A Chemical Model of Phosphate Adsorption by Soils: II. Noncalcareous Soils[1]

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ABSTRACT

The Constant Capacitance model provided a quantitative description of o-phosphate adsorption by 44 noncalcareous soils whose pH values ranged from 4.9 to 7.6. The intrinsic surface protonation-dissociation constants, capacitance density, and phosphate packing area parameters required by the model were adopted from model calculations on reference hydrous oxide minerals. The intrinsic phosphate surface complexation constants were calculated through the application of a nonlinear least squares fitting program to the soil o-phosphate adsorption data. Two of these intrinsic constants were found to be independent of pH over the range investigated, as required by the model. However, the intrinsic constant for the formation of the neutral o-phosphate surface species exhibited a statistically significant dependence on pH. The Constant Capacitance model was best able to describe o-phosphate adsorption by noncalcareous soils, including pH effects, if a soil-specific set of intrinsic phosphate surface complexation constants was employed.

Additional Index Words: anion adsorption, ligand exchange, surface chemistry.

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IN Part I of this study (Goldberg and Sposito, 1984), the Constant Capacitance model (Stumm et al., 1980) was applied successfully to describe o-phosphate adsorption by aluminum and iron oxide minerals. This model is based on a ligand exchange mechanism of adsorption, which is considered to be appropriate for o-phosphate on hydrous oxide surfaces (Mott, 1981). Both the charge on the adsorbent surface and the charge on the adsorptive anion are considered in the model, which then is able to predict phosphate adsorption under changing conditions of pH value and o-phosphate concentration. The model produced good fits to experimental adsorption data (conventional isotherms and "adsorption envelopes") for both crystalline and amorphous aluminum and iron hydrous oxides.

In this paper, the Constant Capacitance model is extended for the first time to o-phosphate adsorption by noncalcareous mineral soils. This application of the model is predicated on four basic assumptions: (i) The principal phosphate adsorption mechanism is ligand exchange with surface hydroxyl groups bound to metal cations (Berkheiser et al., 1980; Mott, 1981); (ii) The protonation-dissociation constants for the surface hydroxyl groups reacting with o-phosphate do not depend on the kind of metal (i.e., Al or Fe) to which the hydroxyl groups are bound (Goldberg and Sposito, 1984); (iii) The surface area occupied by an adsorbed o-phosphate ion may be represented by the average

value of 0.6 nm^2; (iv) The phosphate surface complexation constants do not depend on the kind of metal to which the reactive surface hydroxyl groups are bound.

These four assumptions are essentially uniformity hypotheses concerning the reactions of o-phosphate with soils. Assumption (i) should be applicable to noncalcareous soils that do not contain large amounts of allophanic minerals. Soils containing allophane as a significant component are excluded, since phosphate sorption on these soils can involve a precipitation mechanism (Veith and Sposito, 1977). Calcareous soils are excluded because the mechanism of o-phosphate adsorption may involve ligand exchange with surface carbonate groups as well as surface hydroxyl groups. Assumptions (ii) and (iv) are special cases of the hypothesis that, to a first approximation, the protonation-dissociation and o-phosphate exchange reactions of surface hydroxyl groups in soils are independent of the bulk solid phase to which the hydroxyl groups are bound. In support of this assumption, Goldberg and Sposito (1984) found that the common logarithms of the intrinsic protonation-dissociation constants, K_+ (int) and K_- (int), and of the phosphate surface complexation constants for aluminum and iron oxide minerals were not significantly different. Assumption (iii) simplifies the model calculation and will be discussed under Data and Methods.

