

## Phosphate Adsorption in Virginia Piedmont Ultisols under Long-Term Phosphorus Applications

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**ABSTRACT.** Phosphorus (P) adsorption is a determinant in agricultural production and environmental quality. Phosphorus adsorption behavior was studied with the Langmuir and two-site Langmuir models in two soil series that received P applications for over three decades, namely, Davidson clay loam (clayey, kaolinitic, thermic, Rhodic Paleudults), and Tatum silt loam (clayey, mixed, thermic, Typic Hapludults).

Phosphorus adsorption data for the two soil series used, closely fitted to the two-site Langmuir model than the original Langmuir model as evidenced from the lowest residual sums of squares. The P adsorption maxima in the non-fertilized treatments were 4,007 mg kg<sup>-1</sup> in the Davidson soil and 2,179 mg kg<sup>-1</sup> in the Tatum soil. The maximum P sorption capacities in both soils were decreased only by 5% due to 30 years of continuous P fertilization. The Davidson soil as compared to the Tatum soil had a lower pH (5.4 vs 6.2), slightly higher amount of clay (40% vs 30%), higher content of dithionite-citrate-bicarbonate extractable iron oxides (16.7% vs 6.5%), and higher amount of aluminum oxides (1.5% vs 0.8%). Negligible effect of many years of P application on the P adsorption power of the soils was perhaps due to the transformation of adsorbed P into non-labile forms such as reductant soluble P and occluded P as well as creation of new sites and exposing of original sites due to weathering. The results suggest that rate of P fertilization cannot be reduced even after continuous long term P fertilization specially in highly weathered soils

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## INTRODUCTION

Plants and soil microorganisms actively compete for meager levels of soil solution phosphorus (P) present as orthophosphates, the level of which is controlled by adsorption, precipitation and desorption processes. Adsorption of phosphates onto soil colloids takes place through an inner-sphere complexation process (McBride, 1994). Thus, a reasonable fraction of adsorbed phosphate is rapidly converted into non-labile forms that are not readily extracted by plants. Of the adsorbed phosphates, only the mononuclear fraction is considered to be labile and exchangeable with  $^{32}\text{P}$  within a specific time (Okajima *et al.*, 1983). Thus, rapid release of the labile pool P recharges the soil solution P compensating the P uptake by growing plants and the soil biota.

Literature demonstrate the importance of P adsorption to soil particles in agricultural use as well as in environmental quality. What motivates the usage of adsorption isotherms in this study are primarily identification of soil constituents involved in adsorption and postulation of the nature and mechanism of the adsorption process, and the possibility of their use in the prediction of fertilizer requirements to attain optimum yields while maintaining environmental quality (Adams *et al.*, 1987; Barrow, 1987).

Soils are known to vary widely in their capacities to supply P to crops due to differences in parent material and climate as well as the heterogeneous nature of soil components that leads to complex reactions between native P, added fertilizer P and P present in different soil constituent phases. Phosphorus adsorption/desorption, transformation and availability are influenced by the clay content, free Fe and Al oxides, pH, the ionic strength of soil solution, organic matter and soil mineralogy (Bolan *et al.*, 1986; Sanyal and De Datta, 1991).

Properties such as soil texture and sesquioxide content are not markedly altered by soil management and fertilization practices (Mullins, 1991). The chemical properties of the soil environment such as soil pH, organic matter content, CEC, and extractable nutrient contents are altered by long-term cultivation. Thus, soil management and fertilization are likely to affect P dynamics in soils both directly and indirectly. The long-term application of soluble phosphate fertilizer is considered to reduce P adsorption capacity since reactive sites could be partially occupied. Failure of the adsorption maxima to be decreased by long-term P addition would imply the transformation of P to non-exchangeable forms. Therefore, it would be

beneficial to investigate how P sorption, availability and transformation are affected by long-term P fertilization in agricultural soils. The objectives of this study were to evaluate changes in phosphate adsorption due to long-term application of P fertilizer and the role of soil physio-chemical and mineralogical properties in controlling P adsorption of highly weathered soils.

