

## NITRATE SORPTION IN A VARIABLE-CHARGE FOREST SOIL OF THE PACIFIC NORTHWEST

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Despite the general acceptance that soils of the Pacific Northwest (United States) have a high retention capacity for phosphate ( $\text{PO}_4^{-3}$ ), and perhaps even sulfate ( $\text{SO}_4^{-2}$ ), few studies in the region have investigated the potential of physicochemical mechanisms to retain nitrate ( $\text{NO}_3^-$ ). The specific objectives of this study were to (i) determine the capacity of different horizons of a mesic, Typic Fulvudand under intensive forest management in southwestern Washington to sorb  $\text{NO}_3^-$ , (ii) determine the point of zero net charge for each horizon of this soil, and (iii) relate specific mineralogical characteristics to the physicochemical soil properties. Five soil pits were excavated to a depth of approximately 150 cm, and soil samples were composited by genetic horizon, including A, AB, 2Bw1, and 2Bw2 horizons. Through batch equilibration,  $\text{NO}_3^-$  sorption isotherms were created for each horizon and showed an increase in sorption with both depth and increased  $\text{NO}_3\text{-N}$  solution concentrations. The point of zero net charge of the two Bw horizons was determined to exist between a pH range of 3.5 to 3.6. Selective dissolution techniques of the mineral soil were used to determine the presence of crystalline and noncrystalline aluminosilicates. Allophane and imogolite contents of the less than the 2-mm mineral soil fraction ranged from 0.6% to 3.0% across all observations, although noncrystalline forms of Fe and Al comprised a majority of the subsurface horizons, and increased with depth. The presence of variable charge soil components on this site, coupled with the acidic soil pH regime associated with the coniferous forest stand, allows for the concentration-dependent sorption of  $\text{NO}_3^-$ , which may serve to retain a significant proportion of an otherwise highly mobile form of an essential plant nutrient. (Soil Science 2006;171:313-321)

**Key words:** Nitrogen retention, point of zero net charge, allophane, imogolite, nitrate adsorption.

**N**ITROGEN is widely regarded as a limiting nutrient for plant growth in many temperate coniferous forest ecosystems (Gessel et al., 1973). As such, numerous studies have investigated N leaching fluxes associated with the management of these ecosystems (Briggs et al., 2000; Katzensteiner, 2003; Ranger et al., 2002; Ring, 1995). In all of the studies mentioned,  $\text{NO}_3^-$  was the primary form of N leached from surface soil horizons. Although the potential of biological and hydrological mechanisms to mitigate  $\text{NO}_3^-$

leaching losses has been discussed, none of these studies have investigated the potential of physicochemical mechanisms to retain  $\text{NO}_3^-$ . This is likely due to: (i) the weak affinity of  $\text{NO}_3^-$  to form surface complexes (Parfitt 1980), (ii) the tendency of most soils, via isomorphic substitution, to more strongly adsorb cations compared with anions (Kimmins, 1997), and (iii) typical soil pH values above the point of zero net charge (PZNC) for the predominant mineral components of most systems (Langmuir, 1997).

Coniferous forest soils of the Pacific Northwest have a combination of factors unique to other forest soils of temperate latitudes however, and may require the investigation of physicochemical mechanisms on  $\text{NO}_3^-$  mobility. Singh and

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Uehara (1999) define net soil surface charge as a function of soil pH, PZNC, electrolyte concentration, and the valence of the counterion. In these temperate coniferous forest ecosystems, soil pH is generally acidic, associated with a mor forest floor regime (Kimmins, 1997). Furthermore, despite comprising only 0.7% of the global ice-free land surface area and less than 2% of the United States (Soil Survey Staff, 1999b), soils of the Andisol order occupy a disproportionately large area of the Pacific Northwest. These soils have a high proportion of Fe and Al oxides and often contain the short-range-order minerals allophane and imogolite (Wada, 1980) which weather rapidly from extruded volcanic tephra (Goldin, 1982). Soils with these mineralogical characteristics are termed variable charge soils (Bowden et al., 1980) because these minerals can contribute positive colloidal surface charge under acidic soil conditions.

