

Modeling Phosphate Adsorption by Agricultural and Natural Soils

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The nonideal competitive adsorption model (NICA) was developed from the Langmuir adsorption theory and the Freundlich empirical equation. It is well suited to describing ion adsorption in complex systems like soils, which have multiple ions, highly heterogeneous surfaces, and a variety of adsorption sites on the particle surfaces. It has been successfully used to model the binding of protons and metal ions to humic substances, but its application for the adsorption of anions to heterogeneous surfaces has not been documented. The purpose of this study was to adapt the NICA model to describe hydroxyl and phosphate adsorption. Results show that by considering two types of surface sites, the NICA model can provide an excellent fit ($R^2 > 0.99$) of the hydroxyl adsorption data obtained from -11 to -4 of $\log[\text{OH}]$, which corresponds to soil pH from 3 to 10. By using the parameters generated from hydroxyl adsorption, including adsorption maxima ($Q_{\text{max,OH}}$), binding strength (K_{OH}), and nonideality (m), the NICA model gave a remarkable goodness of fit ($R^2 > 0.98$) for the phosphate adsorption data obtained at different pH values. The model sensitivity test showed that the Type 1 surface (SOH_2^+) has up to 100 times greater contribution to phosphate adsorption than the Type 2 surface (SOH). Thus, the model may be simplified into a three-parameter model by only considering the Type 1 surface for phosphate adsorption in acidic soils. The adapted NICA model can thus describe phosphate adsorption combined with hydroxyl adsorption and the parameters ($n_{\text{PO}_4,1}/n_{\text{OH},1} < 1$, where $n_{\text{PO}_4,1}$ accounts for nonideality of PO_4^{3-} and $n_{\text{OH},1}$ accounts for nonideality of OH^- , both on a Type 1 surface) reveal the multidentate binding of phosphate. It provides a promising tool for analyzing competitive anion adsorption processes in soils.

Abbreviations: NICA, nonideal competitive adsorption.

Phosphate adsorption by soils plays a crucial role on phosphate retention and affects phosphate transport from soils to waterways. The quantitative description of soil phosphate adsorption is important for the prediction of phosphate fertilizer requirements for optimum plant growth (Fox and Kamprath, 1970). It may also be used to evaluate potential phosphate loss from a soil. There are many models used to describe the relationship between phosphate sorbed on soil and phosphate concentrations in solution. Among them, the Langmuir one-surface isotherm and the Freundlich equation are most frequently adopted to model phosphate adsorption. The Langmuir one-surface isotherm (Langmuir, 1918) was derived as

$$Q = Q_{\text{max}} \frac{Kc}{1 + Kc} \quad [1]$$

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where Q is the amount of phosphate adsorbed per unit weight of soil, Q_{max} is the phosphate sorption maximum, K is the constant presumably related to the binding strength of phosphate on soil surfaces, and c is the concentration of phosphate in the solution at equilibrium. The Freundlich equation (Freundlich, 1926) takes the form

$$Q = Kc^m \quad [2]$$

where K and m are constants. The combined Langmuir-Freundlich equation (Eq. [3]) was also developed to describe atomic and ionic adsorption (Sips, 1948):

$$\theta = \frac{(Kc)^m}{1 + (Kc)^m} \quad [3]$$

where θ is the fraction of the total sites occupied by the adsorbed species.

These equations normally fit sorption data for only a limited range of solution phosphate concentrations (Holford et al., 1974; Fitter and Sutton, 1975), and they are regarded as empirical isotherms used to fit the curve of adsorption data (Harter and Smith, 1981). The limitation of these models is that they are valid only for the conditions under which the adsorption experiment was conducted and cannot be used to predict adsorption under changing conditions of solution concentration, ionic strength, and pH (Goldberg, 1995).

In fact, both the Langmuir and Freundlich equations were originally developed to model pure gas adsorption on uniform solid surfaces. They only deal with monocomponent adsorption. In soils, there are always many ions in the soil solution that may

interfere with phosphate adsorption, and the soil surface is heterogeneous. Thus, it is not possible to analyze competitive ion adsorption by using the simple Langmuir and Freundlich equations. Koopal et al. (1994) derived an equation for multicomponent adsorption on heterogeneous surfaces by combining the extended Henderson–Hasselbalch equation as a nonideal local isotherm with the Langmuir–Freundlich affinity distribution function. It was named the nonideal competitive adsorption (NICA) model:

$$\theta = \frac{(K_{i,c,i})^{n_i} \left[\sum (K_{i,c,i})^{n_i} \right]^p}{\sum (K_{i,c,i})^{n_i} 1 + \left[\sum (K_{i,c,i})^{n_i} \right]^p} \quad [4]$$

Numerous studies have demonstrated that the NICA model fit experimental data for the competitive binding of metal ions to humic substances and closely predicted the binding of Cu and Cd with changes in field conditions (Benedetti et al., 1996; Koopal et al., 2005). So far, however, it has only been used in describing the binding of protons and metal ions to negatively charged surfaces. We are not aware of the application of the NICA model for anion adsorption on heterogeneous surfaces.