## MATERIALS AND METHODS

### Site description

Two soil series that had long-term P fertilization, namely, Davidson clay loam (clayey, kaolinitic, thermic, Rhodic Kandudults) and Tatum silt loam (clayey, mixed, thermic, Typic Hapludults) were selected for the study from Virginia Piedmont soils in the eastern United States. These soils were derived from metamorphic rocks. The parent rock was Catoclin greenstone for the Davidson soil and Sericite schist for the Tatum soil. The soils used in the study have been cultivated with corn (*Zea mays* L.) Over a long period of time. The Davidson soil received annual broadcast of superphosphate applications at the rate 30 kg P ha<sup>-1</sup> yr<sup>-1</sup> for the 34 year period from 1960 to 1993 while the Tatum silt loam received superphosphate applications at the rate 25 kg P ha<sup>-1</sup> yr<sup>-1</sup> for a period of 39 years from 1954 to 1993 (Table 1). In both locations, a control plot (with no P application) was maintained for the same duration. Soil samples for the study were taken in the spring of 1993, from the 0 to 15 cm depth at the rate of 10 cores per plot from all four replicates in a treatment.

### Soil analysis

The air dried soil samples were sieved to remove coarse fragments (>2 mm) and thoroughly mixed. Textural analysis was carried out by the pipette method (Day, 1965). Soil pH measurements were obtained from a 1:1 soil:deionized water suspension. Organic matter was determined by the Walkley and Black (1934) method. Dithionite-citrate-bicarbonate (DCB) soluble Fe, Al, and Mn were extracted by the Mehra and Jackson (1960) procedure and exchangeable Al (1 M KCl) by the Barnishel and Bertsch (1982) technique. Elemental concentrations in these extractions were determined by inductively-coupled argon plasma spectroscopy (ICP).

**Table 1. Fertilization history of the treatments of the two soil series used in the investigation.**

Soil Series	Taxonomic classification	Treatments			Duration (yr)
		Fertilizer level (kg ha <sup>-1</sup> yr <sup>-1</sup> )			
		N*	P*	K*	
Davidson	clayey, kaolinitic, thermic, Rhodic Kandudults	170	0	112	34
		170	30	112	34
Tatum	clayey, mixed, thermic, Typid Hapludults	200	0	25	39
		200	25	25	39

\* Sources of fertilizer: N = Ammonium nitrate, P = Super phosphate, K = Muriate of potash.

### Adsorption isotherms

Three-gram (3.0 g) duplicated sub-samples of air dried soil were weighed into nine 100 ml polypropylene centrifuge tubes. Fifty ml of 0.01 M CaCl<sub>2</sub> solutions with 0, 1, 5, 10, 15, 25, 50, 100 and 200 µg ml<sup>-1</sup> P concentration were added to the tubes. The tubes were stoppered and shaken twice daily for 1 minute over a six-day period at 22°C to achieve equilibrium. Samples were then centrifuged (14,500 × g), and filtered through Whatman No. 42 filter paper. Phosphorus in the filtrate was determined by inductively-coupled argon plasma emission spectroscopy.

Ideally, adsorption should be determined in a system in which the surface would be free of the adsorbate ion. Usually, the ideal conditions are not feasible and, hence, require correction for initial surface phosphate. The correction was carried out by adding an amount of surface desorbed P (0 µg P ml<sup>-1</sup> treatment) to the adsorbed P (x/m µg g<sup>-1</sup>) value. The amounts added were 1.27, 9.59, 0.82 and 7.58 µg P g<sup>-1</sup> for Davidson control and Davidson fertilized, and Tatum control and fertilized treatments, respectively. The need for a

similar correction was identified and used by Olsen and Watanabe (1957). The correction values were greater in the P fertilized than in control treatments in both soil series. Average data from these P analyses were plotted using the basic Langmuir model;

$$\frac{x}{m} = \frac{V_m b c}{(1 + b c)} \quad (1)$$

and by the two-site Langmuir model;

$$\frac{x}{m} = \frac{V_{m_1} b_1 c}{(1 + b_1 c)} + \frac{V_{m_2} b_2 c}{(1 + b_2 c)} \quad (2)$$

Where,  $x/m$  is P sorbed per unit weight at an equilibrium concentration of  $c$ ,  $b$  is the coefficient related to the free energy of transfer of P from solution to soil,  $V_m$  is the adsorption maximum of volume of monolayer ( $\mu\text{g P g soil}^{-1}$ ), and the subscripts represent discrete energy sites and  $V_{m_1}$  and  $V_{m_2}$  represents the adsorption capacity due to sites of the  $n$ th discrete energy. Total maximum adsorption capacity of the soil is  $V_{m_1} + V_{m_2}$ .

