

Mineral and Organic Matter Controls on the Sorption of Macronutrient Anions in Variable-Charge Soils

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Partitioning ions between the solid and solution phase is one of the most important processes controlling nutrient mobility and bioavailability. Despite this, less research has focused on the interactions of nutrient anions at soil interfaces, although variable-charge components are present to some extent in nearly all soils. The objective of this study was to develop equations using commonly measured soil properties (particle size analysis, organic matter content, and extractable Fe and Al fractions) to predict sorption isotherms for NO_3^- , SO_4^{2-} , and H_2PO_4^- . Six subsurface soils, ranging spatially and temporally from heavily weathered Oxisols of the tropics to a recently glaciated Entisol from the U.S. Pacific Northwest, were used to generate sorption isotherms of the three macronutrient anions using initial solution concentrations from 0.1 to 5 mmol L^{-1} . Before batch sorption experiments, soils were saturated with KCl, rinsed free of excess salts, and adjusted to $\text{pH} = 4.0 \pm 0.1$ to eliminate the confounding effects of competing ions or differing pH regimes. Almost all soils from temperate latitudes had a greater capacity to sorb anions than the Oxisols included in this study for comparison. This was particularly true for the soils with volcanic parent materials from the Pacific Northwest. For any given soil, the capacity to sorb the macronutrient anions was in the order $\text{H}_2\text{PO}_4^- > \text{SO}_4^{2-} > \text{NO}_3^-$. Multiple regression analyses generally suggest that the electrostatic sorption of NO_3^- and SO_4^{2-} is positively related to the presence of active Al fractions and negatively correlated with organic C content.

Abbreviations: AEC, anion exchange capacity; Al_{ORG} , organically bound aluminum; Al_{SUB} , aluminum substituted for iron in iron oxides; CEC, cation exchange capacity; Fe_{SRO} , short-range order iron; PZNC, point of zero net charge.

Soils are responsible for supplying nearly all of the 18 elements that plants require, and most of those as inorganic ions. Thus, charge development in soils and the electrochemical interactions between soil particles and nutrient ions are essential for both the accrual of nutrients and the regulation of nutrient supply to the biota. Despite the fact that a significant proportion of those ions exist as anions, particularly the macronutrients, relatively little attention has been paid to the development of positive electrostatic charge on the soil surface and the resulting anion sorption and exchange reactions. This is probably due to the fact that much of modern soil science, specifically the study of plant–soil interactions, has developed from an agricultural background and inherited many similar agricultural biases. Forest soils and many natural ecosystems, however, differ markedly from these cropping systems in terms of physical, chemi-

cal, and biological properties, and should be evaluated separately with regard to the resulting processes that characterize them.

Variable-charge soils, or soils in which the electrostatic charge is dependent on pH (Brady and Weil, 2002), are present to some extent in nearly all terrestrial ecosystems; however, they are predominately found in five soil orders: Oxisols, Ultisols, Alfisols, Spodosols, and Andisols (Theng, 1980), which collectively cover nearly one-third of both the global and U.S. ice-free land surface area (Buol et al., 2003). Forests are among the dominant forms of vegetative cover on these soils (Brady and Weil, 2002). In the United States, forest vegetation predominates the Andisol and Ultisol orders in the Pacific Northwest and Southeast, respectively. Through intensive forest management, these two regions produce the majority of the national softwood timber supply (Smith et al., 2004). The acidic, mor forest floor regime associated with coniferous forests (Kimmins, 1997), coupled with the variable-charge soil components common in these soils, allow the potential development of a positive electrostatic charge on the soil surface that can result in anion sorption.

The complex interactions between such amphoteric soil colloids and ions in solution are critical in regulating many soil chemical reactions. This is particularly true in terms of plant nutrition, as the partitioning of nutrients between the solid and solution phases is widely considered the most important factor controlling nutrient transport, including both availability to plant roots and leaching (Barrow, 1987; Johnson and Cole, 1980). This is exemplified by the macronutrient anions of N and P, which are two of the most important nutrient anions in soils (Parfitt, 1980). The former (NO_3^-) is

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Table 1. Soil sample identifications (comprised of the abbreviation of the place of origin and the series name), horizons, and U.S. taxonomic classifications of the six soils investigated in this study.

Soil (origin and series)	Horizon	Taxonomic classification
HI-Wahiawa, Hawaii	Bo1	very-fine, kaolinitic, isohyperthermic Rhodic Haplustox
ME-Rawsonville, Maine	Bh	coarse-loamy, isotic, frigid Typic Haplohumods
NC-Cecil, North Carolina	Bt1	fine, kaolinitic, thermic Typic Kanhapludults
PR-Bayamon, Puerto Rico	Bo1	very-fine, kaolinitic, isohyperthermic Typic Hapludox
WA-Boistfort, Washington	Bw1	medial over clayey, ferrihydritic over parasquic, mesic Typic Fulvudands
WA-Grove, Washington	Bw2	sandy-skeletal, mixed, mesic Dystric Xerorthents

one of the most weakly held anions, thus facilitating nutrient depletion through leaching; while the anions of the latter (H_2PO_4^- or HPO_4^{2-}) are among the most strongly held, thus limiting plant uptake. In this respect, SO_4^{2-} exists somewhere between the two and is regarded as the only macronutrient anion that is held in an exchangeable form (Bohn et al., 2001).