The influence of Fe and Al oxide formation on  $\text{NO}_3^-$  sorption has been well characterized in many different soil orders in tropical latitudes (Kinjo and Pratt, 1971), particularly Oxisols (Cahn et al., 1992; Dynia, 2000). Furthermore, Eick et al. (1999) and Toner et al. (1989) have made similar investigation into Ultisols of the southeastern and mid-Atlantic United States. Although the rates and processes of oxide formation may differ between these soils and those of volcanic influence, studies into the sorptive capacities of Andisols extend the range of this potential mechanism for  $\text{NO}_3^-$  retention well beyond tropical and subtropical latitudes (Espinoza et al., 1975 and Katou et al., 1996).

In this study, the physicochemical and mineralogical properties of an Andisol, under intensive forest management in southwestern Washington, were investigated to determine if the presence of noncrystalline minerals resulted in pH-dependent charge characteristics and allowed for the concentration-dependent sorption of  $\text{NO}_3^-$  at ambient field pH values. Nitrate sorption isotherms were generated for each genetic horizon and related to the net surface charge of the less than 2-mm soil fraction across a range of pH values. Quantification of allophane and imogolite was also performed to assess their role in the observed physicochemical interactions.

#### MATERIALS AND METHODS

Soils investigated were of the Boistfort series (mesic, Typic Fulvudand) from the Fall River long-term soil productivity (LTSP) study in the

Twin Harbors South operating area of the Weyerhaeuser Company (46°44 N, 123°24 W) in Pacific County, Washington, U.S.A. The climate of western WA is characterized by cool dry summers and moderate wet winters, with a 5-year (May 2000 to April 2005) on-site mean annual air temperature (at 25 cm) of 8.7°C and mean annual precipitation of 1480 mm (Davis Instruments, Hayward, Calif). The site supports a highly productive, planted Douglas fir [*Pseudotsuga menziesii* (Mirb.) Franco] stand and lies within the *Tsuga heterophylla* zone as described by Franklin and Dyrness (1988). The soils on-site are deep, well drained, medium-textured to moderately fine textured silt loam to silty clay developed from Miocene basalt with andic properties in the surface horizon (Soil Survey Staff, 1999a; Steinbrenner and Gehrke, 1966).

Five soil pits were sampled by genetic horizon to a depth of approximately 150 cm, including A, AB, 2Bw1, and 2Bw2 horizons with average depths of 16.5, 45.5, 95.5, and 150+ cm, respectively. Samples were air-dried and ground to pass through a 2-mm sieve. A 10-g sample of each horizon from each pit was used to determine soil pH using a 1:1 soil/solution ratio in solutions of distilled deionized (DI) water, 0.01 M KCl and 1 M KCl. Samples were stirred and allowed to equilibrate for 30 min before pH measurement (Orion Research Model 230A, 1997). Remaining soil was then composited by mass from each horizon for further analysis.

$\text{NO}_3^-$  sorption was determined via batch equilibration techniques adapted from Cahn et al. (1992), Eick et al. (1999), Kinjo and Pratt (1971), and Kowalenko and Yu (1995) in which 5 g of air-dry soil from each horizon was equilibrated with 20 mL of a known concentration of  $\text{NaNO}_3$ . Equilibration was assumed to have occurred after the mixture was shaken at room temperature for 1 h on a reciprocal shaker at a rate of approximately 100 oscillations/min. After equilibration, the mixtures were centrifuged for 15 min at a force of 1200g. The visible presence of suspended solids in the supernatant of some samples led to the filtration of all samples after centrifugation using prewashed Whatman no. 42 ashless filter papers (Whatman International Ltd., Maidstone, England). After the supernatants were decanted, the remaining soil and solution were weighed to determine the gravitational water content entrained within the soil. Determination of initial soil  $\text{NO}_3\text{-N}$  concentrations was made via a similar process in