#### Clay mineral identification

Prior to mineralogical analysis, samples were pre-treated to remove organic matter and free iron oxide fraction (Mehra and Jackson, 1960). The less than 0.002 mm was prepared for clay separation. Oriented clay mounts were prepared by deposition of approximately 250 mg in suspension on an unglazed ceramic tile mounted on suction apparatus. Mineral identification was obtained through X-ray diffractograms. Kaolinite and gibbsite were quantified by mass-equivalent calibration of endothermic peak areas for poorly crystalline Georgia kaolinite and Reynolds synthetic gibbsite as standards. Other minerals were quantified using the following relationship:

$$I_x/I_k = C(M_x/M_k)$$

Where  $I_x$  and  $I_k$  are integrated intensities of the unknown mineral and kaolinite,  $C$  is a constant determined empirically as the slope of  $I_x/I_k$  vs  $M_x/M_k$  for known

mixture of a standard mineral and kaolinite, and  $M_x$  and  $M_k$  are masses of the unknown minerals and kaolinite, respectively.

The value  $M_k$  for the samples studied was taken as the mass percentage of kaolinite as determined from DSC calibration.

### Statistical analysis

A nonlinear regression method was used to fit averaged values of the duplicated P sorption data to the original Langmuir and two surface model Langmuir equations. The residual sums of square (RSS) values of the two models were calculated and compared for selection of the best fit of the equations.

## RESULTS AND DISCUSSION

### P adsorption

Phosphorous adsorption isotherms in Figure 1 show basic characteristics of a L-curve isotherm (Sposito, 1984). Phosphorus sorption by the four treatments had a strong initial phase with a relatively steep slope at low equilibrium concentrations, and then a weaker sorption phase at higher concentrations with a decreasing slope which did not approach an asymptotic maximum within the P concentration range of the experiment. The strong adsorption phase is attributed to the existence of unoccupied high affinity sorption sites on the soil surfaces (Pratiff *et al.*, 1989). The weaker reaction phase is probably due to the penetration of phosphate into Fe and Al (hydro) oxides-crystals or insertion between aggregates of microcrystals (Barrow, 1989). Given the curvilinear nature of the data, it is evident that the original Langmuir model (monolayer model) tended to overestimate P adsorption at moderate levels of equilibrium P concentrations, and underestimate P adsorption at high concentrations.

The two-site Langmuir model fits the data closely and is free of the estimation problems observed in the original Langmuir model (Figure 2). The goodness of fit of the two models show that, in all cases, the magnitude of the error for the two-site model is much smaller than for the one-site model (Table 2). The lower error in the two site model implies the existence of multiple adsorption sites, or the involvement of adsorption sites which have widely

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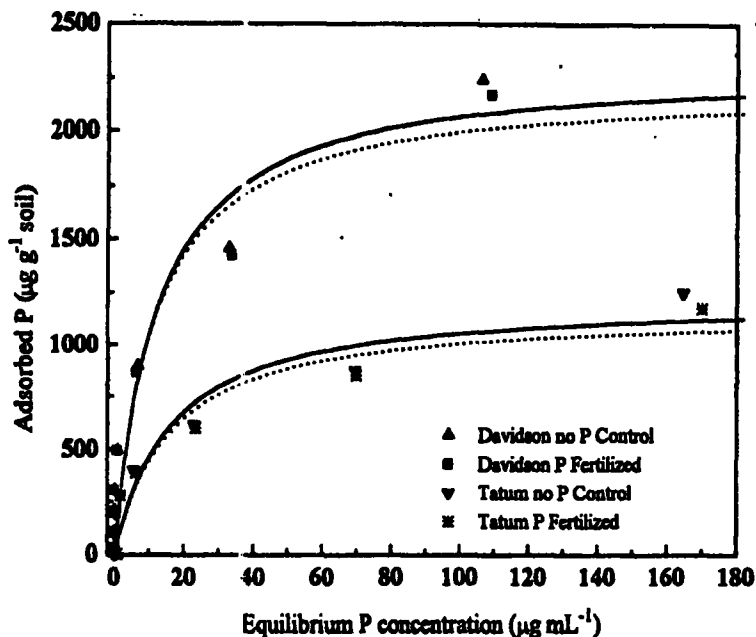


