Aluminum is more tightly bound in soil after wollastonite treatment to a forest watershed

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Abstract

Aluminum concentrations decreased on soil exchange sites and in soil solutions after a whole-watershed wollastonite ($CaSiO_3$) treatment at the Hubbard Brook Experimental Forest in New Hampshire. This study was conducted to determine whether these decreases could be explained by changes in organically bound Al (Al_{org}) in soils. The concentrations of Al_{org}, exchangeable Al (Al_{KCl}) and other chemical properties in organic (Oi + Oe, Oa) and 0-10 cm mineral soil layers were measured using samples collected prior to treatment (1998) and afterwards (2002, 2006, 2010 and 2014). Compared to pre-treatment values, Al_{org} concentrations in the Oa horizon and the 0-10 cm mineral soil layer increased by 312% and 803%, respectively. Over the same period, Al_{KCl} concentrations in these horizons decreased by 57% and 15%, respectively. Through 2014, the Al_{org} pool in the 0-10 cm mineral soil layer increased by 602% compared to the pretreatment value, whereas the Al_{KCl} pool in the Oa horizon decreased by 84%. In the surface Oi + Oe horizon, no significant changes in soil Al concentrations and pools were observed after the treatment, though Al_{KCl} concentrations showed a slight decrease. Aluminum is migrating downward from the Oa horizon to the 0-10 cm mineral layer. The predominant form of Al binding has shifted from weaker exchangeable Al to stronger organically bound Al. This conversion of exchangeable Al to organically bound Al has reduced Al solubility and contributed to improved forest health.

Key words: cation exchange, forest health, organically bound aluminum, soil acidity, watershed, wollastonite

1. Introduction

Aluminum (Al) exists in different forms in the soil environment. In addition to Al-bearing minerals such as gibbsite ($Al(OH)_3$) and kaolinite ($Al_2Si_2O_5(OH)_4$), Al can participate in strong complexation reactions with soil organic matter (SOM). Aluminum bound in this way is generally referred to as organically bound Al (Al_{org}). It can also form weaker electrostatic associations with SOM and clay minerals, resulting in exchangeable Al. Considering the important pH buffer effect of Al compounds (Skyllberg, 1999; Li and Johnson, 2016) and the toxicity of dissolved Al^{3+} in forest soils (Berggren and Mulder, 1995; Foy et al., 1999), the investigation of Al speciation in forest soils is crucial to understand the acid-base properties of soils, their chemical and biological response to changes in atmospheric acid inputs (i.e., “acid rain”), and the effects of potential mitigation strategies.

Many previous studies have focused on modeling the relationship between pH, Al solubility and solid-phase Al. Warfvinge and Sverdrup (1992) used the reaction between $Al(OH)_3$ and H^+ as the controller of pH and Al solubility in models of acidic deposition to soils and waters (Equations 1, 2). Berggren and Mulder (1995) suggested that this gibbsite solubility model is valid at pH>4.2:

$$Al(OH)_3\,(s) + 3H^+ \leftrightarrow Al^{3+} + 3H_2O \quad (1)$$

$$pAl = 3pH + pK_s \quad (2)$$

where K_s is the equilibrium constant for the reaction in (1).

Mulder and Stein (1994) suggested that organically adsorbed Al controls the Al solubility in acidic forest soils when pH is less than 4.2 and soil solutions are generally undersaturated with respect to $Al(OH)_3$. In this situation, Al^{3+} is the dominant form of dissolved monomeric inorganic Al. The binding reaction for Al^{3+} on SOM can be written as (Wesselink et al., 1996):

$$RAl^{(3-x)+} + xH^+ \leftrightarrow RH_x + Al^{3+} \quad (3)$$

where $RAl^{(3-x)+}$ represents organically bound Al sites and RH_x represents protonated humic binding sites. The equilibrium for reaction (3) can be described by the following relationship:

$$\frac{(Al^{3+})}{(H^{+})^{x}} = K_{H-Al}\ \frac{[RAl^{(3-x)^{+}}]}{[RH_{x}]} \tag{4}$$

where parentheses represent solute activities (mol L^{-1}), square brackets represent concentrations (mol kg^{-1} soil) and $K_{H\text{-}Al}$ is the complexation constant for the reaction shown in equation (3)。

Although the Clean Air Act has been in place for decades, forest and aquatic ecosystems in the northeastern United States have only recovered slowly from chronic acid deposition. Most soils in the region have high Al saturation and the base saturation remains low (Likens et al., 1996). In order to promote the recovery of forest soils from acidic deposition, mitigation strategies including calcium amendments have great potential. These amendments are generally effective in increasing soil pH, base saturation, cation exchange capacity and microbial activity (e.g., Frostegard et al., 1996). Many studies have also investigated the influence of calcium additions on the Al saturation in soils. Ingerslev (1999) reported that the concentration of exchangeable Al decreased in the upper soil horizons after eight years of liming in a Norway spruce stand in Denmark; Mijangos et al. (2010) also observed significantly lower values of Al saturation in the Gorbeia Natural Park in northern Spain. However, the effect of calcium treatment on Al in soils still includes some important uncertainties. While most studies have documented decreases in Al saturation and exchangeable Al after calcium treatment, few have examined effects on Al distribution in soils, especially the influence on organically bound Al; there is also a lack of systematic investigations tracking the change in Al forms and distribution over longer periods after calcium treatment.

The Hubbard Brook Experimental Forest (HBEF) in New Hampshire is one of the most intensively studied forest research sites in the northeastern United States. The focus of much of the research at Hubbard Brook is the small watershed ecosystem. In 1999, wollastonite ($CaSiO_3$) was applied to watershed 1 at the HBEF in order to examine the ecological and biogeochemical response of the watershed ecosystem to Ca amendment. Johnson et al. (2014) observed significant decreases in the concentration of exchangeable Al in Oi + Oe and Oa horizons, as well as the top 10 cm of the mineral soil; Shao et al. (2016) documented significant declines in the concentration of inorganic monomeric Al in soil solutions and stream water between 1997 and 2013. Our objective was to determine whether these decreases in exchangeable Al and Al concentrations in soil solutions could be explained by changes in organically bound Al in soils.

2. Materials and methods

2.1. Site description

The HBEF is located within the White Mountain National Forest in New Hampshire. Watershed 1 (W1) has an area of 11.8 ha, with an elevation range of 488 to 747 m. The HBEF has a cool, humid, continental climate, with average monthly temperatures ranging from -9°C in January to 18°C in July. Mean annual precipitation is 1400 mm, with about one-third falling as snow (Campbell et al., 2011). The major tree species in W1 are sugar maple (*Acer saccharum*), American beech (*Fagus grandifolia*) and yellow birch (*Betula alleghaniensis*), with some red spruce (*Picea rubens*), balsam fir (*Abies balsamea*), and paper birch (*Betula papyrifera*) in the uppermost zone of the watershed (Fahey et al., 2005).

Soils at the HBEF are diverse. The most common are acidic Spodosols (Haplorthods and Fragiothords), developed from till left behind after the last glaciation, with a sandy loam texture (Wang, 1997). The soil depth is highly variable, with an average of 57 cm to the C horizon in nearby watershed 5 (W5) (Johnson et al., 1991). A well-developed O horizon, averaging 7 cm in thickness, lies atop the mineral soil (50 cm). Schists and gneisses of the

Rangeley formation are the most common bedrock types.

The effective base saturation, based on neutral-salt extraction, in W1 was estimated to be 10% prior to treatment (Peters et al., 2004). In order to increase the base saturation to the estimated pre-industrial level of 19%, wollastonite ($CaSiO_3$) was applied to W1 in October 1999. An estimated load of 1028 kg Ca ha^{-1} was spread via helicopter with a nearly uniform distribution pattern (Peters et al., 2004).

2.2. Soil sampling and analysis

Watershed 1 soil samples were collected in July 1998 (pre-treatment) at 96 randomly chosen sites and in July 2002, 2006, 2010 and 2014 (post-treatment) at 100 sites. O-horizon samples were collected as combined Oi + Oe and Oa horizons using 15- by 15-cm wooden or polyvinyl chloride templates (Johnson et al., 2014). Soils in the 0-10 cm mineral soil layer (upper mineral horizons) were collected using a 3.5-cm-diameter stainless steel corer (Johnson et al., 2014). Soil samples from the combined Oi + Oe horizon were air dried and ground in a Wiley mill; samples from the Oa and the upper mineral soil were air dried and screened using 5- and 2-mm stainless steel screens, respectively (Johnson et al., 2014). Soil masses were determined based on oven-dried weight (Johnson et al., 2014).