which a 20 mL solution of 2 M KCl was used as the equilibrating solution. Before equilibration, two to three drops of toluene were added to each mixture to prevent any biologically mediated N transformations. Supernatant concentrations of NO<sub>3</sub>-N were immediately determined using an autoanalyzer (Perstorp Analytical 500 Series Flow-injection, Silver Spring, Md). The quantity of NO<sub>3</sub>-N sorbed, adapted from Cahn et al. (1992), was determined as:

$$N_s = \frac{(V \cdot N_i) + \left( \frac{W \cdot N_x \cdot V}{W_x} \right) - N_f(V + V_0)}{W} \quad (1)$$

where,  $N_s$  is the amount of NO<sub>3</sub>-N sorbed per weight of oven-dried soil (mg/g),  $N_i$  is the initial concentration (mg/L) of NO<sub>3</sub>-N added via solution,  $N_x$  is the concentration (mg/L) of NO<sub>3</sub>-N of the supernatant from the equilibration with 2 M KCl,  $N_f$  is the concentration (mg/L) of NO<sub>3</sub>-N of the solution from the equilibration with NaNO<sub>3</sub>,  $V$  is the volume (L) of  $N_i$  or  $N_f$  added and  $V_0$  is the gravitational water content (L) of the sample after the supernatant has been decanted. Concurrent to the equilibration procedure, the oven-dry weight (105°C for 24 h) of a thoroughly homogenized 5-g subsample of soil was determined so that sorption values could be presented on a dry weight basis. Thus, from Eq. (1),  $W$  is the equivalent oven-dry weight (mg) of the sample equilibrated with NaNO<sub>3</sub>, and  $W_x$  is the equivalent oven-dry weight (mg) of the sample equilibrated with 2 M KCl. The procedure was repeated in triplicate with 10 different concentrations of NaNO<sub>3</sub> ranging from 3 to 395 mg NO<sub>3</sub>-N per liter (3, 6, 9, 12, 15, 24, 47, 94, 187, and 395 mg NO<sub>3</sub>-N per liter) for the generation of sorption isotherms. To provide better resolution of the sorptive capacity of the soils across the range of ambient NO<sub>3</sub>-N solution concentrations observed on-site (Strahm et al., 2005), half of the NaNO<sub>3</sub> solutions represent a more narrow range of 0 to 15 mg NO<sub>3</sub>-N per liter.

PZNC was determined via simultaneous determination of cation exchange capacity (CEC) and anion exchange capacity (AEC) for 10 pH values (2 ≤ pH ≤ 9) for the less than 2-mm mineral soil fraction and defined as the pH value at which CEC equals AEC (Zelazny et al., 1996). In this procedure, individual subsamples of each horizon were saturated with KCl and rinsed free of any excess salts before pH adjustment with HCl and KOH. The pH of each sample was recorded after a 4-h equilibration after which

NaNO<sub>3</sub> was used to displace K<sup>+</sup> and Cl<sup>-</sup> from the sample and used to determine CEC and AEC, respectively (Zelazny et al., 1996). For pH values at which CEC and AEC were not specifically determined, regression techniques were used to represent exchange capacities (SigmaPlot 2000, SPSS, Inc., Chicago, Ill). Net surface charge was determined by subtracting predicted AEC from CEC across the continuum of measured pH values.

Organically bound, noncrystalline and crystalline forms of Fe, Al, and Si were determined on the less than 2-mm mineral soil fraction via selective dissolution techniques using pyrophosphate, acid oxalate, and dithionite citrate reagents, respectively (Dahlgren, 1994; Jackson et al., 1986; Parfitt and Childs, 1988). All selective dissolutions were performed in quadruplicate. Quantities of allophane and imogolite were estimated by multiplying acid oxalate-extractable Si (Si<sub>o</sub>) by a correction factor derived from the molar Al/Si ratio and based on the empirical formula of their proposed noncrystalline structure (Parfitt, 1990). Molar Al/Si ratios were calculated as (Al<sub>o</sub> - Al<sub>p</sub>)/Si<sub>o</sub>, where Al<sub>o</sub> and Al<sub>p</sub> represent the Al extracted via acid oxalate and pyrophosphate reagents, respectively.