The aim of this work was to adapt the NICA model so it will describe hydroxyl and phosphate adsorption by soils.

MATERIALS AND METHODS

Soils

Four soils were chosen for this study. Two Typic Endoaquents were collected from the Macdonald Research Farm of McGill University, Ste. Anne de Bellevue, QC, Canada (45°28' N, 73°45' W, elevation 35.7 m). These soils came from experiment plots under continuous corn (*Zea mays* L.) production that received 45 kg P ha⁻¹ either from composted cattle manure or from triple superphosphate fertilizer for 4 yr. Details of the experiment are provided in Jiao (2005). The other two soils were collected from the Morgan Arboretum of McGill University, within 2 km of the first site. One is a Typic Endoaquent under hay production and the second is a Cryorthod (U.S. Soil Taxonomy) or a Humic-Ferric Podzol (Canadian System of Soil Classification) under a mixed deciduous–coniferous forest. All samples were air dried and crumbled by hand to pass through a 2-mm sieve.

Soils were analyzed for pH (1:2 soil/water) and effective cation exchange capacity (CEC) at field pH (Hendershot and Duquette, 1986). Total C and N in the soils were measured with a Carlo-Erba Flash EA CN analyzer (Milan, Italy). The total P in the soils was determined in H₂O₂–H₂SO₄ digests (Parkinson and Allen, 1975). Total inorganic phosphate was measured in 0.5 mol L⁻¹ H₂SO₄ extracts (O'Halloran, 1993), and Mehlich-3 extractable Fe, Al, and P were determined using the method described by Tran and Simard (1993). Labile P, collected with an anion-exchange resin, and water-extractable phosphate were also measured (Sibbesen, 1977); the difference between labile P and water-extractable phosphate was considered to represent the native adsorbed phosphate in soils (Holford et al., 1974; Wolf et al., 1986). Phosphate in solution was quantified colorimetrically with the ammonium molybdate–ascorbic acid method (Murphy and Riley, 1962) on a Lachat Quik-Chem AE flow-injection autoanalyzer (Lachat Instruments, Milwaukee, WI). Mehlich-3 extractable Fe and Al were analyzed by atomic absorption spectrometry. Characteristics of the soils are provided in Table 1.

Table 1. Physical and chemical properties of the soils used in this study.

Soil†	Classification	Soil series	Texture	Vegetation	Fertilizer	pH _{H2O} (1:2)	CEC‡	Total nutrient				Mehlich-3			Labile P	Q _{nat,P} \$
								C	N	P	Inorganic P	P	Fe	Al		
							cmol kg ⁻¹			g kg ⁻¹				mg kg ⁻¹		
Man.-soil	Typic Endoaquent	St. Damas	sandy loam	corn	organic P	5.81	10.0	28.33	3.33	1.45	1.18	278	348	1170	149.81	112.92
	Typic Endoaquent	St. Damas	sandy loam	corn	inorganic P	5.06	7.61	20.02	2.36	1.28	1.14	222	348	1170	100.39	84.15
Hay field	Typic Endoaquent	St. Rosalie	clay	hay	none	5.99	12.6	19.43	2.21	0.84	0.54	19.2	243	960	25.31	24.18
	Cryorthod	Uplands	loamy sand	beech & maple	none	4.17	4.95	53.17	3.80	0.24	0.02	5.83	429	990	14.52	14.08

† Man.-soil, manure-amended soil; TSP-soil, triple superphosphate fertilized soil.

‡ Cation exchange capacity.

§ Native adsorbed P.

Adsorption Experiment

Hydroxyl Adsorption

A back-titration method (Duquette and Hendershot, 1993) was adapted to determine OH^- adsorption. It involved two procedures. First, samples were titrated by weighing 2 g of soil into a 100-mL beaker, adding 30 mL of 0.1 mol L^{-1} KCl solution as the supporting electrolyte, then titrating the suspension with 0.1-mL aliquots of standardized 0.1 mol L^{-1} HCl, with 2-min equilibration periods between each addition, to pH 3. A continuous back titration was then performed with standardized 0.02 mol L^{-1} KOH at a rate of 0.2 mL min^{-1} to pH 10. We recorded the pH and the volumes of acid and base added. The second procedure was a reference titration, in which a second soil suspension (2 g of soil with 30 mL of 0.1 mol L^{-1} KCl) was prepared and titrated to pH 3 following the procedure in the sample titration. The suspension was then transferred into a 50-mL centrifuge tube and centrifuged at $7800 \times g$ for 20 min. The supernatant was filtered ($<0.45\text{-}\mu\text{m}$ Millipore polycarbonate membrane) into a 100-mL preweighed beaker. The filtrate was weighed and back titrated to pH 10. During both sample and reference titrations, the suspension or solution was agitated continuously with a magnetic stirrer and purged with ultrapure N_2 gas.