Copper chloride ($CuCl_2$) and Na-pyrophosphate have both been used as extractants to estimate extractable soil Al. It has been suggested that $CuCl_2$ is a better extractant than the more widely used Na-pyrophosphate (Eriksson and Skyllberg 2001). Previous studies have reported that the extraction by Na-pyrophosphate releases greater amounts of Al. Skyllberg et al. (2001) reported a consistently higher amount of Al extracted by Na-pyrophosphate than $CuCl_2$ during the extraction of podzolic mineral soils in south-west Denmark; Gruba and Mulder (2008) reported the same pattern with similar mineral soils in southern Poland. In addition to exchangeable and organically bound Al, Na-pyrophosphate can dissolve amorphous Al hydroxides and hydroxy-interlayered Al (Kaiser and Zech, 1996), which $CuCl_2$

does not extract (Skyllberg et al., 2001).

Exchangeable Al, which includes Al in weak electrostatic attraction to clays and SOM, is also extracted by $CuCl_2$ (Skyllberg, 1999; Gruba and Mulder, 2008). To estimate organically bound Al, it is therefore necessary to subtract exchangeable Al from the $CuCl_2$-extractable Al (Al_{CuCl2}). If exchangeable Al is determined by KCl extraction (Al_{KCl}; Thomas, 1982; Gruba and Mulder, 2008; Johnson et al., 2014), organically bound Al can be estimated by:

$$Al_{org} = Al_{CuCl2} - Al_{KCl} \qquad (5)$$

where Al_{org} is the estimated organically bound Al, Al_{CuCl2} is the amount of $CuCl_2$-extractable Al, and Al_{KCl} is the amount of Al extracted by KCl, all typically expressed in $cmol_c$ kg^{-1}.

For each type of extraction, 3.000±0.010 g subsamples were measured and placed in 50-ml centrifuge tubes. The soil:solution ratio was 1g:20ml for the 1M KCl extraction and 1g:10ml for the 0.5M $CuCl_2$ extraction. The KCl extraction was performed for 14 hours using a mechanical vacuum extractor (Johnson et al., 2014). The $CuCl_2$ extraction was performed for 2 hours using a wrist-action shaker. The $CuCl_2$ extracts were then collected by filtration through Whatman glass fiber filters. Exchangeable Al (Al_{KCl}) was calculated from the concentration of Al in the KCl extracts measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Total extractable Al (Al_{CuCl2}) was calculated from the concentration of Al in the $CuCl_2$ extracts, measured by ICP-OES (sampling years 1998 and 2002) and flame atomic absorption spectroscopy (FAAS: sampling years 2006, 2010 and 2014). Fifteen of the $CuCl_2$ extracts from sampling year 2014 were measured by both ICP-OES and FAAS in order to examine the consistency between methods. The results showed <5% difference between the two techniques.

The corresponding soil Al pools in each horizon were calculated using the following equations:

$$\text{Exch. Al } (\text{mol}_c\ \text{m}^{-2}) = \text{Al}_{\text{KCl}}\ (\text{cmol}_c\ \text{kg}^{-1}) * \text{Soil mass } (\text{kg m}^{-2}) * 0.01 \quad (6)$$

$$\text{Org. bound Al } (\text{mol}_c\ \text{m}^{-2}) = \text{Al}_{\text{org}}\ (\text{cmol}_c\ \text{kg}^{-1}) * \text{Soil mass } (\text{kg m}^{-2}) * 0.01 \quad (7)$$

$$\text{Extract. Al } (\text{mol}_c\ \text{m}^{-2}) = \text{Exch. Al } (\text{mol}_c\ \text{m}^{-2}) + \text{Org. bound Al } (\text{mol}_c\ \text{m}^{-2}) \quad (8)$$

Where soil mass is calculated separately by three horizons.

Exchangeable acidity was measured by NaOH titration to the phenolphthalein point after 1 M KCl extraction under the conditions described above (Johnson et al., 2014). Exchangeable H (H_{KCl}) was then calculated as:

$$H_{KCl} = \text{Acidity}_{KCl} - \text{Al}_{KCl} \quad (9)$$

Total acidity (Acidity_{BaCl2}) was measured by $BaCl_2$ extraction using the $BaCl_2$-TEA method (Thomas, 1982). The 0.5 M $BaCl_2$ extracting solution was buffered to pH 8.20 using triethanolamine. Soils were then extracted using a soil:solution ratio of 1g:10ml. The extraction was performed for 30 minutes using a wrist-action shaker. The filtered extracts and blanks were titrated to pH 7.0 using either 0.2M HCl or 0.1M NaOH. Total acidity was then calculated using the difference in titrant volume between samples and blanks (Thomas, 1982).

Organically bound H (H_{org}) was calculated as:

$$H_{org} = \text{Acidity}_{BaCl2} - \text{Acidity}_{KCl} - \text{Al}_{org} \quad (10)$$

Soil pH was measured in deionized water using a water:soil ratio of 5g:1g for the O horizon and 1g:1g for the upper mineral horizon. Exchangeable bases (Ca, Na, K, Mg) were measured by ICP-OES after a 1 M NH_4Cl extraction using a soil:solution ratio of 1g:20ml for 14h in a mechanical vacuum extractor (Johnson et al., 2014). Effective cation exchange capacity (CEC_e) was calculated as:

$$CEC_e = \text{Exchangeable bases} + \text{Acidity}_{KCl} \quad (11)$$

2.3. Statistical methods

Minitab 17 was used as the statistical analysis tool. One-way analysis of variance

(ANOVA) was performed for the various soil properties, using sampling year as the "treatment" variable. To determine significant differences between samples from different years, Tukey's honestly significant difference method was used with an α-value of 0.05. Post-treatment means that were significantly different from the pre-treatment (1998) mean were interpreted as effects of the wollastonite treatment.

The Al_{CuCl2} and $Acidity_{BaCl2}$ were measured on subsets (approximately 50%) of the samples used in the research reported by Johnson et al. (2014). In order to make proper comparisons, the other data (Al_{KCl}, $Acidity_{KCl}$, etc.) were limited to the same subsets. As a result, the values reported here for exchangeable cations are slightly different from the values in Johnson et al. (2014). However, the patterns among different sampling years observed here are the same as those reported in Johnson et al. (2014) for properties common to both papers.

3. Results

3.1. Aluminum concentrations

The concentrations of organically bound Al exhibited different patterns of change in different horizons. In the Oi + Oe horizon, the organically bound Al concentration did not change significantly in the 16-year post-treatment period compared to the pretreatment value (4.62 ± 1.08 $cmol_c\ kg^{-1}$; Table 1). In the Oa horizon, the concentration of organically bound Al was significantly greater in 2002, 3 yr after the treatment (7.6 ± 1.78 $cmol_c\ kg^{-1}$), compared to the pretreatment value (4.04 ± 1.00 $cmol_c\ kg^{-1}$), and continued to increase steadily until the last year of our analysis (12.61 ± 2.98 $cmol_c\ kg^{-1}$). In the upper 10 cm of mineral soil, an even more significant increasing pattern was observed. The concentration of organically bound Al increased from 1.58±0.44 $cmol_c\ kg^{-1}$ to 2.49 ± 0.76 $cmol_c\ kg^{-1}$ in the first three years after the treatment, then the concentration nearly quadrupled by 2010 (6.72 ± 1.40 $cmol_c\ kg^{-1}$), and doubled again in 2014 (12.69 ± 1.70 $cmol_c\ kg^{-1}$) (Table 1).

The concentrations of exchangeable Al decreased slightly in the Oi + Oe horizon after the treatment, compared to the pretreatment value (1.184 ± 0.26 $\mathrm{cmol_c\ kg^{-1}}$). While this decrease was not statistically significant in the subset of the data used in this analysis, it was significant for the entire dataset (Johnson et al., 2014). In the Oa horizon, exchangeable Al concentrations decreased from 7.14 ± 0.86 $\mathrm{cmol_c\ kg^{-1}}$ to 4.52 ± 0.68 $\mathrm{cmol_c\ kg^{-1}}$ three years after the treatment. The concentration then remained significantly lower than the pretreatment value in the years that followed. There was no noticeable trend in exchangeable Al concentration in the upper mineral soil (Table 1).

No significant changes were observed for total extractable Al, the sum of organically bound Al and exchangeable Al, in the Oi + Oe horizon (Table 1). In the Oa horizon, there was an increasing, but non-significant, trend in the extractable Al concentration after the wollastonite treatment. Extractable Al concentrations continuously increased in the 0-10 cm mineral layer after the treatment, though this pattern only became significant in 2010 (Table 1).

