

9-2010

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Recommended Citation

Cho, Youngil, Charles T. Driscoll, Chris E. Johnson, and Thomas G. Siccama. 2009. "Chemical Changes in Soil and Soil Solution after Calcium Silicate Addition to a Northern Hardwood Forest." *Biogeochemistry* 100 (1-3): 3–20. doi:10.1007/s10533-009-9397-6.

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**Chemical Changes in Soil and Soil Solution after Calcium Silicate Addition to
a Northern Hardwood Forest**

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Published in *Biogeochemistry*, volume 100, pages 3-20 (2010)

Abstract

Liming has been used to mitigate effects of acidic deposition in forest ecosystems. This study was designed to examine the effects of calcium (Ca) supply on the spatial patterns and the relations between soil and soil solution chemistry in a base-poor forest watershed. Watershed 1 at the Hubbard Brook Experimental Forest in New Hampshire, USA was experimentally treated with wollastonite (CaSiO_3) in October, 1999. Exchangeable Ca (Ex-Ca), soil pH_s (in 0.01M CaCl_2), effective cation exchange capacity (CEC_e), and effective base saturation (BS_e) increased, while exchangeable acidity (Ex-Acid) decreased in organic soil horizons in 2000 and 2002. Mineral soils experienced either small increases in Ex-Ca, pH_s , CEC_e , BS_e , small decreases in Ex-Acid or no changes. Thus, most of the added Ca remained in the forest floor during the study period. Prior to the treatment the BS_e decreased with increasing elevation in organic and mineral soil horizons. This spatial pattern changed significantly in the forest floor after the treatment, suggesting that soils at higher elevations were more responsive to the chemical addition than at lower elevations. Soil solutions draining the forest floor responded to the treatment by increases in concentrations of Ca, dissolved silica, pH, and acid neutralizing capacity (ANC), and a decrease in inorganic monomeric Al (Al_i). Treatment effects diminished with increasing soil depth and decreasing elevation. Positive correlations between Ca/Al_m in soil solution and Ex-Ca/Ex-Al ratios in soil indicated that changes in the chemistry of soils significantly influenced the chemistry of soil water, and that Ca derived from the dissolution of wollastonite mitigated the mobilization of Al within the experimental watershed.

Key words: calcium, Hubbard Brook Experimental Forest, soil, soil solution, wollastonite

Introduction

Elevated atmospheric deposition of strong acid anions (e.g. SO_4^{2-} , NO_3^-) during the 20th century and continuing today contributes to the acidification of base-poor northern hardwood forests in the northeastern U.S. (Likens et al. 1996; Warby et al. 2005, 2009). SO_4^{2-} is the dominant anion in atmospheric deposition and drainage waters at Hubbard Brook (Likens et al. 2001). The forest floor of watersheds at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire (NH), and many other regions in the northeastern U.S. are acidic, with limited ability to neutralize strong acid inputs by the supply of base cations (e.g. Ca^{2+} , Mg^{2+} , Na^+ , and K^+) due to minimal mineral weathering and/or low concentrations of exchangeable basic cations in the O horizon (Lawrence et al. 1995; Likens et al. 1996). Sulfate exhibited pH-dependent adsorption in mineral soil (Nodvin et al. 1988). Mineral soils at the HBEF have shown depletion of exchangeable Ca and this depletion has resulted in the mobilization of elevated concentrations of Al to the O horizon and drainage waters (Likens et al. 1998; Palmer et al. 2004). These conditions may stress forest vegetation (Hawley et al. 2006; Juice et al. 2006) and limit the recovery of acid-impacted surface waters (Likens et al. 2001; Driscoll et al. 2001).

Calcium is a major base cation in soils and drainage waters at Hubbard Brook soils and in most other regions, and is an important element for wood formation (Lawrence et al. 1995). The HBEF has exhibited depletion of Ca from the forest floor (Lawrence et al. 1995; Palmer et al. 2004) and low base saturation (BS) in mineral soil horizons (Johnson et al. 1991b). In addition, soils in the watersheds at the HBEF have thicker forest floor and shallow soil depth at higher elevations, and deeper deposits of glacial till at lower elevations (Likens et al. 1998; Johnson et

al. 2000). Consequently, understanding elevational and horizontal variations of the Ca supply across the landscape is important to elucidate responses of watershed ecosystems to atmospheric acidic deposition and potential mitigation strategies.

The application of basic materials such as CaCO_3 has been used as a management approach to improve the acid-base status of forest and aquatic ecosystems by increasing exchangeable Ca, cation exchange capacity, and decreasing exchangeable Al concentrations in soils (Blette & Newton 1996). Previous studies of base additions to forest soils from the 1970s to the 1990s have shown: (1) changes in the composition of the soil decomposer community and increases in microbial activity (Zelles et al. 1987; Illmer & Schinner 1991); (2) increases in mineralization of soil organic carbon and changes in nitrogen mineralization (Adams et al. 1978; Marschner et al. 1989); (3) increases in nitrification (Tamm & Popovic 1989); (4) changes in species distribution and abundance of soil invertebrates (Persson 1988); (5) changes in root growth, and plant nutrient uptake and productivity (Smallidge et al. 1993); and (6) improvements in the acid-base status of drainage waters and the composition of the aquatic biotic communities (Baker & Christensen 1991; Driscoll et al. 1996).

In October, 1999 a readily weatherable calcium silicate mineral, wollastonite (CaSiO_3), was added to watershed 1 (W1) at the HBEF to enhance the supply of Ca to the forest ecosystem. Supplying Ca by the dissolution of a calcium silicate mineral is similar to the natural weathering source of this element at Hubbard Brook, and is an alternative to the liming approach used in other studies (Adams and Dickson 1973; Cirimo and Driscoll 1996; Nihlgard et al. 1988; Nodar et al. 1992). Cho et al (2009) observed the wollastonite treatment mitigated episodic acidification in streamwater during summer storm events. In addition, Hawley et al (2006) and Juice et al (2006) found that foliar (i.e. red spruce) winter injury in W1 was reduced in comparison with red

spruce foliage in W6 and that regeneration of sugar maples increased markedly in the treated watershed as compared with the untreated reference watershed.

This research focused on investigating the effects of the Ca supply on soil and soil solution chemistry in organic and mineral soil horizons of W1, examining the linkage between soil and soil solution chemistry. To investigate these effects, we made spatially and temporally detailed and coupled measurements of soil and soil solution chemistry by horizon and along the elevational gradient of W1 to evaluate changes in the acid-base status of the watershed prior to and following the chemical treatment. We hypothesized that: (1) exchangeable Ca in soils would increase, decreasing exchangeable acidity; (2) the enhanced supply of Ca derived from the wollastonite dissolution would increase Ca^{2+} , pH, and acid neutralizing capacity (ANC) in soil waters; and (3) there would be longitudinal variations among subcatchments in the acid-base response to the wollastonite application.

Materials and Methods

Study site features

The HBEF is located in the southern portion of the White Mountain National Forest in central New Hampshire, USA. Watershed 1 has an area of 11.8 ha and an elevation range from 488 m to 747 m (Figure 1). The principal bedrock is the Silurian Rangely Formation which is comprised of metamorphic rocks of igneous and sedimentary origin: quartz mica schist and quartzite, interbedded with sulfidic schist and calc-silicate granulite (Johnson et al. 2000). The

soils at the HBEF are predominately Spodosols (Typic Haplorthods) derived from glacial till, and the average depths of the organic and the mineral soils are 7 cm and 50 cm, respectively (Johnson et al. 1991a, b; Johnson 2002). Mineral soils increase in depth with decreasing elevation, providing more opportunity for the neutralization of either strong acid anions from atmospheric deposition or organic anions naturally released from litter and organic soils (Palmer et al. 2004). In addition, the thickness of the forest floor increases at high elevations. The dominant vegetation type on W1 consists of northern hardwood species (sugar maple (*Acer saccharum*), American beech (*Fagus grandifolia*) and yellow birch (*Betula alleghaniensis*)) on the lower 90 % of the watershed, and a montane boreal transition forest of red spruce (*Picea rubens*), balsam fir (*Abies balsamea*) and white birch (*Betula papyrifera*) at high elevation (Likens & Bormann 1994). The climate at the HBEF is humid-continental, characterized by long, cold winters (average temperature for January is -9°C) and short cool summers (average for July is 10°C) with 1,400 mm of average annual precipitation, approximately 30% of which falls as snow (Federer et al. 1990). The Ca-treated watershed is located on a south-facing slope with average slope of 20-30% (Juice et al. 2006) and has three distinct landscape zones: (1) the higher elevation spruce-fir-white birch (SFB) zone which is characterized by relatively flat topography, shallow soils and flowpaths, bedrock outcrops, spruce-fir-white birch canopy trees, and 38% of the fine roots at O horizon (T.J. Fahey, Cornell University, unpublished data); (2) the high elevation hardwood (HH) zone which has steep slopes, deeper soils, often lying on bedrock with no C horizon, 33% of the fine roots at O horizon, and is dominated by deciduous vegetation; and (3) the lower elevation hardwood (LH) zone which is dominated by deeper soils, dense glacial till, deciduous canopy trees, and 42% of the fine roots at O horizon.

