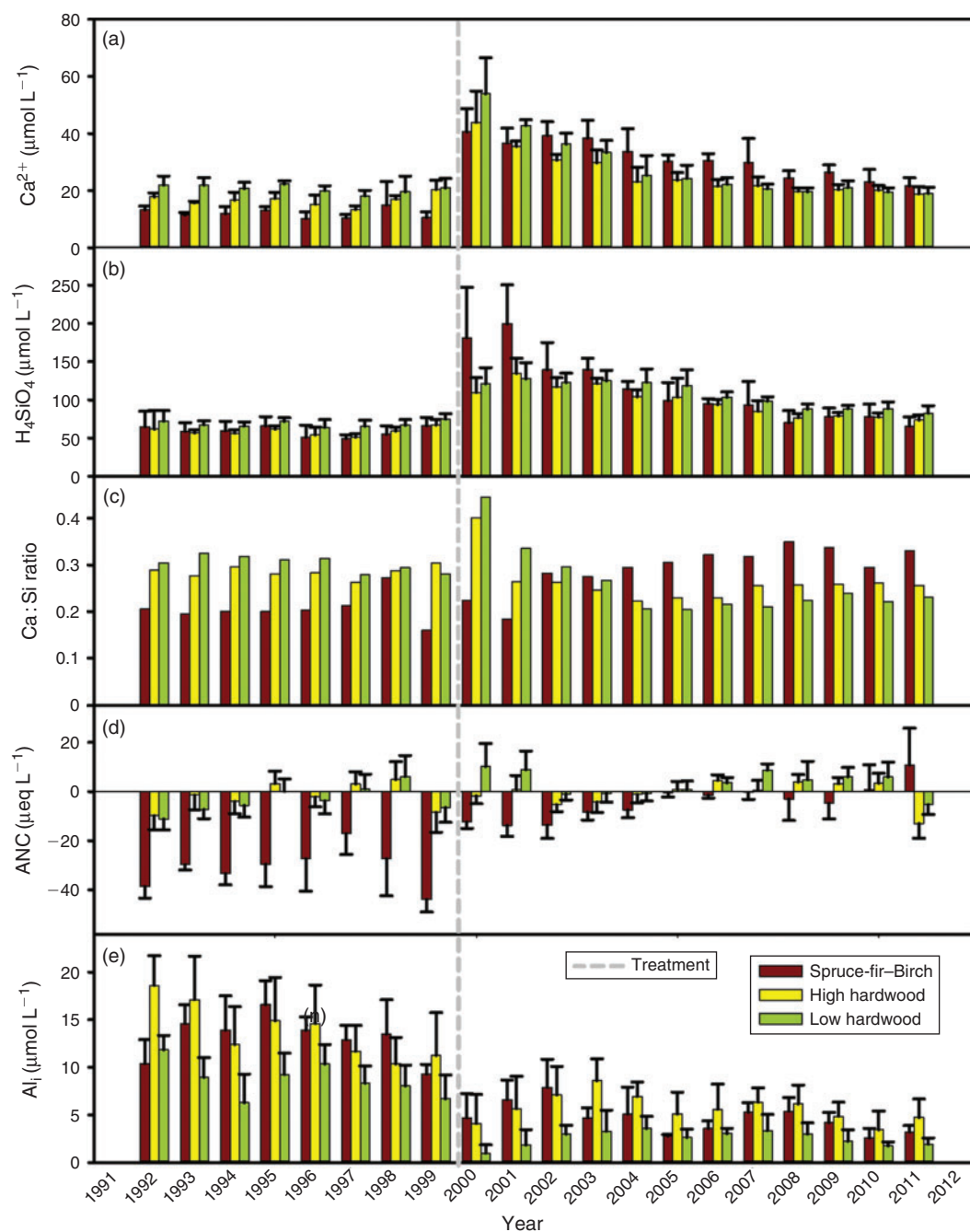


Fig. 2. Spatial and temporal patterns in concentrations of Ca, H_4SiO_4 , Ca:Si, acid-neutralising capacity (ANC) and Al_i in stream water from Watershed 1 (W1) of the Hubbard Brook Experimental Forest (HBEF). Data are shown for three elevation zones: the spruce-fir-white birch zone (SFB), the high-elevation hardwood zone (HH) and the low-elevation hardwood zone (LH). Wollastonite was added in October 1999. Annual mean values are expressed on a water year basis (from 1 October to 30 September). Error bars represent standard deviations for each water year. The vertical line separates the pretreatment and post-treatment periods.

remain potentially harmful for aquatic organisms.^[5] During the pretreatment period (1999), the average ANC in the SFB sub-watershed was much lower than the average ANC in the HH and LH sub-watersheds (SFB: $-33.9 \pm 23.1 \mu\text{eq L}^{-1}$, HH: $-11.1 \pm 9.4 \mu\text{eq L}^{-1}$, LH: $-6.3 \pm 9.4 \mu\text{eq L}^{-1}$). At the end of study period (2011), the ANC values in the SFB sub-watershed remained significantly higher than pretreatment values, whereas the ANC in the HH and LH sub-watersheds were similar

to the pretreatment values (SFB: $10.9 \pm 43.3 \mu\text{eq L}^{-1}$, HH: $-11.9 \pm 13.3 \mu\text{eq L}^{-1}$, LH: $-5.1 \pm 16.4 \mu\text{eq L}^{-1}$).