The OH^- consumption on the sample surface, an estimate of the amount of OH^- adsorbed, was calculated by subtracting the OH^- consumption of the reference titration from that of the sample titration at the same pH. The calculated OH^- consumption was zero at pH 3, the starting point of the titration. We rescaled the OH^- consumption data by adjusting the curve to pass through the measured CEC at field pH.

Phosphate Adsorption

A batch adsorption experiment was performed to assess phosphate adsorption by soils at different pH levels. Two grams of soil was weighed into a 50-mL centrifuge tube. Then 30 mL of 0.1 mol L^{-1} KCl solution, containing 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 or 1.0 mmol L^{-1} P from KH_2PO_4 , was added as initial P. Soil suspensions were adjusted to pH 4 or 7 for the two agricultural soils and pH 4, 5.5, or 7 for the hay field and forest soils using diluted HCl or KOH. A preliminary study revealed that the two soils from the hay field and the forest had strong phosphate adsorption capacities. To obtain the effective phosphate adsorption, initial P concentrations for these soils included 1.4 and 2.0 mmol L^{-1} P for pH 4 and 7, and omitted 0.3 and 0.5 mmol L^{-1} P at pH 7. This gave 97 tubes in total. The soil-P solution mixture was shaken on an end-over-end shaker (15 cycles min^{-1}) at $22 \pm 1^\circ\text{C}$. The suspension pH was readjusted to the desired pH value twice during the 24-h shaking: after 20 h with 0.1 mol L^{-1} HCl or KOH and after 22 h with 0.01 mol L^{-1} HCl or KOH. The volume of added HCl or KOH was recorded. After a total of 24 h shaking, the tubes were removed from the shaker and the suspension was centrifuged at $7800 \times g$ for 20 min. After measuring the pH, the supernatant was filtered ($<0.45\text{-}\mu\text{m}$ membrane), and the filtrate was analyzed for phosphate (Murphy and Riley, 1962). Adsorbed phosphate was calculated as the difference between the amount of phosphate added and the phosphate remaining in solution, accounting for the dilution effect from adding HCl and KOH to the suspension.

A set of duplicate soils were weighed and treated with 0.6 mmol L^{-1} P from KH_2PO_4 to calculate the coefficient of variation using (USEPA, 1979)

$$\text{CV}(\%) = \frac{200|A-B|}{\sqrt{2}(A+B)} \quad [5]$$

where A and B are the adsorbed phosphate for the replicate samples. The phosphate adsorption experiment was highly repeatable since the CV for all duplicate soils was $<1.5\%$.

Adaptation of the Nonideal Competitive Adsorption Model for Anion Adsorption

We assumed the following reactions for hydroxyl and anion (L^-) adsorption:



where S refers to a metal ion in a hydroxylated mineral and SOH to a reactive surface hydroxyl. According to the form of the NICA model for proton or metal ion binding (Koopal et al., 1994; Kinniburgh et al., 1999), we used the following equation to describe hydroxyl adsorption:

$$Q = Q_{\text{OH},1} + Q_{\text{OH},2} = Q_{\text{max,OH},1} \frac{(K_{\text{OH},1}[\text{OH}])^{m_1}}{1 + (K_{\text{OH},1}[\text{OH}])^{m_1}} + Q_{\text{max,OH},2} \frac{(K_{\text{OH},2}[\text{OH}])^{m_2}}{1 + (K_{\text{OH},2}[\text{OH}])^{m_2}} \quad [8]$$

where Q is the total amount of OH^- adsorbed ($\text{cmol}_c \text{ kg}^{-1}$) to a soil at hydroxyl concentration of $[\text{OH}]$ (mol L^{-1}), the subscripts 1 and 2 denote Type 1 and Type 2 surfaces, $Q_{\text{max,OH}}$ is the adsorption maximum, K_{OH} is a median affinity constant for OH^- , and m accounts for the intrinsic chemical heterogeneity of a surface and the OH^- -specific nonideality.

The analytical equation for OH^- and PO_4^{3-} adsorption to two heterogeneous surfaces can be written as

$$Q_{\text{PO}_4} = Q_{\text{PO}_4,1} + Q_{\text{PO}_4,2} = Q_{\text{max,PO}_4,1} \frac{(K_{\text{PO}_4,1}[\text{PO}_4])^{n_{\text{PO}_4,1}}}{(K_{\text{OH},1}[\text{OH}])^{m_1/p_1} + (K_{\text{PO}_4,1}[\text{PO}_4])^{n_{\text{PO}_4,1}}} \times \frac{[(K_{\text{OH},1}[\text{OH}])^{m_1/p_1} + (K_{\text{PO}_4,1}[\text{PO}_4])^{n_{\text{PO}_4,1}}]^{p_1}}{1 + [(K_{\text{OH},1}[\text{OH}])^{m_1/p_1} + (K_{\text{PO}_4,1}[\text{PO}_4])^{n_{\text{PO}_4,1}}]^{p_1}} + Q_{\text{max,PO}_4,2} \frac{(K_{\text{PO}_4,2}[\text{PO}_4])^{n_{\text{PO}_4,2}}}{(K_{\text{OH},2}[\text{OH}])^{m_2/p_2} + (K_{\text{PO}_4,2}[\text{PO}_4])^{n_{\text{PO}_4,2}}} \times \frac{[(K_{\text{OH},2}[\text{OH}])^{m_2/p_2} + (K_{\text{PO}_4,2}[\text{PO}_4])^{n_{\text{PO}_4,2}}]^{p_2}}{1 + [(K_{\text{OH},2}[\text{OH}])^{m_2/p_2} + (K_{\text{PO}_4,2}[\text{PO}_4])^{n_{\text{PO}_4,2}}]^{p_2}} \quad [9]$$

