



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 (CaSiO₃) 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.

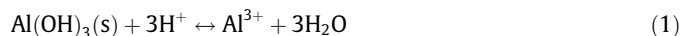
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1. Introduction

Aluminum (Al) exists in different forms in the soil environment. In addition to Al-bearing minerals such as gibbsite (Al(OH)₃) and kaolinite (Al₂Si₂O₅(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 (Skylberg, 1999; Li and Johnson, 2016) and the toxicity of dissolved Al³⁺ 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 (Eqs. (1), (2)). Berggren and Mulder (1995) suggested that this gibbsite solubility model is valid at pH > 4.2:



$$\text{pAl} = 3\text{pH} + \text{pK}_s \quad (2)$$

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, Al³⁺ is the dominant form of dissolved monomeric inorganic Al. The binding reaction for Al³⁺ on SOM can be written as (Wesselink et al., 1996):



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:

$$\frac{[\text{Al}^{3+}]}{[\text{H}^+]^x} = K_{\text{H-Al}} \frac{[\text{RAI}^{(3-x)+}]}{[\text{RH}_x]} \quad (4)$$

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where parentheses represent solute activities (mol L^{-1}), square brackets represent concentrations (mol kg^{-1} soil) and $K_{\text{H-Al}}$ is the complexation constant for the reaction shown in Eq. (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., Frostegård 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 Fragiorthods), developed from till left behind after the last glaciation, with a sandy loam texture (Wang and Benoit, 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 $1028 \text{ kg Ca ha}^{-1}$ 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 Skjyllberg, 2001). Previous studies have reported that the extraction by Na-pyrophosphate releases greater amounts of Al. Skjyllberg 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 southwest 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 (Skjyllberg et al., 2001).

Exchangeable Al, which includes Al in weak electrostatic attraction to clays and SOM, is also extracted by CuCl_2 (Skjyllberg, 1999; Gruba and Mulder, 2008). To estimate organically bound Al, it is therefore necessary to subtract exchangeable Al from the CuCl_2 -extractable Al ($\text{Al}_{\text{CuCl}_2}$). If exchangeable Al is determined by KCl extraction (Al_{KCl} ; Thomas, 1982; Gruba and Mulder, 2008; Johnson, 2013; Johnson et al., 2014), organically bound Al can be estimated by:

$$\text{Al}_{\text{org}} = \text{Al}_{\text{CuCl}_2} - \text{Al}_{\text{KCl}} \quad (5)$$

where Al_{org} is the estimated organically bound Al, $\text{Al}_{\text{CuCl}_2}$ is the amount of CuCl_2 -extractable Al, and Al_{KCl} is the amount of Al extracted by KCl, all typically expressed in $\text{cmol}_c \text{ kg}^{-1}$.

For each type of extraction, $3.000 \pm 0.010 \text{ g}$ subsamples were measured and placed in 50-ml centrifuge tubes. The soil:solution ratio was 1 g:20 ml for the 1 M KCl extraction and 1 g:10 ml for the 0.5 M CuCl_2 extraction. The KCl extraction was performed for 14 h using a mechanical vacuum extractor (Johnson et al., 2014). The CuCl_2 extraction was performed for 2 h 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 ($\text{Al}_{\text{CuCl}_2}$) 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

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