Fate of Applied Sulfate in Volcanic Ash-Influenced Forest Soils

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ABSTRACT

Forests in the Inland Northwest, USA, commonly show SO_4 deficiency, suggesting limited SO_4 availability in the soils. Regional soils, which lie between the east slopes of the northern Cascade Range and the west slopes of the northern Rocky Mountains, are influenced to varying degrees by poorly crystalline aluminosilicates and ferrihydrite, and are often classified as Andisols (Andosols). Research has shown that SO_4 retention is greatly influenced by Fe and Al oxides. However, little is known of the sorption behavior exhibited by poorly crystalline andic soils of the region. In this study we investigated the mineralogy and SO_4 sorption capacity of ash-influenced soils found in the Inland Northwest. Batch SO_4 adsorption experiments showed that up to 40% of added SO_4 was adsorbed. Furthermore, there were positive correlations between soil SO_4 adsorption capacity and increasing ash influence as measured by (i) the andic soil parameter $\%Al_o + 0.5\%Fe_o$ ($R^2 = 0.89$), (ii) P retention ($R^2 = 0.91$), and (iii) NaF pH ($R^2 = 0.48$). Soil pH, total organic C (TOC), and percentage of clay showed insignificant or inconclusive relationships with SO_4 adsorption. Release of adsorbed SO_4 was significantly lower in volcanic ash-influenced soils as compared with non-ash soils, indicating a greater affinity for SO_4. These results indicate that poorly crystalline aluminosilicates and Fe oxides significantly influence the amount of SO_4 present in forest soil solutions. Successful nutrient management plans must recognize the sorption behavior of these andic soils.

F OREST SOILS in the Inland Northwest are heterogeneous in composition with varying amounts of residual, colluvial, and eolian materials intermixed. Most soils of this region have also been influenced to some degree by the deposition of volcanic ash from the eruption of Mt. Mazama (now Crater Lake, OR) approximately 7600 calendar yr BP (Zdanowicz et al., 1999). Many of these soils still retain relatively thick mantles of weathered volcanic ash and are classified as Andisols in Soil Taxonomy (Soil Survey Staff, 1999) and Andosols in the World Reference Base (FAO/ISRIC/ISSS, 1998).

As volcanic ash weathers, poorly crystalline aluminosilicates (allophane and imogolite) and ferrihydrite are formed (Dahlgren et al., 1993). At soil pHs typically found in the Inland Northwest (5.6–6.6), these minerals exhibit a positive variable charge, creating a significant anion exchange capacity (AEC) (Nanzyo et al., 1993). Consequently, SO_4 will adsorb through electrostatic or ligand exchange reactions to the variable-charged soil minerals (Edwards, 1998; Eggleston et al., 1998; Hug,

1997; Marsh et al., 1988; Peak et al., 1999; Rietra et al., 2001; Wijnja and Schulthess, 2000; Zhang et al., 1987).

Over the past few decades, several studies have focused on Fe and Al oxide-rich soils and their ability to adsorb SO_4. Soils with varying amounts of crystalline oxides were found to adsorb 300 to 11 000 kg SO_4 ha^{-1} (Barton et al., 1994; Camps Aberstain et al., 2002; Curtin and Syers, 1990a, 1990b; Fumoto et al., 1996; Gebhardt and Coleman, 1974; Haque and Walmsley, 1973; Hue et al., 1990; Marsh et al., 1988; Wolt et al., 1992). Similarly, poorly crystalline Fe and Al oxides in highly weathered soils of Brazil were significantly correlated with SO_4 adsorption (Alves and Lavorenti, 2004). Andic soils from NW Galatia, Spain placed in a 0.4-mmol L^{-1} SO_4 solution, were shown to adsorb on average 4.5 mmol of SO_4 per kilogram of soil (Camps Aberstain et al., 2001).

These previous studies address the SO_4 adsorption potential of Fe and Al oxide rich soils; however, their findings are not entirely applicable to Holocene andic soils weathered under a Mediterranean climate as found in the Inland Northwest, USA. Sulfate adsorption capacities, such as those found in the above cited studies, could significantly affect the efficiency of current commercial fertilizer applications, which are critical to overcoming sulfate deficiencies found in forests throughout this region (Blake et al., 1990; Shaw et al., 2001; Xiao et al., 2001).

Tree response to SO_4 fertilization is dependent on the amount of SO_4 that resides in solution, which is a function of the SO_4 adsorption and desorption behavior of the soil. Adsorption and consequent desorption is dependent on soil pH, ionic strength of the soil solution, and the sulfate-metal bonding mechanisms present. The first two factors, pH and ionic strength, have variable effects on SO_4 adsorption (Barrow, 1972; Bolan et al., 1986; Courchesne, 1991; Elkins and Ensminger, 1971; Langmuir, 1997; Zhang et al., 1996), and play a critical role in determining the SO_4 bonding mechanism, and therefore adsorption–desorption behavior (Evangelou, 1998a).