The concentrations of Al_i decreased significantly in stream water of all three sub-watersheds in response to the CaSiO_3 addition (Figs 2, 3). The LH sub-watershed had the lowest Al_i concentration among three sub-watersheds. By 2011, Al_i concentrations in all the sub-watersheds (SFB: $3.2 \pm 0.7 \mu\text{mol L}^{-1}$, HH: $4.3 \pm 2.2 \mu\text{mol L}^{-1}$, LH: $1.9 \pm 1.0 \mu\text{mol L}^{-1}$) were

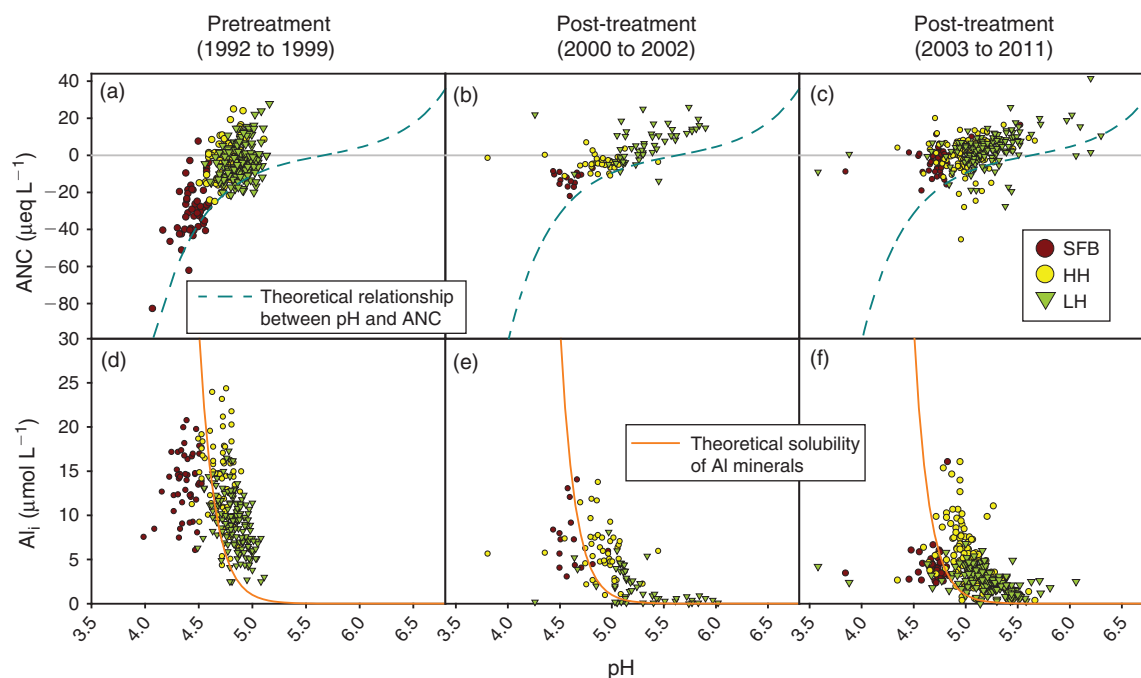


Fig. 3. Relationships between pH and acid-neutralising capacity (ANC), and pH and Al_i in stream water of Watershed 1 (W1) at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire before and after wollastonite treatment. Data are shown for three elevation zones: the spruce-fir-white birch zone (SFB), the high-elevation hardwood zone (HH) and the low-elevation hardwood zone (LH). Indicated values of acidification status are shown $\text{pH} < 5.5$,^[39] $\text{ANC} < 0 \mu\text{eq L}^{-1}$ ^[5] and $\text{Al}_i > 2 \mu\text{mol L}^{-1}$.^[5] Theoretical relationship between pH and ANC is shown for open system that has partial pressure of carbon dioxide ($p\text{CO}_2$) = $\sim 32 \text{ Pa}$ ($10^{-3.5} \text{ atm}$). Theoretical relationship between pH and Al_i is shown for the logarithm of the mineral solubility constant (K_{s0}) of $\text{Al}(\text{OH})_3 = 8.99$.

significantly lower than in the pretreatment period (SFB: $13.1 \pm 2.3 \mu\text{mol L}^{-1}$, HH: $13.9 \pm 2.9 \mu\text{mol L}^{-1}$, LH: $8.7 \pm 1.8 \mu\text{mol L}^{-1}$). However, Al_i concentrations remained above $2 \mu\text{mol L}^{-1}$ for many of the observations, a level that is potentially toxic to aquatic organisms.^[5]

Solute fluxes

Soil solutions draining the Oa, Bh and Bs horizons showed low fluxes of Ca and dissolved Si and high fluxes of H^+ and Al_i before CaSiO_3 treatment (Fig. 4; Table 2). The fluxes of Ca, dissolved Si and H^+ decreased with increasing soil depth in all sub-watersheds before and after treatment, whereas the fluxes of Al_i had a pattern of increasing flux with soil depth (Fig. 4). The CaSiO_3 addition resulted in increases in the fluxes of Ca and dissolved Si, and decreases in the fluxes of H^+ and Al_i throughout the soil profile in W1 (Fig. 4). The fluxes of Ca in soil solutions draining all soil horizons gradually increased during the first 3 years after treatment (2000–02). In contrast, the fluxes of dissolved Si rapidly increased immediately following the treatment and then decreased slightly through 2011 in all sub-watersheds. The decreases in the fluxes of H^+ and Al_i in soil solutions draining all soil horizons were most evident in the first 3 years after CaSiO_3 addition (2000 to 2002), and then the fluxes of H^+ and Al_i remained stable through 2011 (Fig. 4).