3.2. Aluminum pools

The pool of organically bound Al in Oi + Oe and Oa horizons showed little change through the 16-year analysis period (Table 2). In the Oi + Oe horizon, the organically bound Al pool ranged from 0.158 ± 0.038 $\mathrm{mol_c\ m^{-2}}$ to 0.326 ± 0.098 $\mathrm{mol_c\ m^{-2}}$ without any trends or differences between post-treatment and pre-treatment values. A similar pattern was observed in the Oa horizon. In the upper mineral soil, the amount of organically bound Al increased significantly from the pretreatment value (0.714 ± 0.165 $\mathrm{mol_c\ m^{-2}}$) to the last analysis year (4.295 ± 0.570 $\mathrm{mol_c\ m^{-2}}$) (Table 2).

Similar to the organically bound Al pools, exchangeable Al pools did not change significantly in the Oi + Oe horizon. In the Oa horizon, however, the amount of exchangeable Al decreased after the treatment, and the difference between the pre-treatment value (1.227 ±

0.293 $mol_c\ m^{-2}$) and the post-treatment value became statistically significant in 2002 (0.607 ± 0.168 $mol_c\ m^{-2}$). The decreasing trend in exchangeable Al in the Oa horizon persisted through 2014 (0.191 ± 0.044 $mol_c\ m^{-2}$). In the 0-10 cm mineral layer, the exchangeable Al pool showed little change until 2014 (1.697 ± 0.158 $mol_c\ m^{-2}$), which was significantly lower than the pretreatment value (2.886 ± 0.157 $mol_c\ m^{-2}$) (Table 2).

Extractable Al pools showed no significant change in the Oi + Oe horizon. In the Oa horizon, the pool decreased steadily and remained about 50% lower than the pretreatment value (2.200 ± 0.698 $mol_c\ m^{-2}$) in post-treatment years. In the upper mineral soil, the amount of extractable Al started to increase significantly in 2010 (4.782 ± 0.518 $mol_c\ m^{-2}$) and reached 5.972 ± 0.689 $mol_c\ m^{-2}$ in 2014 (Table 2).

3.3. Organically bound H

Prior to the wollastonite treatment, the concentration of organically bound H in the Oi+Oe horizon was 62.64 ± 2.45 $cmol_c\ kg^{-1}$ (Table 1). The concentration of organically bound H significantly decreased to 48.86 ± 1.98 $cmol_c\ kg^{-1}$ in 2002 due to the wollastonite treatment, then recovered to the pretreatment level after 2010. In the Oa horizon, none of the post-treatment concentrations of organically bound H were significantly different from the pre-treatment mean (Table 1). No significant changes in organically bound H were observed in the upper mineral soil (Table 1).

The organically bound H pools were the predominant pools of the total acidity in all three horizons. Organically bound H accounted for more than 80% and 65% of total acidity in the Oi+Oe horizon and Oa horizon, respectively. In the upper mineral soil, over 50% of the total acidity could be attributed to organically bound H.

4. Discussion

In the Oi + Oe horizon, both the exchangeable Al and organically bound Al concentrations were relatively constant over time. Also, most of the extractable aluminum was in the organically bound form (4 to 6 $\text{cmol}_c\ \text{kg}^{-1}$), compared to the exchangeable form (around 1 $\text{cmol}_c\ \text{kg}^{-1}$). In the Oa horizon, the concentrations of exchangeable Al and organically bound Al showed strikingly different trends after the treatment. Exchangeable Al concentrations have decreased by about 50%, whereas organically bound Al concentrations have approximately tripled (Figure 1). Thus, the predominant form of extractable Al in Oa horizons has shifted from exchangeable Al (pretreatment) to organically bound Al (after treatment). In the upper mineral soil (0-10 cm), although exchangeable Al concentrations remained relatively constant after the treatment, organically bound Al concentrations increased significantly and eventually surpassed exchangeable Al in 2010. By 2014, organically bound Al in the 0-10 cm mineral soil layer was more than twice the concentration of exchangeable Al. Total extractable Al concentrations remained relatively constant in Oi + Oe and Oa horizons, but increased significantly in upper mineral soils due to the increase in the organically bound Al concentration (Fig. 1).

The size of the Al pools in different horizons reflects the combination of the Al concentrations and the soil masses. In the Oi + Oe horizon, no significant changes were observed in soil mass, exchangeable Al or organically bound Al concentrations. As a result, the various Al pools in this layer remained relatively constant after treatment. The pattern in the Oa horizon was much different. Since the mass of soil in the Oa horizon decreased continuously and significantly after the treatment (Johnson et al., 2014; Table 2), this change affected pools of both exchangeable and organically bound Al. Since the concentration of exchangeable Al in the Oa horizon decreased significantly after the wollastonite treatment, the exchangeable Al pool in the Oa horizon dramatically decreased through the 16-year study period (Table 2). However, the pool of organically bound Al remained approximately constant in the Oa horizon as the increasing Al_{org} concentrations were offset by the declining soil mass. In the 0-10 cm mineral layer, although exchangeable Al concentration showed little change, the corresponding pool value decreased and was significantly lower in 2014 compared to the pretreatment value due to lower soil mass (Table 2). This result is surprising, though, because there is no reason to believe that mineral soil mass would be affected by the wollastonite treatment. Incorporation of organic matter migrating downward from the Oa horizon may partly explain this apparent decrease in soil mass, but we did not see a consistent increase in soil C in the 0-10 cm mineral soil layer after treatment (Johnson et al., 2014). The soil coring method we used is subject to considerable uncertainty due to compression of soil in the corer and refusal of the corer by stones. Despite the apparent trend in soil mass, the pool of organically bound Al in the upper mineral soil increased dramatically, from 0.714 ± 0.165 to 4.295 ± 0.575 mol_c m^{-2} due to the increasing soil concentration (Table 2).

The distribution of the extractable Al pool among the three horizons also changed after the wollastonite treatment. The upper mineral soil contained an increasingly larger proportion of the extractable Al in these layers over time. In 1998, prior to treatment, about 60% of the extractable Al was in the 0-10 cm mineral soil layer. This value has increased to 70% in 2010 and nearly 85% in 2014 (Fig. 2). Also the importance of organically bound Al has increased in the Oa horizon and 0-10 cm mineral soil layer after treatment. Prior to treatment, the sum of the pools of organically bound Al in Oa and upper mineral horizons represented 30% of the extractable Al in the three horizons, while this percentage increased to 41% in 2006, 55% in 2010 and nearly 71% in 2014. In contrast, the importance of exchangeable Al significantly decreased from 67% in 1998 to 53% in 2006, 40% in 2010 and 25% in 2014. These results indicate that extractable Al has migrated to the deeper horizons after wollastonite treatment and has become more tightly bound to the soil.

4.1. Downward migration of Al

Johnson et al. (2014) showed that Ca derived from the wollastonite moved progressively downward through the three horizons after the treatment. They also found that the migration of Ca was accompanied by progressive decreases in soil exchangeable acidity. The replacement of H and Al by Ca on exchange sites of soil organic matter in organic horizons could facilitate the progressive downward migration of Al and H to lower soil horizons. For instance, the decrease in exchangeable H in the Oi + Oe horizon shortly after the wollastonite addition was accompanied by a significant decrease in pH_w in the Oa horizon one year after the treatment (Johnson et al., 2014). Similarly, the increasing organically bound Al in the upper mineral soil layers is likely the result of migration of Al from the Oa horizon. Although the organically bound Al pool in the Oa horizon did not change significantly after treatment, exchangeable Al pools decreased rapidly: the pool had been halved 4 years after the treatment and had decreased by 85% by 2014 (Table 2). The loss of exchangeable Al from the Oa horizon thus supplied reactive Al, most of which was retained in the 0-10 cm mineral soil layer as organically bound Al. The concentration of Al_{org} was only very weakly correlated with soil C in the Oa horizon and upper mineral soil (Fig. 3), suggesting that the concentrations of organically bound Al were not controlled by the availability of binding sites on SOM. We did observe a correspondence between the temporal patterns in pH and Al:C ratios in the Oa horizon, which is consistent with equation (4) (Fig. 4). However, the relationship was not observed in the 0-10 cm mineral soil layer, suggesting that the formation of organically adsorbed Al was not controlled by equation (4) in this layer. The increasing range of Al:C ratios during the post-treatment period in both layers (Fig. 4) indicates a heterogeneous Al binding capability in SOM. We did not observe significant downward migration of Al from the Oi + Oe horizon. Aluminum concentrations were relatively low in the Oi + Oe horizon prior to the treatment.