Studies have shown that SO_4 forms primarily outer-sphere (i.e., electrostatic) bonds with crystalline Al oxides, and inner-sphere bonds (i.e., ligand exchange) with crystalline Fe (Hug, 1997; Peak et al., 1999; Wijnja and Schulthess, 2000). Sulfate also tends to form stronger bonds to crystalline Fe oxides as compared with Al oxides (Johnson and Todd, 1983; Singh, 1984). These differences in binding strengths are primarily attributed to the binding mechanisms involved. Electrostatic bonds are created when SO_4 is attracted to an opposite charge on a metal surface. However, this attraction is not strong

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Abbreviations: Al_o, oxalate extractable aluminum; Al_p, pyrophosphate extractable aluminum; Fe_o, oxalate extractable iron; Fe_c, (citrate, bicarbonate, dithionite)–(oxalate) extractable iron; MAP, mean annual precipitation; Si_o, oxalate extractable silica; TOC, total organic carbon.

enough to displace the hydroxyl groups attached to the surface of the metal. In contrast, ligand exchange occurs when the sulfate-metal attraction is strong enough to displace the hydroxyl groups, forming a monodentate, inner-sphere complex (Evangelou, 1998b). Raman spectra and in situ attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) of SO_4 sorption on goethite shows primarily inner-sphere coordination at soil pHs < 6; however, outer-sphere complexes did form at all pH levels. Above pH 6, sorption is primarily outer-sphere (Elzinga et al., 2001; Peak et al., 1999; Wijnja and Schulthess, 2000). It could be hypothesized that similar bonding mechanisms are responsible for SO_4 adsorption on allophane and ferrihydrite.

Sulfate desorption is necessary for maintenance of nutrient balances in tree foliage. If SO_4 was adsorbed by poorly crystalline minerals and not readily desorbed it would be unavailable for tree nutrition. Harrison et al. (1989) found that significant quantities of SO_4 were irreversibly held in an Andisol of northwest Washington, USA. Conversely, Dahlgren et al. (1990) and Dahlgren and Ugolini (1989) showed that SO_4 readily desorbed from tephra-derived Spodosols in the same region. It is unclear which soil properties enhance SO_4 availability for tree nutrition and which are responsible for irreversibly bonding sulfate, especially with respect to regional andic soils.

Therefore, the objectives of this research were twofold. The first objective was to characterize the expression of andic properties in an array of forest soils from the Inland Northwest region. A second objective was to determine the effect of andic properties on the fate of SO_4 applied to these soils in a manner that mimics typical fertilizer inputs used across the region.

MATERIALS AND METHODS

Study Sites

The study sites (Fig. 1) are located in three subregions of the Inland Northwest: (i) the Blue Mountain region of northeast Oregon/southeast Washington, (ii) the south-central Washington Cascades, and (iii) the Idaho Batholith region of central Idaho. Nineteen established forest research sites were selected from these subregions for study. Sites were selected to represent a wide range in volcanic ash influence. Volcanic ash presence was determined in the field by color and texture analysis. Field assessment of volcanic ash influence ranged from nondetectable to a 55-cm thick ash mantle. Volcanic ash was often found mixed with loessal deposits and colluvium derived from granite or basalt. Soils are classified as Andisols, Inceptisols, Mollisols, and Alfisols (Soil Survey Staff, 1999) (Table 1). Annual precipitation varies widely across the study areas, with the greatest mean annual precipitation (MAP) occurring in the Blue Mountain region and south-central Cascades (700–2200 mm). Lowest MAP occurs on the lower slopes of the Blue Mountains and in the Batholith region of central Idaho (440–670 mm) (Table 1). Landscapes are generally characterized as mountainous, with elevations ranging from 600 to 1700 m above sea level.

Sample Collection

At each of the 19 research sites, 5 soil samples were collected at random locations within the forest research control plots

Fig. 1. Locations of 19 plots investigated for andic properties and SO_4 adsorption–desorption patterns within the Inland Northwest, USA.

(0.324 ha). For sampling, the organic layer was removed to expose mineral soil, after which soil was collected using a 1430-cm³ bucket auger to a uniform depth of 30 cm. Soil morphology at our research plots typically transitioned from an Oe to a Bw horizon, with A horizons largely being absent or very thin. Therefore, the sampling of an A horizon during collection was deemed impractical and was not done. Soil samples were placed in a bucket and thoroughly mixed, resulting in a single representative bulk soil sample for each of the 19 research sites. For comparison, two additional soils were selected from laboratory soil archives: a humid Andisol from Costa Rica and a loessal soil from the Palouse region of north-central Idaho with minimal ash influence.

Soil Characterization

Bulk soil samples were air-dried, gently crushed, and passed through a 2-mm sieve. The < 2-mm air-dried samples were then used in subsequent analyses. Soil pH was measured in H_2O using a 1:1 soil/solution ratio. Sodium fluoride pH at 2 min (Fieldes and Perrott, 1966) was measured to determine the presence of poorly crystalline aluminosilicates and Fe oxides. Phosphorus retention was measured on all soils using the New Zealand P retention test (Soil Survey Laboratory Staff, 1995). Phosphorus extracts were analyzed on a PerkinElmer spectrophotometer (MBA 2000, Life Sciences, Boston, MA). Total organic carbon was measured using an Elementar carbon analyzer (Elementar VarioMax, Hanau, Germany). Particle-size distribution by centrifuge was determined for a subset of research sites that showed a range in andic properties.

Organically bound Fe and Al were extracted using sodium pyrophosphate (Fe_p and Al_p) according to McKeague et al. (1971). Poorly crystalline and organically bound Fe, Si, and Al were extracted using ammonium oxalate (Fe_o, Si_o, and Al_o) (Bascomb, 1968). Citrate-bicarbonate-dithionite extraction (Fe_d) was used to remove all secondary Fe mineral fractions (Jackson et al., 1986). Selective soil dissolutions were performed separately on all soil samples. Metal concentrations in the extracts were measured using inductively coupled plasma–atomic emission spectroscopy (ICP–AES) (Thermo Jarrell Ash, Franklin, MA).