DATA AND METHODS

Constant Capacitance Model

A description of the Constant Capacitance model (Stumm et al., 1980) was given in Part I (Goldberg and Sposito, 1984). The model parameters determined previously in Part I and adopted in the present study are: K_+ (int) $= 10^{7.35}$, K_- (int) $= 10^{-8.95}$, and $C = 1.06$ F m^{-2}. The specific surface area, S, of the adsorbent is a parameter required by the model whose values in the hydrous oxide application had been determined experimentally. In the model applications to published studies on soils, however, experimental values of this parameter were not available. A method was developed for calculating the specific surface area of the phosphate-reactive fraction in a soil based on information gained from the study of reference oxide minerals in Part I. Since the assumption has been made that phosphate-reactive surfaces in soil exhibit phosphate adsorption behavior similar to reference metal oxides, the average area occupied by an adsorbed phosphate ion (the packing area) can be considered to be of similar magnitude in both cases. The packing area can be calculated from measurements of the specific surface area and the maximum phosphate adsorption by reference oxides. This calculation was performed with the oxide mineral data compiled in Part I. The resulting packing areas are listed in Table 1 along with other values reported independently by Hingston (1981). The average value of the packing areas in Table 1, 0.6 nm^2, was used in modeling the soil data. With the packing area and the maximum phosphate adsorption (an available experimental parameter), the specific surface area needed in the model can be calculated for any soil. The specific surface area so calculated represents the amount of soil surface area *attributable to phosphate-reactive compounds* per unit mass of whole soil.

Table 1—Packing areas of phosphate adsorbed by
hydrous oxide minerals.

Solid	Specific surface area	Maximum adsorption	Packing area	Source of data
	10^4 m^2 kg^{-1}	mol P kg^{-1}	nm^2	
Aluminum oxides				
γ-Al$_2$O$_3$	9.8	0.28	0.784	Anderson and Malotky (1979)
γ-Al$_2$O$_3$	11.7	0.397	0.490	Huang (1975)
Hydrous alumina	19.72	0.918	0.356	Rajan et al. (1974)
Gibbsite	4.5	0.0700	1.06	Parfitt et al. (1977)
Gibbsite	4.7	0.0798	0.977	Hingston et al. (1974)
Gibbsite	0.83	0.0231	0.598	Helyar et al. (1976)
Gibbsite			0.46	Hingston (1981)
Gibbsite			0.60	Hingston (1981)
Iron oxides				
Iron oxide gel	28.0	1.55	0.30	Ryden et al. (1977)
Hematite	2.1	0.0742	0.471	Breeuwsma and Lyklema (1973)
Goethite-C	3.2	0.0890	0.598	Hingston et al. (1972)
Goethite-E	8.1	0.203	0.662	Hingston et al. (1972)
Goethite	3.0	0.210	0.237	Sigg (1979)
Goethite			0.61	Hingston (1981)
Goethite			0.63	Hingston (1981)
Goethite			0.68	Hingston (1981)

Average = 0.6 ± 0.2 nm^2

Fig. 1—Phosphate "adsorption envelope" calculated with experimental data from Ballard and Fiskell (1974) and Yuan (1980).

Table 2—Average common logarithms of the intrinsic phosphate
surface complexation constants (44 soils).

Intrinsic constant	Mean	Standard deviation
log K1 (int)	8.71	0.56
log K2 (int)	2.41	2.38
log K3 (int)	−5.14	1.71

Phosphate Adsorption Data

Values for the three intrinsic phosphate surface complexation constants (See Part I) were obtained using the computer program FITEQL (Westall, 1982). This program fits equilibrium constants to adsorption data using a least-squares optimization technique. The experimental data used were those of Magalhaes (1969), Holford et al. (1974), Ballard and Fiskell (1974), Parfitt (1977), Yuan (1980), and Mead (1981). Adsorption was assumed to be the only phenomenon represented by these data. The soils studied consisted of 38 soils from eastern Australia, three from Florida, one from southern England, one from California, and one from Papua, New Guinea. The set of soils chosen for study ranged in pH value from 4.9 to 7.6. Their selection was based on the following criteria: (i) Allophanic soils and soils containing > 1.0% CaCO$_3$ were not considered. (ii) Phosphate adsorption data determined in the absence of a background electrolyte to maintain constant ionic strength were rejected. For the soils studied, the ionic strength ranged from 10 mol m^{-3} to 100 mol m^{-3}. (iii) Soil phosphate adsorption isotherms consisting of fewer than five data points were not included.