4.2. The shift in soil Al forms

The shift from exchangeable Al to organically bound Al that was observed in Oa and upper mineral horizons was a complex response to the Ca amendment. Because Ca has a much lower affinity for organic binding sites than Al (Tam and McColl, 1990), it would need to be present in very high concentrations in soil solution to displace significant amounts of Al_{org}. However, the Ca amendment may also affect organically bound Al indirectly. The displacement of exchangeable Al by Ca would elevate reactive Al concentrations in pore waters near soil particle surfaces. According to equation (4), if the concentrations of organically bound H are approximately constant (Table 1), organically bound Al should be positively correlated with the ratio $(Al^{3+}) / (H^+)^x$ in soil solution. Lower H^+ activities in soil solutions, due to the neutralization of H^+ during wollastonite dissolution, would increase the $(Al^{3+}) / (H^+)^x$ ratio and thus favor elevated concentrations of organically bound Al in soil. This explanation is consistent with Skyllberg (1999), who suggested that the concentration of organically bound Al in O and E horizons in acidic forest soils is a result of interactions between organic acidity and Al alkalinity generated through mineral weathering. In our study, however, the alkalinity is generated by Ca-silicate (wollastonite) rather than Al-silicate weathering. Combined with the increase in pH, these two conditions allow Al to compete favorably with H on SOM binding sites and result in the accumulation of organically bound Al. Although Al may also compete for weaker exchangeable sites, the relatively high concentration of Ca in the soil solution after wollastonite addition resulted in a decrease in exchangeable Al.

The shift in the binding strength of Al in the Oa horizon did not increase the pool of organically bound Al because of the large decrease in the mass of the Oa horizon after treatment (Table 2). In the upper mineral horizon, however, there were large and significant increases in both the concentration and pool of organically bound Al. This increase appears to be unrelated to pH. Indeed, organically bound Al concentrations increased by about 65% in the 0-10 cm mineral soil layer, while pH significantly decreased through 2002 (Table 1). This pattern suggests that a large amount of reactive Al must have entered and been immobilized in the upper mineral soil after the treatment. The pH in the upper mineral horizon eventually increased in the late post-treatment years, contributing to accelerated increases in organically bound Al in 2006-2014 (Tables 1, 2).

4.3. Soil solution observations

Considering the large changes in organically bound Al concentrations and pools in the Oa horizon and upper mineral soil after the wollastonite treatment, soil solution chemistry may provide insight into the chemistry and transport of Al in W1 soils. Shao et al. (2016) reported monthly soil solution data for the Oa and Bh horizons at 13 locations in Watershed 1. They observed significant decreasing trends in organic monomeric Al (Al_o) and inorganic monomeric Al (Al_i) concentrations from 1997 to 2014. After the wollastonite treatment, the Al_o concentration significantly decreased, compared to the pretreatment level. Inorganic monomeric Al concentration showed a similar pattern, but with an even more dramatic decrease. Over the same period, organically bound Al concentrations in the soil tripled (Fig. 5).

The negative correlation between the trends of organically bound Al in the soil and Al concentrations in soil solutions is not a coincidence. The solubility of organically bound Al in soils is highly pH dependent (Equation 3, 4) (Fakhraei and Driscoll, 2015). The increasing pH observed in Oa horizon soil solutions can largely explain the decreasing Al_o concentrations in soil solutions since dissolved organic carbon (DOC) concentrations were not significantly affected by the treatment (Shao et al., 2016). The reduction in Al_o losses in soil solution likely contributed to the increasing concentrations of organically bound Al in the

Oa horizon. The changes in Al_i concentrations are also consistent with the results in this study. The replacement of exchangeable Al by Ca in the first few post-treatment years partially compensated for the reduced Al solubility due to pH increases, resulting in moderate declines in Al_i. After 2002, exchangeable Al concentrations no longer decreased significantly (Table 1) and Al_i concentrations in soil solution started to decrease sharply (Shao et al., 2016).

Dissolved aluminum fluxes, including both Al_o and Al_i, were also influenced by the wollastonite treatment. Using watershed 6 (W6) as the reference watershed, the post-treatment difference in the Bh horizon Al fluxes between W6 and W1 (W6 – W1) represents the net immobilization of Al in the upper three soil layers. The bottom of the Bh horizon, where the Bh lysimeters are located, lies approximately 10 cm below the organic-mineral boundary (Johnson et al., 1991). The annual Al flux out of the Bh horizon was consistently lower on W1 than W6 from 2003 to 2014, though this discrepancy was not observed before 2003 due to the delayed response to the wollastonite treatment (Fig. 6). Summing the differences in Al fluxes for 1999-2014, there was a net decrease of 0.15 mol_c m^{-2} of Al exiting the Bh horizon on W1 relative to W6. Over that same period, extractable Al in the Oi + Oe, Oa and 0-10 cm mineral soil layers increased by 1.42 mol_c m^{-2} (Table 2), more than enough to account for the decreases in soil solution fluxes. Formation and dissolution of secondary mineral phases such as gibbsite and kaolinite may also contribute to the decreasing Al concentrations and fluxes in soil solutions and stream waters observed in W1 after the wollastonite treatment.

4.4. Response of organically bound H

Organically bound H concentrations decreased less and showed much more resilience to the Ca amendment than organically bound Al concentrations in the Oa and 0-10 cm mineral soil layers (Table 1). This pattern is not a surprise since the H_{org} concentrations are much larger than Al_{org} and both exchangeable Al and H. Thus, the amount of H and Al released from exchange sites after displacement by Ca are relatively small compared to the H_{org} pool. However, there is an ongoing shift from R-H_x (H_{org}) to R-Al (Al_{org}), consistent with increased pH in soil solutions (Equations 3, 4) and soils. Organically bound Al has been the major sink for reactive Al after the wollastonite treatment. In contrast, H^+ in the soil solution on W1 is largely neutralized by H_4SiO_4 formation in the dissolution of the wollastonite ($CaSiO_3$). Organically bound H pools decreased in the Oa horizon in tandem with the decreasing soil mass, but unlike Al, H_{org} did not accumulate in the 0-10 cm mineral soil layer. With Ca largely displacing the weakly bound (exchangeable) Al and H in the Oa and 0-10 cm mineral soil layers, and Al_{org} displacing H_{org}, the net effect has been an increase in Ca-saturation on weak binding sites, an increase in Al-saturation on strong binding sites, and the loss of H from both.

4.5. Biogeochemical implications

The wollastonite treatment on W1 at Hubbard Brook in 1999 had a significant impact on the distribution of Al among fractions and among organic and mineral horizons. Soil Al has migrated from the Oa horizon to the upper mineral soil and is more tightly bound after the treatment. The predominant form of Al-SOM binding has shifted from the weaker exchangeable Al form to organically bound Al. Cation-exchange reactions between Ca derived from the added wollastonite and exchangeable H and Al have caused reductions in exchangeable H and Al. The Al released from exchange sites was largely retained as Al_{org}, while H was neutralized in weathering reactions.

The immobilization of Al observed in the Oa horizon and upper mineral soil on W1 contributed to the improvement of tree health. Improvement in the health and vigor of red spruce and sugar maple was observed on watershed 1 after the $CaSiO_3$ treatment. Halman et al. (2008) reported a significant increase in foliar Ca and total sugar concentrations in red spruce, while Juice et al. (2006) and Halman et al. (2013) observed an increase in survival and foliar Ca concentrations of sugar maple. In particular, a decrease in fine root Ca/Al molar ratios was proposed as a major factor in these changes. The immobilization of Al in the soil can also improve fish survival in downstream aquatic systems by decreasing the flux of Al from the terrestrial to the aquatic environment (e.g., Baker and Schofield, 1982). By increasing Ca availability and immobilizing Al, widespread $CaSiO_3$ treatment could benefit forest and aquatic systems in the northeast United States that were impacted by chronic acidification in the 20th century, though the level of acid rain itself has declined substantially.

The conversion of exchangeable Al to organically bound Al observed in this study has reduced the Al solubility in the Oa and upper mineral horizons after wollastonite treatment. The degree to which Al-binding by SOM is reversible will largely determine the long-term effects. The increased pH in organic and upper mineral soil layers may begin to reverse when the influence of Ca amendment has been diminished. Once this happens, Al may be released to the soil solution through decomplexation or solubilization of Al_{org}. Depending on the equilibrium between organic Al and toxic inorganic monomeric Al in soil solution, future mobilization of organically bound Al may have consequences for forest health and downstream aquatic ecosystems.

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Table 1

Organically bound aluminum, exchangeable aluminum and total extractable aluminum concentrations in soils at the Hubbard Brook Experimental Forest before and after the wollastonite ($CaSiO_3$) treatment on watershed 1. † Means ± standard errors. Means followed by different letters in a row are significantly different ($P < 0.05$).