The quantity of Fe contained in crystalline (hydr)oxides (Fe_c) minerals was estimated as follows:

$$Fe_c = Fe_d - Fe_o \qquad [1]$$

Ferrihydrite content was estimated using the equation proposed by Nanzyo et al. (1993):

$$Ferrihydrite\ \% = Fe_o\% \times 1.7 \qquad [2]$$

Allophane content was estimated using an equation from Dahlgren (1994):

$$Allophane = f \times Si_o \qquad [3]$$

where f is a function of the ratio between poorly crystalline Al and Si. For an Al/Si ratio of 1:1, the factor would be 5. An Al/Si ratio of 2:1 would yield a factor of 7, and an Al/Si ratio of 2.5:1 would yield $f = 10$. Aluminum and Si ratios were calculated for each sample, from which it was determined that a factor of 7 and 10 could be used for the calculation of allophane/imogolite in this study.

Sulfate Adsorption

Current nutrient management for forest soils in the Inland Northwest prescribe field application of 270 to 300 kg SO_4 ha⁻¹, which, assuming a typical andic soil porosity of 0.50 and a 10-cm depth, corresponds to 2.08 mmol L⁻¹ SO_4. To encompass high and low SO_4 fertilizer application rates, a range of concentrations (0.52, 1.04, 2.08, 4.17, 8.33 mmol L⁻¹) was used in our sorption experiments. A blank was also run to measure desorbed native SO_4. Results indicated that the amount of native SO_4 desorbed in the blank was nearly one order of magnitude less than the lowest initial concentration of the isotherm, and therefore was deemed insignificant. Bulk SO_4 solutions were made using Na_2SO_4 and deionized H_2O. Duplicate samples containing 5 g of soil and 25 mL of SO_4 solution were placed in 50 mL centrifuge tubes. The soil solu-

Table 1. Selected morphological, climatological, chemical, and mineralogical characteristics of soils used in the study.†

Location	Taxonomic classification	Soil parent material	Ash depth	Annual precipitation	Soil pH	NaF pH	Al_o	Al_p	Fe_o	Fe_c	Si_o	Al_o + 0.5 Fe_o	TOC
			cm	mm						%			
SN	Haploxeroll	L	–‡	630	5.7	8.5	0.6	0.1	0.5	tr¶	0.1	0.9	2.3
LB	Dystrocryept	GC	–	560	6.4	9.8	0.3	0.1	0.3	0.1	tr	0.5	1.7
N3§	Vitrixerand	VA,L,BC	–	440	6.6	9.5	0.3	0.1	0.5	0.2	0.1	0.6	2.1
FC	Xeropsamment	GC	–	560	6.0	9.8	0.5	0.1	0.3	0.1	0.1	0.7	1.1
MH§	Udivitrand	VA,BR	–	840	5.6	9.7	0.6	0.1	0.7	0.3	0.1	1.0	2.5
L1	Haplocryoll	BR	–	670	6.0	9.4	0.4	0.1	1.2	0.6	0.1	1.0	2.0
HS	Haploxeralf	BR	–	2160	6.0	9.9	0.6	0.1	0.9	0.6	0.1	1.1	2.2
L2	Haplocryoll	BC	–	670	6.2	9.6	0.5	0.1	1.2	0.3	0.1	1.1	2.0
UK	Udivitrand	VA,L	74	440	6.2	10.4	0.9	0.2	0.5	0.1	0.3	1.2	3.4
NS2	Udivitrand	VA,BR	30	760	6.0	10.2	1.1	0.2	0.7	tr	0.4	1.5	2.2
NC	Udivitrand	VA,TS	54	760	6.3	10.0	1.2	0.1	0.6	0.4	0.6	1.5	1.8
NG	Udivitrand	VA,TS	45	760	6.0	10.6	1.3	0.2	0.7	0.2	0.6	1.7	2.6
N1	Udivitrand	VA,BC	48	440	6.2	10.9	1.3	0.3	0.7	0.1	0.5	1.7	1.9
N2	Vitrixerand	VA,L,BC	39	440	6.5	10.8	1.3	0.2	0.7	tr	0.6	1.7	2.9
UF	Udivitrand	VA,L,BC	54	700	5.8	10.7	1.1	0.2	1.1	0.4	0.3	1.7	2.7
CC	Udivitrand	VA,TS	55	760	5.7	10.5	1.4	0.2	0.7	0.2	0.6	1.8	2.3
UP	Udivitrand	VA,BR	36	700	5.7	10.8	1.3	0.3	1.2	0.2	0.4	1.9	5.0
BZ	Dystroxerept	BR	–	2160	6.2	10.8	1.6	0.2	0.9	0.3	0.6	2.1	1.8
TS1	Udivitrand	VA,L,BC	48	1450	5.8	11.2	1.6	0.4	1.0	0.3	0.5	2.1	5.0
TS2	Udivitrand	VA,L,BC	43	1450	5.8	11.3	1.9	0.4	1.1	0.3	0.6	2.5	4.5
GR	Hapludand	VA	>100	2000	4.4	9.9	1.0	–#	1.9	2.8	0.2	2.0	3.5

† L = loess; GC = granite colluvium; VA = volcanic ash; BC = basalt colluvium; BR = basalt residuum; TS = tertiary sediments; Al_o = oxalate extractable aluminum; Al_p = pyrophosphate extractable aluminum; Fe_o = oxalate extractable iron; Fe_c = (citrate, bicarbonate, dithionite)–(oxalate) extractable iron; Si_o = oxalate extractable silica; TOC = total organic carbon.
‡ No distinct volcanic ash mantle present.
§ Significant soil disturbance from logging activities.
¶ Trace (<0.05%).
# Not determined.