## RESULTS

As the concentration of NO<sub>3</sub><sup>-</sup> in solution increased, a greater amount of NO<sub>3</sub><sup>-</sup> was observed to have sorbed to the mineral surface across all horizons (Figs. 1 and 2). The fraction sorbed was highest at lower solution concentrations, a behavior typical of all ions in solution (Langmuir, 1997), and evidenced here by the curvilinear form of the sorption isotherm. Data generated from each horizon adhere to the Freundlich-type isotherm as given by:

$$\frac{x}{m} = KC^n \quad (2)$$

where,  $x/m$  represents mg NO<sub>3</sub>-N sorbed per gram of dry soil,  $C$  is the concentration of solution (milligrams of NO<sub>3</sub>-N per liter), and  $K$  (distribution coefficient) and  $n$  are constants where  $K$  has units of mg NO<sub>3</sub>-N per gram of dry soil per liter and represents the maximum percentage of NO<sub>3</sub><sup>-</sup> sorbed (slope of the isotherm at the origin) when  $n = 1$  (Langmuir 1997). From Eq. (2), the horizons investigated in this study show an increase in the sorption of NO<sub>3</sub><sup>-</sup> with depth, as expressed by the following  $K$  values (in milligrams of NO<sub>3</sub>-N per gram of

dry soil per liter): A =  $1.76 \times 10^{-4}$ , AB =  $3.38 \times 10^{-4}$ , 2Bw1 =  $1.06 \times 10^{-3}$ , and 2Bw2 =  $1.77 \times 10^{-3}$ . However, calculated  $n$  values ranging from 0.94 to 1.18 result in a deviation from the strict linear interpretation of the distribution constant even across the range of  $\text{NO}_3\text{-N}$  solution concentrations more commonly found at ambient soil solution concentrations (Fig. 2).

The chosen method for the determination of PZNC failed to generate clearly defined PZNC values for the organic-rich A and AB horizons, although a minimum net surface charge of  $-6.5$  and  $-4.2$   $\text{cmol}_c/\text{kg}$  were calculated at pH values of 4.7 and 3.7 for those horizons, respectively (Fig. 3). Under basic pH regimes, maximum cation sorption was approached and determined at a pH of 7.7 to be  $-24.5$   $\text{cmol}_c/\text{kg}$  for the A horizon and  $-21.0$   $\text{cmol}_c/\text{kg}$  for the AB horizon. Determination of the PZNC for the subsurface horizons was possible and calculated as 3.59 and 3.46 for the 2Bw1 and 2Bw2 horizons, respectively. AEC maxima for the subsurface horizons were approached as the system became more acidic and measured as 6.6  $\text{cmol}_c/\text{kg}$  for the 2Bw1 horizon (at pH 2.3) and 7.8  $\text{cmol}_c/\text{kg}$  for the

2Bw2 horizon (at pH 2.2). Conversely, CEC maxima were approached at the highest measured pH values (pH 9) and determined to be  $-27.8$  and  $-27.4$   $\text{cmol}_c/\text{kg}$  for the 2Bw1 and 2Bw2 horizons, respectively. Only in the A horizon did the minimum net surface charge occur above the measured soil pH as determined in a weak electrolyte solution (0.01 M KCl) or DI water (Table 1).

Selective dissolutions for the determination of Fe, Al, and Si yielded decreasing concentrations of all constituents with depth, with the exception of the acid oxalate extractions of the A horizon (Table 1). Conversely, the Al/Si molar ratio increased with depth and influenced the estimates of allophane and imogolite concentrations similarly. Despite calculated Al/Si ratios of more than 4 in the subsurface horizons, allophane and imogolite concentrations were never greater than 3% of less than 2-mm mineral soil fraction, due to low ( $<0.2\%$ )  $\text{Si}_o$  concentrations.