Property	**Year**				
Oi + Oe horizon	1998	2002	2006	2010	2014
Organically bound Al, cmol$_c$ kg^{-1}	4.62±1.08 A†	3.13±0.71 A	3.85±0.82 A	6.07±1.30 A	5.94±1.40 A
Exchangeable Al, cmol$_c$ kg^{-1}	1.184±0.26 A	0.76±0.15 A	1.052±0.22 A	0.973±0.10 A	0.738±0.25 A
Total extractable Al, cmol$_c$ kg^{-1}	5.81±1.31 A	3.89±0.83 A	4.9±1.01 A	7.02±1.40A	6.68±1.62 A
Organically bound H, cmol$_c$ kg^{-1}	62.64±2.45 A	48.86±1.98 B	52.31±1.56 B	60.44±2.39 A	66.5±1.98 A
Exchangeable H, cmol$_c$ kg^{-1}	7.055±0.446 A	3.623±0.282 C	4.881±0.290 B	4.149±0.261 B C	3.627±0.192 C
Exchangeable Ca, cmol$_c$ kg^{-1}	5.487±0.376 C	36.44±2.48 A	32.07±1.59 A	24.56±1.45 B	24.40±1.08 B
Bases, cmolc/kg	7.575±0.465 C	40.17±2.65 A	36.71±1.70 A	28.39±1.59 B	28.92±1.18 B
Exchangeable acidity, cmol$_c$ kg^{-1}	8.192±0.450 A	4.383±0.263 C	5.932±0.326 B	5.117±0.339 B C	4.365±0.263 C
Total acidity, cmol$_c$ kg^{-1}	75.46±2.07 A	56.38±2.10 B	62.09±1.66 B	71.63±2.63 A	76.81±1.80 A
CEC$_e$, cmol$_c$ kg^{-1}	15.767±0.618 C	44.55±2.64 A	42.65±1.60 A	33.51±1.55 B	33.29±1.06 B
pH$_w$	3.89±0.03 C	4.53±0.07 A B	4.48±0.05 B	4.68±0.05 A	4.38±0.05 B

Property	**Year**				
Oa horizon	1998	2002	2006	2010	2014
Organically bound Al, cmol$_c$ kg^{-1}	4.04±1.00 B	7.60±1.78 A B	9.47±1.69 A B	10.11±1.81 A B	12.61±2.98 A
Exchangeable Al, cmol$_c$ kg^{-1}	7.14±0.86 A	4.52±0.68 B	4.68±0.61 B	3.06±0.47 B	2.97±0.52 B
Total extractable Al, cmol$_c$ kg^{-1}	11.12±1.73 A	12.12±2.36 A	14.15±2.2 A	13.17±2.19 A	15.58±3.14 A
Organically bound H, cmol$_c$ kg^{-1}	44.70±2.36 A B C	41.73±2.93 C	55.23±2.99 A	44.03±2.84 B C	54.62±3.39 A B
Exchangeable H, cmol$_c$ kg^{-1}	4.894±0.443 A	3.625±0.332 A B	2.346±0.240 B	2.237±0.346 B	4.332±0.557 A
Exchangeable Ca, cmol$_c$ kg^{-1}	3.707±0.494 C	11.49±1.36 A	10.90±1.20 A	7.033±0.704 B C	9.79±1.26 A B
Bases, cmol$_c$ kg^{-1}	5.434±0.565 C	13.3±1.44 A	12.70±1.29 A	8.260±0.756 B C	11.54±1.33 A B
Exchangeable acidity, cmol$_c$ kg^{-1}	11.952±0.662 A	7.944±0.636 B	6.926±0.519 B C	5.283±0.463 C	7.266±0.662 B C
Total acidity, cmol$_c$ kg^{-1}	60.69±2.61 B C	57.27±3.00 C	71.62±3.18 A B	59.42±3.25 C	74.50±3.20 A
CEC$_e$, cmol$_c$ kg^{-1}	17.386±0.850 A B	21.25±1.30 A	19.63±1.14 A	13.543±0.734 B	18.81±1.14 A
pH$_w$	3.84±0.06 C	3.85±0.08 C	4.11±0.05 B	4.42±0.04 A	4.01±0.06 B C

Property	**Year**				
0-10 cm mineral soil layer	1998	2002	2006	2010	2014
Organically bound Al, cmol$_c$ kg^{-1}	1.58±0.44 C	2.49±0.76 B C	4.79±1.1 B C	6.72±1.40 B	12.69±1.7 A
Exchangeable Al, cmol$_c$ kg^{-1}	5.78±0.47 A	5.74±0.61 A	6.07±0.62 A	5.65±0.34 A	4.94±0.49 A
Total extractable Al, cmol$_c$ kg^{-1}	7.00±0.79 B	7.78±1.27 B	10.52±1.6 B	12.18±1.51 A B	17.55±2.07 A
Organically bound H, cmol$_c$ kg^{-1}	25.45±2.04 A	22.86±1.82 A	29.3±2.05 A	28.73±1.95 A	23.76±2.55 A
Exchangeable H, cmol$_c$ kg^{-1}	1.848±0.239 A	2.011±0.229 A	0.998±0.131 B	0.754±0.122 B	2.103±0.157 A
Exchangeable Ca, cmol$_c$ kg^{-1}	0.661±0.158 C	0.933±0.119 A B C	1.854±0.365 A B	0.823±0.083 B C	1.934±0.451 A
Bases, cmol$_c$ kg^{-1}	1.169±0.194 A B	1.350±0.148 A B	2.410±0.417 A	1.189±0.099 B	2.373±0.472 A B
Exchangeable acidity, cmol$_c$ kg^{-1}	7.536±0.426 A	7.718±0.710 A	6.848±0.596 A	6.281±0.276 A	6.925±0.558 A
Total acidity, cmol$_c$ kg^{-1}	34.52±2.53 A	33.06±2.86 A	40.94±3.00 A	41.11±2.49 A	42.32±3.01 A
CEC$_e$, cmol$_c$ kg^{-1}	8.704±0.502 A	9.068±0.778 A	9.257±0.777 A	7.469±0.278 A	9.298±0.673 A
pH$_w$	3.94±0.06 B	3.65±0.07 C	4.02±0.05 A B	4.18±0.04 A	4.08±0.05 A B

Table 2

Organically bound aluminum, exchangeable aluminum and extractable aluminum pools in soils at the Hubbard Brook Experimental Forest before and after the wollastonite ($CaSiO_3$) treatment on watershed 1. † Means ± standard errors. Means followed by different letters in a row are significantly different ($P < 0.05$).

Property	**Year**				
Oi + Oe horizon	1998	2002	2006	2010	2014
Dry mass, kg m^{-2}	3.887±0.317 A B†	4.699±0.446 A	3.972±0.249 A B	4.425±0.604 A	2.844±0.230 B
Organically bound Al, mol$_c$ m^{-2}	0.187±0.052 A	0.200±0.071 A	0.158±0.038 A	0.326±0.098 A	0.250±0.129 A
Exchangeable Al, mol$_c$ m^{-2}	0.058±0.022 A	0.051±0.015 A	0.046±0.011 A	0.068±0.030 A	0.036±0.021 A
Total extractable Al, mol$_c$ m^{-2}	0.245±0.073 A	0.251±0.083 A	0.203±0.047 A	0.393±0.122 A	0.286±0.149 A
Organically bound H, mol$_c$ m^{-2}	2.444±0.235 A	2.293±0.247 A	2.036±0.128 A	2.711±0.396 A	1.879±0.148 A
Exchangeable H, mol$_c$ m^{-2}	0.277±0.033 A	0.164±0.019 B C	0.193±0.018 B	0.159±0.022 B C	0.101±0.010 C
Exchangeable Ca, mol$_c$ m^{-2}	0.205±0.019 D	1.553±0.145 A	1.196±0.079 B	0.912±0.077 B C	0.647±0.043 C
Bases, mol$_c$ m^{-2}	0.281±0.024 D	1.710±0.157 A	1.370±0.087 A B	1.052±0.085 B C	0.763±0.048 C
Exchangeable acidity, mol$_c$ m^{-2}	0.330±0.036 A	0.215±0.025 A B	0.239±0.020 A B	0.226±0.035 A B	0.137±0.024 B
Total acidity, mol$_c$ m^{-2}	2.961±0.268 A	2.708±0.297 A	2.432±0.150 A	3.263±0.475 A	2.266±0.227 A
CEC$_e$, mol$_c$ m^{-2}	0.611±0.055 D	1.925±0.171 A	1.608±0.098 A B	1.278±0.106 B C	0.900±0.058 C D