tion ionic strength and pH were allowed to vary to account for the natural variation found in forest soils. We acknowledge the role increasing ionic strength has on SO_4 sorption; however, controlling ionic strength would reduce the applicability of our findings to actual forest soil conditions. Samples were placed on a rotating shaker at 220 rpm for 8 h at room temperature, after which they were centrifuged at 27 000 × g for 15 min and the supernatant filtered through a 0.2-μm membrane disk filter. Preliminary SO_4 adsorption kinetic studies showed that 8 h was sufficient to achieve equilibrium (Kimsey, 2003). Measurement of supernatant pH showed that equilibrium pH was on average within 0.2 pH units of the soil pH (1:1 soil/ water ratio), thus minimizing artifacts created from varying pH. This small change in soil pH was acceptable because: (i) we wished to mimic actual soil conditions on fertilization, and; (ii) the change in SO_4 adsorption as a function of pH is minimal at the pH values of our soil samples (Pigna and Violante, 2003). After filtering, the supernatant was diluted 1:10 with deionized-H_2O and analyzed for SO_4 concentration by ion chromatography (Dionex, #AS-11, Sunnyvale, CA). The amount of SO_4 adsorbed was determined by the difference between the initial and equilibrium SO_4 concentration.

Sulfate Desorption

Three soils that reflected a wide range in volcanic ash influence (none to high) were selected to measure SO_4 desorption. Each soil was treated with a 2.08 mmol L^{-1} SO_4 solution for the adsorption phase (see adsorption methods above). The desorption experiment was initiated by resuspending the centrifuged soil back to the 5:25 solid/solution ratio by adding 0.01 M $CaCl_2$. Calcium chloride, a weak electrolyte, was chosen as an artificial soil solution to determine the effect of a non-specific ionic pore-water solution on SO_4 desorption. Following resuspension, the samples were then placed on a 220-rpm rotational shaker for 48 h at room temperature. Sulfate desorption experiments on an array of ash-influenced soils showed that equilibrium was reached within 48 h. In a literature review by Edwards (1998) on S cycling in soils, it was noted that most SO_4 desorption from soil-solution mixtures reached equilibrium after 0.5 h. Dahlgren et al. (1990) found that adsorption/desorption equilibrium times are approximately the same, although at time lengths much longer than 0.5 h. For this experiment, it must be noted that this adsorption–desorption extraction is one in which equilibrium is drastically perturbed and therefore is not an indicator of reversibility, but one of retention against desorption for the specified length of the desorption experiment (Essington, 2004). After 48 h, samples were removed from the shaker, centrifuged at 27 000 × g for 15 min, filtered through a 0.2-μm membrane disk filter, and analyzed by ion chromatography. Suspension pH was on average within 0.2 pH units of the soil pH. The amount of SO_4 desorbed was calculated by subtracting the amount of SO_4 in the entrained Na_2SO_4 solution from the amount of SO_4 detected in the desorbing $CaCl_2$ solution.

Statistical Analyses

Coefficients of determination were calculated to determine the strength of proposed linear relationships between SO_4 adsorption and measured mineralogical and chemical properties. Differences in SO_4 desorption patterns were analyzed for significance using t tests and mean standard deviation.

RESULTS AND DISCUSSION

Mineral Composition

The Si_o content of sampled soils ranged from 0.1% at LB to 0.6% at TS2, indicating little volcanic ash influ-

ence at LB and significantly higher influence at TS2 (Table 1). There is an increase in Si_o content between L2 and UK, 0.1 and 0.3%, respectively. Sample UK, unlike L2, exhibits an observable volcanic ash presence in the field (Table 1). For the research sites with observable ash caps, Si_o content ranges between 0.3 and 0.6%, suggesting an increase in volcanic ash influence. Si_o is an important factor in the formation of allophane and is influenced by climate, drainage, vegetation, and tephra thickness (Parfitt, 1990). The Si_o data suggest a positive relationship with the presence of volcanic ash and increasing MAP (Table 1). Sample GR from Costa Rica contains only 0.2% Si_o, approximately one-third of TS2. This suggests more intense weathering and the subsequent loss of silica through the process of desilication in this soil from a humid, tropical environment (Buol et al., 2003).

The Fe_o content ranged between 0.3% at LB to 1.2% at L1. Fe_o is found both in weathered volcanic ash and in soils weathered from Fe-rich basalt parent material. The use of Fe_o values as indicators of volcanic ash influence on soil mineralogy is problematic since Fe-rich basalt parent materials, which can also produce large quantities of Fe_o, are common parent materials at many of the study sites. Thus, Fe_o was used in concert with Si_o values to assess volcanic ash influence. Four research sites, L1, L2, MH, and HS, had comparatively high Fe_o concentrations at 1.2, 1.2, 0.7, and 0.9%, respectively. However, Si_o content was extremely low with a value of 0.1% at all four sites. Thus, these poorly crystalline Fe concentrations may be attributable to weathering of basalt parent material. Additionally, examination of soil pits at these sites showed no morphological evidence of volcanic ash in the profiles.

Oxalate extractable iron contributes > 60% of total extractable Fe_d in Inland Northwest soils. Fe_c values ranged from trace to 0.6% (Table 1). Higher Fe_c/Fe_o ratios were found in soils dominated by weathered basalt parent material, with lower ratios occurring primarily in ash-influenced soils. Higher Fe_o concentrations have also been attributed to partially dissolved magnetic minerals such as maghemite and magnetite (Walker, 1983; van Oorschot and Dekkers, 2001). This may explain the higher Fe_o values found in basalt-derived soils as opposed to volcanic ash soils. Magnetic minerals were observed in the soil samples on application of a magnet. The Fe_c/Fe_o ratio for sample GR, the highly weathered Andisol from Costa Rica, was very high compared with Inland Northwest Andisols. This may be due to dissolution of poorly crystalline Fe minerals and the subsequent formation of crystalline Fe under a more intense weathering regime. Ferrihydrite was estimated to range from a trace in soils with little ash influence to 1.9% in soils with relatively high ash influence (Table 2).