where Q_{PO_4} is the amount of phosphate adsorbed plus native adsorbed phosphate, K_{PO_4} is a median affinity constant for PO_4^{3-} , $[\text{PO}_4]$ is the concentration of PO_4^{3-} in the equilibrium solution, n_{PO_4} accounts for nonideality of PO_4^{3-} ($0 < n_{\text{PO}_4} \leq 1$), p reflects the intrinsic chemical heterogeneity of a surface and is the same for OH^- and PO_4^{3-} (0

$< p \leq 1$), and $Q_{\max, \text{PO}_4}$ is defined (according to the suggestion of Kinniburgh et al. [1999] for the NICA model) as

$$Q_{\max, \text{PO}_4} = (n_{\text{PO}_4} / n_{\text{OH}}) Q_{\max, \text{OH}} = [n_{\text{PO}_4} / (m/p)] Q_{\max, \text{OH}} \quad [10]$$

We considered the adsorption of both OH^- and PO_4^{3-} on two types of surfaces, as indicated by subscripts 1 and 2 in Eq. [8] and [9], since there are two clear inflection points in the surface charge evaluation for a wide range of acid soils (Ge and Hendershot, 2004). Also, many studies have revealed that phosphate adsorption data were fitted very well by the Langmuir two-surface model, indicating that two types of surfaces were responsible for phosphate adsorption (Holford et al., 1974; Jiao et al., 2007).

Data Analysis

The SAS nonlinear procedure (Proc NLIN) was used to generate the parameters of the NICA model (SAS Institute, 2003). The influence of pH on phosphate speciation, i.e., the proportions of H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} in soil solution, was estimated using Visual MINTEQ (Gustafsson, 2004).

RESULTS

Experimental Data

Hydroxyl

The results of sample and reference titrations are illustrated in Fig. 1. The relationship between OH^- adsorption (Q) and $\log[\text{OH}]$ were presented in Fig. 2. The OH^- adsorption curves for the soils from the agricultural sites showed that OH^- adsorption increased continuously with the increase of $\log[\text{OH}]$ between -11 and -4 (Fig. 2). For the forest soil, the OH^- adsorption increased from -11 to -9.2 of $\log[\text{OH}]$, decreased between -9.2 and -8.8 of $\log[\text{OH}]$, and then increased from -8.8 to -4 of $\log[\text{OH}]$ (Fig. 2). The zone of declining OH^- adsorption corresponds to values between pH 4.8 and 5.2 in the soil suspension. We speculate that abundant Al in the solution of the forest soil may consume OH^- at around pH 5.0 when $\text{Al}(\text{OH})_3$ precipitates are formed (Fig. 1b), resulting in the decrease in OH^- adsorption (Fig. 2). The Al concentration in solutions separated from the suspensions, titrated to pH 3, was $22.8 \text{ mg Al L}^{-1}$ in the forest soil, at least twice that in the other three soils. Generally, more OH^- in the soil suspension resulted in more OH^- adsorption on the soil particle surface, and there are two inflection points on each charge curve in the experimental condition of $\log[\text{OH}]$ from -11 to -4 (Fig. 2).

Phosphate

Several phosphate forms (H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-}) exist in soil solutions, but free trivalent phosphate (PO_4^{3-}) was considered to be the most important competitor with OH^- for binding on the adsorption sites. The Visual MINTEQ program (Gustafsson, 2004) estimated that the concentration of PO_4^{3-} was 4.34×10^5 times greater at pH 7 than at pH 4. This corresponds with our observation of greater phosphate adsorption at pH 7 than at pH 4 for all soils studied (for example, see Fig. 3 for the results of the agricultural soil amended with manure). Thus, for phosphate adsorption, data were organized as phosphate on the surface (adsorbed phosphate plus native phosphate) vs. the solution concentration of PO_4^{3-} ($\log[\text{PO}_4]$),