An understanding of the relationships between soil properties and the partitioning of these anions between the solid and solution phases is important to accurately predict their soluble fluxes in response to direct (e.g., fertilization) and indirect (e.g., atmospheric deposition) landscape manipulations. Alves and Lavorenti (2004) argued that efforts to achieve such an understanding are lacking with regard to SO_4^{2-} relative to phosphate. Such investigations are almost nonexistent with respect to NO_3^- , and those that do exist focus predominately on the relationships with soil physical properties (Black and Waring, 1976, 1979). Furthermore, attempts to relate SO_4^{2-} sorption to specific fractions of Fe and Al, as determined by selective dissolution analyses, have produced equivocal and often contradictory results with predominantly positive correlations attributed to Fe oxides (Johnson and Todd, 1983), Al oxides (Camps Arbestain et al., 2001), organically bound Fe and Al (Bhatti et al., 1997), oxalate-extractable Fe and Al (Alves and Lavorenti, 2004; Camps Arbestain et al., 1999b; Barreal et al., 2001), dithionite-extractable Fe and Al (Comfort et al., 1992), or various Fe and Al combinations (Camps Arbestain et al., 1999a). Furthermore, despite a widely recognized negative relationship between SO_4^{2-} sorption and organic matter (Camps Arbestain et al., 1999a, 2001; Comfort et al., 1992; Johnson and Todd, 1983; Pigna and Violante, 2003; Shanley, 1992; Vance and David, 1992) as well as pH (Motavalli et al., 1993; Pigna and Violante, 2003; Shanley, 1992; Zhang et al., 1996), some studies continue to produce inconclusive (Kimsey et al., 2005) or contradictory results (Harrison et al., 1989) with respect to those properties.

The inability of such studies to converge on a common set of variables to predict the sorption of a particular anion is probably due to the confounding factors inherent in utilizing soils across large spatial scales. Singh and Uehara (1998) stated that the factors influencing surface charge, and thus many sorption reactions, are: (i) pH; (ii) the chemical composition of the soil particles; (iii) the ionic strength of the solution; and (iv) the presence and nature (specifically the valence) of any counterions. Thus, soils from different sites will inherently vary in all four of these parameters due in part to differences in parent materials, vegetative cover, previous land management practices, and atmospheric deposition regimes. Such differences could confound attempts to relate anion sorption reactions to other soil properties, particularly Fe and Al fractionation schemes, as is often done.

With a few exceptions (Comfort et al., 1992; Syers et al., 1973), most investigations attempting to relate anion sorption to soil physical or chemical properties evaluate sorption at only a single anion concentration. For any system in

which ions in solution and an oppositely charged surface exist, however, the percentage of the ion sorbed is typically highest at the lowest solution concentrations and the fraction sorbed tends to decrease as the concentration increases, giving rise to a curvilinear sorption isotherm (Langmuir, 1997). This study related the parameters that define the behavior of Langmuir sorption isotherms with the physical and chemical composition of the bulk soil while holding the effects of pH and ion competition constant. Such data increase the applicability of the derived relationships across a range of sites and anion concentrations.

MATERIALS AND METHODS

Study Sites

Subsurface (B horizon) soil samples were collected from four pedogenically diverse sites across the United States where forest management is practiced (Table 1). The soils, abbreviated by origin and soil series name are: ME-Rawsonville from the Bear Brook Watershed in Maine (Norton et al., 1999), NC-Cecil from the Henderson Long-Term Site Productivity (LTSP) study in North Carolina (Allen et al., 1995), and two soils from Washington state, WA-Boistfort from the Fall River LTSP study (Terry et al., 2001), and WA-Grove from the Matlock LTSP study (Meehan, 2006). Despite their close geographic proximity, the soils of the two sites in Washington are dramatically different. The WA-Grove soil was formed in glacial outwash from the retreat of the Puget Lobe of the Cordilleran Ice Sheet during the last glacial maximum (Burns, 1985). The WA-Boistfort soil was formed in Miocene basalt flows south of the furthest extent of subsequent glacial events (Burns, 1985; Christiansen and Yeats, 1992). Additionally, because tropical Oxisols are widely regarded to have the greatest composition of variable-charge mineralogy, two Oxisols (HI-Wahiawa and PR-Bayamon, from Hawaii and Puerto Rico, respectively) were included to capture greater variability in soil mineralogical composition. Following collection, soils were air dried and passed through a 2-mm sieve before all subsequent analyses.

Soil Physical and Chemical Analysis

Selective dissolution analyses of Fe, Al, and Si were used to estimate pedogenically significant mineralogical fractions. Although it is often assumed that pyrophosphate-, oxalate-, and dithionite-citrate-extractable Fe and Al are related to organically bound, noncrystalline, and crystalline mineralogical fractions, respectively, research has clearly demonstrated that the actual relationships are often less clear and that such a simplistic model is inappropriate (Parfitt and Childs, 1988; Soil Survey Staff, 2004).

The use of selective dissolution analyses as a tool in soil taxonomy (Soil Survey Staff, 2004), however, has resulted in the generation of a large set of such data by the National Soil Survey Center (NSSC) Soil Survey Laboratory (Soil Survey Staff, 2007). Available for public use, the data generated by the NSSC Soil Survey Laboratory comprise the most extensive database for soil series-level physical and chemical characterization. Thus, despite problems relating values from selective dissolution analysis to spe-

cific mineralogical fractions, the widespread availability of such data, when coupled with the results of this study, could still be of use in guiding land management decisions as well as future modeling efforts where opportunities for more intensive soil characterization may be limited.