The stream water in W1 exhibited low fluxes of Ca and dissolved Si, and high fluxes of H^+ and Al_i before CaSiO_3 treatment. The CaSiO_3 addition resulted in increases in fluxes of Ca and dissolved Si, and decreases in fluxes of H^+ and Al_i in stream water (Fig. 5). These patterns were most evident in the SFB sub-watershed. The fluxes of Ca increased 198 % in the SFB zone, 173 % in the HH zone and 133 % in the LH zone immediately following the treatment (2000) compared with

average pretreatment fluxes (1992–99). The SFB sub-watershed had the highest average Ca fluxes during the post-treatment period (2000–11) (SFB: $29.9 \pm 4.2 \text{ mmol m}^{-2} \text{ year}^{-1}$, HH: $24.9 \pm 3.9 \text{ mmol m}^{-2} \text{ year}^{-1}$, LH: $26.4 \pm 3.2 \text{ mmol m}^{-2} \text{ year}^{-1}$). The fluxes of dissolved Si increased in all sub-watersheds after the treatment. The SFB sub-watershed was the most responsive to CaSiO_3 addition, with dissolved Si increasing by 176 % compared with average pretreatment fluxes (HH: +61 %, LH: +53 %) (1992–99). The fluxes of H^+ and Al_i in all sub-watersheds decreased immediately following the CaSiO_3 addition (Fig. 5). There were marked increases in H^+ fluxes in all sub-watersheds in 2003, resulting from low pH associated with elevated discharge (132 mm) during the snow-melt period in late March of that year. The mean fluxes of Al_i in the post-treatment period (2000 to 2011) decreased 64 % in the SFB zone, 55 % in the HH zone and 70 % in the LH zone compared with pretreatment (1992 to 1999) fluxes.

Discussion

Acidification indicators

Several chemical parameters are used to indicate the acid-base status of drainage waters. Cronan and Grigal^[38] suggested that molar Ca : Al ratios in soil solutions below 1 are indicative of acidification stress in forest soils and may be indicative of conditions that could impair the health of forest vegetation. Prior to treatment, Ca : Al_i ratios were below 1 in the SFB zone and low but somewhat above 1 in the HH zone, particularly in the mineral soil waters. Following treatment, we observed marked increases in Ca : Al_i , particularly in Oa horizons (Fig. 1). Juice et al.^[14] reported marked improvements in regeneration of sugar maple in response to CaSiO_3 treatment and Battles et al.^[16] saw a recovery of tree biomass increment of sugar maple. The