The Al_o content showed two distinct populations. Soils with little or no ash influence ranged between 0.3 and 0.6%, while ash-influenced soils ranged between 0.9 and 1.9% (Table 1). The Al_o dominated over Fe_o (nearly 2:1) in ash-influenced soils. This trend is reversed for GR, as Al_o is the smallest mineral fraction extracted except for Si_o. This suggests allophane has

Table 2. Selected physical and mineralogical characteristics for a subset of research soils.

Location	Sand	Silt	Clay	A/I†	FH‡
			%		
SN	11.3	78.6	10.1	tr§	tr
N3	13.6	63.0	13.0	0.7	0.9
NS2	19.8	72.8	7.4	3.4	1.2
NG	17.5	73.9	8.6	4.0	1.2
CC	17.3	74.7	8.0	4.2	1.2
TS2	13.6	76.9	9.5	6.0	1.9

† A/I = allophane and imogolite as estimated by Dahlgren (1994).
‡ FH = ferrihydrite as estimated by Nanzyo et al. (1993).
§ Trace.

further weathered to halloysite or kaolinite in this Costa Rican soil (Alvarado and Buol, 1975; Martini, 1976). Organically bound Al (Al_p) accounted for approximately 15% of oxalate extracted Al in volcanic ash soils and 21% for low ash-influenced soils. The bulk of remaining Al_o is attributable to allophane/imogolite, partial hydroxy-Al interlayer extraction, and/or Al-substituted ferrihydrite. Allophane content was estimated to range between trace in low ash-influenced soils to 6% in high ash-influenced soils (Table 2).

The Soil Taxonomy and World Reference Base parameter for andic properties, $\%Al_o + 0.5\%Fe_o$, ranges between 0.5% at LB and 2.5% at TS2. A sharp upward inflection occurs at a $\%Al_o + 0.5\%Fe_o$ value of 1.5 (Table 1). This increase in Fe_o and Al_o may be explained by increased volcanic ash influence and/or increased precipitation, as both of these factors encourage the formation of poorly crystalline, secondary aluminosilicates and Fe oxides. Consequently, these data indicate that there is a wide range in volcanic ash influence in the forest soils used in this study.

The NaF pH value is often used as an indicator of the presence of reactive allophane or other poorly crystalline minerals that have edge sites available for hydroxyl-anion exchange (Fieldes and Perrott, 1966; Soil Survey Staff, 1998). pH values > 9.4 suggest the presence of poorly crystalline minerals, and indicate volcanic ash influence. Soils in this study had NaF pH values from 9.4 to 11.3 (Table 1). Since all soils have NaF pH values ≥ 9.4, it was expected that each soil would contain a significant amount of poorly crystalline minerals. TS2 contains the largest combined fraction of Fe_o, Al_o, and Si_o at 3.6%, while LB has the smallest fraction at 0.6% (Table 1). There is a strong correlation between increasing NaF pH values and the andic parameter $\%Al_o + 0.5\%Fe_o$ ($R^2 = 0.48$, $P < 0.01$) (Fig. 2). This knowledge is of particular use, since NaF pH is a relatively simple, inexpensive analysis that can be conducted in the field with the use of a field pH kit and a bottle of NaF solution (Soil Survey Laboratory Staff, 1995).

Sulfate Adsorption

In 12 of the 19 regional soils, the maximum percentage of SO_4 adsorbed occurred at an initial concentration of 1.04 mmol L^{-1}, with the remaining soils reaching maximum percentage of SO_4 adsorbed at a concentration of 2.08 mmol L^{-1} (Table 3). Percentage of SO_4 removed from solution decreased or remained constant
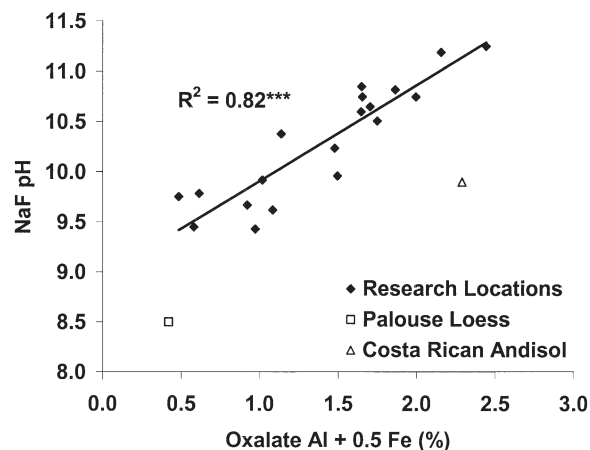
Fig. 2. NaF pH dependence on poorly crystalline minerals ($\%Al_o + 0.5\%Fe_o$) in sampled regional forest soils. Solid symbols represent research plots and open symbols represent comparison soils. The line shown is the best-fit linear relationship to the research plot data.

in the majority of soils at initial concentrations of 4.17 and 8.33 mmol L^{-1}. These observations are consistent with research showing that a larger proportion of an anion is adsorbed at lower solution concentrations, followed by smaller proportions at higher concentrations (Langmuir, 1997).

A subset of SO_4 adsorption isotherms, TS2, NG, and N3, illustrates the range in soil SO_4 adsorption capacity observed in the Inland Northwest soils studied (Fig. 3). Sample TS2 exhibits the highest SO_4 adsorption capacity of the Inland Northwest soils and N3 the lowest. NG represents a comparatively moderate SO_4 adsorption capacity. Sample GR (weathered Costa Rican Andisol) had the highest SO_4 adsorption affinity, adsorbing nearly

Table 3. Sulfate retention as a function of initial solution concentration and New Zealand P data from test results (values represent mean of duplicate samples).