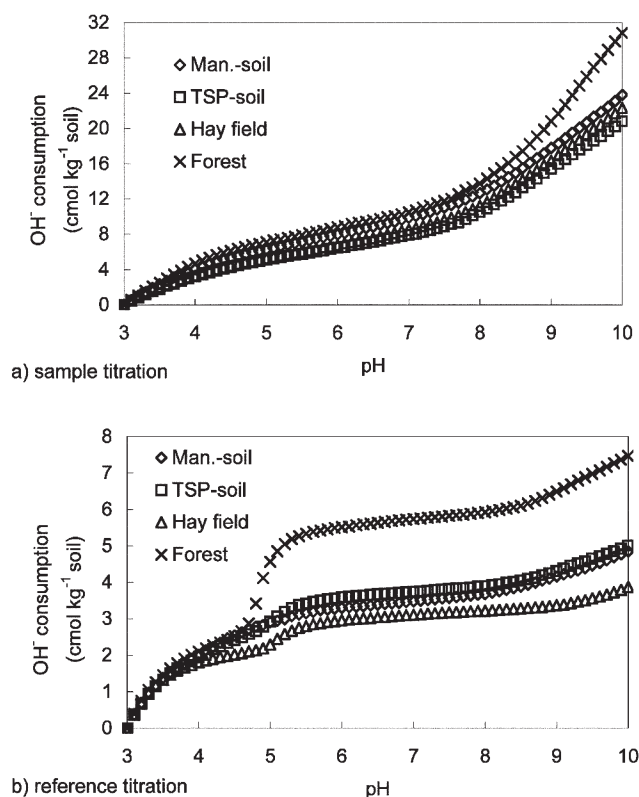


Fig. 1. Hydroxyl consumption during (a) sample titration and (b) reference titration of manure-amended soil (Man.-soil), triple superphosphate fertilized soil (TSP-soil), hay field soil, and forest soil. Points are observations ($n = 70$) for each soil.

which was calculated with Visual MINTEQ from the total phosphate concentration measured experimentally.

Modeling

Hydroxyl Adsorption

We used the SAS nonlinear procedure (Proc NLIN) to obtain the parameters in Eq. [8]. Input data included $[\text{OH}]$ and Q obtained in the titration experiment (Fig. 2). The initial estimates of parameters, taking the manure-amended soil in

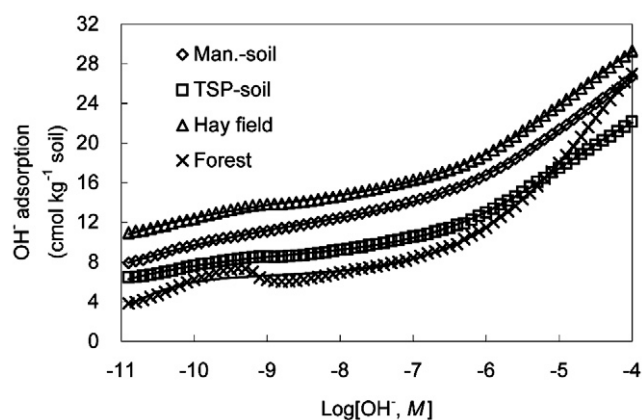


Fig. 2. Hydroxyl adsorption by manure-amended soil (Man.-soil), triple superphosphate fertilized soil (TSP-soil), hay field soil, and forest soil. Points are observations ($n = 70$) for each soil and lines are calculated from the nonideal competitive adsorption (NICA) model. The range of $\log[\text{OH}]$ between -11 and -4 corresponds to pH between 3 and 10.

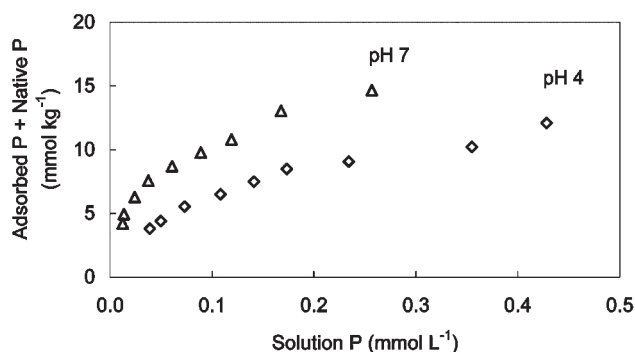


Fig. 3. Phosphate adsorption on the manure-amended soil as influenced by solution pH, showing higher phosphate adsorption at pH 7 than that at pH 4; $n = 9$ for each soil.

Fig. 2 as an example, were $Q_{\max, \text{OH}, 1} = 12$ (the plateau of first peak), $\log K_{\text{OH}, 1} = 10$ ($-\log[\text{OH}^-]$ around the first inflection point), $m_1 = 0.5$ ($0 < m_1 \leq 1$); $Q_{\max, \text{OH}, 2} = 15$ (end point of the charge curve minus $Q_{\max, \text{OH}, 1}$), $\log K_{\text{OH}, 2} = 5$ ($-\log[\text{OH}^-]$ around the second inflection point), $m_2 = 0.5$ ($0 < m_2 \leq 1$). The above-mentioned initial estimation of the parameters is crucial to facilitate SAS convergence.