Thus, this study attempted to use data from selective dissolution analyses to define pedogenically significant Fe and Al fractions, and relate these fractions to the parameters defining anion sorption. Table 2 gives a list of these parameters and their relationships to commonly observed selective dissolution analyses, as synthesized from Parfitt and Childs (1988), Parfitt (1990), and Soil Survey Staff (2004). Here the "pedogenically active" fraction represents the Fe and Al that exists outside of a highly ordered crystalline matrix and thus may be expected to interact more extensively with other soil constituents (Camps Arbestain et al., 2001; Soil Survey Staff, 2004). Similarly, other, more well identified, Fe and Al fractions are also listed. In this way, we hope to offer a tool that can be used to predict sorption capacity across the landscape, as well as provide the context to discuss potential sorption mechanisms. Standard methods for pyrophosphate-extractable, oxalate-extractable (Dahlgren, 1994; Jackson et al., 1986; Parfitt and Childs, 1988) and dithionite-citrate-extractable (Soil Survey Staff, 2004) Fe, Al, and Si were used. All selective dissolutions were performed in triplicate.

Subsamples of each soil sample were analyzed for C using a PerkinElmer Model 2400 CHN analyzer (PerkinElmer, Wellesley, MA) after grinding to a fine powder with a mortar and pestle for homogenization. Sand, silt, and clay contents were determined by sedimentation in a hexametaphosphate solution to ensure particle dispersion (Soil Survey Staff, 2004) after sequential pretreatment to remove organic matter with H₂O₂ and oxide cementation using a bicarbonate-buffered dithionite-citrate solution (Soil Survey Staff, 2004). All physical and chemical analyses are reported on a dry-mass percentage basis.

Charge Characteristics

The point of zero net charge (PZNC) was determined by simultaneous determination of the cation exchange capacity (CEC) and the anion exchange capacity (AEC) at eight pH values (2 ≤ pH ≤ 9), and defined as the pH at which CEC equals AEC (Zelazny et al., 1996). In this procedure, individual subsamples of each horizon were saturated with 1 mol L⁻¹ KCl and rinsed free of excess salts with 0.01 mol L⁻¹ KCl before pH adjustment with 1 mol L⁻¹ HCl and 1 mol L⁻¹ KOH. The pH of each sample was recorded following a 4-h equilibration after which 0.5 mol L⁻¹ NaNO₃ was used to displace K⁺ and Cl⁻ from the sample and used to determine CEC and AEC, respectively (Zelazny et al., 1996). Potassium was analyzed using inductively coupled Ar plasma spectroscopy (ICAP Model 61E, Thermo-Jarrell Ash Corp., Franklin, MA), and Cl⁻ via ion chromatography (Dionex DX-120 Ion Chromatograph, Dionex Corp., Sunnyvale, CA). For pH values (2 ≤ pH ≤ 9) at which CEC and AEC were not specifically determined, nonlinear regression was used to represent exchange capacities (SigmaPlot 2000, SPSS, Inc., Chicago, IL). Net surface charge was determined by subtracting predicted AEC from CEC across the continuum of measured pH values.

Anion Sorption Isotherms

Before anion sorption equilibrations, steps were taken to control the pH of both the soil and solution. All soils were adjusted to pH 4.0 ± 0.1 following KCl saturation to remove any competing ions (other than K⁺ and Cl⁻), and subsequently rinsed to remove excess salts via the procedure outlined above and by Zelazny et al. (1996), for the deter-

Table 2. Abbreviation, description, and method of determination (from data derived from selective dissolution analysis for Fe, Al, and Si) for independent variables used in regression analysis with Langmuir isotherm parameters.

Variable	Description	Estimation†
Fe _{PED}	pedogenically active Fe fraction	Fe _d
Al _{PED}	pedogenically active Al fraction	Al _o
Fe _{SRO}	short-range-order Fe fraction	Fe _o
Al _{SRO}	short-range-order Al fraction	Al _o - Al _p
Al _{ORG}	organically bound Al	Al _p
Al _{SUB}	Al substituted in Fe oxides	Al _d
Al/Si	short-range order Al/Si ratio	(Al _o - Al _p)/Si _o
Fe _{G+H}	Fe in goethite and hematite	Fe _d - Fe _o
Clay	clay particle size fraction	
Organic C	organic C content	

† Pyrophosphate (Al_p), acid oxalate (Fe_o, Al_o, and Si_o), and dithionite-citrate (Fe_d and Al_d) extractable fractions.

mination of the PZNC. Following these pretreatment steps, soils were again air dried and passed through a 2-mm sieve before use in the batch equilibration experiment. Six different concentrations of KNO₃, K₂SO₄, and K₂HPO₄ were prepared, ranging from 0.1 to 5 mmol L⁻¹. All solutions were adjusted to pH 4.0 ± 0.05 through the dropwise addition of dilute HCl or KOH. This experiment was performed at pH 4.0 ± 0.1 to maximize the potential for anion sorption while still remaining close to the native pH range of these soils in the presence of a dilute electrolyte solution (Table 3), such as that used during the process of determining the PZNC.