Figure 1. Curvilinear Langmuir isotherms for phosphate adsorption by two soil series.

different P affinities (Muljadi *et al.*, 1966a, 1966b, 1966c; Kuo, 1988). Since the soils used in the study were highly weathered, and have been cultivated with corn (*Zea mays* L.) over a long duration, the observed behavior is compatible with similar soils having high amounts of clay and  $\text{Fe}_2\text{O}_3$  (Table 3).

The calculated adsorption maximum for the two-site model ( $V_{m_1} + V_{m_2}$ ) shows an increase of about 42% over that of the original Langmuir model (Table 2). This increase is lower than the increases of 48–140% reported in the literature (Holford *et al.*, 1974). The adsorption maxima for the control treatments were slightly higher than for the P fertilized treatments (Table 2). The small difference in P adsorption suggests that the fertilized and non-fertilized soils had similar numbers of unoccupied adsorption sites. Kurtz and Quirk (1965) observed little or no reduction in adsorption maxima as a result of the past P fertilization of a Red Brown Earth from South Australia, but residual effects of P application were evident in brunizen and lateritic soils. Mullins (1991) reported that in the southern United States, long-term P fertilization had a small influence on the adsorption capacity for recently added fertilizer P.

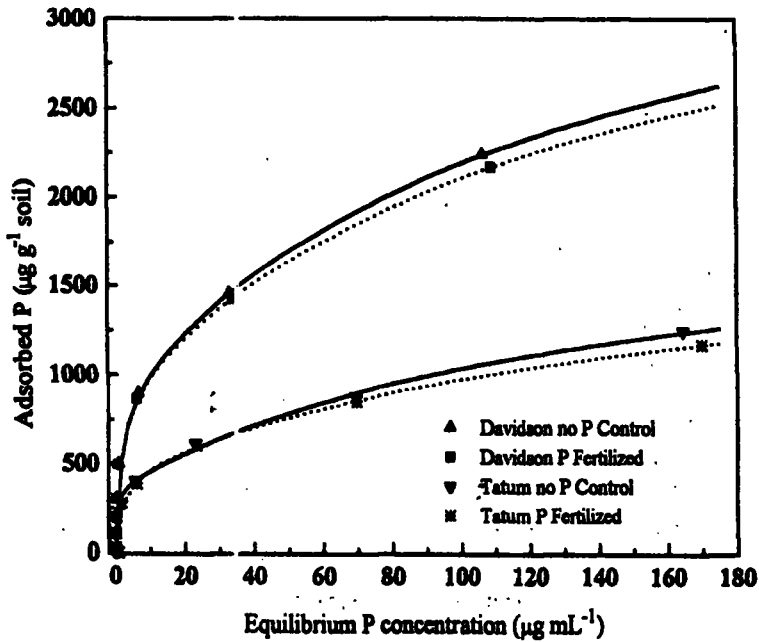


Figure 2. Two site Langmuir isotherms for phosphate adsorption by two soil series.