Evaluation of Fe + Al bound in three components of the soil (organic, noncrystalline, and crystalline fractions) shows mineralogical differences between the surface (A and AB horizons) and the subsoil (2Bw horizons).

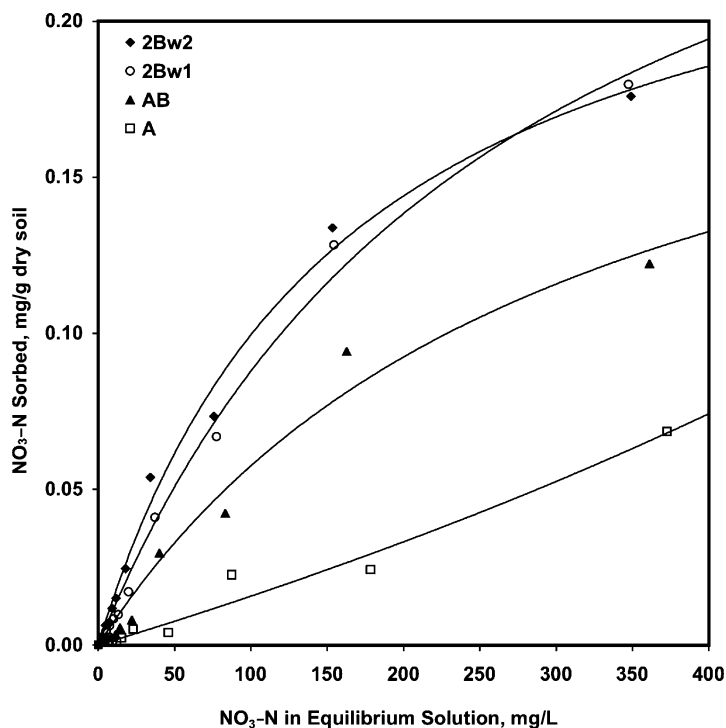


Fig. 1. Quantity of  $\text{NO}_3\text{-N}$  sorbed per gram of dry soil over a range of equilibrium  $\text{NO}_3\text{-N}$  solution concentrations for four horizons of the Boistfort series from the Fall River LTSP study. Best-fit lines shown for visual representation.

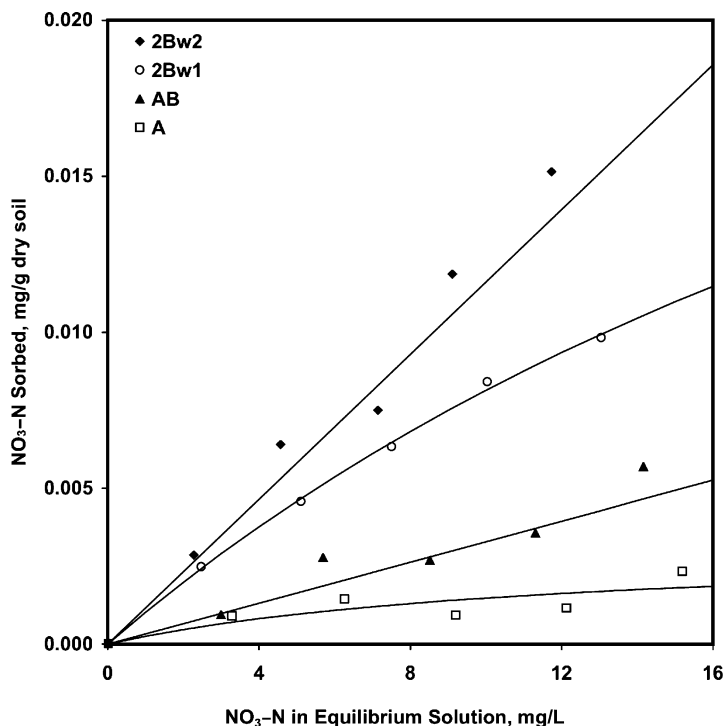


Fig. 2. Recreation of Figure 1 with a focus on the range of equilibrium solution concentrations between 0 and 15 mg NO<sub>3</sub>-N per liter. Lines added for visual representation only.