The application of wollastonite

The experimental addition of wollastonite to W1 was designed to restore the base saturation of the soil to a level estimated to have existed at the advent of acidic deposition (Likens et al. 1998; Gbondo-Tugbawa & Driscoll 2003). Wollastonite is similar in composition to the naturally occurring Ca-silicate minerals, such as plagioclase and hornblende, that occur at the HBEF (Likens et al. 1998). Theoretically, the amount of Ca required to restore the overall base saturation of W1 soils from 10% to 19% was approximately 850 kg Ca/ha, equivalent to 30.2 tons of wollastonite over the area of W1. After considering the differences in the dissolution rate of wollastonite between pilot laboratory studies and the field with imperfect wetting of mineral surfaces, accumulation of weathering products, and possible fouling of the surfaces by organic and metal oxide coatings, it was estimated that at least 7 years would be required for the dissolution of the wollastonite added to W1 (Peters et al. 2004). These phenomena were observed during an experimental addition of calcium carbonate (CaCO_3) to the Woods Lake watershed in New York (Driscoll et al. 1996). To account for potential losses or inefficiencies in wollastonite dissolution, a “safety factor” of 50% was added to the dose, resulting in an application of 45 tons of wollastonite, or 1,316 kg Ca/ha. The wollastonite was pelletized into 1.5 – 4 mm diameter pellets with a water-soluble binder, which allowed the pellets to disintegrate to individual particles (mean diameter 16 μm) in the presence of moisture after the manipulation (Peters et al. 2004). The application was made in October of 1999, after leaf fall, by helicopter. The application rate was remarkably uniform across the watershed (Peters et al. 2004).

Soil sample collection and analyses

Since the short-term impacts of the Ca addition were likely to be limited to the forest floor and upper mineral soil, the monitoring effort for this research focused on these horizons. Soil samples were collected at 100 randomly selected sites in W1 prior to (1998) and after (2000 and 2002) the treatment. Soil samples were collected from the Oi+Oe (Oie) and Oa layers, using 15 cm x 15 cm forest floor blocks (Federer et al. 1993). After the O horizon sampling, the upper mineral soil was sampled using a 5-cm diameter stainless steel corer. The depth of the cores was a maximum of 10 cm, but often less due to refusal of the corer by rocks.

The soil samples from the Oie horizons were oven dried at 80 °C to a constant weight, and ground in a Wiley mill. Large sticks and roots larger than the size of a pencil were removed and weighed prior to grinding. The Oa and upper mineral horizon samples were air dried, weighed, and sieved through 5-mm and 2-mm stainless steel screens, respectively. Sticks, roots, and debris (coarse fraction) not passing through the screen with mild pressure were weighed. Stones, which were rarely present in the Oa horizon, were also included in the coarse fraction. Material passing through the screen was weighed and rebagged. All soil samples that were pre-treated and sieved were analyzed for pH_s. Exchangeable cations (Ca, Mg, K, Na, Al) were extracted with 1.0 M of ammonium chloride (NH₄Cl) for 12 hrs. Blette and Newton (1996) observed that NH₄Cl does not dissolve significant amounts of soil minerals. Furthermore, we observed high Ca/Si molar ratios in the NH₄Cl extracts from a subset of soil samples that were analyzed for both Ca and Si. For the Oie horizon of the LH zone, the mean molar Ca/Si of NH₄Cl extracts was 511 for 1998 samples (prior to treatment) and 193 for 2002 samples (after treatment). For the Oa horizon of the LH zone, the mean molar Ca/Si of NH₄Cl extracts was 525 for 1998 samples (prior to treatment) and 320 for 2002 samples (after treatment). The Ca/Si values were not significantly different for the two years. These high Ca/Si values in the NH₄Cl

extracts suggest that dissolution of wollastonite was not an important source of Ca in the Ex-Ca measurements.

Specific chemical methods for Ex-Acid, CEC_e , and BS_e , which is computed as the sum of exchangeable bases divided by the CEC_e and multiplied by 100, in soil samples are detailed and referenced in Table 1.

Soil solution collection and analyses

Zero-tension lysimeters were constructed of PVC troughs filled with acid-washed quartz sand and installed in the wall of excavated soil pits below the forest floor (Oa horizon) and below the Bh and Bs horizons. Soil solutions were collected at monthly intervals throughout the year from the lysimeters at thirteen sites (6, 11, 15, 42, 46, and 47 on the grid system at the SFB zone; 88, 89, and 121 at the HH zone; 154, 158, 159, and 199 at the LH zone) within W1 (Figure 1) as part of a long-term monitoring program. All of the soil solution samples were analyzed for Ca, total Al (Al_t), total monomeric Al (Al_m), organic monomeric Al (Al_o), H_4SiO_4 , pH, Mg, Na, K, NH_4^+ , SO_4^{2-} , NO_3^- , Cl^- , and F^- , using the methods described in Table 1. Inorganic monomeric Al (Al_i) concentrations were calculated as measured total monomeric Al concentration minus measured organic monomeric Al concentration (i.e. $Al_i = Al_m - Al_o$) (Driscoll 1984). ANC values were also calculated based on the composition of major ions in solution (Table 1).

Statistical analyses

To test for changes in soil chemistry between the pre- and post-treatment period, the two-sample t-test for independent samples was used (MINITAB version 14; statistical software), considering the statistical significance by p -values based on an α -value = 0.05 and a 95 %

confidence interval. We also applied geostatistical models in order to examine changes in spatial patterns of soil chemistry. To evaluate the spatial structure of the soil chemical response to the wollastonite treatment, we calculated semivariograms and fit standard mathematical models of semivariance. For prediction, we used the simplest model that fit the semivariogram, and employed ordinary Kriging to estimate base saturation on a prediction grid of x- and y-coordinate points (Webster & Oliver 2004). The geostatistical program GS+ (version 7.0) was used to calculate semivariance. Kriged values of soil BS_e were displayed on 2-dimensional contour graphs.

Results

Soil chemistry

The results of this study are presented as one pre-treatment (1998) and two post-treatment data sets. Mean soil chemistry values in the pre-treatment and post-treatment samples are shown by horizon in Table 2.

Prior to the treatment, exchangeable Ca, pH_s , CEC_e , and BS_e at Oie, Oa, and upper mineral horizons in W1 were characterized by relatively low values. Coincidentally, W1 showed high concentrations in exchangeable Al and exchangeable acidity at all horizons (Table 2). Most of the Ex-Acid in the Oie soil horizon was attributed to exchangeable hydrogen ions, while acidity in the mineral soil horizon was largely due to Ex-Al.

Following wollastonite addition, the soil chemistry in the Oie horizon changed significantly by 2000, while effects in the Oa horizon occurred by 2002 (Table 2). Though smaller in magnitude, significant changes in soil chemistry were also evident in the mineral soil. By 2002, Ex-Ca had increased to 35 $cmol_c/kg$ in the Oie horizon, 11 $cmol_c/kg$ in the Oa horizon,

and 0.85 cmol_c/kg in the upper mineral horizon due to wollastonite addition, resulting in increases in pH_s to 4.34 in the Oie, 3.48 in the Oa, and 3.44 in the mineral horizon, respectively, by the third year following the treatment (2002; Table 2). Decreases in Ex-Al were modest, from 6.9 to 5.3 cmol_c/kg in the Oa horizon, and there was the only statistically significant effect in 2002 (Table 2). However, Ex-Acid decreased by 2002 to 5.1 cmol_c/kg in the Oie, 8.5 cmol_c/kg in the Oa, and 7.7 cmol_c/kg in the mineral horizon, respectively (Table 2). CEC_e increased in all horizons due to the large increases in Ex-Ca in the organic and the upper mineral horizon. BS_e increased to nearly 86% in the Oie horizon and approximately 56% in the Oa horizon by 2002. There was no statistically significant change in BS_e in the upper mineral soil between pre- and post-treatment observation due to the small increase in Ex-Ca (Table 2).

The elevational patterns in organic (weighted average of Oie and Oa) and mineral soil chemistry are shown in Figure 2, including mean values, standard deviations, and statistical significance. The organic soil horizon at all elevations exhibited a marked response to the wollastonite treatment in comparison with the mineral soil, with the exception of Ex-Al (Figure 2). The magnitudes of changes in concentrations of Ex-Ca, Ex-Acid, CEC_e, and BS_e in the organic soil were greater at higher elevation than lower elevation after the Ca manipulation. The forest floor appears to have retained most of the added wollastonite, as little transport into the mineral soil was evident by 2002. The exception occurred in the SFB zone, where mineral-soil Ex-Ca more than doubled between 1998 and 2002 (Figure 2). The SFB zone had the lowest Ex-Ca values prior to treatment, so this increase brought the SFB mineral soil Ex-Ca up to a level similar to the pretreatment values in the hardwood zones.