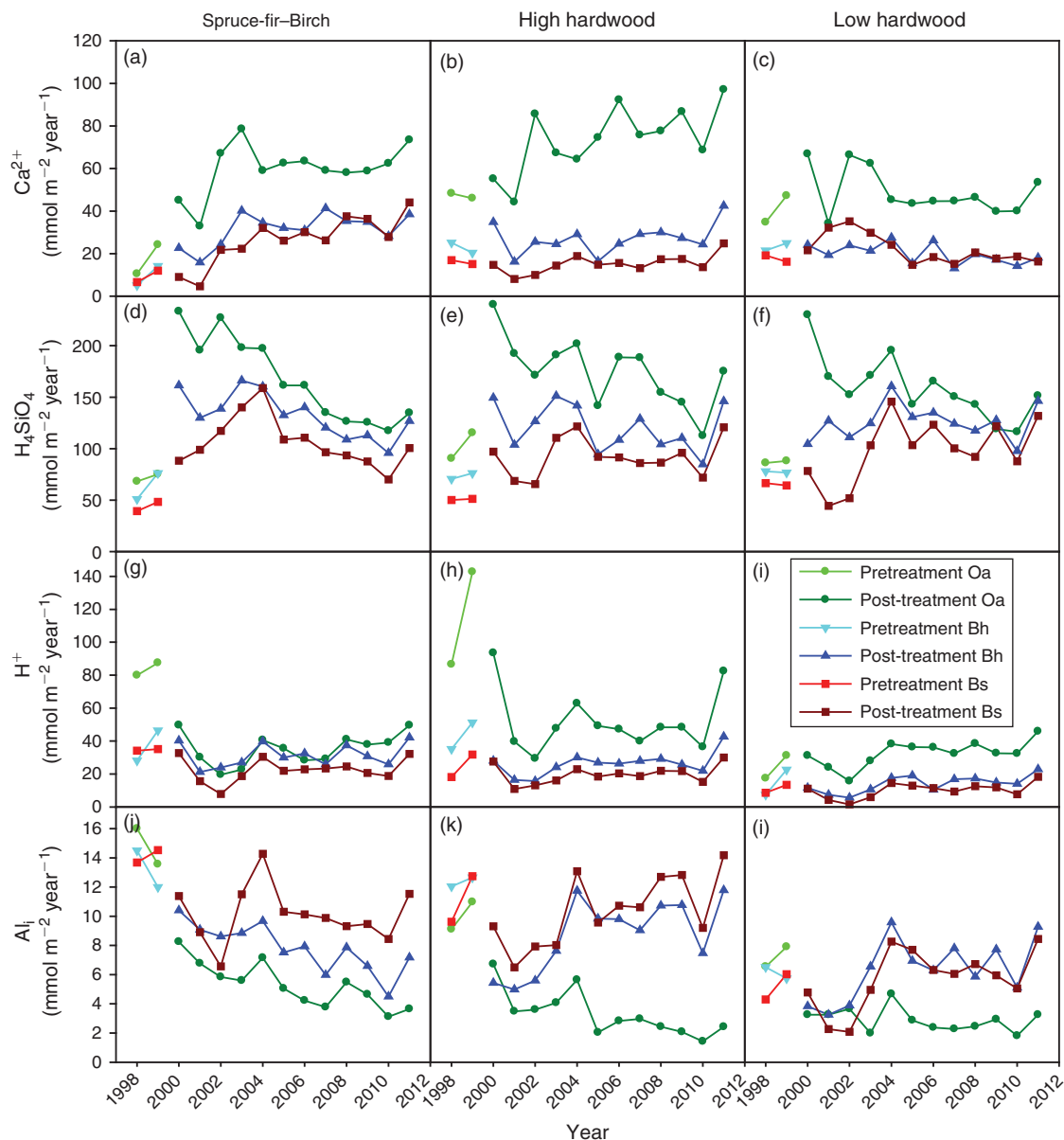


Fig. 4. Solute fluxes (Ca , H_4SiO_4 , H^+ and Al_i) in soil solution in three sub-watersheds of Watershed 1 (W1) at the Hubbard Brook Experimental Forest (HBEF) before and after treatment. Data are shown for three elevation zones: the spruce-fir-white birch zone (SFB), the high-elevation hardwood zone (HH) and the low-elevation hardwood zone (LH). Wollastonite was added in October 1999. Annual mean values are expressed on a water year basis (from 1 October to 30 September).

improved Ca nutrition also promoted higher aboveground net primary production and increased the photosynthetic surface area in the treated watershed relative to a reference watershed. These results suggest that $\text{Ca} : \text{Al}_i$ near 1 or maybe somewhat above 1 is indicative of conditions of acidification stress to sugar maple.

Stream water is considered acidic when its pH is below 5.5^[39]; stream water exhibits chronic acidification when ANC is less than $0 \mu\text{eq L}^{-1}$ ^[5]; and stream water is potentially toxic to aquatic biota when concentrations of Al_i exceed $2 \mu\text{mol L}^{-1}$ ^[5]. According to these acidification indicators, stream water in W1 was routinely acidic and had potential toxicity to aquatic biota before the CaSiO_3 addition. All stream water samples collected before CaSiO_3 treatment had pH less than 5.5 and concentrations of Al_i were above $2 \mu\text{mol L}^{-1}$. In addition, most stream water samples had ANC values below $0 \mu\text{eq L}^{-1}$; the range of

stream water ANC was from -83 to 26 before CaSiO_3 addition (Fig. 3).

After CaSiO_3 treatment, stream water generally had higher pH and ANC values and lower concentrations of Al_i compared with pretreatment values, which indicates that the conditions of acidification and Al_i toxicity were improved for stream water in W1. In particular, stream water in the LH sub-watershed showed some alleviation of acidification and Al_i toxicity (Fig. 3). The CaSiO_3 treatment clearly shifted the acid-base status of the watershed to higher values of ANC, with some values, particularly in the LH zone, above the inflection point of positive ANC. In general, the measured ANC was greater than the values predicted by assuming equilibrium with atmospheric CO_2 at a given pH (Fig. 5). This discrepancy is likely due to the presence of naturally occurring organic anions, hydrolysed forms of Al_i and, to a lesser extent, bicarbonate associated with the elevated

Table 2. Ca fluxes of soil solutions draining Oa, Bh and Bs horizons and stream water in Watershed 1 (W1)Each value represents the annual flux of Ca in W1 (weighted average of three sub-watersheds). 1998 represent the water year from Oct 1997 to Sep 1998. Uncertainties (\pm) are standard deviations