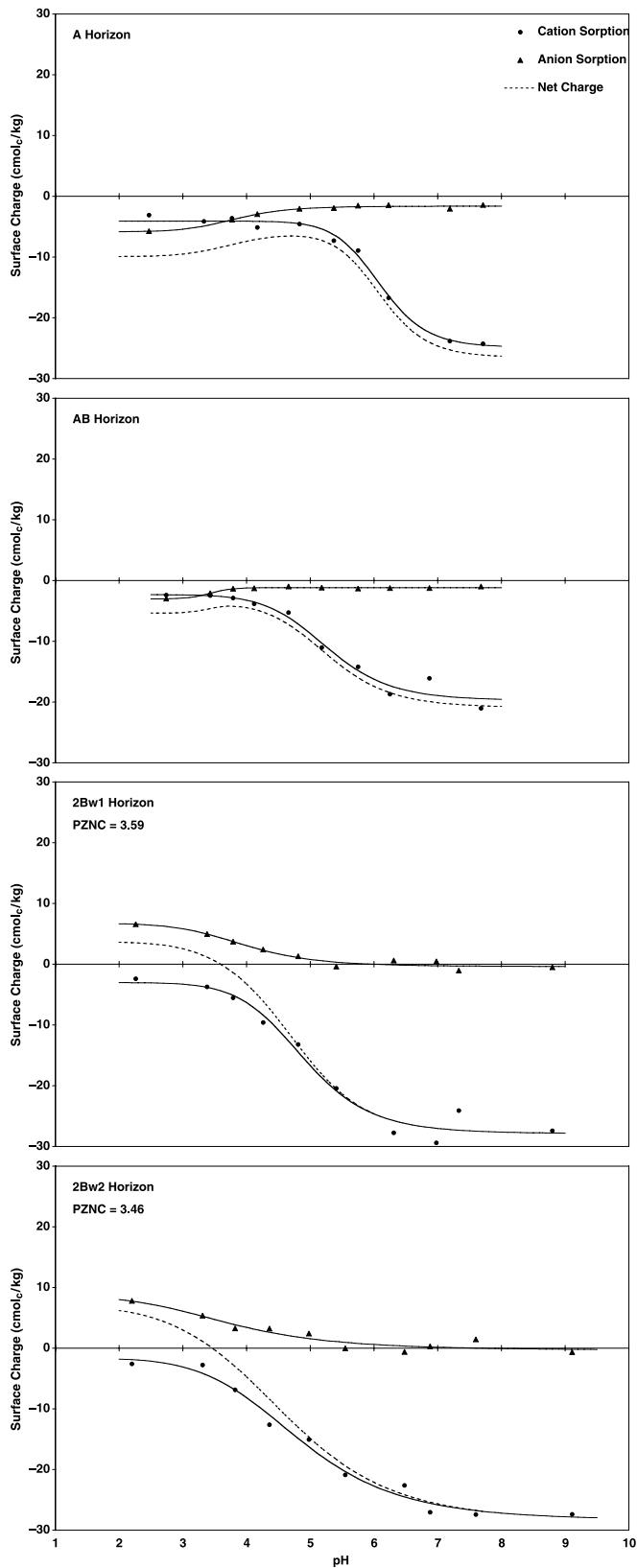
Approximately 50% or more of the Fe and Al are bound with organic matter in the surface horizons (Table 1). The fraction of Fe and Al that is organically bound decreases with depth from 62.5% in the A horizon to 19.3% in the 2Bw2 horizon. The inverse is true of the non-crystalline Fe and Al fraction, with only 3.4% in the A horizon and more than 55% in the Bw2 horizons. Despite these clear trends with depth, Fe and Al bound in a crystalline matrix show less variability with depth and range from 21.8% to 34.1% to a depth of 150 cm.