The only significant change in the concentration of Ex-Al in either organic or mineral soil occurred in SFB organic horizons (Figure 2), but this decrease of 3.6 cmol_c/kg was small in

comparison to the 21 cmol_c/kg increase in Ex-Ca that was observed in these horizons. Aluminum was the dominant cation associated with the mineral soil exchange sites (Table 2, Figure 2). The decreases in Ex-Acid in organic horizons were closely linked to the increase in pH_s, since exchangeable hydrogen ions were the predominant form of exchangeable acidity in O-horizon soils. As pH_s increased, Ex-Acid decreased in the organic soil horizon in all zones except in the HH zone during 2000. In contrast, there was a slight increase in pH_s and decrease in Ex-Acid in the HH zone and no statistically significant change in the SFB and LH zones in mineral soil horizons. Increases in CEC_e and BS_e were also largely associated with increases in Ex-Ca in the organic soil horizon, while there was either a slight increase or no change in the mineral soil.

Soil solution chemistry

For consistency, we compare soil solution data from 1998, 2000, and 2002 to correspond with the soil sampling program. Prior to wollastonite addition, soil solutions draining the O horizon had higher Ca, H₄SiO₄, Al_i, SO₄²⁻, and DOC and lower pH and ANC than solutions draining the mineral horizons (Table 3). Higher concentrations of Ca in the O horizon compared to the mineral horizon prior to the Ca application probably reflect the cycling of Ca by trees and throughfall and litter inputs of Ca.

During the first year after the wollastonite treatment (2000), concentrations of Ca, H₄SiO₄, and ANC all significantly increased in both the O and the mineral horizon soil solutions (Table 3). Increases in Ca, H₄SiO₄, and ANC were also evident during the third year (2002), probably reflecting the continuing dissolution of wollastonite and downward transport of the dissolution products (Table 3). The pH of soil water for all horizons did not change significantly in 2000 but increased to 4.72 in the O horizon and to 4.74 in the mineral soil by the third year after the

manipulation (Table 3). In contrast, the concentrations of Al_i in O horizon solutions decreased significantly in both 2000 and 2002, whereas a decrease in Al_i concentration in mineral soil solutions was not evident until 2002. The Ca application on W1 also resulted in an increase in the concentrations of SO_4^{2-} in the first year after the treatment (Table 3). Sulfate concentrations subsequently decreased to 33 $\mu\text{mol/L}$ in the O horizon and 45 $\mu\text{mol/L}$ in the mineral horizon solutions, respectively, by the third year following the treatment.

Unlike the gradual increasing patterns in soil solution Ca, pH, and ANC concentrations, dissolved H_4SiO_4 rapidly increased for the first year following the treatment and then decreased during the third year. This initial H_4SiO_4 response may be attributed to rapid dissolution of Si from the added wollastonite following the application. Whereas a substantial amount of Ca was retained as exchangeable Ca in the O horizon, much of the H_4SiO_4 released during dissolution apparently remained in solution. As a result, the Ca/Si molar ratio decreased during the first year after $CaSiO_3$ application from 0.45 to 0.18 in organic soil solution and from 0.25 to 0.14 in mineral soil solution. Following this initial period, there was an increase in the Ca/Si ratio (i.e. mean ratio: 0.45 in organic and 0.36 in mineral soil solution in 2002) back to pre-treatment levels (Figure 3). This pattern indicates that with additional time, the dissolution of wollastonite had diminished somewhat resulting in lower (but still elevated relative to pre-treatment levels) concentrations of H_4SiO_4 in O horizon solutions. Retention of Ca by exchange sites in the O horizon appears to have decreased as well, resulting in increasing Ca concentrations in soil solutions and higher Ca/Si ratios. DOC concentrations exhibited no significant changes in any horizon between the pre- and post-treatment.

Six sets of lysimeters in the SFB zone, 3 in the HH zone, and 4 in the LH zone (Figure 1) were used to investigate landscape patterns in solute concentrations in soil solutions draining

organic and mineral soil horizons in W1 prior to (1998) and after (2000 and 2002) the Ca manipulation (Figure 4). Prior to the wollastonite treatment, Ca, H_4SiO_4 , pH, and ANC were low and Al_i concentration was high in both the organic and the mineral soil solution across almost all elevations, especially in the SFB zone. This pattern could be linked to the fact that concentrations of exchangeable Ca were low in soil at higher elevations and increased with decreasing elevation (Figure 2; Johnson et al. 2000).

The magnitude of both increases in Ca, H_4SiO_4 , pH, and ANC, and decreases in Al_i was greater at the SFB zone (higher elevation) than at the HH and LH zones (lower elevations). This phenomenon was attributed to lower concentrations of Ca, H_4SiO_4 , pH, and ANC, and higher Al_i concentrations at the SFB zone than at the HH and LH prior to the Ca treatment. The increase in SO_4^{2-} concentrations was more evident at the higher elevation than at the lower elevation in both organic and mineral soil solutions during the first year following the treatment. There were no significant changes in DOC concentrations at any of the elevations (Figure 4). The SFB zone has shallow soil depth, relatively flat topography resulting in high soil moisture, and limited mineral weathering (Johnson et al. 2000). As a result, the effects of the wollastonite treatment are likely to be more pronounced than in the deeper and drier soils of lower elevations.

The concentrations of total Al and organically bound monomeric Al showed different behavior from inorganic monomeric Al concentrations. There were significant increases in Al_i in the SFB (annual mean values: 22 $\mu\text{mol/L}$ in 1998 to 30 $\mu\text{mol/L}$ in 2000; $p < 0.05$) and the LH (8 $\mu\text{mol/L}$ in 1998 to 18 $\mu\text{mol/L}$ in 2000; $p < 0.05$) sites, and there was an insignificant increase in Al_i at the HH (18 $\mu\text{mol/L}$ in 1998 to 26 $\mu\text{mol/L}$ in 2000; $p > 0.05$) site in the O horizon soil solution. These values decreased to 20 $\mu\text{mol/L}$ at SFB and 13 $\mu\text{mol/L}$ at the both HH and the LH sites in 2002. Soil solutions draining mineral horizon soils also showed significant increases in

Al_t at the SFB (annual mean values: 24 $\mu\text{mol/L}$ in 1998 to 39 $\mu\text{mol/L}$ in 2000; $p<0.05$), the HH (22 $\mu\text{mol/L}$ in 1998 to 37 $\mu\text{mol/L}$ in 2000; $p<0.05$), and the LH (10 $\mu\text{mol/L}$ in 1998 to 17 $\mu\text{mol/L}$ in 2000; $p<0.05$) sites, and then these increased Al_t concentrations decreased to 31 $\mu\text{mol/L}$ at the SFB, to 32 $\mu\text{mol/L}$ at the HH, and to 14 $\mu\text{mol/L}$ at the LH during the third year following the wollastonite treatment, respectively. There were no significant changes in Al_o at the SFB site in both the O (9 $\mu\text{mol/L}$ in 1998, 11 $\mu\text{mol/L}$ in 2000, and 7 $\mu\text{mol/L}$ in 2002; $p>0.05$) and mineral (6 $\mu\text{mol/L}$ in 1998, 9 $\mu\text{mol/L}$ in 2000, and 7 $\mu\text{mol/L}$ in 2002; $p>0.05$) horizon soil solutions. Nor were there distinct patterns at the hardwood sites. Al_o concentrations at the HH and the LH sites in the O horizon soil solutions averaged 10 and 5 $\mu\text{mol/L}$ in 1998, 10 and 8 $\mu\text{mol/L}$ in 2000, and 6 and 5 $\mu\text{mol/L}$ in 2002, respectively. Al_o concentrations in mineral soil solutions at the HH and the LH sites were 6 and 1 $\mu\text{mol/L}$ (1998), 8 and 3 $\mu\text{mol/L}$ (2000), and 7 and 2 (2002), respectively.

Discussion

Horizontal patterns

Retention of Ca and Al immobilization

Prior to wollastonite application, the CEC_e was significantly negatively correlated with pH_s in both the O horizon (average of O_{ie} and O_a, $p<0.05$, $r=-0.323$) and the mineral soil ($p>0.05$, $r=-0.147$; Table 4, Figure 5). Negative correlations between CEC_e and pH_s at Hubbard Brook and in other forest soils in the northeastern U.S.A have been ascribed to the contribution

of soil organic matter to CEC and soil acidity (Johnson 2002). The O horizon contains an abundance of carboxyl groups (R-COOH) that both lower pH and provide sites for cation binding. In mineral horizons, Ex-Al is the predominant exchangeable cation, which results from the dissolution of mineral Al. Thus, there is more Al available for release to mineral soil solutions than organic soil waters (Figure 3). The importance of Ca to CEC_e decreases with soil depth, perhaps due to Ca cycling by vegetation and natural soil pedogenesis. In the O horizon, Ca accounted for 27% of CEC_e , whereas it comprised only 7% in the upper mineral horizon (Figure 5). Exchangeable H^+ represented 35% of the CEC_e in the O horizon, whereas exchangeable Al was 70% of the CEC_e in the upper mineral horizon (Figure 5).

After Ca addition, the correlations between CEC_e and pH_s in the O horizon were significantly positive in 2002 ($p < 0.01$, $r = +0.433$), corresponding with significant positive correlations between Ex-Ca and pH_s ($p < 0.01$, $r = +0.340$ in 2000; and $p < 0.01$, $r = +0.570$ in 2002, respectively). In the mineral horizons, however, no significant correlations were observed between either CEC_e and pH_s or Ex-Ca and pH_s (Table 4).