Property	**Year**				
Oa horizon	1998	2002	2006	2010	2014
Dry mass, kg m^{-2}	15.11±3.07 A	9.26±1.74 A B	7.123±0.989 B	8.21±1.31 B	5.174±0.554 B
Organically bound Al, mol$_c$ m^{-2}	0.990±0.432 A	1.177±0.425 A	0.743±0.188 A	1.203±0.333 A	0.811±0.253 A
Exchangeable Al, mol$_c$ m^{-2}	1.227±0.293 A	0.607±0.168 A B	0.434±0.102 B	0.356±0.091 B	0.191±0.044 B
Total extractable Al, mol$_c$ m^{-2}	2.200±0.698 A	1.784±0.583 A	1.178±0.281 A	1.559±0.414 A	1.002±0.263 A
Organically bound H, mol$_c$ m^{-2}	6.470±1.360 A	3.591±0.681 A B	3.275±0.342 B	3.304±0.411 B	2.496±0.293 B
Exchangeable H, mol$_c$ m^{-2}	0.572±0.140 A	0.259±0.043 B	0.112±0.014 B	0.127±0.022 B	0.266±0.066 B
Exchangeable Ca, mol$_c$ m^{-2}	0.403±0.094 C	0.702±0.065 A	0.487±0.052 A	0.408±0.056 B	0.403±0.051 B
Bases, mol$_c$ m^{-2}	0.606±0.123 A B	0.842±0.073 A	0.581±0.056 A B	0.488±0.061 B	0.479±0.056 B
Exchangeable acidity, mol$_c$ m^{-2}	1.765±0.343 A	0.832±0.172 B	0.531±0.097 B	0.479±0.089 B	0.457±0.084 B
Total acidity, mol$_c$ m^{-2}	9.23±1.96 A	5.60±1.19 A B	4.549±0.575 B	4.986±0.770 B	3.762±0.448 B
CEC$_e$, mol$_c$ m^{-2}	2.370±0.433 A	1.674±0.204 A B	1.111±0.110 B	0.967±0.113 B	0.935±0.114 B
Property	**Year**				
0-10 cm mineral soil layer	1998	2002	2006	2010	2014
Dry mass, kg m^{-2}	56.78±2.81 A	57.6±3.34 A	55.61±3.58 A	44.13±2.74 B	36.31±2.55 B
Organically bound Al, mol$_c$ m^{-2}	0.714±0.165 C	0.890±0.244 B C	1.570±0.290 B C	2.455±0.492 B	4.295±0.575 A
Exchangeable Al, mol$_c$ m^{-2}	2.886±0.157 A	2.732±0.202 A	2.624±0.164 A	2.389±0.154 A	1.697±0.158 B
Total extractable Al, mol$_c$ m^{-2}	3.391±0.254 B	3.359±0.324 B	4.020±0.376 B	4.782±0.518 A B	5.972±0.689 A
Organically bound H, mol$_c$ m^{-2}	12.364±0.550 A	11.359±0.618 A	13.434±0.808 A	11.657±0.726 A	7.856±0.929 B
Exchangeable H, mol$_c$ m^{-2}	1.013±0.115 A B	1.060±0.105 A	0.512±0.069 C D	0.310±0.061 D	0.713±0.067 B C
Exchangeable Ca, mol$_c$ m^{-2}	0.311±0.042 B	0.491±0.060 B	0.720±0.076 A	0.335±0.031 B	0.435±0.048 B
Bases, mol$_c$ m^{-2}	0.555±0.049 B	0.690±0.063 B	0.933±0.080 A	0.482±0.041 B	0.565±0.051 B
Exchangeable acidity, mol$_c$ m^{-2}	3.871±0.155 A	3.775±0.225 A	3.050±0.155 B	2.654±0.143 B C	2.409±0.188 C
Total acidity, mol$_c$ m^{-2}	16.90±0.66 A B	16.03±0.75 A B	18.05±0.90 A	16.49±0.86 A B	14.26±1.22 B
CEC$_e$, mol$_c$ m^{-2}	4.426±0.144 A	4.465±0.229 A	3.984±0.152 A	3.136±0.159 B	2.941±0.203 B

Figure Legends

Fig. 1. Trends in exchangeable Al, organically bound Al and total extractable Al concentrations in Oi + Oe, Oa and upper mineral horizons from 1998 to 2014. Treatment with wollastonite ($CaSiO_3$) occurred in October, 1999.

Fig. 2. Distribution of Al among exchangeable and organically bound pools in Oie, Oa and 0-10 cm mineral soil layers. The upper graph shows the amount of different types of extractable Al, the lower graph shows the distribution. Treatment with wollastonite ($CaSiO_3$) occurred in October, 1999.

Fig. 3. Relationship between percent carbon and Al_{org} concentrations ($cmol_c$ kg^{-1}) in the Oa horizon and 0-10 cm mineral soil layer at the Hubbard Brook Experimental Forest. Data were classified as pretreatment (1998) and post-treatment (2002, 2006, 2010 and 2014).

Fig. 4. pH and Al_{org} :C ratios ($cmol_c$ g^{-1}) in the Oa horizon (blue boxes) and 0-10 cm mineral soil layer (gray boxes) on W1 at the Hubbard Brook Experimental Forest, including data from before (1998) and after (2002, 2006, 2010 and 2014) the wollastonite ($CaSiO_3$) treatment. Treatment occurred in October, 1999.

Fig. 5. Influence of the Ca amendment on soluble Al concentrations in the Oa horizon. The solid line represents organic monomeric Al (Al_o) concentrations in soil solutions. The dashed line represents concentrations of inorganic monomeric Al (Al_i). Box charts represent box-and-whisker plots of organically bound Al concentrations on the soil binding sites, where

the center line in the box represents median value and the "△" represents the mean value. Extreme outliers have been omitted from the box plots for clarity. Soil solution samples were collected from 1997 to 2014. Soil samples were collected in 1998, 2002, 2006, 2010 and 2014. Treatment with wollastonite ($CaSiO_3$) occurred in October, 1999 (Red line).

Fig. 6. Annual dissolved Al fluxes in Bh horizon soil solutions was calculated from 1997 to 2014. The difference between W6 and W1 (W6-W1) represents the net immobilization of Al due to the treatment, assuming the pretreatment Al flux between the two watersheds was comparable. Treatment with wollastonite ($CaSiO_3$) occurred in October, 1999. Data from Shao et al. (2016).

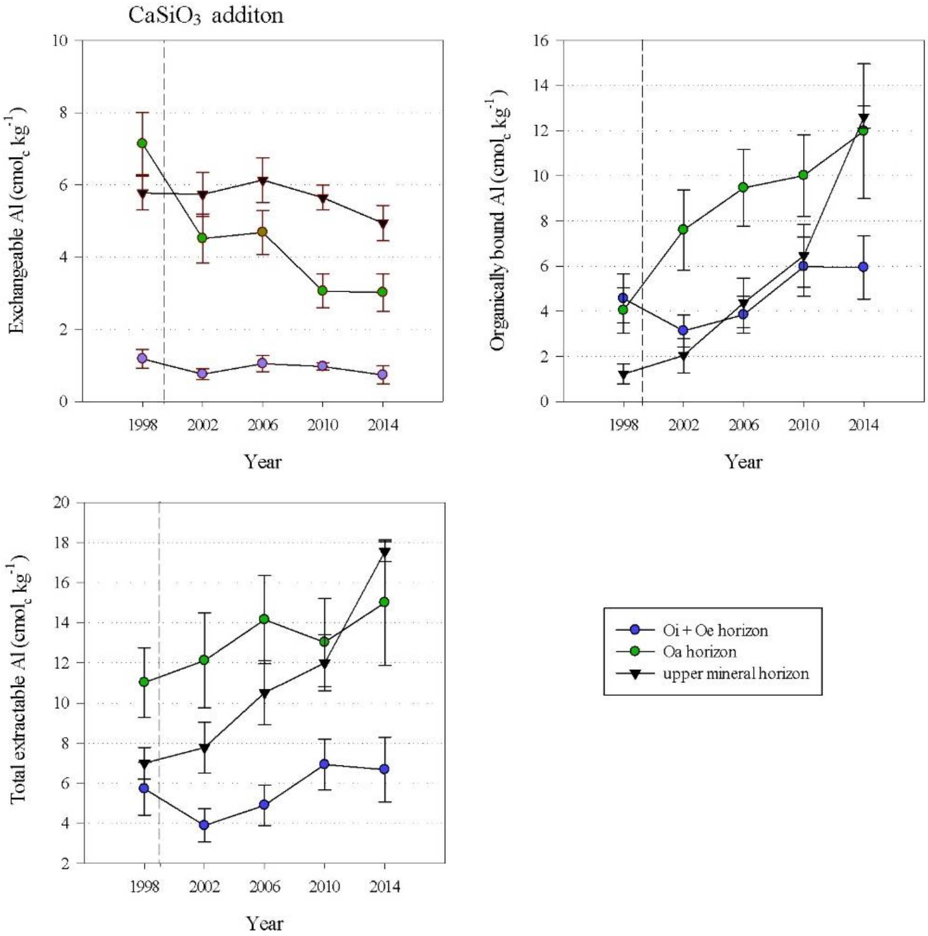
CaSiO$_3$ additon
Exchangeable Al (cmol$_c$ kg^{-1})
0
2
4
6
8
10
1998
2002
2006
2010
2014
Year
Organically bound Al (cmol$_c$ kg^{-1})
0
2
4
6
8
10
12
14
16
Total extractable Al (cmol$_c$ kg^{-1})
2
4
6
8
10
12
14
16
18
20
Oi + Oe horizon
Oa horizon
upper mineral horizon

Fig. 1.