Location	0.52†	1.04	2.08	4.17	8.33	NZP‡
			mmol kg^{-1}			
SN	0.14	0.55	1.19	2.66	4.27	−§
LB	0.36	0.64	1.34	2.26	3.50	31.8
N3	0.19	0.56	1.18	2.17	3.68	35.5
FC	0.18	0.89	1.35	1.99	3.60	36.7
MH	0.26	–	0.93	2.24	5.25	43.1
L1	0.24	0.69	1.59	2.56	5.77	48.8
HS	0.43	0.90	1.54	2.90	4.79	51.8
L2	0.08	0.69	1.07	2.43	4.53	55.5
UK	0.19	0.58	1.19	2.26	4.81	56.4
NS2	0.26	0.69	1.15	2.69	5.00	57.1
NC	0.42	–	1.42	3.77	6.66	62.9
NG	0.44	1.09	2.01	4.14	7.41	65.7
N1	0.33	0.74	1.60	3.11	5.95	68.6
N2	0.31	0.80	1.70	2.73	6.13	68.5
UF	0.52	1.03	2.10	4.45	7.42	70.7
CC	0.56	–	2.41	4.86	7.94	72.9
UP	0.56	1.25	2.09	3.23	5.51	74.4
BZ	0.80	1.66	2.84	4.63	6.77	75.9
TS1	0.78	1.84	3.43	6.76	10.72	86.5
TS2	0.95	2.03	3.64	6.90	11.08	89.5
GR	1.70	3.61	7.36	11.98	17.25	–

† Initial solution concentration units are in mmol L^{-1}.
‡ PO_4 retained from 10.53 mmol L^{-1} solution as measured by the New Zealand P retention test.
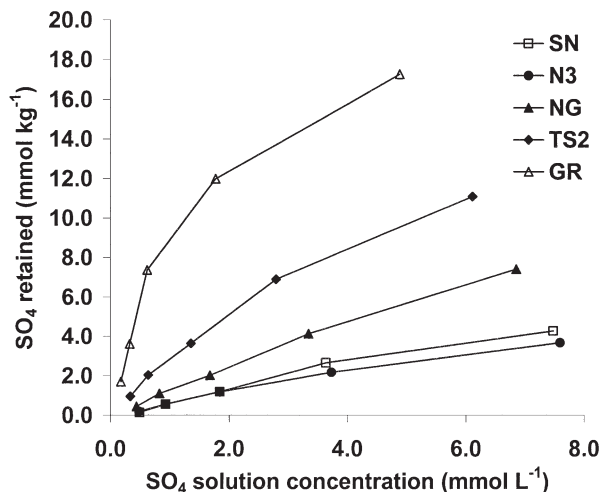§ Not determined.

Fig. 3. Sulfate adsorption isotherms for initial solution concentrations of 0.52, 1.04, 2.08, 4.17, and 8.33 mmol SO_4 L^{-1}. Closed symbols distinguish selected research soils and open symbols comparison soils.

Fig. 4. Sulfate adsorption as a function of the andic parameter %Al_o + 0.5%Fe_o for sampled soils. Initial SO_4 concentration was 2.08 mmol L^{-1}. Solid lines represent the best-fit linear relationship for the two separate data populations, accompanied by their respective coefficient of determination.

200% more SO_4 than TS2. Conversely, sample SN (loessal soil with minimal ash influence) had the lowest, adsorbing approximately the same quantities of SO_4 as N3.

The amount of SO_4 adsorbed from an initial concentration of 2.08 mmol L^{-1} varied widely (Table 3). Soils minimally influenced by volcanic ash adsorbed between 8.9 and 15.3% of added SO_4. Soils with established volcanic ash influence adsorbed between 11.0 and 34.9%. These results indicate that a significant quantity of commercially applied SO_4 fertilizer on volcanic ash-influenced forest soils would be adsorbed. A recent forest fertilization trial on an Andisol in northeast Oregon, USA found no response to SO_4 fertilizer in the foliage tissue, but a large increase in soil extractable SO_4 (Shaw et al., 2005). Further, the study found that there was statistically no difference in SO_4 resin capsule extracts between the control and treated plots. These findings support our observations that volcanic ash retains significant quantities of SO_4.

No relationship was found between soil pH and the percentage of SO_4 adsorbed ($R^2 = 0.08$). The mean soil pH value was 6.1, with a standard deviation of 0.3. The small variance is the likely reason for the lack of correlation between soil pH and SO_4 adsorption. Other studies have shown a correlation between SO_4 adsorption and soil pH (Curtin and Syers, 1990a; Elkins and Ensminger, 1971; Gebhardt and Coleman, 1974; He et al., 1997; Marsh et al., 1988; Pigna and Violante, 2003; Zhang et al., 1987), yet many of these studies acidified their soils to atypical levels to obtain pH/SO_4 adsorption curves.

Additionally, soils showed no relationship between TOC and SO_4 adsorption. The lack of an A horizon at our research sites prevent any comparison of SO_4 adsorption between a high organic carbon A horizon and an underlying ash-influenced Bw horizon. However, Johnson and Todd (1983) found no consistent relationship between the percentage of C and SO_4 adsorption in a Cryand and Spodosol sequence in northwest Washington, USA. Thus, we conclude that in the soils of the

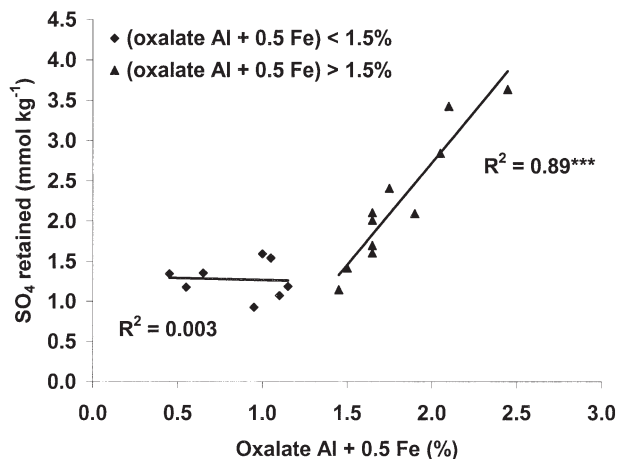Inland Northwest, the presence of organic C does not significantly influence SO_4 adsorption.