The large and continuing increase in Ex-Ca and CEC_e in O horizons implies that much of the Ca released from the dissolution of the added wollastonite was retained by forest floor exchange sites for the period shortly after treatment. In fact, Ca largely remained in the forest floor, accounting for 49% of CEC_e in 2000 and 66% of CEC_e in 2002, and limiting penetration to the mineral soil. The large increases in Ex-Ca in organic horizons coincide with much smaller decreases in Ex-Al and Ex-Acid (Table 2, Figure 2). Thus, the release of Ca from wollastonite dissolution resulted in an increase of CEC_e rather than the displacement of exchangeable acidic cations by Ca. This pattern of increases in CEC_e following the wollastonite application was evident at all elevations. The mechanism of increases in CEC_e in response to the treatment is

likely due to the deprotonation of carboxyl sites associated with soil organic matter, thus creating pH-dependent cation exchange capacity. This pattern was also reported following CaCO_3 application to Woods Lake watershed in the Adirondack (Blette & Newton 1996).

SO_4^{2-} desorption

Previous investigators at the HBEF have shown that SO_4^{2-} adsorption is pH-dependent, particularly in B horizon soils (Fuller et al. 1985; Mitchell et al. 1989; Nodvin et al. 1986; 1988). Therefore, increases in Ca concentrations and concomitant decreases in H^+ concentration in W1 soil solutions after the wollastonite addition were expected to cause SO_4^{2-} desorption, and an increase in soil solution SO_4^{2-} concentrations. This response was only significant in mineral soil solutions, and was a transient phenomenon, evident only during the first year (2000) following the treatment (Figure 3). By 2002, mineral soil SO_4^{2-} concentrations returned to the pre-treatment levels in all subcatchments. This pattern appears to be consistent with pH-dependent adsorption of SO_4^{2-} on iron and aluminum sesquioxides in the mineral soil (Nodvin et al. 1986).

We observed significant decreases in SO_4^{2-} concentrations in organic horizon soil solutions throughout the watershed in 2002 (Table 3, Figure 3). This pattern occurred despite large increases in the pH_s of both Oie and Oa soils (Table 2). The mechanism responsible for this decrease in SO_4^{2-} in O horizon solutions is not evident.

Landscape patterns

Change in BS_e

As part of our evaluation of the effects of the Ca addition to watershed 1, we evaluated the spatial patterns of biogeochemical changes. The effective base saturation in the mineral soil can be used as general indicator of ecosystem stress from elevated Al concentrations at the HBEF, with a threshold value of 15% BS_e suggestive of adverse conditions for tree health and surface water acidification (Cronan & Grigal 1995; Cronan & Schofield 1990; Palmer et al. 2004). To determine spatial patterns in BS_e , we interpolated the soils data by Kriging from maps with coordinate values. This approach allowed us to map the modeled output and identify areas sensitive to changes in atmospheric deposition prior to treatment and evaluate the intra-watershed response to the experimental addition of wollastonite.

The BS_e was less than 20% in the upper mineral soil everywhere in W1 except a few restricted locations prior to the treatment, with the lowest values in the upper areas of the watershed (Figure 6). After the treatment, the fraction of the watershed with very low BS_e (<10%) decreased substantially, and a few locations showed BS_e values >30% (Figure 6). Changes in the spatial patterns in the O horizon (weighted average of Oie and Oa) were more evident than changes in the upper mineral horizon. The BS_e of the O horizon decreased with increasing elevation prior to the treatment and more than half of the watershed had BS_e below 50% (Figure 6). However, this pattern changed after the treatment. By 2002, organic horizons throughout W1 had BS_e greater than 60%, and values were relatively constant throughout the watershed. The application rate of wollastonite was relatively uniform across the watershed (Peters et al. 2004). Thus, the application of wollastonite to wetter soil provides a more immediate change in watershed soils and drainage waters of the SFB zone than application to more well-drained soils at lower elevations. The differing responses of organic and mineral soils (Figure 6) support the conclusion that much of the Ca released by wollastonite dissolution

remained in the forest floor. Whereas the BS_e increased by as much as 60% or more in O horizons, the greatest increase observed in mineral soil was only 20-30%.

Ca/Al ratio

Cronan and Grigal (1995) suggested that there is a 50% risk of harmful effects on tree growth and nutrition when the Ca/Al molar ratio in soil solution is less than 1, with the risk increasing to 75% and 100% risk when the Ca/Al ratio decreases below 0.5 and 0.2, respectively. We used total monomeric Al (Al_m) to calculate the Ca/Al molar ratio in soil solutions, and Ex-Ca and Ex-Al to calculate the Ca/Al in soil. Prior to the treatment the mean Ca/ Al_m molar ratios were 0.4 and 0.4 in the SFB zone, 1.6 and 0.8 in the HH zone, 2.1 and 1.5 in the LH zone in the organic and the mineral soil solutions, respectively. These values suggest that there may be evidence for Al stress on acid sensitive vegetation in the SFB zone and the HH zone.

After the wollastonite treatment, increases in solution Ca/ Al_m were evident at all landscape positions due to increases in Ca and decreases in Al_m . Although the Ex-Ca/Ex-Al ratio is not as widely used as soil solution Ca/Al as an indicator of Al stress, it is useful to evaluate the coupling of these stoichiometric relationships. Prior to the treatment there were consistent spatial patterns in solution and soil Ca/Al, with the lowest values in the SFB zone, increasing in the HH and the LH zones (Figure 7). Broadly speaking, solution and soil Ca/Al ratios were similar in magnitude in O horizon samples. In mineral soil, however, the soil Ex-Ca/Ex-Al ratios were much lower than solution values due to the dominance of Ex-Al on soil exchange sites. Following the wollastonite application, Ca/Al ratios increased in both soils and solutions in organic and mineral horizons except Ca/Al ratio in mineral soils of the HH zone during the first year (Figure 7).

Hawley et al. (2006) showed that winter injury to red spruce, due to cold temperature coupled with depletion of available Ca in soils, decreased in W1 compared with the untreated reference watershed (W6). This response coincided with increases in foliar Ca concentrations derived from the dissolution of added wollastonite. Juice et al. (2006) examined the response of sugar maple to the Ca addition and found that increased foliar Ca concentrations of canopy sugar maples in W1 increased health, growth, and survivorship after the treatment.

The magnitude of the increases in Ca/Al ratios was much greater in the organic horizon than mineral soil. This response is likely due to the strong retention of Ca in the forest floor. Also, the solubility of Al decreases with increases in pH to neutral values (Driscoll and Postek 1995; Cho et al. 2009). In the O-horizon there was an uncoupling of the spatial pattern in Ca/Al ratios due to enhanced wollastonite dissolution in the SFB zone, such that in 2002 the Ex-Ca/Ex-Al ratio in the SFB zone was greater than the HH zone and comparable to the LH zone. Less striking changes were evident in the mineral soil, although the SFB zone exhibited marked increases in both solution and soil Ca/Al, probably due to the shallow, wet soils which allowed for greater dissolution of wollastonite than the HH and the LH zones. The LH zone demonstrated large changes in solution Ca/Al with little change in exchangeable Ca/Al (Figure 7). Tracking these shifts in Ca/Al stoichiometry over the long-term, along with the associated forest vegetation response, should provide insight on the use of Ca/Al ratios as indicators of forest health.

Conclusions

The magnitude of increases (Ex-Ca, pH_s, CEC_e, and BS_e in soil; Ca, pH, and ANC in soil water) and decreases (Ex-Al and Ex-Acid in soil; Al_i concentrations in soil water) in both soils and soil solutions was greater in the third year than in the first year after the Ca manipulation. In contrast, H₄SiO₄ concentrations were highest in the first year after the treatment, suggesting relatively rapid direct dissolution of wollastonite. The changes in soil and soil solution chemistry were most evident within the organic horizon, since most of the Ca derived from the dissolution of added wollastonite was retained in the forest floor due to increases in CEC_e. The increase in CEC_e was likely due to the deprotonation of carboxyl sites associated with soil organic matter. Wollastonite dissolution was greatest in the high-elevation SFB zone due to shallow soils and a relatively high water table. There were positive relationships between Ca/Al_m in soil water and Ex-Ca/Ex-Al in soil in both the pre-treatment and the post-treatment periods, suggesting that concentrations of Ca and Al_m in soil solution were correlated with the patterns in Ex-Ca and Ex-Al concentrations in soil horizons. The Ca/Al_m ratio in soil solution increased following the treatment, possibly alleviating acidification stress and resulting in the improvement in the health of red spruce and sugar maple.

Acknowledgements

This work was supported by the National Science Foundation including the Long-Term Ecological Research (LTER) program. We appreciate the help of Joseph Denkenberger, Jason Dittman, Colin Fuss, and Mary Margaret Koppers in field research and laboratory analyses. This is a contribution of the Hubbard Brook Ecosystem Study. The HBEF is a LTER site and is

administered by the United States Department of Agriculture (USDA) Forest Service, Northeastern Research Station, Newtown Square, Pennsylvania.