Ca flux (mmol m ⁻² year ⁻¹)	Year													
	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
Oa horizon	31.2 ± 19.1	39.2 ± 13.0	55.7 ± 10.9	37.2 ± 6.2	73.0 ± 10.9	69.5 ± 8.3	56.2 ± 9.9	60.2 ± 15.6	66.8 ± 24	59.9 ± 15.5	60.7 ± 15.8	61.8 ± 23.6	57.0 ± 15.0	74.7 ± 21.8
Bh horizon	17.3 ± 10.7	19.9 ± 5.4	27.2 ± 6.6	17.1 ± 1.9	24.6 ± 0.9	28.7 ± 10.1	30.4 ± 3.7	21.3 ± 9.3	27.3 ± 3.3	27.9 ± 14.2	28.4 ± 7.9	26.5 ± 8.9	22.3 ± 7.3	33.0 ± 13.1
Bs horizon	14.3 ± 6.7	14.5 ± 2.2	15.1 ± 6.3	15.0 ± 11.2	22.3 ± 12.6	22.2 ± 7.7	25.0 ± 6.6	18.5 ± 6.5	21.4 ± 7.7	18.2 ± 7.0	25.2 ± 10.9	23.8 ± 10.8	20.0 ± 7.2	28.4 ± 9.5
Stream water	16.2 ± 1.3	15.3 ± 5.2	40.2 ± 5.7	20.2 ± 2.1	20.5 ± 2.6	26.7 ± 3.1	32.4 ± 6.1	25.3 ± 2.9	29.1 ± 6.0	24.2 ± 4.8	26.1 ± 3.0	28.4 ± 4.1	21.7 ± 2.2	29.8 ± 2.6

partial pressure of CO_2 above atmospheric values that contribute to ANC in natural waters.^[40] The patterns of decreasing acidity and Al_i after CaSiO_3 treatment are consistent with the pH-dependent mobilisation of Al_i . This is also consistent with the close correspondence between annual H^+ fluxes and annual Al_i fluxes in soil solution and stream water (Figs 4, 5).

The concentrations of Al_i were negatively correlated with pH in W1 before ($r = -0.44$, $P < 0.001$) and after (2000 to 2002: $r = -0.57$, $P < 0.001$; 2003 to 2011: $r = -0.47$, $P < 0.001$) CaSiO_3 treatment (Fig. 3). After treatment, the concentrations of Al_i in all three sub-watersheds decreased. In particular, stream water in the LH sub-watershed showed some alleviation of conditions of Al toxicity (i.e. $\text{Al}_i < 2 \mu\text{mol L}^{-1}$). The magnitudes of the slopes of the Al_i v. pH relationships in the post-treatment period (-4.2 in 2000–02; -4.3 in 2003–11) were less than in the pretreatment period (-9.3). This pattern is generally consistent with the theoretical pH-dependent solubility of Al minerals, in which Al_i approaches a solubility minimum near pH 6.^[41] In the HH and LH zones, the stream water shows a pH-dependent pattern that is consistent with the theoretical solubility of $\text{Al}(\text{OH})_3$. In the SFB sub-watershed, the Al_i concentrations also decreased in response to the CaSiO_3 treatment, but in contrast to hardwood drainage reaches, these solutions were generally undersaturated with respect to the solubility of Al minerals (Fig. 3).

The fate of wollastonite-derived calcium and silica

In order to trace the release of CaSiO_3 -derived Ca and Si and their transport through the soil profile, we defined the ‘added’ Ca and Si flux as the amount of Ca and Si derived from the dissolution of applied CaSiO_3 . This value was computed by subtracting the average pretreatment Ca and Si fluxes (soil solution: 1998 to 1999; stream water: 1992 to 1999) from the post-treatment Ca and Si fluxes. Using this approach, we estimated the amount of the dissolved Ca and Si derived from added CaSiO_3 leaving each soil horizon (Table 3). We compare the added Ca fluxes with changes in soil Ca pools in W1^[24] and with a conceptual model of the phases of CaSiO_3 dissolution on W1 hypothesised by Nezat et al.^[37]

Nezat et al.^[37] proposed that the elevated Ca in stream water during the first year after CaSiO_3 treatment was largely due to dissolution of CaSiO_3 deposited directly in the stream channel during the helicopter application. The fluxes of Ca associated with the added CaSiO_3 leaving in stream water were indeed greater than the added Ca flux from the Bs horizon (Bs: $0.7 \text{ mmol m}^{-2} \text{ year}^{-1}$; stream: $24.4 \text{ mmol m}^{-2} \text{ year}^{-1}$) in 2000. In 2001, added Ca fluxes in soil solutions and stream waters both decreased, with the added Ca leaving the Bs horizon remaining much lower than added Ca in stream water (Bs: $0.6 \text{ mmol m}^{-2} \text{ year}^{-1}$; stream: $4.4 \text{ mmol m}^{-2} \text{ year}^{-1}$). This pattern is consistent with Ca release from the exchange pool in the hyporheic zone or dissolution of residual CaSiO_3 in the stream channel, as suggested by Nezat et al.^[37] In later years (2002–10), we observed elevated added Ca fluxes from the forest floor and mineral soil solutions. These patterns indicate that during this period, the added Ca penetrated deeper in the soil profile and contributed to the increases in Ca fluxes of stream water. Our analysis of the dynamics of added Ca within the soil is thus generally consistent with conceptual model of Nezat et al.^[37] of three phases of CaSiO_3 dissolution.