The experimental data for OH^- adsorption corresponded well to the values estimated by the NICA model ($R^2 > 0.999$, Table 2). This supports our consideration of two types of functional surface charge sites for OH^- adsorption. For all soils, the Type 1 surface had a smaller adsorption maximum ($Q_{\max, \text{OH}, 1}$) but a stronger binding strength ($\log K_{\text{OH}, 1}$) than the Type 2 surface (Table 2).

Phosphate Adsorption

The same procedure (SAS Proc NLIN) was used to generate the parameters in the NICA model (Eq. [9]). Input data included three variables: $\log[\text{OH}^-]$, $\log[\text{PO}_4]$ and Q_{PO_4} (adsorbed phosphate plus native phosphate). The initial parameters in Eq. [9] were estimated as (manure-amended soil as an example): $\log K_{\text{PO}_4, 1} = 15$ ($> \log K_{\text{OH}, 1}$ by considering the higher binding strength of PO_4^{3-} than OH^-), $n_{\text{PO}_4, 1} = 0.5$ ($0 < n_{\text{PO}_4, 1} \leq 1$), $p_1 = 0.5$ ($m_1 < p_1 \leq 1$); $\log K_{\text{PO}_4, 2} = 5$ ($> \log K_{\text{OH}, 2}$ by considering the higher binding strength of PO_4^{3-} than OH^-), $n_{\text{PO}_4, 2} = 0.9$ ($0 < n_{\text{PO}_4, 2} \leq 1$), $p_2 = 0.5$ ($m_2 < p_2 \leq 1$). The above estimation of initial parameters promotes the convergence of Proc NLIN in SAS. The constants in Eq. [9] include $Q_{\max, \text{OH}, 1}$, $K_{\text{OH}, 1}$, m_1 , $Q_{\max, \text{OH}, 2}$, $K_{\text{OH}, 2}$, and m_2 , which are the results from Eq. [8] (Table 2).

Table 2. Parameters† obtained from the nonideal competitive adsorption model (Eq. [8]) for OH^- adsorption data.

Soil‡	$Q_{\max, \text{OH}, 1}$	$\log K_{\text{OH}, 1}$	m_1	$Q_{\max, \text{OH}, 2}$	$\log K_{\text{OH}, 2}$	m_2	R^2
	cmol _c kg ⁻¹			cmol _c kg ⁻¹			
Man.-soil	12.5	11.7	0.312	22.7	4.55	0.413	1.000
TSP-soil	8.88	11.8	0.415	18.1	4.90	0.475	1.000
Hay field	14.9	12.3	0.303	20.3	4.80	0.481	1.000
Forest	6.51	11.0	0.950	33.2	4.43	0.482	0.999

† $Q_{\max, \text{OH}}$ is the adsorption maximum and K_{OH} is a median affinity constant for OH^- ; m accounts for the intrinsic chemical heterogeneity of a surface and the OH^- -specific nonideality. The subscripts 1 and 2 denote Type 1 and Type 2 surfaces, respectively.

‡ Man.-soil, manure-amended soil; TSP-soil, triple superphosphate fertilized soil.

Table 3. Parameters† obtained from the nonideal competitive adsorption model (Eq. [9]) with two types of surfaces (SOH_2^+ and SOH) for soil P adsorption data.

Soil‡	$\log K_{\text{PO}_4, 1}$	$n_{\text{PO}_4, 1}$	p_1	$\log K_{\text{PO}_4, 2}$	$n_{\text{PO}_4, 2}$	p_2	R^2
Man.-soil	15.8	0.462	0.379	0–4§	1.000	0.413	0.998
TSP-soil	17.5	0.466	0.415	5.29	0.487	0.475	0.999
Hay field	18.3	0.447	0.304	5.14	0.452	0.481	0.999
Forest	15.8	0.532	1.000	2.05	0.004	0.494	0.987

† K_{PO_4} is a median affinity constant for PO_4^{3-} , n_{PO_4} accounts for nonideality of PO_4^{3-} ($0 < n_{\text{PO}_4} \leq 1$), and p reflects the intrinsic chemical heterogeneity of a surface and is the same for OH^- and PO_4^{3-} ($0 < p \leq 1$). The subscripts 1 and 2 denote Type 1 and Type 2 surfaces, respectively.

‡ Man.-soil, manure-amended soil; TSP-soil, triple superphosphate fertilized soil.

§ Any given value between 0 and 4, same modeling result ($R^2 = 0.998$).

The SAS output is listed in Table 3. Similarly to OH^- adsorption, the Type 1 surface has a stronger binding strength ($\log K_{\text{PO}_4, 1}$) for PO_4^{3-} than the Type 2 surface ($\log K_{\text{PO}_4, 2}$). Since p accounts for the intrinsic chemical heterogeneity of the surface, a larger p_1 value for the forest Cryorthod indicates that the Type 1 surface in this soil is more homogeneous than that of the other soils.