## DISCUSSION

The soils of the Fall River LTSP study exhibit concentration-dependent sorption of NO<sub>3</sub><sup>-</sup> across all horizons at ambient pH levels, despite the fact that none of these horizons were determined to have a PZNC greater than the measured soil pH (as determined by DI water and 0.01 M KCl). This may seem counterintuitive, in that anion sorption is observed in conjunction with a net mineral surface charge that is negative. However, Toner et al. (1989) showed that the point of zero salt effect, a different method for

determining the zero point of charge of the mineral surface, was a poor indicator of AEC, and they suggest that regions of anion sorption could occur despite a net negative charge of the bulk soil sample. In the 2Bw1 and 2Bw2 horizons, for example, despite a net negative charge at the native pH determined using a weak electrolyte (0.01 M KCl), AEC was estimated to be 2.4 and 2.8 cmol<sub>c</sub>/kg, respectively.

The inability to determine the PZNC of the organic-rich A and AB horizons is likely the result of a predominance of Al humus complexes in these horizons. In the absence of allophane and imogolite, the Al oxides present in the form of Al humus complexes behave differently from those in a mineral matrix, and no positive charge is exhibited (Wada 1980). Furthermore, decreases in pH would increase the solubility of Al. This newly solubilized polyvalent cation would then have two potential impacts on the system: (1) reducing the quantity of Al oxides present in the solid phase and (2) requiring an increase of counterion valence in solution to maintain a charge balance. In addition, the decrease in pH may facilitate the precipitation of soluble organic acids, which,



from a charge standpoint, can function as anions in solution. This would further necessitate desorption of anions from the solid phase to maintain charge balance in solution.

The calculated allophane and imogolite content of the less than 2-mm mineral soil fraction seems very low, relative to other Andisols found globally. In a synthesis of 823 allophanic horizons of Andisols from 20 countries, Parfitt and Kimble (1989) reported allophane contents of the less than 2-mm mineral soil fraction ranging from near zero up to 60%. The low allophane and imogolite contents estimated in this study are driven primarily by low Si<sub>o</sub> concentrations (Table 1). These low Si<sub>o</sub> concentrations further influence the Al/Si ratios as estimated by (Al<sub>o</sub> - Al<sub>p</sub>)/Si<sub>o</sub> and result in reported ratios of more than 4 in the 2Bw1 and 2Bw2 horizons. These values fall well above the median for the global distribution of 2.0 (Parfitt and Kimble, 1989). This suggests either that, in the presence of low Si, the weathering sequence has favored the formation of gibbsite (Flach et al., 1980) over allophane and imogolite, or that there are large amounts of ferrihydrite present that may interfere with the quantification of allophane via the chosen method (Parfitt and Childs, 1988). However, multiplying the acid oxalate-extractable Fe by a factor of 1.7 to estimate ferrihydrite concentrations by weight (Parfitt and Childs, 1988) yields ferrihydrite contents of less than 2%, which falls below the range of 6% to 9% proposed to interfere with the chosen method for allophane and imogolite determination used in this study (Parfitt and Kimble, 1989). In either case, our data point to the secondary formation of nonallophane or imogolite Fe and Al oxide precipitates which are likely driving the variable charge nature of the less than 2-mm soil fraction and govern the observed NO<sub>3</sub><sup>-</sup> sorption.

Regarded as a highly mobile form of a limiting nutrient in temperate coniferous forest ecosystems, the fate of NO<sub>3</sub><sup>-</sup> is often investigated with regard to plant availability in terms of leaching beyond the rooting zone. This study defines a mechanism that may serve to increase

Fig. 3. Net surface charge (dashed line), cation sorption (closed circles), and anion sorption (closed triangles) for four horizons of the Boistfort soil series from the Fall River LTSP study. Net charge determined by the difference between positive surface charge (anion sorption) and negative surface charge (cation sorption). PZNC is defined as the pH at which the net surface charge is neutral and is listed for the 2Bw1 and 2Bw2 horizons.

TABLE 1  
Specific physical, chemical, and mineralogical characteristics of the soils of the Fall River LTSP study.