Adsorption maxima values (Table 2) show that the difference in P adsorbed to high affinity sites identified by  $V_m$ , was small between the fertilized and non-fertilized soils. These sites accounted for 23% of monolayer P adsorbed in the Davidson soil and 20% of monolayer P adsorbed in the Tatum soil. The difference in P adsorbed to low-affinity sites was greater both in absolute terms as well as in relative terms. The rapid initial-phase P adsorption may have been caused by an inner-sphere complexation mechanism (McBride, 1994). In this high affinity phase, the adsorbed P is incorporated into the adsorbent structure with transfer of its charge to the surface (White and Zelazny, 1986). Thus, P adsorbed during this initial adsorption phase could be transformed to crystalline forms. As the solution P concentration in the soil increases, Al-P and Fe-P transformation occurs at a faster rate (Hsu, 1982a, 1982b). Juo and Ellis (1968) reported that Fe-P crystallization rate is faster than that of Al-P. As soil undergoes weathering new adsorption sites are created and these sites enable the soils to adsorb P.



**Table 2. Residual sums of squares and adsorption parameters obtained from the Langmuir models for treatments of the two soil series.**

Soil	Residual sums of squares $\times 10^3$		Adsorption Maxima ( $\mu\text{g g}^{-1}$ )				Binding Constant		
	Langmuir	Two site Langmuir	Langmuir	Two site Langmuir			Langmuir	Two site Langmuir	
				$V_{m_1}$	$V_{m_2}$	Total		$b_1$	$b_2$
Davidson - Control	124.6	13.0	2308.9	898.5	3108.5	4007.0	0.086	0.665	0.007
Davidson - Fertilized	106.3	51.0	2211.9	875.5	2967.5	3843.0	0.092	0.765	0.007
Tatum - Control	341.6	185.8	1242.2	424.6	1754.3	2178.8	0.062	0.748	0.007
Tatum - Fertilized	369.7	217.2	1165.5	398.4	1635.5	2033.9	0.072	0.821	0.005

**Table 3. The physio-chemical properties and clay mineralogy of the two soils.**

Parameter	Davidson soil	Tatum soil
<b>Physio - chemical properties</b>		
Texture - sand (%)	20.4	24.5
silt (%)	39.6	45.1
clay (%)	40.0	30.4
pH (1:1, soil water)	5.4	6.2
Organic matter (%)	2.5	2.1
Exchangeable Al (mg kg <sup>-1</sup> soil)	3.9	4.0
DCB extractable - Fe <sub>2</sub> O <sub>3</sub> (%)	16.7	6.5
Al <sub>2</sub> O <sub>3</sub> (%)	1.5	0.8
<b>Mineralogical analysis (%)</b>		
Kaolinite	60.0	62.0
Interstratified	-	22.0
Intergrade	27.0	-
Vermiculite	-	10.0
Mica	10.0	-
Gibbsite	0.2	-
Quartz	2.0	1.0

Adsorbed P at low affinity adsorption phase is not as strongly held as the initial phase (Barrow, 1987). Therefore, P adsorbed in this phase replenishes the P removed from soil solution due to microbial and plant uptake. The rate of P crystallization from this loosely held P is lower than for the rapid

initial-phase adsorbed  $P$ . In this study, the number of occupied adsorption sites in the fertilized soils does not appear to be considerably lower than those of the non-fertilized soils. This small difference in available P sorption sites may be related to the fact that the rates of P fertilization were only marginally higher than the P removal levels of corn. A crop of corn producing a grain yield of 9.5 tons  $ha^{-1}$  removes about 27 kg P  $ha^{-1}$  (Mengel and Kirkby, 1987). Thus, the net amount of retained fertilizer P content in the fertilized soil could have been relatively low.

The  $b_1$  and  $b_2$  coefficients of the two-site Langmuir model represent the free energy of transfer of  $PO_4^{3-}$  from solution to solid adsorbent surfaces of soil (Table 2). The  $b_1$  coefficient represents free energy required for initial structural adsorption mechanisms. Structural adsorption of  $PO_4^{3-}$  by inner-sphere complexation reactions has a high free energy requirements. The adsorption phase represented by  $b_2$  is a low-energy consuming physisorption process that consists of both adsorption and precipitation reactions. In all cases binding energy values in the slower adsorption phase suggest that P is loosely held in quasi-equilibrium with soil solution P.