The phosphate adsorption changes, as a function of solution pH, were predicted by the NICA model (Fig. 4–7). For all soils, the NICA model fit the experimental data very well ($R^2 > 0.98$ in Table 3). It not only correctly estimated the phosphate adsorption change from pH 4 to 7, but also gave a very good estimation for phosphate adsorption at pH 5.5 for the soils from the hay field and forest (Fig. 6 and 7; no experimental data were obtained for the two agricultural soils at pH 5.5).

DISCUSSION

Two Surfaces for Hydroxyl Adsorption

The OH^- adsorption curve from pH 3 to 10, i.e., -11 to -4 of $\log[\text{OH}^-]$ reveals two types of surfaces. We consider the Type 1 surface to be the positively charged functional groups (SOH_2^+) of Fe and Al oxide and hydroxide minerals. These metal oxides have a strong protonation tendency in acidic soils and thus have been recognized as the most important component to control anion adsorption (Sparks, 2003). This surface should have a high binding strength. The Type 2 surface was hypothesized to be the functional group (SOH) of minerals (Ryden et al., 1977) and phenols. Based on the bond characteristics (Sparks, 2003), phenol-OH in soil organic matter could

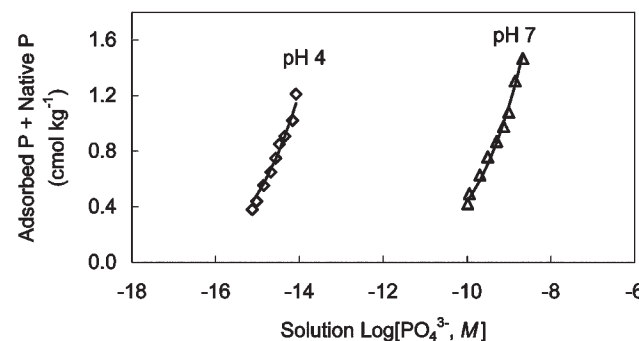


Fig. 4. Phosphate adsorption by manure-amended soil at pH 4 and 7. Points are observations and lines are calculated from the nonideal competitive adsorption (NICA) model.

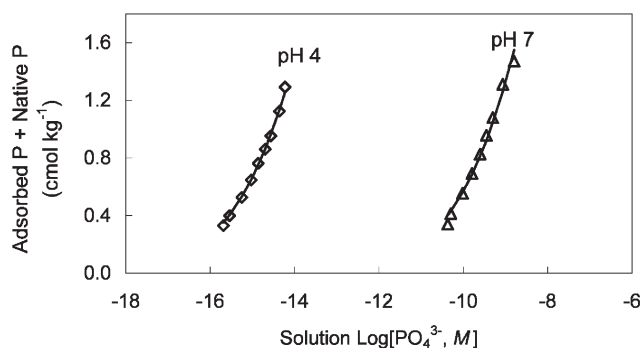


Fig. 5. Phosphate adsorption by triple superphosphate fertilized soil at pH 4 and 7. Points are observations and lines are calculated from the nonideal competitive adsorption (NICA) model.

be the second most important component after the functional group of metal oxides for anion adsorption.

Phosphate Speciation and the Nonideal Competitive Adsorption Model

Because of its higher binding strength, we chose to use PO_4^{3-} in the NICA model. Sigg and Stumm (1981) reported that the intrinsic complexation constant ($\log K$) is 1.5 for PO_4^{3-} binding on the hydrous goethite, while it is only -6.5 and -8.5 for HPO_4^{2-} and H_2PO_4^- , respectively. This means that the binding strength of PO_4^{3-} is millions of times stronger than the other phosphate species, HPO_4^{2-} and H_2PO_4^- . We also realize that pH has a large influence on phosphate speciation. For example, at pH 7, PO_4^{3-} is almost negligible and HPO_4^{2-} and H_2PO_4^- each account for about 50% of total phosphate (Lindsay, 1979); but the PO_4^{3-} still exists, and the adsorption of PO_4^{3-} to the soil particle surface will shift the equilibrium from HPO_4^{2-} and H_2PO_4^- to PO_4^{3-} .

The binding of PO_4^{3-} is considered to be specific adsorption and >1 mol of OH^- might be released due to 1 mol of PO_4^{3-} adsorption. The average stoichiometry with respect to the hydroxyl reaction can be reflected by the ratio of the non-ideality parameters: n_i/n_{H} , which was used to scale the bound amount of species i to maintain thermodynamic consistency (Kinniburgh et al., 1999). According to the suggestion of Kinniburgh et al. (1999), as indicated in Eq. [10], when $n_{\text{PO}_4}/n_{\text{OH}}$ is <1 , then the maximum binding of PO_4^{3-} is less than the total site density as defined by the hydroxyls. This could reflect some degree of multidentate binding of PO_4^{3-} . This

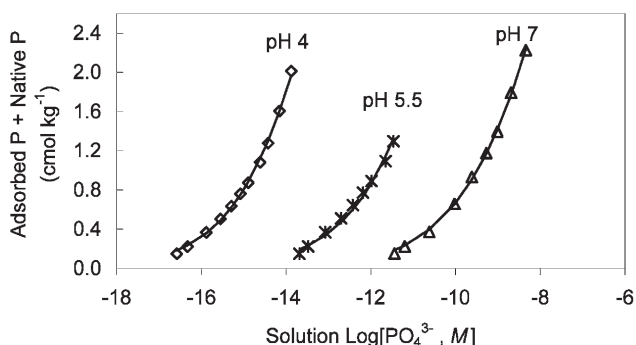


Fig. 6. Phosphate adsorption by soil from a permanent hay field at pH 4, 5.5, and 7. Points are observations and lines are calculated from the nonideal competitive adsorption (NICA) model.