Sulfate adsorption was not dependent on the presence of layer silicate clays. Sample SN has approximately 10% clay as vermiculite, illite, and trace amounts of poorly crystalline minerals, and had a low SO_4 adsorption capacity. Allophane and ferrihydrite compose a larger portion of the clay fraction in the ash-influenced soils TS2 and N3. These poorly crystalline mineral fractions comprise approximately 83% of the clay percentage in TS2 and 12% in N3 (Table 2). The TS2 exhibited the greatest SO_4 adsorptive capacity and N3 a similar capacity to that of SN, thus indicating that allophane and ferrihydrite rather than silicate clays are responsible for a large portion of SO_4 adsorption in regional ash-influenced soils.

Two distinct SO_4 adsorption patterns were detected as a function of the andic parameter %Al_o + 0.5%Fe_o. Correlation of SO_4 adsorbed with %Al_o + 0.5%Fe_o shows a break at approximately 1.5% (Fig. 4). The %Al_o + 0.5%Fe_o values < 1.5% displayed relatively low SO_4 adsorption levels, with only 10 to 12% of added SO_4 being adsorbed. However, once this value is exceeded, there is an abrupt increase in SO_4 adsorption ($R^2 = 0.89$, $P < 0.01$). Sulfate adsorption increased 300 to 400% across study sites with %Al_o + 0.5%Fe_o values ≥ 1.5%. GR adsorbed up to 700% more SO_4 than soils with %Al_o + 0.5%Fe_o values < 1.5%. SN exhibited the same adsorption capacity as soils with values < 1.5%.

The SO_4 vs. PO_4 retention test results were similar to the SO_4 vs. %Al_o + 0.5%Fe_o adsorption trends; that is, two populations of SO_4 adsorption behavior were observed (Fig. 5). Sulfate retention averaged only 1.25 mmol kg^{-1} in the range where 30 to 60 mmol kg^{-1} of PO_4 were retained. Beyond 60 mmol kg^{-1} of PO_4 retained, SO_4 retention increased as a function of PO_4 retention. This indicates that as andic mineralogy increases, sorption of both anions increases in a somewhat similar manner. This is in contrast to the population of soils with less SO_4 and PO_4 sorption, in which PO_4 sorp-

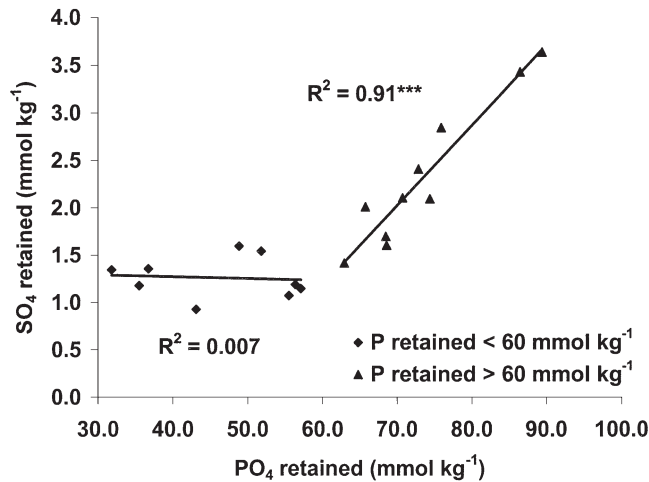**Fig. 5. Sulfate adsorption as a function of PO_4 retention capacity based on the New Zealand P retention test. Initial solution concentrations for SO_4 and PO_4 were 2.08 mmol L^{-1} and 10.53 mmol L^{-1}, respectively. Solid lines represent the best-fit linear relationship for the two separate data populations, accompanied by their respective coefficient of determination.**

Fig. 6. Sulfate adsorption as a function of NaF pH for sampled soils. Initial solution concentration was 2.08 SO_4 mmol L^{-1}. Solid lines represent the best-fit linear relationship for the two separate data populations, accompanied by their respective coefficient of determination.

tion increased but SO_4 sorption did not, suggesting that PO_4 is sorbing to sites that are inaccessible to SO_4. The variable sorption amounts observed between all the soils must be related to the binding mechanisms for SO_4 and PO_4. In general, PO_4 is thought to form primarily strong inner-sphere bonds, while SO_4 can form both inner-sphere and outer-sphere bonds with minerals, depending on the type of mineral and solution properties (i.e., pH and ionic strength) (Evangelou, 1998b; Hug, 1997; Peak et al., 1999).

The SO_4 sorption as a function of NaF pH (Fig. 6) was also similar to the trend observed for SO_4 sorption as a function of $\%Al_o + 0.5\%Fe_o$ and PO_4 retention. There was a sharp increase in SO_4 adsorbed at NaF pH values > 10.5 ($R^2 = 0.48$, $P < 0.01$). Soils with a NaF pH < 10.5 showed no correlation ($R^2 = 0.02$) with SO_4 adsorption. These results suggest that forest managers could utilize NaF pH as a relatively simple and inexpensive predictor of soil SO_4 adsorption.