By the end of 2010, the cumulative amount of added Ca leaving the forest floor in soil solution ($271.2 \text{ mmol m}^{-2}$) was

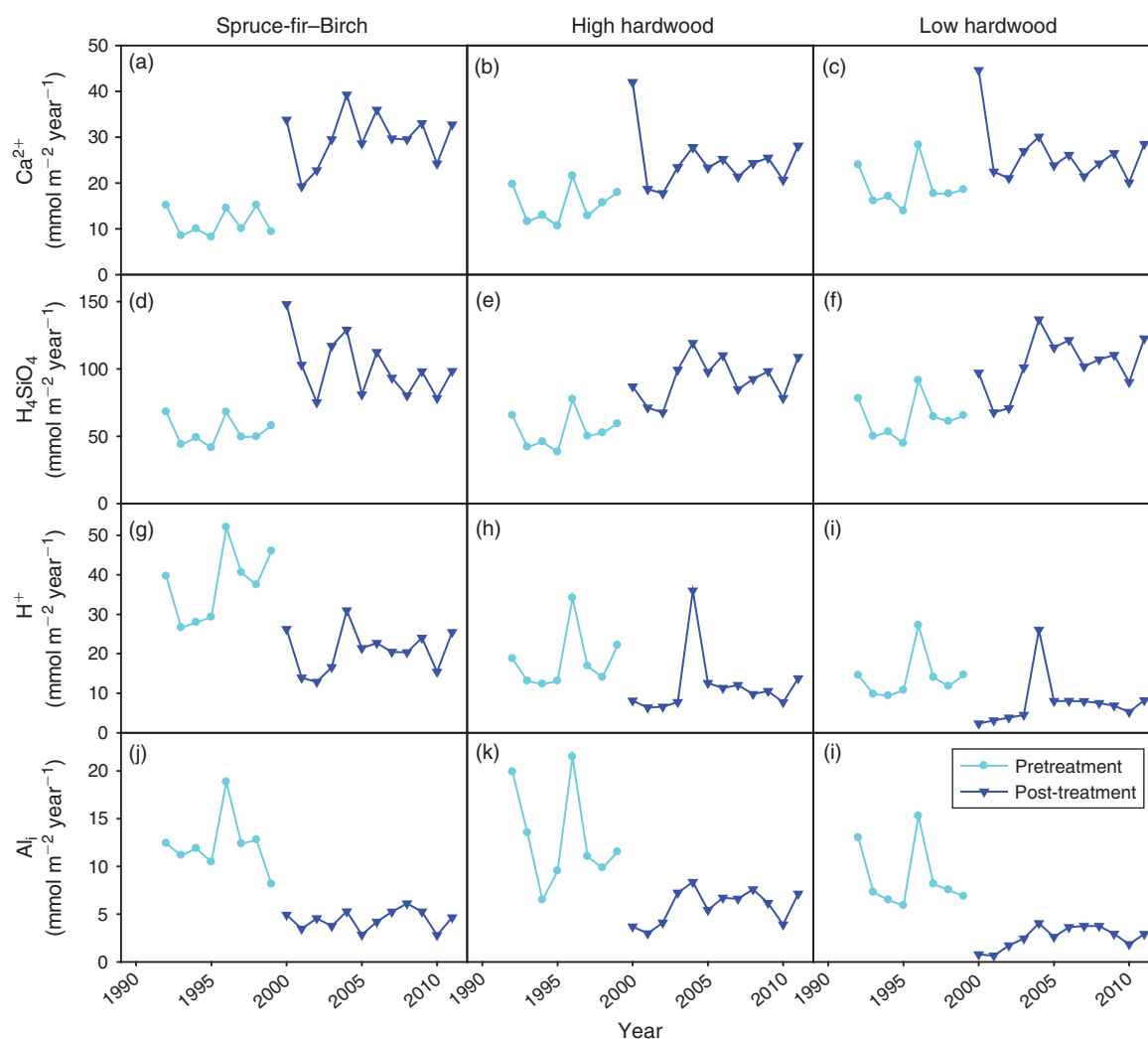


Fig. 5. Solute fluxes (Ca , H_4SiO_4 , H^+ and Al_i) of stream water in three sub-watersheds of Watershed 1 (W1) at the Hubbard Brook Experimental Forest (HBEF) before and after treatment. Data are shown for three elevation zones: the spruce-fir-white birch zone (SFB), the high-elevation hardwood zone (HH) and the low-elevation hardwood zone (LH). Wollastonite was added in October 1999. Annual mean values are expressed on a water year basis (from 1 October to 30 September).

Table 3. The amount of Ca derived from the dissolution of applied wollastonite ('added' Ca fluxes) leaving Oa, Bh and Bs horizons and stream water in Watershed 1 (W1)

These values were calculated by subtracting average pretreatment Ca fluxes (soil solution: 1998 to 1999; stream water: 1992 to 1999) from annual post-treatment Ca fluxes. The three phases of wollastonite dissolution suggested by Nezat et al.^[37] are given for perspective

Ca ($\text{mmol m}^{-2} \text{ year}^{-1}$)	Year											Total
	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	
Three phases of wollastonite dissolution ^[37]	In-stream dissolution	Hyporheic exchange period							Infiltration period			
Oa horizon	20.5	2	37.8	34.3	21	25	31.6	24.7	25.5	26.6	21.9	270.9
Bh horizon	8.7	-1.4	6.1	10.1	11.9	2.8	8.8	9.3	9.8	7.9	3.7	77.6
Bs horizon	0.7	0.6	7.9	7.8	10.6	4.2	7	3.8	10.8	9.5	5.7	68.5
Stream water	24.4	4.4	4.8	10.9	16.7	9.6	13.4	8.5	10.3	12.6	6	121.7

much smaller than the amount of Ca applied to W1 in the 1999 treatment (2570 mmol m^{-2}). Johnson et al.^[24] reported that the pool of total Ca in the forest floor in 2010 was $642.5 \text{ mmol m}^{-2}$ greater than pretreatment values (1998). Thus, $1662.5 \text{ mmol m}^{-2}$ of Ca added from CaSiO_3 has been exported from the O horizon

by other means. Possible mechanisms include Ca uptake from forest floor horizons by vegetation,^[42,43] undissolved CaSiO_3 particles remaining in the forest floor or migrating to the mineral soil, and lateral transport of added Ca from the forest floor to stream water, bypassing the Oa-horizon lysimeters.