The maximum phosphate adsorption for a soil was estimated by plotting K_d, the distribution coefficient, vs. q, the amount of phosphate adsorbed. (The distribution coefficient is defined as the ratio of the amount adsorbed to the solution concentration.) The maximum adsorption, b, is found by extrapolating the graph to $K_d = 0$ where $q = b$. Sposito (1982, Fig. 2) has illustrated this method for one of the phosphate adsorption data sets used in this study. Phosphate adsorption by soils usually is at a maximum around pH 3 to 5 and decreases steadily with increasing pH value (see, e.g., Obihara and Russell, 1972; Hingston et al., 1972). The Constant Capacitance model predicts this effect of pH on adsorption (Goldberg and Sposito, 1984, Fig. 4). However, since the phosphate adsorption maximum in the model is used to calculate the total quantity of reactive surface hydroxyl groups present in the soil, the value used in the FITEQL program must be the *largest* phosphate adsorption maximum possible at any pH value.

The "adsorption envelope" is a plot of the maximum adsorption vs. pH. A plot of this type, showing the percent of the absolute maximum adsorption as a function of pH, is needed to estimate what should be the effective phosphate adsorption maximum for a soil at a given pH value. With the phosphate surface complexation constants obtained in Part I for oxides, a phosphate "adsorption envelope" was simulated with the Constant Capacitance model. The simulation was based on the phosphate adsorption data of Ballard and Fiskell (1974) for a soil at pH 4.9 and of Yuan (1980) for a soil at pH 5.05. The assumption was made that the phosphate adsorption maxima determined at these two pH values were equal to the largest maximum adsorption values for the two soils (Chen et al., 1973; Huang, 1975; Obihara and Russell, 1972). When expressed as percent of maximum adsorption, the simulation results for the two soils reduced to a single curve, validating the assumption of maximum adsorption at these pH values. From this graph, working values for the effective adsorption maxima were obtained and used to estimate phosphate surface complexation constants from the soil adsorption data. A new phosphate "adsorption envelope" then was calculated using the three average values of the common logarithms of the intrinsic phosphate surface complexation constants obtained for the 44 soils studied. This "universal" phosphate adsorption envelope is shown in Fig. 1. For any pH value between 4 and 8, a value of the percent of the absolute maximum adsorption can be read off the graph and used to back-calculate what should be the effective maximum adsorption for a soil.

RESULTS AND DISCUSSION

Table 2 lists average log Ki (int) ($i = 1, 2, 3$) for the intrinsic phosphate surface complexation constants obtained from FITEQL computations applied to adsorption data for 44 soils. For these soils, the intrinsic equilibrium constants, K1 (int) and K3 (int), exhibited smaller standard deviations in the logarithms than were observed for hydrous oxide minerals in Part I. The standard deviation of the logarithm of K2 (int) was large, however, and probably reflects the fact that FITEQL convergence for this constant was achieved for only nine soils. Indeed, good fits were
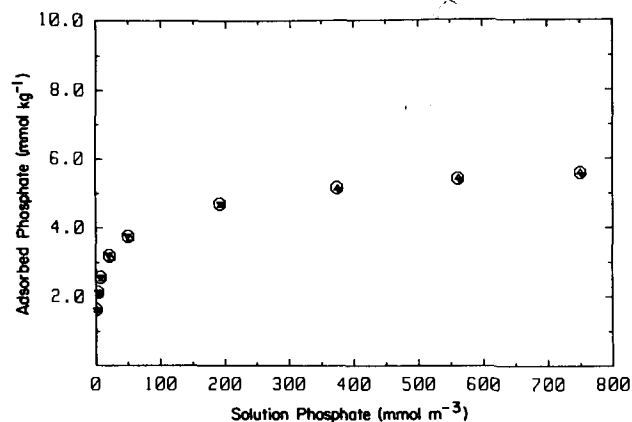
Fig. 2—Effect of changes in the packing area, a, of phosphate by ±1 standard deviation on phosphate adsorption. Based on experimental data for the Anderson soil (pH = 6.25) from Holford et al. (1974): a = 0.6 nm², open circles; a = 0.8 nm², open triangles; a = 0.4 nm², filled triangles.

Fig. 3—Model fit to experimental data (filled triangles) for Chipley soil (pH = 4.9) from Ballard and Fiskell (1974). Model results are represented by open triangles.

possible without the use of this constant (see Fig. 3 and 4).