Anion sorption was determined for NO₃⁻, SO₄²⁻, and H₂PO₄⁻ using a batch equilibration technique adapted from Cahn et al. (1992), Eick et al. (1999), Kinjo and Pratt (1971), and Kowalenko and Yu (1995). Before all equilibrations, two to three drops of toluene were added to each mixture to prevent any biologically mediated N transformations. Five-gram subsamples of each soil were equilibrated with 20 mL of one of the six concentrations of KNO₃, K₂SO₄, and K₂HPO₄. Equilibrations were performed in triplicate. After the mixture was shaken at room temperature for 1 h on a reciprocal shaker at a rate of approximately 100 oscillations min⁻¹, equilibration was assumed to have occurred. Following equilibration, the mixtures were centrifuged for 15 min at a force of 1200 × g, after which the supernatants were decanted. Random samples were selected for pH measurement following equilibration to assess any pH changes during the procedure. All post-equilibration pH values remained within ±0.1 of the target pH level. After decanting, the remaining soil and solution was

Table 3. Particle size fractions, organic C content, and pH for the <2-mm fraction of the six soils investigated in this study.

Soil	Particle size analysis			Organic C	pH (1:1)	
	Sand	Silt	Clay		Distilled, deionized H ₂ O	0.01 mol L ⁻¹ KCl
	%					
HI-Wahiawa	10	10	80	1.6	5.16	4.68
ME-Rawsonville†	45	33	22	9.5	3.59‡	—
NC-Cecil	25	20	55	0.3	5.19	4.61
PR-Bayamon	55	3	42	0.2	5.25	4.93
WA-Boistfort	12	48	40	0.7	4.65	4.31
WA-Grove	86	2	12	1.3	5.08	4.83

† Not enough sample mass remaining for additional pH measurement.

‡ Value taken from Fernandez et al. (2003) for samples from same study site and horizon.

Table 4. Iron, Al, and Si values from selective dissolution analyses and the pedogenically significant Fe and Al fractions derived from them as defined in Table 2. Values reported on a percentage dry mass basis of the <2-mm fraction of the soil.

Soil	Selective dissolution analysis†						Pedogenically significant fractions‡							
	Fe _o	Fe _d	Al _p	Al _o	Al _d	Si _o	Fe _{PED}	Fe _{SRO}	Fe _{G+H}	Al _{PED}	Al _{SRO}	Al _{ORG}	Al _{SUB}	Al/Si
HI-Wahiawa	0.18	7.49	0.06	0.32	0.40	0.02	7.49	0.18	7.31	0.32	0.25	0.06	0.40	10.5
ME-Rawsonville	4.46	6.89	0.74	0.72	0.68	0.02	6.89	4.46	2.43	0.72	-0.02	0.74	0.68	-1.14
NC-Cecil	0.14	5.03	0.03	0.15	0.30	0.05	5.03	0.14	4.89	0.15	0.11	0.03	0.30	2.30
PR-Bayamon	0.03	4.28	0.01	0.05	0.27	0.02	4.28	0.03	4.26	0.05	0.04	0.01	0.27	2.29
WA-Boistfort	0.81	3.83	0.36	0.78	0.58	0.13	3.83	0.81	3.02	0.78	0.42	0.36	0.58	3.18
WA-Grove	0.40	1.24	0.24	0.91	0.32	0.26	1.24	0.40	0.84	0.91	0.67	0.24	0.32	2.56

† Pyrophosphate (Al_p), acid oxalate (Fe_o, Al_o, and Si_o), and dithionite-citrate (Fe_d and Al_d) extractable fractions.

‡ Fe_{PED} and Al_{PED}, pedogenically active Fe and Al; Fe_{SRO} and Al_{SRO}, short-range order Fe and Al; Fe_{G+H}, Fe in goethite and hematite; Al_{ORG}, organically bound Al; Al_{SUB}, Al substituted for Fe in Fe oxides; and Al/Si, short-range order Al/Si ratio.

weighed to determine the gravitational water content entrained within the soil. Supernatant concentrations of NO₃-N were immediately determined using an autoanalyzer (Perstorp Analytical 500 Series Flow-injection, Silver Spring, MD) and SO₄-S and PO₄-P via ICAP (Thermo Jarrell Ash Corp., ICAP 61E Model). The quantity of each anion sorbed was assumed to be the difference between the quantity in solution before and immediately following the equilibration procedure. All sorption values are reported on a millimole per kilogram of dry soil basis as a mean of the three replicates.

Following batch equilibrations, sorption isotherms were generated by the Modified Hyperbola I nonlinear regression technique in SigmaPlot 2000, using the Langmuir isotherm equation:

$$\frac{\text{mmol sorbed}}{\text{kg soil}} = \frac{bN_{\text{max}}(\text{mmol in final solution})}{1 + b(\text{mmol in final solution})} \quad [1]$$

where N_{max} represents the asymptote or theoretical maximum quantity sorbed, and b represents the affinity of the ion to complex with the mineral surface (slope of the tangent of the isotherm at the origin; Langmuir, 1997), also referred to as the binding energy constant (Syers et al., 1973). The Langmuir isotherm was chosen because it provides two independent variables (b and N_{max}) that can then be related to physical and chemical soil properties (Olsen and Watanabe, 1957). This allowed us to evaluate

the relative contributions of soil properties on sorption affinity and maxima independently.

Statistical Analysis

The predictive constants for the Langmuir isotherm equation (b and N_{max}) of each anion were used individually as dependent variables in a stepwise multiple linear regression analysis (SPSS 11.0.2 for Mac, SPSS Inc., Chicago), using the parameters listed in Table 2 as independent variables. Stepwise additions were continued (using independent variable criteria of $P \leq 0.35$ for inclusion, $P \geq 0.5$ for exclusion) until a statistically significant model was achieved ($P < 0.1$). Pearson's correlation coefficients (r) were generated between all regression parameters to ensure that none of the independent variables were significantly correlated.