### P adsorption and soil properties

The amount of P adsorption in the Davidson soil is twice as large as that of the Tatum soil (Table 2). These differences in the adsorption rates can be associated with the following physical, chemical, and mineralogical properties of soils. The Davidson soil has a higher clay content (40%) than the Tatum soil (30%) (Table 3) and, hence, has a larger surface area for P adsorption. Significant correlations between the clay contents and the P adsorption levels have been reported for many soils (Syers *et al.*, 1973; Wada *et al.*, 1989). Clay mineral surfaces in highly weathered soils consist of fine coatings of Al and Fe oxides and hydrous oxides. These coatings effectively increase the surface area available for P adsorption. The high levels of P adsorption in the Davidson soil could have been due to this property.

Kaolinite constitutes 60% of the clay mineral fraction in the Davidson soil and 62% in the Tatum soil (Table 3). The Davidson soil with a higher clay content has a larger kaolinite content than the Tatum soil. The large number of exposed OH<sup>-</sup> groups in the Al layer of kaolinite crystals are preferred sites for P fixation (Muljadi *et al.*, 1966b). In addition, edge faces of kaolinite develop pH dependent charges that can adsorb P. Furthermore, it is suggested that phosphate reacts with kaolinite to form Al-P, thereby moving the adsorption

process towards greater fixation (Lów and Black, 1950). Therefore, the differences in the kaolinite content may partially explain the higher P adsorption capacity in the Davidson soil as compared with the Tatum soil.

Dithionite-citrate-bicarbonate extractable Fe and Al oxyhydroxide contents, respectively, are greater in the Davidson soil (16.7% and 1.5%) than (6.5% and 0.8%) in the Tatum soil (Table 3). The larger adsorption maxima in Davidson soil (Table 2) is probably due to the presence of higher Fe and Al hydrous oxides which increase the P adsorption capacity of soil. The specific adsorption of P on Al and Fe hydrous oxides has been attributed to replacement of OH<sub>2</sub> and OH groups by P in either monodentate (M-H<sub>2</sub>PO<sub>4</sub>-M) or a bidentate (M-O-(POOH)-O-M) linkage (Hingston *et al.*, 1974). Bingham *et al.* (1978) showed that dark red clay soils, which are very similar to the soils studied, were dominated by hematite (67%) and substantial amount of goethite (33%). These minerals are derived toward terminal stages of the weathering process, and are capable of fixing considerable amounts of P (Feldman, 1995). Removal of DCB extractable Fe and Al decreases P adsorption (Weindt *et al.*, 1993), *i.e.*, eliminates the slow adsorption phase, which is probably associated with penetration of phosphate inside Fe and Al (hydro) oxides crystals or between aggregates. Overall, the large amount of Fe<sub>2</sub>O<sub>3</sub> in the Davidson soil induces high P adsorption during both rapid and slower phases.

Soil pH of the Davidson soil was lower than in the Tatum soil (Table 3). The charge and the electrostatic potential of positive pH dependent adsorption sites are increased at the lower pH. At low pH, the higher Al and Fe activities contribute to the higher adsorption capacity observed in the Davidson soil. The relationship has been observed in previous studies by Bolan *et al.* (1988) and Adams and Odom (1985).

## CONCLUSIONS

Phosphorous adsorption behavior in the Davidson clay loam and Tatum silt loam soils was described very well by the two-site Langmuir model. The maximum P sorption capacities of the soils were slightly decreased by the long term application of P. In the Davidson soil, 23% of the total adsorption capacity was accounted by the high-affinity adsorption phase (V<sub>m1</sub>). The high-affinity phase P adsorption capacity in the Tatum soil was 20%. The Davidson soil has a 83% higher P adsorption capacity than the Tatum soil. The differences in factors such as Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, kaolinite, gibbsite, clay content and soil pH explained the higher P adsorption capacity of the Davidson soil. The

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influence of soil parent material and weathering intensity on the level of these factors caused a substantial difference in P adsorption, even though the two soils were in the same taxonomic order and physiographic region. The results suggest that rate of P fertilization cannot be reduced even after continuous long term P fertilization specially in highly weathered soils.

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