The packing area, a, of adsorbed phosphate is a model parameter whose value was not established precisely (Table 1). Figure 2, however, shows, for a representative example, that model fits resulting from variations in the packing area, by plus or minus one standard deviation (0.2 nm²) are almost indistinguishable from the fit obtained by using the average packing area (0.6 nm²). The insensitivity of the model to large changes in the packing area is fortunate and probably occurs because the packing area enters into the isotherm calculations only indirectly.

Theoretically, the intrinsic equilibrium constants in the Constant Capacitance model should be independent of pH. To investigate this property, statistical analyses were carried out to test for linear regression of the common logarithms of the phosphate surface complexation constants on pH. The logarithms of the intrinsic equilibrium constants for the formation of the phosphate species, $SHPO_4^-$ and SPO_4^{2-}, did not show a significant linear relation with pH at the 95% level of confidence. However, for the neutral surface species, SH_2PO_4, there was a significant linear relation between the logarithm of the intrinsic formation con-

stant and the pH value at the 99% level of confidence:

$$\log K1(\text{int}) = 4.38 + 0.712 \text{ pH} \qquad r^2 = 0.566^{**} [1]$$

This relationship points to a failure of the Constant Capacitance model to account for all pH effects on o-phosphate adsorption by the soils in the present study through surface charge and adsorptive ion charge mechanisms alone.

Figures 3, 4, and 5 are representative examples of model fits to soil o-phosphate adsorption data. The points labeled "model" result from using the logarithms of the intrinsic phosphate surface complexation constants calculated by FITEQL for the particular soil. The soils were chosen to be representative of the acid, neutral, and alkaline ranges of soil pH. For individual soils, the fit obtained using soil-specific phosphate surface complexation constants was good. However, the use of the three average phosphate surface complexation constants (Table 2) resulted in an overestimation at lower pH values and an underestimation at higher pH values (data not shown). This effect could be caused by the pH-dependence of log $K1(\text{int})$.

Figure 6 shows a calculated distribution of phosphate surface complexes as a function of pH. The average phosphate surface complexation constants were used to generate the curves, which are illustrative only. The neutral phosphate surface species constitutes the
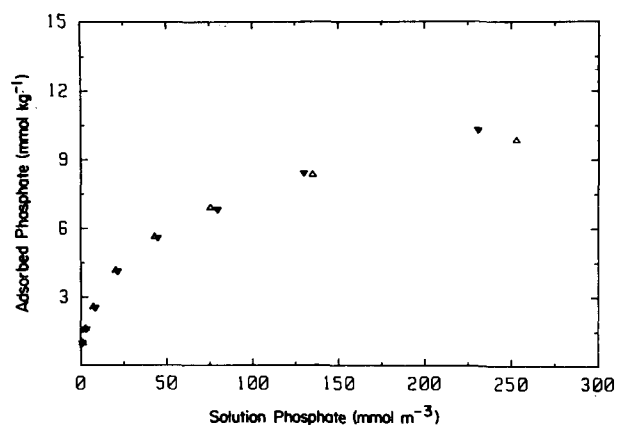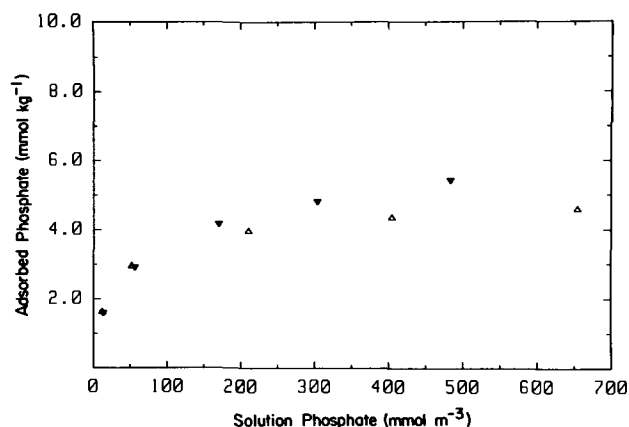