Table 4. The amount of Si derived from the dissolution of applied wollastonite ('added' Si fluxes) leaving Oa, Bh and Bs horizons and stream water in Watershed 1 (W1)

These values were calculated by subtracting average pretreatment Si fluxes (soil solution: 1998 to 1999; stream water: 1992 to 1999) from annual post-treatment Si fluxes

Si flux (mmol m ⁻² year ⁻¹)	Year												Total
	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	
Oa horizon	147.2	98.7	96.3	99.4	110.9	61.4	84.6	70.6	54	42.6	28.2	66.4	960.2
Bh horizon	67	48.9	54.1	76	82.9	47.8	56.5	53.1	38.8	45.6	21.3	68.3	660.3
Bs horizon	34.5	17.3	24.9	64.5	88.6	48	55.1	40.9	37.3	48.4	23.2	64.3	546.9
Stream water	53	23	13.5	48.2	70.6	40.5	56.9	35.7	35.5	44.6	24.6	52.2	498.4

Table 5. The molar ratio of wollastonite-derived (added) Ca : Si in Oa, Bh and Bs horizon soil solutions and stream water in Watershed 1 at the Hubbard Brook Experimental Forest

These values were calculated by subtracting average pretreatment Ca and Si fluxes (soil solution: 1998 to 1999; stream water: 1992 to 1999) from annual post-treatment fluxes

Ca to Si ratio	Year												Mean
	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	
Oa horizon	0.14	0.02	0.39	0.34	0.19	0.41	0.37	0.35	0.47	0.62	0.78	0.59	0.32
Bh horizon	0.13	-0.03	0.11	0.13	0.14	0.06	0.16	0.18	0.25	0.17	0.17	0.21	0.14
Bs horizon	0.02	0.04	0.32	0.12	0.12	0.09	0.13	0.09	0.29	0.2	0.24	0.22	0.15
Stream water	0.46	0.19	0.36	0.23	0.24	0.24	0.24	0.24	0.29	0.28	0.24	0.27	0.27

The CaSiO₃-derived Ca exported in forest floor (Oa) soil solutions through 2010 was 193.3 mmol m⁻² greater than the export of CaSiO₃-derived Ca from Bh soil solutions (Table 3). Johnson et al.^[24] did not observe a significant difference in total Ca in the top 10 cm of mineral soil collected in 1998 and 2010. Thus, the difference in added Ca fluxes in Oa and Bh soil solutions must be explained by Ca uptake by vegetation from the upper mineral soil and lateral flow of soil water. The difference between the amount of added Ca leaving upper mineral soil (Bh) and leaving the lower mineral soil (Bs) via soil solution from 2000 to 2010 was small (9.3 mmol m⁻²), suggesting that little accumulation of added Ca has occurred in deeper mineral horizons to date.

Eleven years after the treatment (2010), the total amount of added Ca exported in stream water was 122.5 mmol m⁻², which represents 4.7% of the initially applied CaSiO₃. Thus, 2447.5 mmol m⁻² of the added Ca still remained in the ecosystem 11 years after the application. Johnson et al.^[24] measured a net accumulation in total Ca of 625.0 mmol m⁻² in the forest floor and upper mineral soil between 1998 and 2010; much of this accumulation was in the Oie layers, probably derived largely by recycling of 'added' litter Ca. Therefore, ~1822.5 mmol m⁻² of the added Ca was transported to lower mineral soils in dissolved form (77.6 mmol m⁻², Table 3) or in particulate form, or was assimilated by forest vegetation and incorporated into the internal Ca cycle of W1. This value is similar to the amount of Ca in living biomass in the watershed before the treatment (1877.5 mmol m⁻²[9]). Although it is likely that some of the added Ca was retained in forest vegetation, it seems unlikely that this sink for Ca can explain the entire discrepancy in the Ca mass balance. Possible explanations of this discrepancy include overestimation of applied CaSiO₃, although Peters et al.^[22] found good agreement between the quantity of CaSiO₃ applied by helicopter and that deposited to the forest floor immediately after treatment, an underestimation of the change in soil pools and underestimation of stream Ca losses.