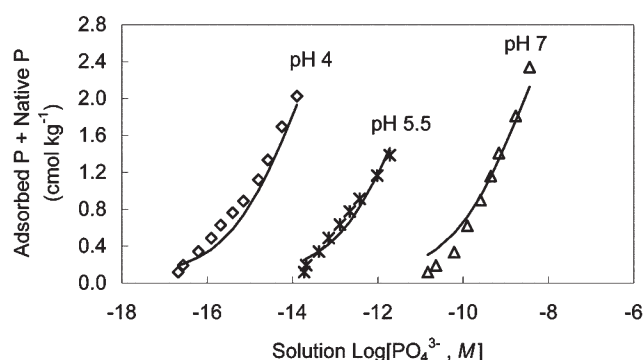


Fig. 7. Phosphate adsorption by a forest soil at pH 4, 5.5, and 7. Points are observations and lines are calculated from the nonideal competitive adsorption (NICA) model.

speculation is confirmed in the study, as the ratio $n_{\text{PO}_4,1}/n_{\text{OH},1}$ was <1 for all soils (Table 4).

Sensitivity Test

The NICA model for all soils is not sensitive to the parameters for the Type 2 surface. Taking the data for the manure-amended soil, for example, and assigning of any value for $\log K_{\text{PO}_4,2}$ from 0 to 4 still provides a good modeling result ($R^2 > 0.99$). In fact, $Q_{\text{PO}_4,1}$ for all soils was about 3 to 100 times larger than $Q_{\text{PO}_4,2}$ in Eq. [9]. This indicates that there is little contribution from the Type 2 surface for phosphate adsorption at pH 4 and 7. Under this experimental condition, i.e., added phosphate concentration up to 2 mmol L^{-1} P and pH from 4 to 7, the maxima of adsorbed phosphate plus native phosphate (Fig. 4–7) were all less than the corresponding $Q_{\text{max,OH},1}$ (Table 2). Thus, almost all the phosphate adsorption would occur on the Type 1 surface. In this case, the NICA model can be simplified to a three-parameter model by only considering the Type 1 surface and it still can fit the experimental data well ($R^2 > 0.98$, Table 4).

CONCLUSIONS

The NICA model developed by Koopal et al. (1994) can be used successfully for anion adsorption based on our assumption for hydroxyl binding on heterogeneous surfaces. The hydroxyl binding curve revealed two types of functional surface sites controlling OH^- adsorption. We assume that they are the positively charged functional groups of Fe and Al oxides (Type

Table 4. Parameters† obtained from the NICA model (considering a Type 1 surface: SOH_2^+) for soil P adsorption data.

Soil‡	$\log K_{\text{PO}_4,1}$	$n_{\text{PO}_4,1}$	p_1	R^2	$n_{\text{PO}_4,1}/n_{\text{OH},1}$ §
Man.-soil	15.8	0.462	0.379	0.998	0.561
TSP-soil	16.6	0.453	0.516	0.999	0.563
Hay field	17.1	0.423	0.390	0.988	0.545
Forest	16.2	0.544	0.950	0.992	0.544

† K_{PO_4} is a median affinity constant for PO_4^{3-} , n_{PO_4} accounts for nonideality of PO_4^{3-} ($0 < n_{\text{PO}_4} \leq 1$), p reflects the intrinsic chemical heterogeneity of a surface and is the same for OH^- and PO_4^{3-} ($0 < p \leq 1$). Subscript 1 denotes Type 1 surface.

‡ Man.-soil, manure-amended soil; TSP-soil, triple superphosphate fertilized soil.

§ $n_{\text{OH},1} = m_1/p_1$, as defined in Eq. [10]. m_1 : refer to Table 2.

1) and the functional group of minerals and phenols (Type 2). The Type 1 surface has smaller adsorption maxima and higher binding energy than the Type 2 surface. The NICA model may be more useful than the simple Langmuir and Freundlich models because it can predict the change in phosphate adsorption with a change in soil solution pH. Since the NICA model includes multiple components in its equation, it may also be used to quantify the competitive adsorption among anions, such as phosphate, sulfate, borate, molybdate, selenate, and arsenate. This remains to be verified, however, and it might be necessary to consider electrostatic interactions by introducing the Donnan submodel (Koopal et al., 2005) to address the nonspecific adsorption.

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