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Figure 2. Elevational patterns in concentrations of Ex-Ca, Ex-Al, Ex-Acid, pH_s , CEC_e , and BS_e from organic (weighted average of Oie and Oa) and mineral soil horizons in W1 prior to (1998) and after (2000 and 2002) wollastonite addition. There is a significant difference in mean values if letters between the pre-treatment and the post-treatment periods are different, (two-sample *t*-test using $\alpha=0.05$ for all tests). The SFB is the high elevation spruce-fir-white birch zone, HH is the high elevation hardwood zone, and LH is the low elevation hardwood zone. Soil samples from 27 organic soil horizon sites and 24 upper mineral soil horizon sites located at the SFB zone, 30 and 32 sites at the HH zone, and 28 and 33 sites at the LH zone were analyzed in 1998, respectively. Soil samples from 32 and 23 sites at the SFB zone, 31 and 28 sites at the HH zone, and 28 and 31 sites at the LH zone from organic and mineral horizons, respectively, were analyzed in 2000. The analyses of soil samples were repeated in 2002 at 24 and 18 sites at SFB, 26 and 32 sites at HH, and 26 and 30 sites at LH from organic and mineral soil horizons, respectively.

Figure 3. Ca/Si ratio ($\mu\text{mol}\cdot\text{L}^{-1}/\mu\text{mol}\cdot\text{L}^{-1}$) in organic and mineral soil solutions in watershed 1 (W1) of the Hubbard Brook Experimental Forest (HBEF).

Figure 4. Elevational patterns in concentrations of Ca, H_4SiO_4 , pH, Al_i , SO_4^{2-} , and ANC from organic and mineral soil solutions from W1 prior to (1998) and after (2000 and 2002) wollastonite addition. Significant differences are indicated by different letters between the pre-treatment and the post-treatment periods (two-sample *t*-test using $\alpha= 0.05$ for all tests). SFB indicates the high elevation spruce-fir-white birch zone, HH is the high elevation hardwood zone, and LH is the low elevation hardwood zone.

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Figure 7. Relationships between Ca/ Al_i ratio in soil solution and Ex-Ca/Ex-Al ratio in soil for spruce-fir-white birch (SFB: high elevation), high hardwood (HH: mid elevation), and low hardwood (LH: low elevation) zones of watershed 1 (W1) at the Hubbard Brook Experimental Forest (HBEF) prior to (1998) and after the Ca application (2000 and 2002).

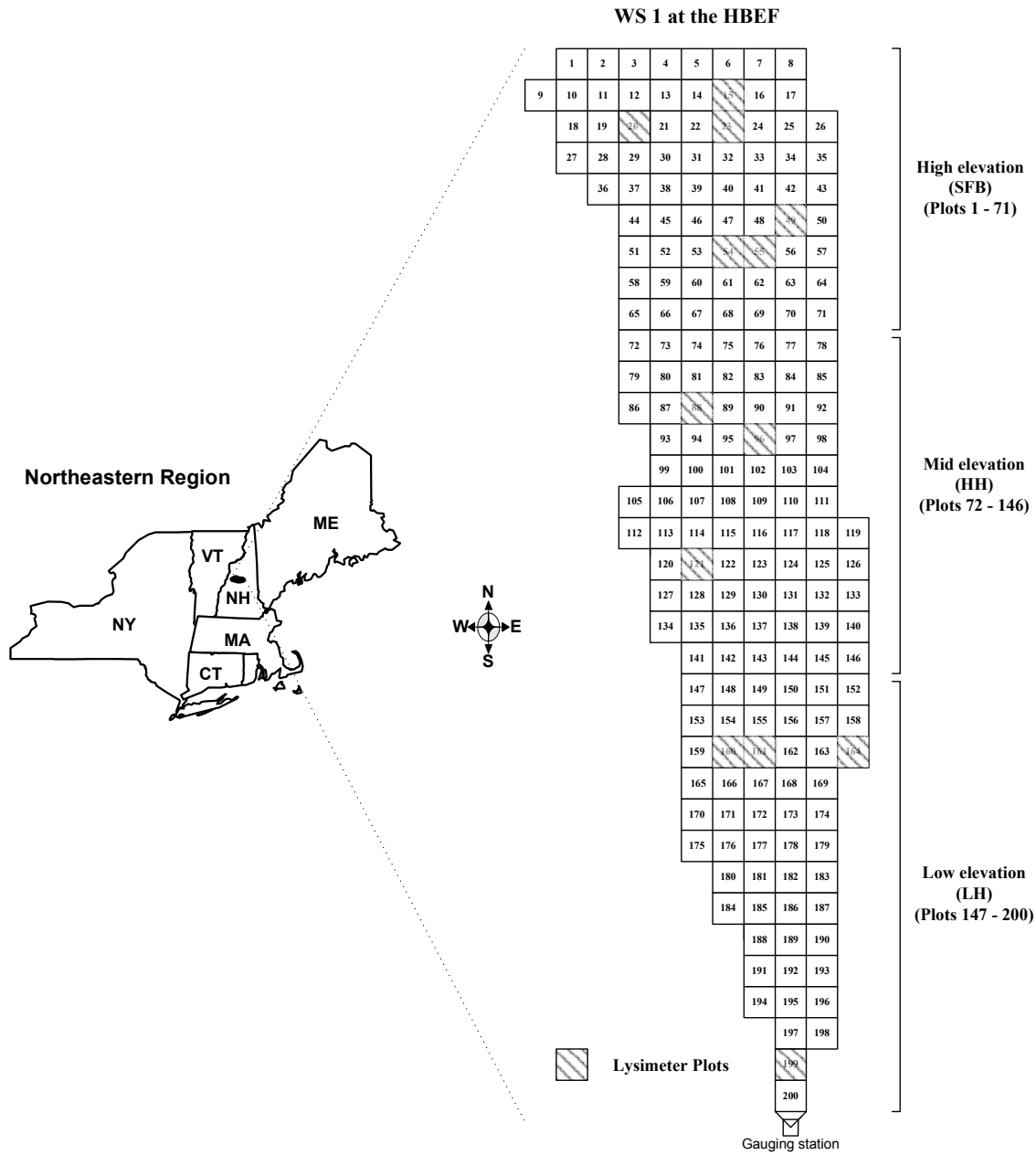


Figure 1.

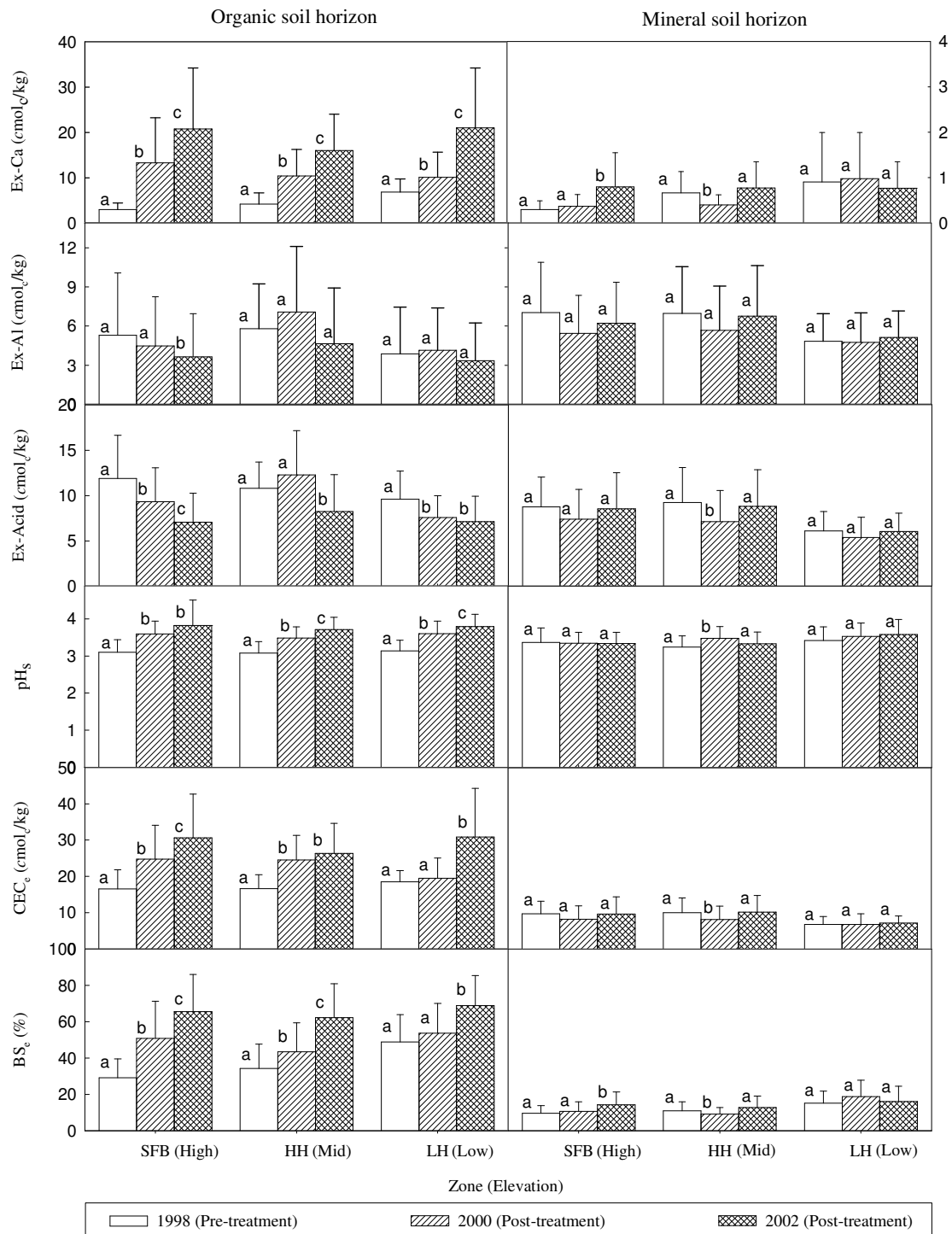


Figure 2.