We also calculated the total amount of added (i.e. CaSiO₃-derived) Si leaving each horizon and in stream water (Table 4). By the end of 2010, 892.8 mmol m⁻² of added Si had been exported from the Oa horizon, ~35 % of the Si added to W1 in 1999 (2571 mmol m⁻²). The amount of added Si leaving the Bh horizon, Bs horizon and stream were 589.2, 482.5 and 446.8 mmol m⁻² respectively. Thus, 2125 mmol m⁻² of the added Si still remained in the ecosystem 11 years after the application, which represents 83 % of the Si applied in 1999. The molar ratio of added Ca : Si in Oa-horizon leachate was small in the first 2 years after the treatment (0.14 and 0.02), then increased over time (Table 5). These initially low ratios may be due to the substantial amount of Ca that was retained as exchangeable Ca in the soil,^[24] while much of the dissolved Si derived from CaSiO₃ dissolution remained in soil solutions. The molar ratio of added Ca : Si in Bh and Bs horizon leachates was lower than in Oa-horizon leachate (Oa: 0.32, Bh: 0.14, Bs: 0.15), possibly owing to retention of exchangeable Ca in upper mineral horizons.

Landscape patterns

The response of watershed solutions to the CaSiO₃ treatment was spatially heterogeneous. Treatment effects were most evident in the SFB sub-watershed (Table S7). The SFB sub-watershed is characterised by gentle topography, shallow soil and till, and elevated concentrations of organic acids.^[25] These characteristics all likely contribute to a higher CaSiO₃ dissolution rate.^[26]

The enhanced dissolution of CaSiO₃ in the SFB zone was evident in the post-treatment trends. Fluxes of Ca increased and Al_i decreased continuously in soil solutions of the SFB sub-watershed for the duration of the study period (Fig. 4). This pattern also occurred in the HH zone for Ca, but the decrease in Al_i flux only occurred in the Oa horizon. In contrast, fluxes of dissolved Si increased in Oa solutions immediately after the treatment and decreased for the duration of the study period in

all zones. Fluxes of dissolved Si in mineral soil solutions increased for a few years after the treatment (2000 to 2005) and have decreased in recent years.

The contrasting patterns of Ca and dissolved Si concentrations and fluxes may reflect differences in the fate of these solutes. A substantial fraction of the Ca released from CaSiO_3 was initially retained on the soil-exchange complex owing to the mass action of the added Ca plus an increase in the cation-exchange capacity due to deprotonation of soil functional groups.^[24,26] The added Ca appears to be steadily migrating downward through the soil profile, with binding on soil-exchange sites and recycling by vegetation attenuating its transport. Although dissolved Si can also be recycled by trees and retained as secondary minerals, its temporal pattern suggests that its transport through soil experiences less attenuation than Ca.

We observed a short-term decrease in fluxes of H^+ and Al_i in 1999 to 2000 in all soil solutions. Fluxes of Al_i have continued to decrease in Oa-horizon solutions in all zones (particularly the SFB and HH), while Al_i fluxes in mineral soil solutions appear to be rebounding after the short-term decrease. The naturally elevated H^+ concentrations in soil solutions in the high-elevation SFB and HH zones facilitate CaSiO_3 dissolution. Additionally, elevated concentrations of dissolved organic carbon (DOC) in SFB soil solutions are indicative of high concentrations of organic acids, which also promote mineral dissolution.^[25] The LH sub-watershed has deeper soil than the SFB sub-watershed and less steep slopes than the HH sub-watershed, increasing the contact time between percolating water and mineral soil.^[25] This extended contact time increases the opportunity for Ca to exchange and for Si to precipitate on soil surfaces, thus delaying the response of soil solutions and stream water to the treatment (Figs 4, 5). In addition, the lower H^+ fluxes of the soil solutions and stream water draining the LH resulted in the lower Al_i fluxes in this sub-watershed, partly due to the lower solubility of Al at higher pH (Fig. 3).^[25]

The average Ca fluxes in stream water after the treatment were higher than those draining the Bs horizon (Table 2). In contrast, the average fluxes of H^+ and Al_i of the stream water were lower than those draining the Bs horizon (Figs 4, 5). These patterns may suggest that additional Ca flux is generated, and H^+ and Al_i are immobilised, in deep mineral horizons below the Bs. Also, release of added Ca from riparian areas and the hyporheic zone, or enhanced transport of Ca-rich soil water through shallow hydrologic flowpaths that bypass the lower mineral soil could contribute to the higher stream Ca fluxes.

Conclusions

Wollastonite treatment significantly increased the concentrations and fluxes of Ca, dissolved Si and ANC, and significantly decreased the concentrations and fluxes of Al_i in both soil solutions and stream water in three different elevation zones of W1 for 12 years after the treatment. The treatment effects were most pronounced in the high-elevation SFB sub-watershed. Wollastonite treatment significantly improved the acid-base status of soil solutions and stream water. After the treatment, stream water tended to be less acidic and these results are generally consistent with theoretical relationships for ANC and Al (OH)₃ solubility. In particular, soil solutions in the upper soil and stream water in the low-elevation zone showed some alleviation of conditions of acidification and Al_i toxicity. Approximately 4.7% of the added Ca was exported from W1 through

stream water and 67.9% of added Ca remained undissolved or assimilated by vegetation in the first 12 years after treatment. A discrepancy was evident between changes in soil pools of available Ca and losses from soil solution, suggesting that a substantial fraction of the added Ca has been assimilated by forest vegetation or transported in particulate form into mineral horizons. The high retention of Ca in the ecosystem after 12 years suggests that CaSiO_3 addition is an effective alternative for replacing Ca depleted from forest soils by chronic acid deposition and to facilitate the recovery of acid-impaired ecosystems.

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