RESULTS AND DISCUSSION

Soil Physical and Chemical Analysis

The six soils utilized in this study varied considerably in terms of their physical and chemical properties. The clay fraction (<0.002 mm) ranged from only 12% in the glacial outwash WA-Grove soil to 80% in the

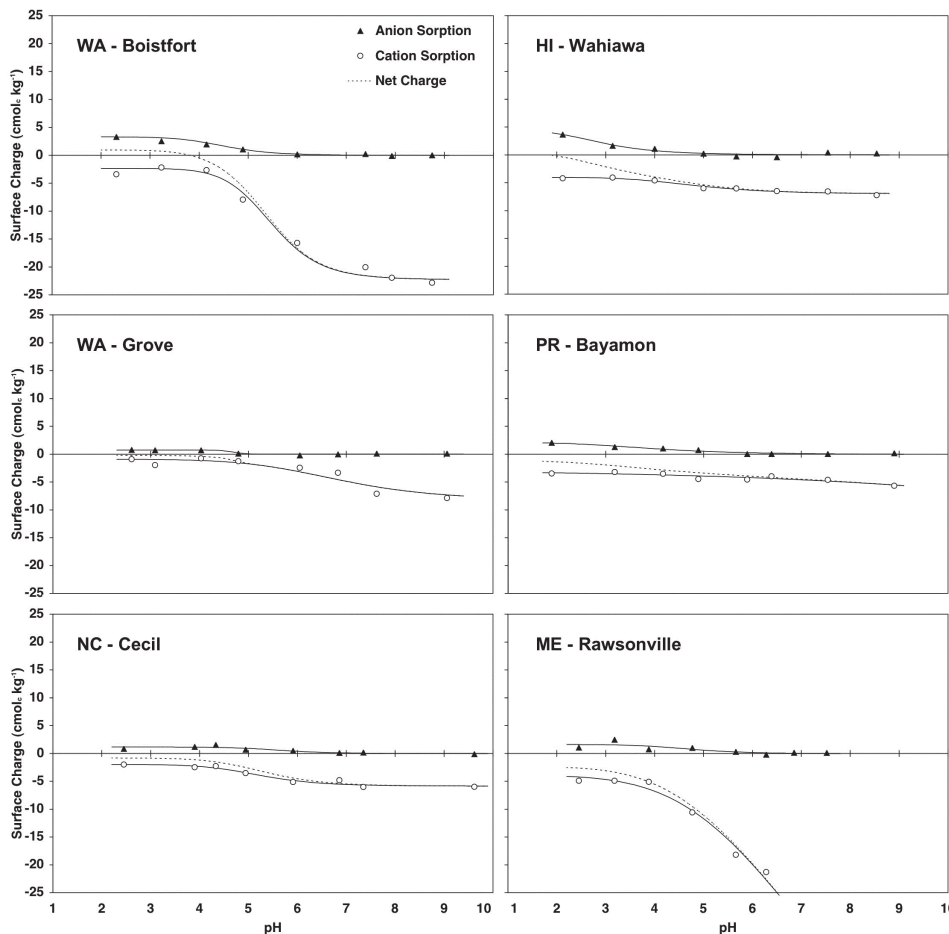


Fig. 1. Net surface charge (dashed line), cation sorption (open circles), and anion sorption (filled triangles) for the <2-mm fraction of each soil. Only WA-Boistfort exhibited a point of zero net charge (pH = 3.8) within the pH range investigated (2 ≤ pH ≤ 9).

HI-Wahiawa soil (Table 3). Due largely to the fact that all soils in this study were from subsurface horizons, the organic C content was <2% with the exception of the Bh horizon of the ME-Rawsonville Spodosol, which approached 10% (Table 3).

Results from the selective dissolution analyses illustrate differences between the soils of the Pacific Northwest and the other samples in terms of chemical composition (Table 4). The WA-Boistfort and WA-Grove soils had the highest quantities of short-range-order Al compounds. This was also true for short-range-order Fe compounds (Fe_{SR0}) and organically bound Al (Al_{ORG}), with the exception of the ME-Rawsonville soil. The Washington soils also had the highest quantities of oxalate-extractable Si, suggesting the presence of the short-range-order aluminosilicates allophane and imogolite (Wada, 1980). These minerals are often associated with inputs of volcanic ash common to the region (Goldin, 1982). The soils from the U.S. Pacific Northwest had the highest amount of pedogenically active Al, yet the lowest percentages of pedogenically active Fe. Trends in Al substituted into crystalline Fe oxides (Al_{SUB}), Al/Si ratio, and estimates of goethite and hematite were less clear (Table 4).

Charge Characteristics

All soils investigated in this study proved to be variable charge and exhibited some positive charge under acidic conditions despite maintaining a net negative surface charge in most cases (Fig. 1). Generally, a positive surface charge increased with acidity and a negative surface charge increased with alkalinity. The WA-Boistfort and ME-Rawsonville soils showed the greatest change in surface charge across the range of pH values. Only the WA-Boistfort soil exhibited a PZNC (pH = 3.8) within the range of pH values investigated. At pH = 4.0, the condition at which the sorption experiments were performed, the CEC was determined to be greater than the AEC for all soils, ranging from 1.1 to 6.8 and 0.7 to 2.5 $cmol_c kg^{-1}$, respectively. This indicates that despite regions of positive charge, probably due to the heterogeneity of the mineral surface, the overall net surface charge of the bulk soil was negative.