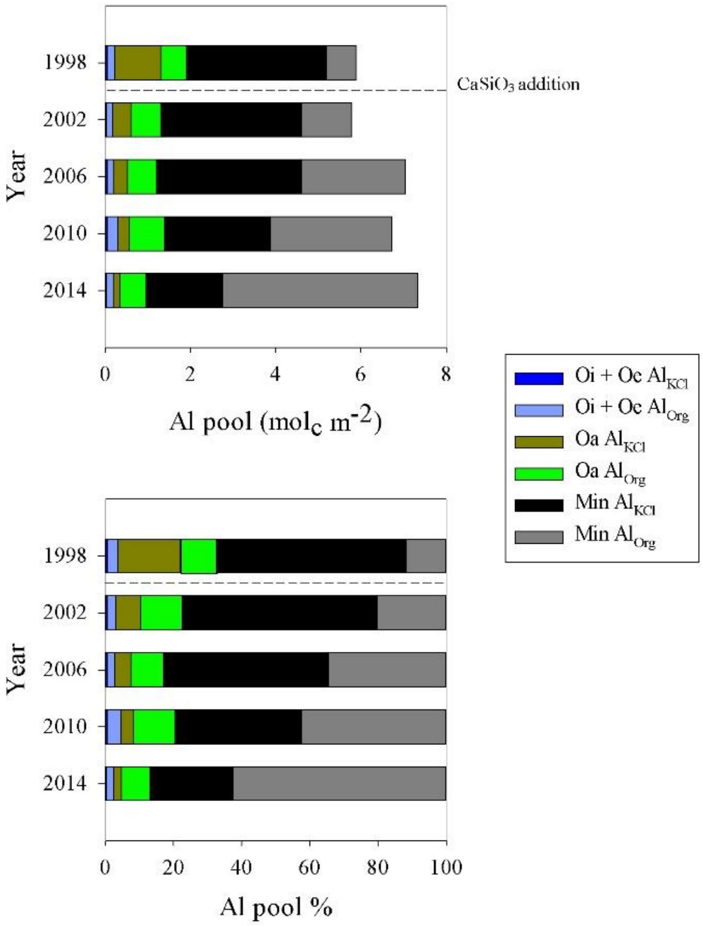
1998
2002
2006
2010
2014
Year
CaSiO₃ addition
0
2
4
6
8
Al pool (molc m-2)
Oi + Oe AlKCl
Oi + Oe AlOrg
Oa AlKCl
Oa AlOrg
Min AlKCl
Min AlOrg
1998
2002
2006
2010
2014
Year
0
20
40
60
80
100
Al pool %

Fig. 2.

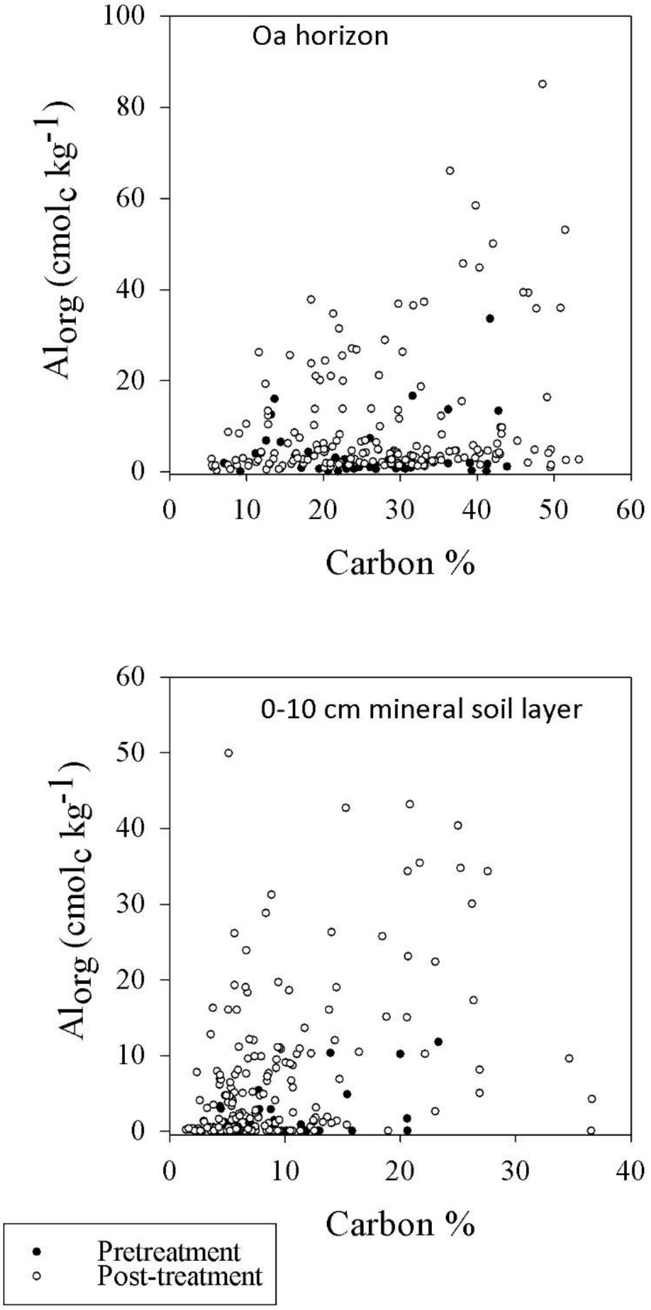
Oa horizon
Al_{org} (cmol$_c$ kg^{-1})
100
80
60
40
20
0
0
10
20
30
40
50
60
Carbon %
0-10 cm mineral soil layer
Al_{org} (cmol$_c$ kg^{-1})
60
50
40
30
20
10
0
0
10
20
30
40
Carbon %
● Pretreatment
○ Post-treatment

Fig. 3.

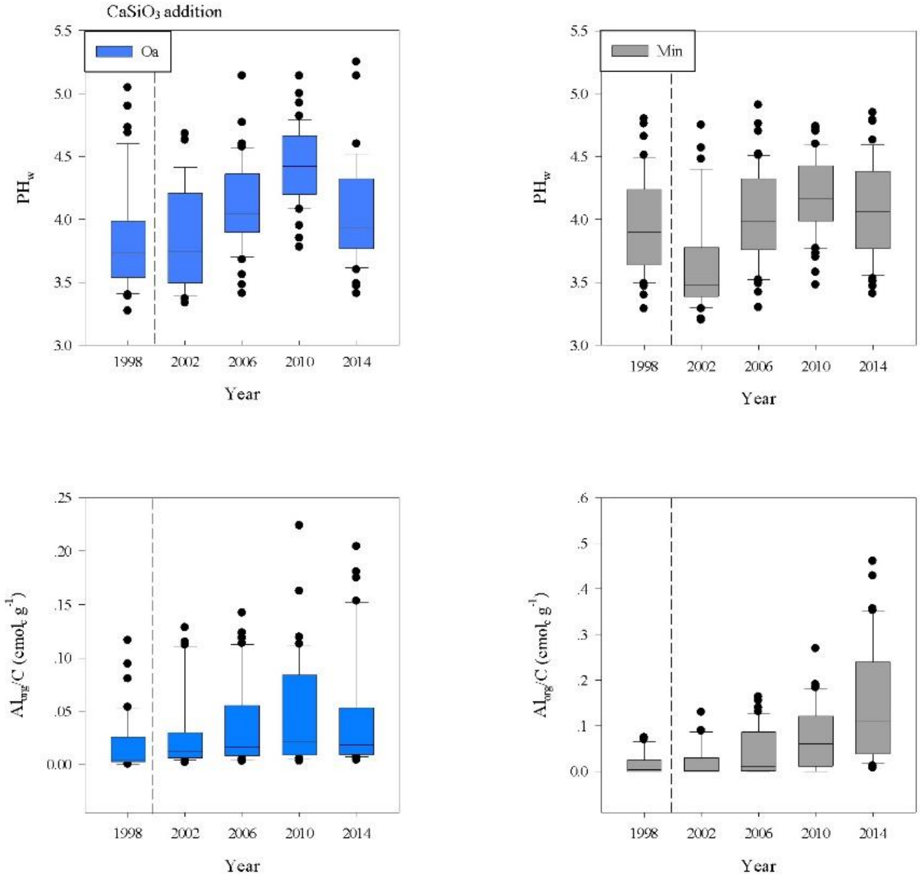
CaSiO3 addition
Oa
Min
PHw
Alorg/C (cmolc g-1)
5.5
5.0
4.5
4.0
3.5
3.0
.25
.20
.15
.10
.05
0.00
.6
.5
.4
.3
.2
.1
0.0
1998
2002
2006
2010
2014
Year

Fig. 4.