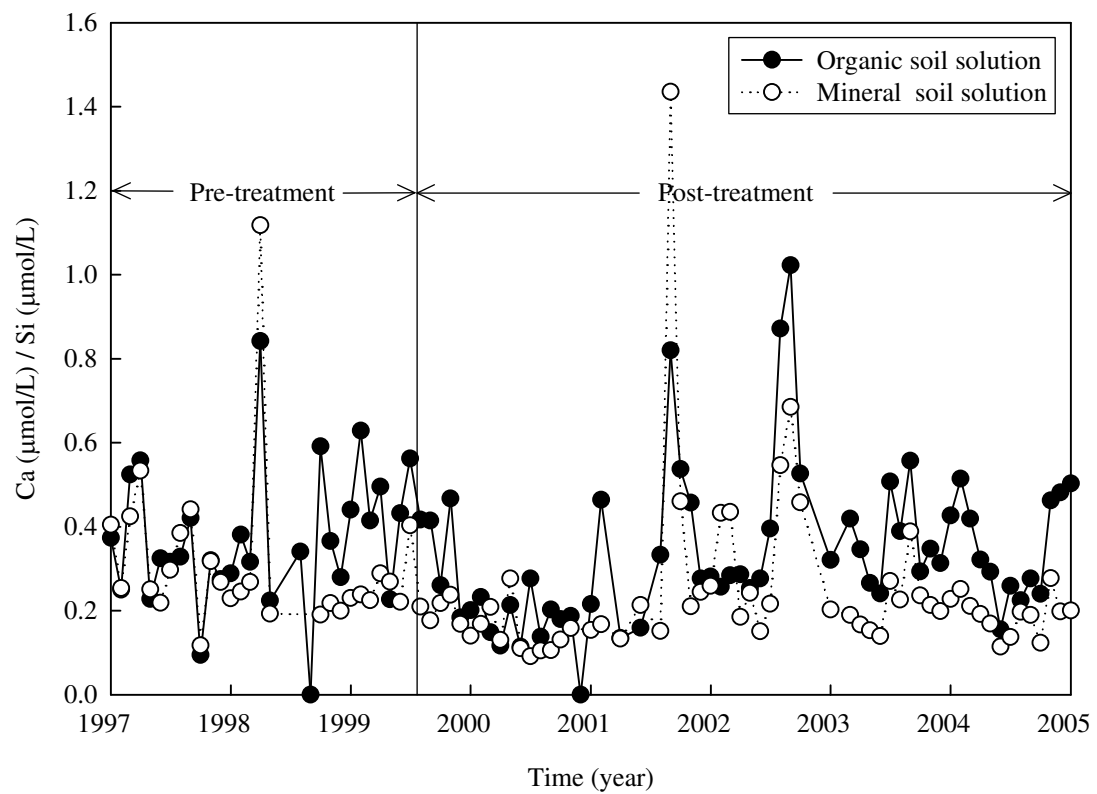


Figure 3.

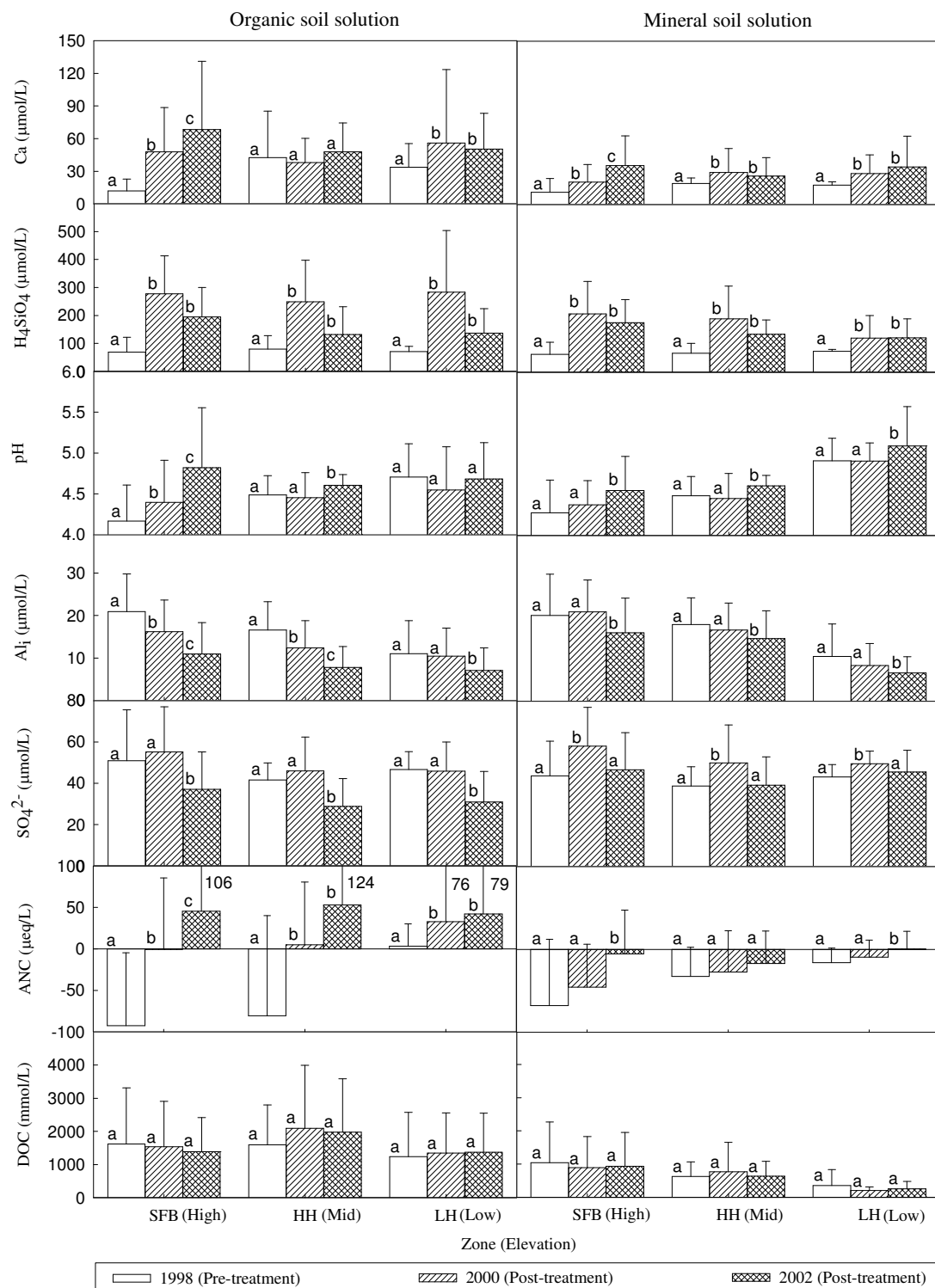


Figure 4.