Anion Sorption

For any individual soil in this study, anion sorption followed the pattern: $H_2PO_4^- > SO_4^{2-} > NO_3^-$. This apparent lack of correlation with ionic valence reinforces the accepted notion that sorption mechanisms for $H_2PO_4^-$, on both Fe and Al oxides alike, are not primarily electrostatic (Parfitt, 1977; Parfitt et al., 1975). Although it is presumed that electrostatic mechanisms are largely responsible for the retention of SO_4^{2-} in an exchangeable form (Bohn et al., 2001), evidence also suggests that interactions between SO_4^{2-} and the mineral surface are more complex. Sulfate, like $H_2PO_4^-$, has been shown to participate in ligand exchange reactions with hydroxylated Fe and Al surfaces (Parfitt, 1980). Sorption of NO_3^- , however, is solely electrostatic. Nitrate is considered to be only weakly attracted to the mineral surface, and can even be repelled by a negative surface charge (Bohn et

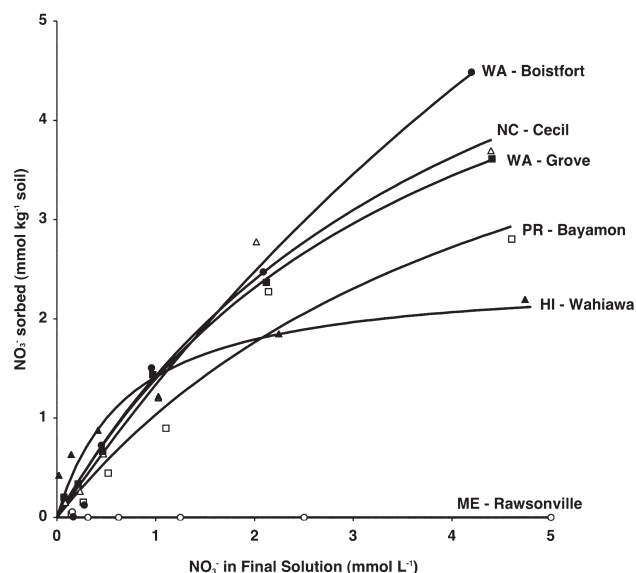


Fig. 2. Quantity of NO_3^- sorbed per kilogram of dry soil across a range of equilibrium NO_3^- solution concentrations at pH = 4.0 ± 0.1 for HI-Wahiawa (filled triangles), ME-Rawsonville (open circles), NC-Cecil (open triangles), PR-Bayamon (open squares), WA-Boistfort (filled circles), and WA-Grove (closed squares) soils. Lines represent Langmuir sorption isotherms.

al., 2001). Thus, the pattern of anion sorption for any given soil in this study is not surprising.

With the exception of the ME-Rawsonville soil, all the soils investigated exhibited some capacity to sorb NO_3^- (Fig. 2). Of those soils, the forest soils from temperate latitudes had the highest amount of NO_3^- sorbed across the widest range of solution concentrations relative to the Bo horizons included from the two Oxisols. Although the HI-Wahiawa soil showed the greatest initial affinity for NO_3^- sorption (b , Table 5), it also had the lowest maximum capacity (N_{max} , Table 5). Conversely, the WA-Boistfort had a theoretical maximum in excess of twice that of any other soil (Table 5).

All soils showed some capacity to sorb SO_4^{2-} (Fig. 3). Trends were similar to those of NO_3^- , with the ME-Rawsonville having both the lowest affinity and the lowest capacity (Table 5). The Bw horizon of the WA-Grove and the two Bo horizons exhibited similar trends in SO_4^{2-} sorption capacity, while the NC-Cecil and WA-Boistfort soils had nearly two and three times that capacity, respectively (Fig. 3, Table 5).

Phosphate sorption patterns were similar to those of SO_4^{2-} and NO_3^- , with one notable exception (Fig. 4). The

Table 5. Langmuir isotherm equation parameters for the theoretical maximum quantity sorbed (N_{max}) and the sorptive affinity (b) for each soil by macronutrient anion combination generated from the data presented in Fig. 2, 3, and 4.

Soil	NO_3^-		SO_4^{2-}		$H_2PO_4^-$	
	N_{max}	b	N_{max}	b	N_{max}	b
	mmol kg^{-1}		mmol kg^{-1}		mmol kg^{-1}	
HI-Wahiawa	2.44	1.38	7.32	3.60	18.6	27.5
ME-Rawsonville	0.00	0.00	2.62	0.42	68.5	5.00
NC-Cecil	7.48	0.24	11.4	37.1	18.5	234
PR-Bayamon	5.97	0.21	5.13	41.0	14.6	47.3
WA-Boistfort	16.8	0.09	16.5	16.3	29.0	512
WA-Grove	6.72	0.26	6.10	21.7	17.3	125