Horizon	Mean Depth (cm)	pH (1:1; Soil/solution)	Pyrophosphate Extractable*			Acid oxalate Extractable*			Dithionite-citrate Extractable*			Al/Si molar Ratio†	% Fe + Al of total for each associated soil component					
			DI H <sub>2</sub> O	0.01 M KCl	1 M KCl	Fe	Al	Si	Fe	Al	Si		Fe	Al	Org‡	Noncryst§	Cryst¶	
A	0-16.5	4.31	4.18	3.90	1.00	1.26	0.23	1.01	1.38	0.12	1.75	1.88	0.37	1.0	0.6	62.5	3.4	34.1
AB	16.5-45.5	4.57	4.26	4.17	0.71	0.90	0.18	1.05	1.41	0.19	1.68	1.66	0.25	2.8	2.2	48.0	25.6	26.4
2Bw1	45.5-95.5	4.69	4.23	3.87	0.21	0.33	0.06	1.01	0.84	0.12	1.46	0.91	0.22	4.6	3.0	22.8	55.4	21.8
2Bw2	95.5-150+	4.78	4.26	3.79	0.15	0.25	0.01	0.95	0.66	0.09	1.37	0.72	0.18	4.8	2.5	19.3	57.4	23.3

\*Values given as percent of soil fraction less than 2 mm on a dry-weight basis.

†Determined by (Al<sub>o</sub> - Al<sub>p</sub>)/Si<sub>o</sub>.

‡Organically bound Fe + Al determined as sodium pyrophosphate-extractable.

§Noncrystalline Fe + Al determined as the difference between acid oxalate-extractable and pyrophosphate-extractable.

¶Crystalline Fe + Al determined as the difference between dithionite citrate-extractable and acid oxalate-extractable.

the residence time of  $\text{NO}_3^-$  in freely percolating soil solutions. A separate investigation of nutrient leaching at this site has observed significantly higher  $\text{NO}_3^-$  concentrations in soil solution in a conventionally harvested treatment when compared with an adjacent uncut forested stand (Strahm et al., 2005). The duration of this difference was sustained up to 5 years after harvest, a period which extends beyond those observed in similar studies on soils with different parent materials (Briggs et al., 2000; Hornbeck and Kropelin, 1982; Katzensteiner, 2003; Titus et al., 1998). Retention of  $\text{NO}_3^-$  through physicochemical means may help explain this discrepancy. For example, by calculating the quantity of  $\text{NO}_3^-$ -N sorbed by each horizon from the Freundlich isotherm equations presented earlier based on mean soil solution concentrations as reported by Strahm et al., (2005) for the harvested (6 mg/L) and uncut stand (0.5 mg/L), it is possible to estimate the pool of soil N that exists as sorbed  $\text{NO}_3^-$  by pairing estimates for bulk density (from Strahm et al., 2005) with mean horizon thickness values. In doing so, it is estimated that sorbed  $\text{NO}_3^-$  represents 50 and 3 kg N/ha to a depth of 1 m in the harvested and uncut stands, respectively. These values represent a small proportion of the total soil N pool of 15,000 kg/ha to a similar depth (Strahm et al., 2005), yet when compared with the mean annual leaching fluxes of the harvested (73 kg N/ha) and uncut stand (2 kg N/ha), the pools of sorbed  $\text{NO}_3^-$  represent 67% and 170%, respectively. Thus, in this system,  $\text{NO}_3^-$  sorption may serve as a mechanism to buffer the rapid export of an otherwise considered highly mobile plant nutrient. In addition to increasing the residence time of a plant available pool of N, this mechanism may also allow more time for the microbial community to transform  $\text{NO}_3^-$  through the process of denitrification and thus may help ameliorate potential negative consequences of  $\text{NO}_3^-$  leaching on ground and surface waters. As such, it may be important to incorporate further investigation of this physicochemical mechanism to retain  $\text{NO}_3^-$  into any investigations in the Pacific Northwest in which the mobility of  $\text{NO}_3^-$  is of interest.

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