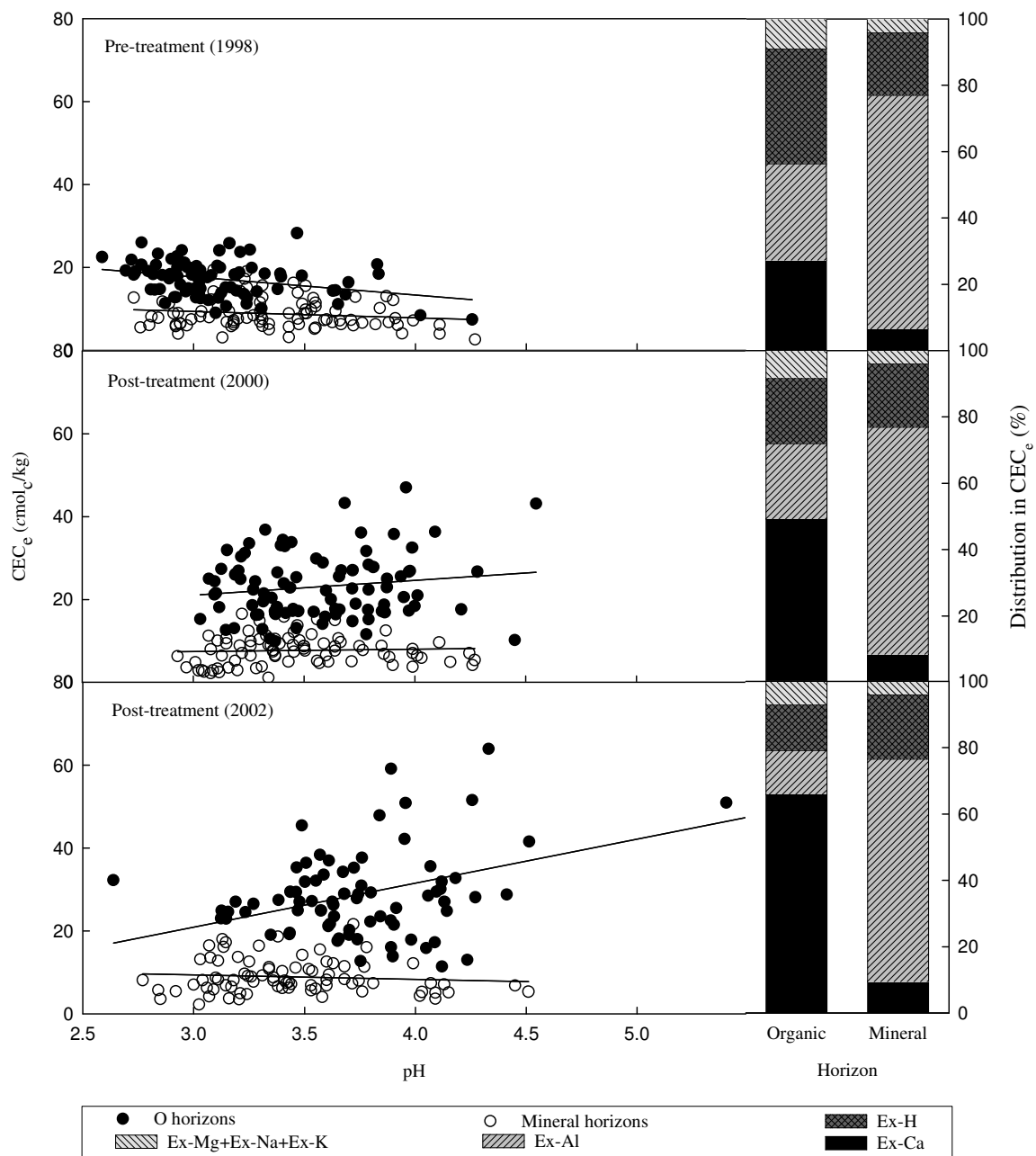


Figure 5.

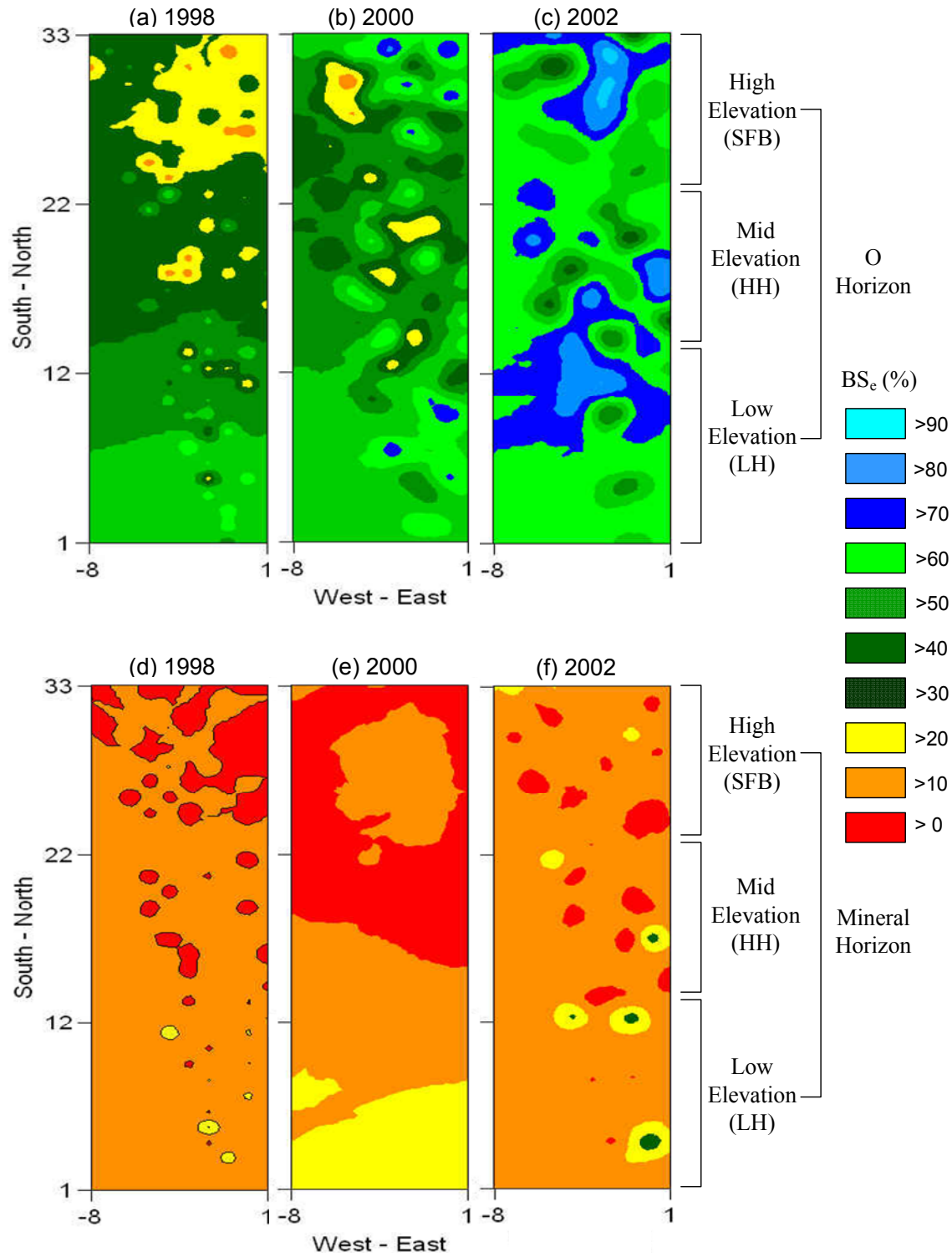


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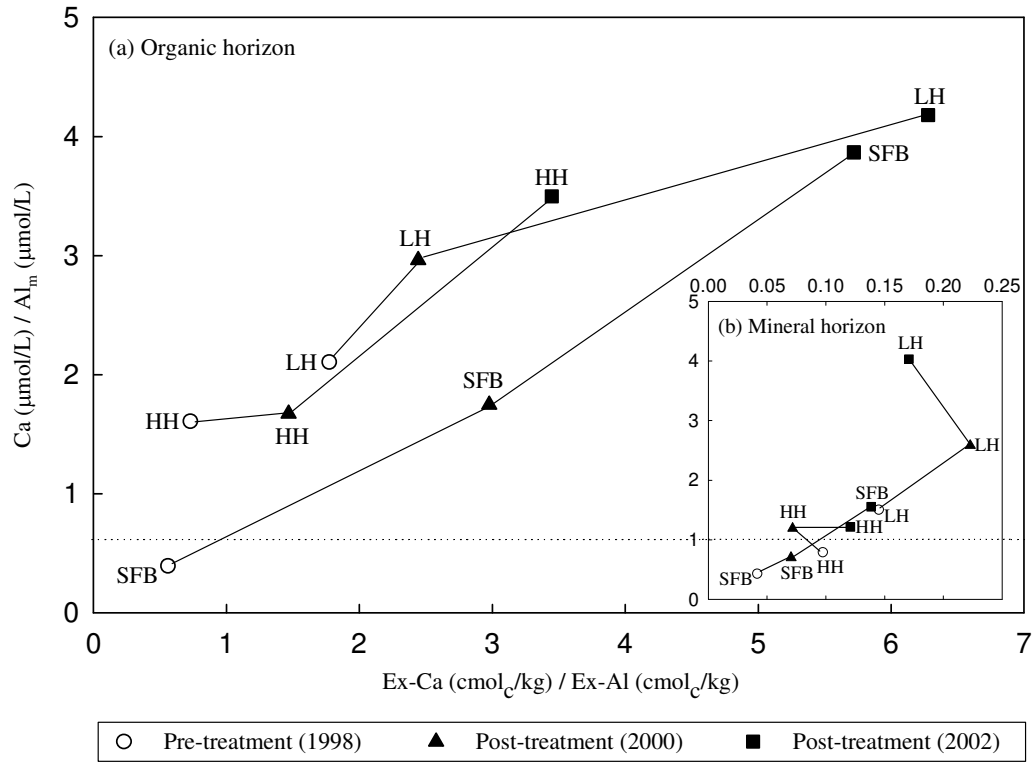


Figure 7.

Table 1.