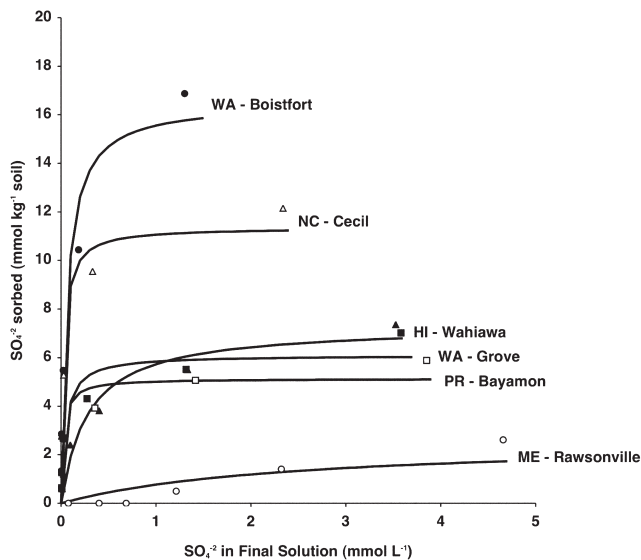


Fig. 3. Quantity of SO_4^{2-} sorbed per kilogram of dry soil across a range of equilibrium SO_4^{2-} solution concentrations at $\text{pH} = 4.0 \pm 0.1$ for HI-Wahiawa (closed triangles), ME-Rawsonville (open circles), NC-Cecil (open triangles), PR-Bayamon (open squares), WA-Boistfort (filled circles), and WA-Grove (filled squares) soils. Lines represent Langmuir sorption isotherms.

ME-Rawsonville Bh horizon, which sorbed the least NO_3^- and SO_4^{2-} , had the highest theoretical maximum sorption capacity of H_2PO_4^- ; however, it also had the lowest initial affinity, possibly suggesting that different mechanisms control the two parameters. The other three temperate forest soils had an affinity for H_2PO_4^-

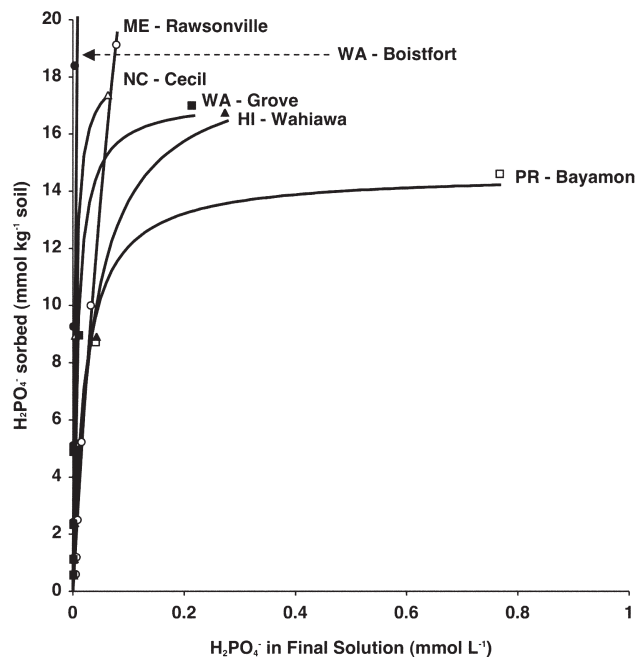


Fig. 4. Quantity of H_2PO_4^- sorbed per kilogram of dry soil across a range of equilibrium H_2PO_4^- solution concentrations at $\text{pH} = 4.0 \pm 0.1$ for HI-Wahiawa (filled triangles), ME-Rawsonville (open circles), NC-Cecil (open triangles), PR-Bayamon (open squares), WA-Boistfort (filled circles), and WA-Grove (closed squares) soils. Lines represent Langmuir sorption isotherms.

sorption that was an order of magnitude greater than the Oxisols (Table 5).

These results indicate similarities in the sorption of NO_3^- and SO_4^{2-} , and suggest a mechanism of interaction with the particle surface that differs from H_2PO_4^- . Nitrate and SO_4^{2-} N_{max} parameters exhibited a negative relationship with organic C, a trend probably due to competition for sorption sites between organic and inorganic anions (Inskeep, 1989) as well as the associated changes in mineral surface characteristics in the presence of organic matter (Johnson and Todd, 1983). Additionally, the value of N_{max} for NO_3^- and SO_4^{2-} sorption showed a positive relationship with various Al fractions (Table 6). Conversely, Fe appeared to play a larger role in the sorption of H_2PO_4^- , as Fe_{SRO} explained more variation in N_{max} than any other combination of factors for any of the other dependent variables (Table 6). Nitrate and SO_4^{2-} N_{max} values also had significant ($P < 0.1$) positive correlations with AEC ($r = 0.78$ and 0.75 , respectively), whereas the N_{max} value for H_2PO_4^- did not ($r = 0.63$, $P = 0.25$). This suggests a mechanism for the sorption of NO_3^- and SO_4^{2-} that is predominantly electrostatic, and supports the accepted notion that phosphate sorption occurs primarily through ligand exchange reactions rather than through electrostatic means (Bohn et al., 2001). Thus, the retention of NO_3^- and SO_4^{2-} in terrestrial ecosystems may be more susceptible to manipulations in the landscape that would affect soil pH and soil surface charge.