Fig. 4—Model fit to experimental data (filled triangles) for Soil no. 15 (pH = 6.4) from Mead (1981). Model results are represented by open triangles.
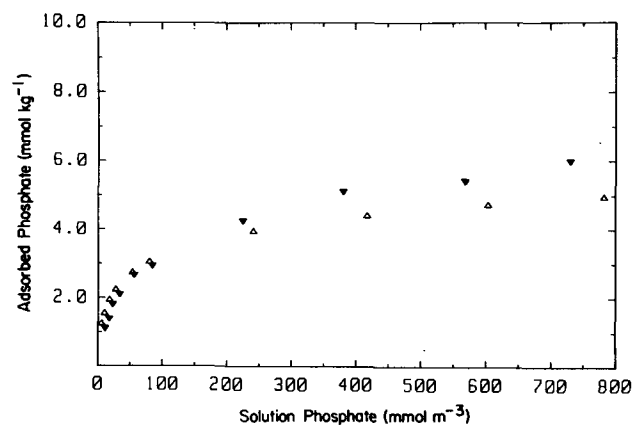

Fig. 5—Model fit to experimental data (filled triangles) for Quast soil (pH = 7.6) from Holford et al. (1974). Model results are represented by open triangles.
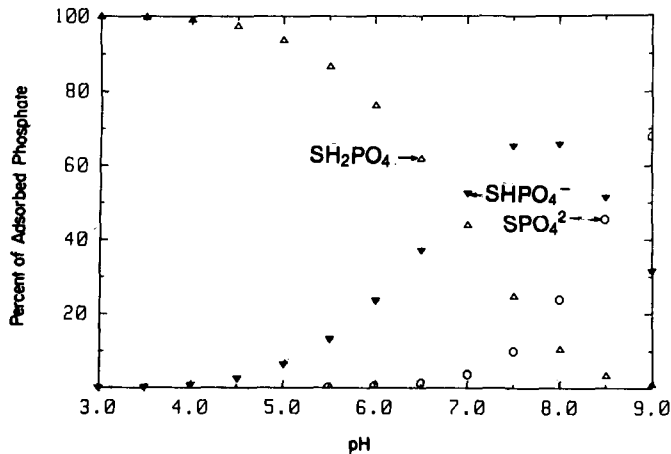
Fig. 6—Illustrative distribution of phosphate surface species as a function of pH: SH_2PO_4, open triangles; $SHPO_4^-$, filled triangles; SPO_4^{2-}, open circles.

dominant species at pH $\leq$ 7. The singly-charged surface species dominates at pH = 7 to 8.5, whereas the doubly-charged surface species dominates above pH 8.5. In the pH range 5 to 8, the model predicts that at least two phosphate surface species are present at significant concentrations in non-calcareous, non-allophanic soils.

CONCLUSIONS

Phosphate adsorption by noncalcareous soils can be described with the Constant Capacitance model incorporating surface protonation-dissociation constants and the packing area of phosphate calculated from data on reference hydrous oxides. With phosphate surface complexation constants calculated by FITEQL for a specific soil, the model was capable of fitting experimental adsorption isotherm data well for that soil.

Theoretically, the surface and adsorptive ion charging mechanisms in the model should account for all pH effects on o-phosphate adsorption, i.e., the intrinsic phosphate surface complexation constants should be independent of pH. This pH independence was found for the intrinsic formation constants for the $SHPO_4^-$ and SPO_4^{2-} surface species. However, the intrinsic equilibrium constant values for the formation of the neutral SH_2PO_4 species exhibited a statistically significant linear dependence on pH. This effect could cause the model to overestimate experimental adsorption data at low pH and underestimate them at high pH when *average* values of the intrinsic phosphate surface complexation constants are used.

The Constant Capacitance model can predict the well known decrease in the phosphate adsorption maximum that occurs with increasing pH (see Fig. 3 to 5). For this reason, the model can be used to predict changes in the phosphate adsorption behavior of a soil resulting from changes in soil pH. However, a soil-specific set of phosphate surface complexation constants obtained with a program like FITEQL should be used. Further research on a broader variety of soils and o-phosphate concentrations is needed to evaluate the model fully.

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