Analyte	Method	Reference
<i>Soil properties</i>		
Exchangeable Ca, Mg, K, Na, Al (Ex-Ca, Ex-Mg, Ex-K, Ex-Na, Ex-Al, cmol _c /kg)	Extracted in 1.0 M NH ₄ Cl + ICP*	Johnson <i>et al.</i> , 1991b
Exchangeable acidity (Ex-Acid, cmol _c /kg)	Extracted in 1.0 M KCl at pH 8.2	Johnson <i>et al.</i> , 1991b
pH _s	Dissociated H ⁺ in 0.1 M CaCl ₂	Johnson, 2002
Effective cation exchange capacity (CEC _e , cmol _c /kg)	Ex-Acid + Ex-Ca + Ex-Mg + Ex-K + Ex-Na	Skyllberg, 1999
Effective base cations (BC _e , cmol _c /kg)	Ex-Ca + Ex-Mg + Ex-K + Ex-Na	Skyllberg, 1999
Effective base saturation (BS _e , %)	100 × (BC _e /CEC _e)	Skyllberg, 1999
<i>Soil solution</i>		
Ca, Mg, Na, K (μmol/L)	Atomic absorption spectroscopy (AAS)	Slavin, 1968
NH ₄ ⁺ (μmol/L)	Automated phenate method	Cappo <i>et al.</i> , 1987
Total monomeric Al (Al _m , μmol/L),	Automated pyrocatechol violet method (PCV)	McAvoy <i>et al.</i> , 1992
Organic monomeric Al (Al _o , μmol/L)	Automated pyrocatechol violet method (PCV)	McAvoy <i>et al.</i> , 1992
Inorganic monomeric Al (Al _i , μmol/L)	Al _m - Al _o	Driscoll, 1984
pH	Potentiometric	APHA, 1992
Dissolved silicate (H ₄ SiO ₄ , μmol/L)	Molybdenum blue colorimetry	APHA, 1992
SO ₄ ²⁻ , NO ₃ ⁻ , Cl ⁻ , F ⁻ (μmol/L)	Ion chromatography (IC)	Tabatabai & Dick, 1983
Acid neutralizing capacity (ANC, μeq/L)**	2[Ca]+2[Mg]+[Na]+[K]+[NH ₄ ⁺]- 2[SO ₄ ²⁻]-[NO ₃ ⁻]-[Cl ⁻]-[F ⁻]	Stumm and Morgan, 1981
Dissolved organic carbon (DOC, μmol/L)	UV enhanced persulfate oxidation, infrared (IR) CO ₂ detection	Dohrman, 1984

*ICP: Inductively coupled plasma spectroscopy

**Ion concentrations are expressed in μmol/L and the unit of ANC is μeq/L.

Table 2.

Parameter	Horizon	Statistics	Pre-treatment		Post-treatment		Significant differences
			1998	2000	2002		
Ex-Ca (cmol _c /kg)	Oie	\bar{x}	5.62	24.4	34.7	1998 < 2000 < 2002	
		SD	2.43	14.6	16.2		
	Oa	\bar{x}	4.44	4.94	11.1	1998, 2000 < 2002	
		SD	3.45	3.79	10.6		
	Mineral	\bar{x}	0.58	0.65	0.85	1998, 2000 < 2002	
		SD	0.44	0.75	0.64		
Ex-Al (cmol _c /kg)	Oie	\bar{x}	1.13	0.84	0.87		
		SD	1.65	2.32	1.32		
	Oa	\bar{x}	6.90	7.07	5.29	1998, 2000 > 2002	
		SD	5.37	5.09	4.45		
	Mineral	\bar{x}	6.19	5.26	6.02	1998 > 2000	
		SD	3.33	2.86	3.17		
Ex-Acid (cmol _c /kg)	Oie	\bar{x}	8.41	5.69	5.11	1998 > 2000, 2002	
		SD	3.91	3.19	2.72		
	Oa	\bar{x}	11.9	11.6	8.48	1998, 2000 > 2002	
		SD	4.16	5.19	4.21		
	Mineral	\bar{x}	7.79	6.68	7.71	1998, 2002 > 2000	
		SD	3.30	3.18	3.69		
pH _s	Oie	\bar{x}	3.26	4.21	4.34	1998 < 2000 < 2002	
		SD	0.23	0.51	0.49		
	Oa	\bar{x}	3.03	3.24	3.48	1998 < 2000 < 2002	
		SD	0.35	0.32	0.57		
	Mineral	\bar{x}	3.35	3.47	3.44	1998 < 2000, 2002	
		SD	0.36	0.33	0.37		
CEC _e (cmol _c /kg)	Oie	\bar{x}	16.2	32.7	43.6	1998 < 2000 < 2002	
		SD	4.08	14.5	17.1		
	Oa	\bar{x}	18.0	18.2	21.4	1998, 2000 < 2002	
		SD	5.30	6.23	9.86		
	Mineral	\bar{x}	8.80	7.68	8.96	1998, 2002 > 2000	
		SD	3.61	3.45	4.07		
BS _e (%)	Oie	\bar{x}	48.7	78.6	86.1	1998 < 2000 < 2002	
		SD	15.7	15.4	9.74		
	Oa	\bar{x}	32.9	35.8	56.0	1998, 2000 < 2002	
		SD	15.8	17.6	21.3		
	Mineral	\bar{x}	12.1	13.1	14.3	1998 < 2002	
		SD	5.85	7.80	7.38		

1. \bar{x} = arithmetic mean, SD = standard deviation

2. Both alternative hypotheses (year > or < year) and null hypotheses (year \approx year) were tested by two sample *t*-test based on *p*-value, using the significance level of 0.05 and 95 % confidence intervals for all tests.

3. Sample numbers are 85 in 1998, 91 in 2000, and 76 in 2002 at Oie and Oa horizons, 88 in 1998, 81 in 2000, and 79 in 2002 at mineral horizon, respectively.

Table 3.

Parameter	Horizon	Statistics	Pre-treatment			Significant differences
			1998	2000	2002	
Ca ($\mu\text{mol/L}$)	O	\bar{x}	27.4	47.9	57.9	1998 < 2000, 2002
		<i>SD</i>	29.6	47.7	48.3	
	Mineral	\bar{x}	15.8	24.8	33.4	1998 < 2000 < 2002
		<i>SD</i>	9.14	18.3	25.9	
H_4SiO_4 ($\mu\text{mol/L}$)	O	\bar{x}	73.0	273	162	1998 < 2002 < 2000
		<i>SD</i>	43.5	165	103	
	Mineral	\bar{x}	68.1	180	152	1998 < 2002 < 2000
		<i>SD</i>	33.5	113	76.5	
pH	O	\bar{x}	4.43	4.46	4.72	1998, 2000 < 2002
		<i>SD</i>	0.42	0.47	0.54	
	Mineral	\bar{x}	4.58	4.56	4.74	1998, 2000 < 2002
		<i>SD</i>	0.41	0.36	0.47	
Al_i ($\mu\text{mol/L}$)	O	\bar{x}	17.0	13.8	9.04	1998 > 2000 > 2002
		<i>SD</i>	8.83	7.40	6.48	
	Mineral	\bar{x}	16.3	21.0	12.8	2000 > 1998 > 2002
		<i>SD</i>	9.03	7.54	7.90	
SO_4^{2-} ($\mu\text{mol/L}$)	O	\bar{x}	47.0	50.3	33.2	2000 > 1998 > 2002
		<i>SD</i>	17.4	19.0	16.3	
	Mineral	\bar{x}	42.4	54.1	45.0	1998, 2002 < 2000
		<i>SD</i>	11.8	16.8	15.4	
ANC ($\mu\text{eq/L}$)	O	\bar{x}	-52.9	11.1	45.8	1998 < 2000 < 2002
		<i>SD</i>	130	81.5	100	
	Mineral	\bar{x}	-40.8	-31.8	-3.57	1998 < 2000 < 2002
		<i>SD</i>	58.1	47.5	46.3	
DOC ($\mu\text{mol/L}$)	O	\bar{x}	1483	1605	1513	1998 \approx 2000 \approx 2002
		<i>SD</i>	1453	1479	1247	
	Mineral	\bar{x}	670	684	649	1998 \approx 2000 \approx 2002
		<i>SD</i>	871	841	792	

1. \bar{x} = arithmetic mean, SD = standard deviation,
2. Both alternative hypotheses (year > or < year) and null hypotheses (year \approx year) were tested by two sample *t*-test based on *p*-value, using the significance level of 0.05 and 95 % confidence intervals for all tests.
3. The range of sample numbers in each constituent is from 69 to 128 in 1998, from 71 to 172 in 2000, and from 93 to 192 in 2002.
4. ANC values were calculated by the equation in Table 1.

Table 4.

Year	O horizon				Mineral horizon			
	$r_{\text{CEC}_{\text{e-pHs}}}$	$p_{\text{CEC}_{\text{e-pHs}}}$	$r_{\text{ExCa-pHs}}$	$p_{\text{ExCa-pHs}}$	$r_{\text{CEC}_{\text{e-pHs}}}$	$p_{\text{CEC}_{\text{e-pHs}}}$	$r_{\text{ExCa-pHs}}$	$p_{\text{ExCa-pHs}}$
1998	-0.323	0.003	-0.366	0.001	-0.147	0.171	-0.337	0.001
2000	+0.153	0.148	+0.340	0.001	+0.055	0.624	-0.157	0.160
2002	+0.433	0.000	+0.570	0.000	-0.097	0.393	-0.023	0.840

1. Pearson correlation coefficients (r) and P-values (p) were tested by the significance level of 0.05 and 95% confidence intervals for all regression analyses.
2. Pre- (1998) and post-treatment (2000, 2002)
3. O horizon is the weighted average of Oie and Oa.