Sulfate Desorption

Sulfate fertilizer efficiency is not only affected by adsorption, but also by desorption. Sulfate desorption controls soil solution SO_4 and thus plant availability. Samples SN, NG, and TS2, which encompass a wide range of $\%Al_o + 0.5\%Fe_o$ values, were chosen for the SO_4 desorption study (Table 1). These selected soils have $\%Al_o + 0.5\%Fe_o$ values of 0.81, 1.64, and 2.44, respectively. It must be clearly stated that this desorption study is not one that was developed to determine the reversibility of SO_4 adsorption, but a perturbed equilibrium extraction analysis. Our intention was to gain a relative indication of the amount of SO_4 that could be desorbed in ash-influenced soils on fertilization.

Sample TS2 (high ash influence) desorbed approximately 0.07 mmol kg^{-1} of adsorbed SO_4; NG (moderate ash influence) desorbed approximately 0.14 mmol kg^{-1}, and SN (minimal ash influence) desorbed approxi-
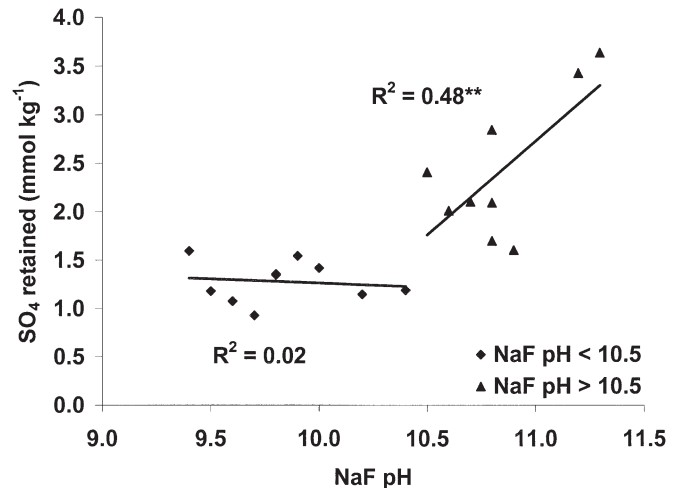
mately 0.27 mmol kg^{-1} (Fig. 7). These desorbed amounts equate to 16% for SN, 6% for NG, and 2% for TS2. The t tests indicated that there is a significant difference in SO_4 desorption between all three soils ($\alpha = 0.05$). The results indicate that as volcanic ash influence increases, SO_4 desorption decreases.

The lack of complete desorption does not necessarily indicate that SO_4 is irreversibly held. True reversibility can only be determined with an experiment in which aqueous concentrations are decreased by small amounts (Essington, 2004), such as in a leaching experiment. Dahlgren et al. (1990) measured SO_4 desorption using a vacuum column leaching experiment, and observed that SO_4 adsorption was reversible in a central Maine Bs horizon. In contrast, Harrison et al. (1989), using similar methods, proposed that a Bs horizon in northwest Washington irreversibly held 36% of adsorbed SO_4. While our results cannot be quantitatively compared with these studies, they do suggest that volcanic ash significantly affects the availability of SO_4, and
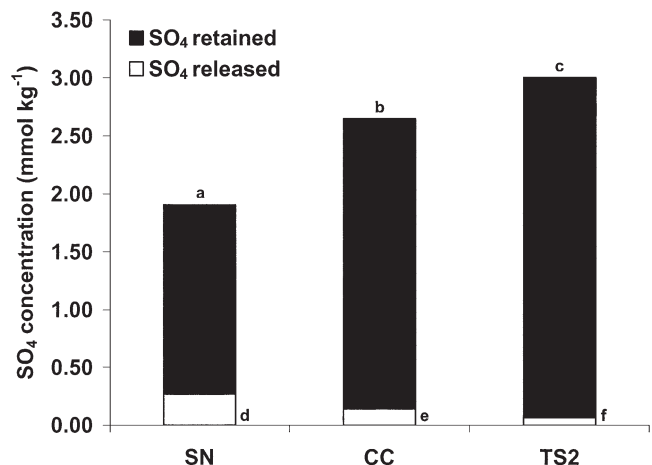

Fig. 7. Sulfate quantities adsorbed and desorbed for selected soils. Values are the mean of three replicates. Letters indicate significant differences in quantities of SO_4 retained and released ($\alpha = 0.05$).

therefore the efficiency of commercial applications of sulfur fertilizer in regional forests.

SUMMARY

This research project has demonstrated that forest soils containing poorly crystalline aluminosilicates and Fe oxides derived from the weathering of volcanic ash have increased SO_4 adsorption capacities. Sulfate adsorption can be estimated from NaF pH, P retention, or $\%Al_o + 0.5\%Fe_o$ data. Based on these estimates, forest managers can adapt sulfur fertilizer prescriptions to account for the SO_4 adsorption capacity of the forest soils in their management area.

Volcanic ash-influenced soils were shown to adsorb up to 40% of added SO_4. Up to 98% of the added SO_4 was retained against rapid desorption directly following application. This retention of adsorbed SO_4 suggests that the majority of the added SO_4 is not bioavailable, thus negatively affecting forest nutrition. This statement is further supported by recent forest S fertilization trials in the region. However, the scope of this experiment did not allow for a quantitative analysis of the nutritional consequences of strongly bound SO_4, nor did we account for continuous removal of SO_4 from solution to measure the "true reversibility" of adsorbed sulfate. Future studies should address the seasonal fluctuations in soil pH and ion concentrations in pore-water and the effect these fluctuations have on SO_4 sorption. Once addressed, and in combination with field-based fertilizer trials, the effect of weathered volcanic ash on SO_4 fertilizer efficiency can be more clearly defined.

ACKNOWLEDGMENTS

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