Predicting Anion Sorption

This study allows a clearer understanding of potential sorption mechanisms by controlling the confounding effects often associated with making such comparisons across sites; however, such an approach can make it more difficult to compare these results with existing research. Despite this, when a consensus can be reached via different methods, we gain a more robust understanding of the factors governing the interactions. In this way, the results of this study are supported by the work of Comfort et al. (1992) in that such approaches are more effective at modeling sorptive maxima than they are initial sorption affinity. The use of soil physical and chemical characteristics to explain the Langmuir isotherm variables for each anion showed a better fit (R^2) for the N_{max} parameter than for the b parameter for models with the same level of significance ($P < 0.1$; Table 6). This calls into question the applicability of using physical and chemical soil data to model anion sorption at lower concentrations, where the affinity parameter (b) has greater influence over the relative proportion sorbed. This is exemplified in this study by the Langmuir parameters for SO_4^{2-} sorption, where the same independent variable, Al_{SUB} , has a negative relationship with b , and a more intuitive, positive relationship with N_{max} .

Such discrepancies between the relationships of the Langmuir parameters to pedogenically active Fe and Al fractions may be due to the choice of independent variables included in the model-building process. Barreal et al. (2003) demonstrated a positive correlation between Al_{SUB} and SO_4^{2-} sorption, and related the relationship to an increase in surface area associated with the substitution of Al into otherwise crystalline Fe minerals (García-Rodeja et al., 1986; Curi and Franzmeier, 1984). Such substitutions have been shown to raise the PZNC of the mineral surface and increase ion exchange capacities (Potter and Yong, 1999). Specifically, increases in surface area have been shown to correlate well with the increased sorption of anions (Hingston, 1981). A similar association with surface area was made by Black

and Waring (1979) regarding NO_3^- sorption. The importance of surface area as a controlling factor in the sorption of macronutrient anions is supported in this study by the positive relationships exhibited between Al_{ORG} and some of the Langmuir isotherm equation parameters (Table 6). Numerous other investigations have documented similar relationships between anion sorption and the development of Al–humus complexes that inhibit crystalline formation and result in an increase in mineral surface area (Alves and Lavorenti, 2004; Camps Arbestain et al., 1999a, 2001; Barreal et al., 2001) and the formation of short-range-order Al oxides with a potential positive surface charge under acidic conditions (Inoue and Huang, 1986). Thus, future attempts at predicting sorption may be benefited by including surface area as a parameter.

Temperate vs. Tropical Soils

One of the more surprising results of this investigation is the relative relationship of the different soils with respect to sorption of the macronutrient anions. The decision to include the Bo horizons of the HI-Wahiawa and PR-Bayamon soils was based on the presumption that Oxisols would exhibit a higher capacity for sorption than any of the temperate forest soil B horizons used, and thus offer some perspective as to where temperate forest soils fall relative to this perceived maximum capacity. In fact, the Bw and Bt horizons (from the WA-Boistfort and NC-Cecil, respectively) consistently sorbed greater quantities of all macronutrient anions across the range of solution concentrations investigated. Even the recently glaciated Bw horizon from the WA-Grove soil, with a clay fraction of only 12%, sorbed anions in greater quantities than the Oxisols across nearly all observations. These trends underscore the influence that volcanic inputs can have on charge development and anion sorption in soils. Weathering of volcanic parent materials can lead to the formation of short-range-order minerals, such as allophane and imogolite, that have high surface area and numerous sites capable of developing positive electrostatic charge (Parfitt, 1980). The Bo horizon samples may also sorb less than Fe and Al mineralogy alone might suggest due to the presence of occluded P on the particle surface. Such pre-existing complexes could prevent additional sorption reactions by physically excluding other ions from interacting with the particle surface (Bohn et al., 2001). This could diminish the number of possible sorption sites for other ions, including the potential-determining ions (H^+ and OH^-), which would then affect the overall surface charge. Specifically, this has been shown to lower the pH of the PZNC (Wann and Uehara, 1978).

CONCLUSIONS

Due to the rigorous controls imposed on the experimental conditions in this study, the isotherms generated can only be viewed as each soil's maximum potential to sorb individual macronutrient anions at the predetermined pH level. The results stress the importance, however, of evaluating the development of positive surface charge and the associated anion sorption or exchange reactions in

Table 6. Stepwise multiple linear regression equations for the Langmuir isotherm equation parameters for the theoretical maximum quantity sorbed (N_{max}) and the sorptive affinity (b) for each soil by macronutrient anion combination listed in Table 5. Adjusted coefficients of determination (R^2) and levels of significance (P) are also listed.

Anion	Parameter	Equation	Adjusted R^2	P
NO_3^-	N_{max}	$6.06 - 3.27(\text{organic C}) + 33.28(\text{organically bound Al})$	0.88	0.020
	b	$-0.049 + 0.125(\text{short-range order Al/Si ratio})$	0.89	0.003
SO_4^{2-}	N_{max}	$-1.643 - 2.00(\text{organic C}) + 33.9(\text{Al substituted in Fe oxides})$	0.77	0.053
	b	$52.5 - 76.4(\text{Al substituted in Fe oxides})$	0.48	0.077
H_2PO_4^-	N_{max}	$15.8 + 11.9(\text{short-range order Fe})$	0.98	<0.001
	b	$-117 - 103(\text{organic C}) + 1160(\text{organically bound Al})$	0.67	0.087

soils across larger spatial scales than previously thought. This may be particularly true in coniferous forest ecosystems, where characteristically acidic soil pH regimes combine with variable-charge soil components to yield an electrostatic mechanism for the abiotic retention of anions. Doing so will allow a more complete understanding of the mobility and bioavailability of these and any related ions in response to changing inputs (fertilization, atmospheric deposition, etc.), and aid our understanding of the associated impacts on nutrient retention, uptake potential, and losses through leaching.

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