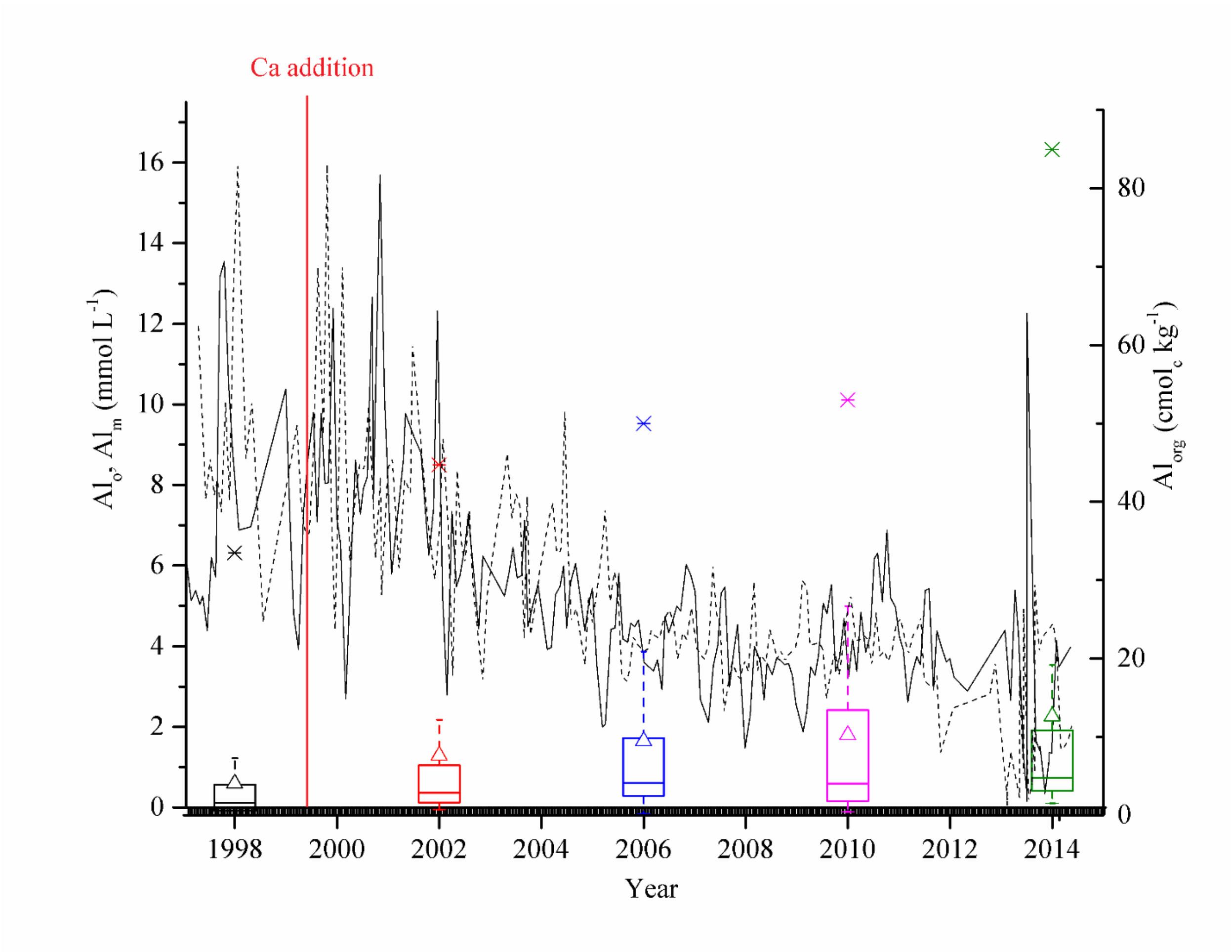
Ca addition
Al_o, Al_m (mmol L^{-1})
0
2
4
6
8
10
12
14
16
Al_{org} ($cmol_c$ kg^{-1})
0
20
40
60
80
1998
2000
2002
2004
2006
2008
2010
2012
2014
Year

Fig. 5.

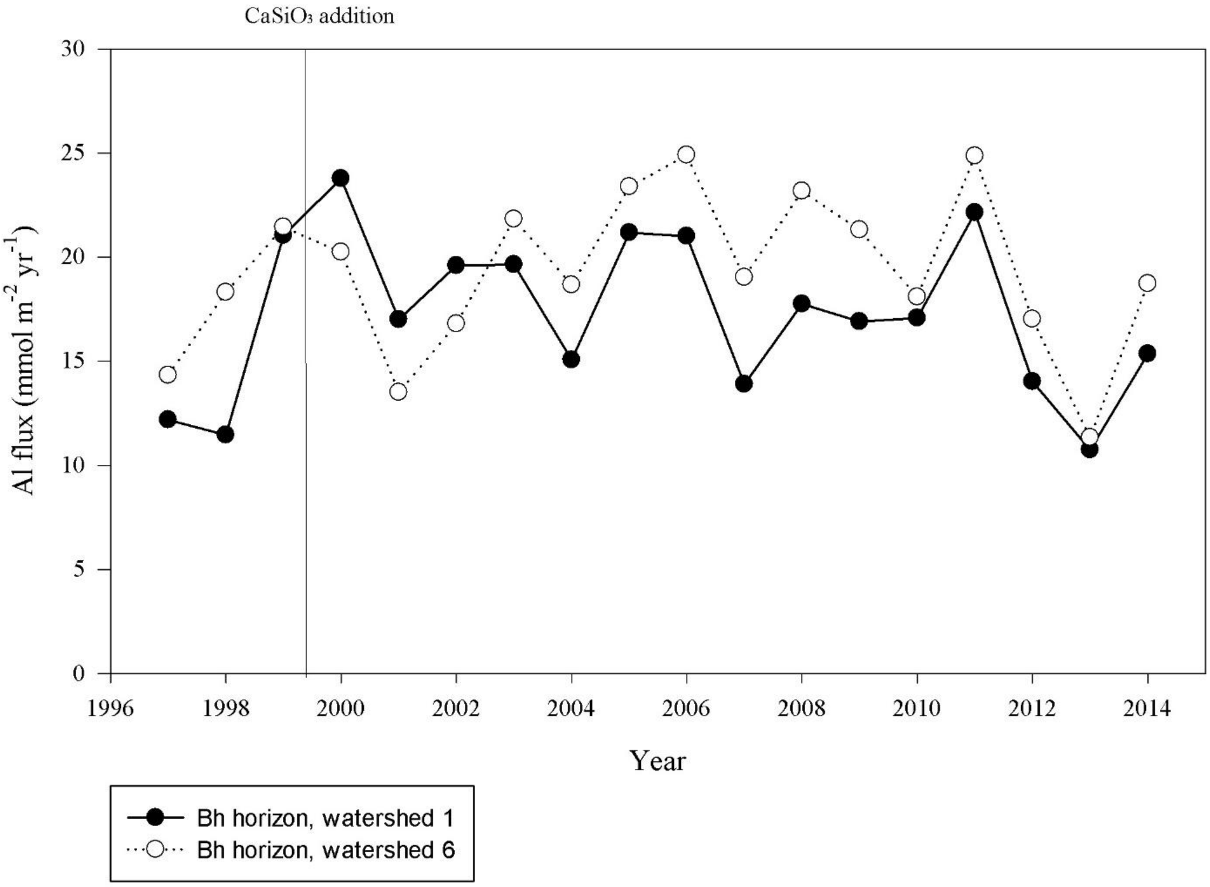
CaSiO₃ addition
Al flux (mmol m⁻² yr⁻¹)
30
25
20
15
10
5
0
1996
1998
2000
2002
2004
2006
2008
2010
2012
2014
Year
Bh horizon, watershed 1
Bh horizon, watershed 6

Fig. 6.