CHAPTER 3

PHOSPHORUS ADSORPTION BY DIVERSE SOILS

ABSTRACT

Phosphorus adsorption greatly affects the capacity of soil to supply P to plants. Application of organic or inorganic P fertilizer to acid soil may not alleviate low P availability because large amounts of P are sorbed through precipitation and adsorption reactions. A laboratory study was conducted to evaluate P sorption in A and B horizons of seven soils with diverse physicochemical properties. Regression analysis of sorption for equilibrium P concentration of 1 to 200 μg P g^{-1} shows that P adsorption data were well fitted to the two sites Langmuir model, i.e., this model had the lowest residual sums of squares.

The P sorption capacity was highest (1385 and 1410 μg P g^{-1}) in Elioak and Vance Piedmont soils, and in the mixed horizons (1099 and 1525 μg P g^{-1}) in mine tailings and Starr soil, respectively. The lowest P adsorption capacity was in Kempsville and Myatt Coastal Plain soils (304.4, and 449μg P g^{-1}), respectively and in a Ridge and Valley Frederick soil (487μg P g^{-1}). All of the Piedmont and mixed horizons soils had high standard P requirements (amount of P requirement to obtain 0.2 ppm P).

Phosphorus adsorption parameters were found to be correlated with clay and Al and Fe oxides. The coefficient of correlation with clay on the Piedmont surface soils was 0.82 and was 0.42 for the Piedmont subsoils. The Al and Fe oxides for the seven subsoils were highly correlated with the P adsorption capacity ($r^2 = 0.89$ and 0.70), whereas the r^2 was <0.51 for the surface soils and was 0.89 and 0.70 for the seven subsoils. This study indicates the importance of soil properties on P adsorption capacity in subsoils as compared to the surface horizon.

3-1 INTRODUCTION

Soil scientists have long recognized the importance of the relationship between P adsorption by soil and plant uptake of P. The big concern is soil acidity where P may be inadequate for plant nutrition, even with a high total P level in soil. The nature and the complexity of P reactions with soil infer a need for research to elucidate the mechanism of P retention in soil (Sample et al., 1980). The adsorption of phosphate ions by soil has been described widely by Barrow (1978). Soluble P added to soil to correct P deficiency reacts rapidly with soil components and, with time, becomes less available for plants (Fox and Kamprath, 1970; Vanderdeelen, 1971). A knowledge of the P adsorption capacity of soil is required to achieve a correct fertilizer diagnosis and to assess the effects of P pollution on environmental degradation of surface water by eutrophication.

The common approach used to determine the P adsorption capacity of soils involves equilibrating soil with a dilute phosphate solution, and then determining the amount P adsorbed by soil (Bache and Williams, 1971). The mechanism of retention has been postulated to involve an initial adsorption of P onto soil surfaces followed by precipitation with Al, Fe, or Ca (Lin, 1983). Several isotherm models including the Langmuir, Freundlich, BET, and Templin equations have been used to describe P adsorption (Olsen and Watanabe, 1957; Fox and Kamprath, 1970). The Langmuir and Freundlich equations have been most commonly used to describe P sorption and solubility relationships.

Various investigators have indicated that P adsorption was correlated with soil physicochemical characteristics such as clay content, pH, organic matter, and free Fe and Al oxides (Syers et al., 1973; White, 1981; Parfitt, 1989; Sanyal and De Datta, 1991). Physicochemical characteristics of soil determine the magnitude of P adsorption and, hence, much effort has been devoted to study the relationship between P adsorbed and physicochemical soil factors. Relevant literature suggested that hydrous oxides of Fe and Al are the most important soil variables that contribute to P adsorption (Singh and Tabatabai, 1977; Sanyal and De Datta,

1991). Highly weathered soils with high Al and Fe oxide contents such as Virginia soils have been recognized for their reactivity with phosphate anions. Bonding of P with hydroxy-Al and Fe on functional groups accounts for positive relationship between the organic matter in soil and P retention (Harter, 1969; Sanyal et al., 1993). Conversely, reaction of negatively charged functional groups from organic acids such as humic acid with positively charged clay surface blocks P retention in soil (Reddy, 1980).

The purpose of this research was to locate soils with low to high P fixation for studies on correction of P deficiency by amendment with inorganic and organic P compounds. Phosphorus adsorption isotherms were used to evaluate the P fixation capacity of soils. A further aim of the research was to investigate the relationships between selected physiochemical soil characteristics and P fixation by soil.

3-1.1 Adsorption Isotherm

Langmuir, Freundlich, Tempkin, and the Brunauer-Emmett-Teller (BET) adsorption isotherms have been used worldwide to model P fixation in soil. The Langmuir and Freundlich equations with only two parameters require simple determination. On the basis of simplicity and convenience, the Langmuir and Freundlich equations have been used extensively in describing P sorption by soil (Kuo, 1988).

3- 1.1.1 Langmuir equation

The Langmuir equation based on the kinetic theory of gases (Langmuir, 1918) was originally developed to model the adsorption of gaseous molecules onto solids. The proposed model involves three assumptions that have been deemed questionable for use in the soil system. (Bohn et al., 1985). First, the energy is constant regardless of the extent of surface coverage. Second, the movement of adsorbate molecules on the surface area occurs without significant interaction. And third, the adsorption maximum process is limited to a monolayer. As developed

by Langmuir (1918), the equation for gas adsorption on a solid surface has the following form:

$$n = \frac{V_m b P}{(1 + bP)}$$

3.1

where;

n = amount of gas adsorbed per unit area,

P= the equilibrium gas pressure,

V_m = the adsorption maximum, and

b = coefficient related to the bonding energy of gas to solid surface.

A linear form of the original Langmuir equation (Langmuir, 1918), was derived by Olsen and Watanabe (1957). This linear form based on desorbed P ions in the equilibrium solution was utilized by Olsen and Watanabe (1957) to study P adsorption in soils. This equation has the following form:

$$\frac{C}{x/m} = \frac{1}{V_m b} + \frac{C}{V_m}$$

3.2

where;

C = the equilibrium concentration of P in solution (ug P ml^{-1}),

x/m= quantity of P adsorbed per unit mass of soil (ug P g^{-1}),

V_m= the adsorption maximum, and

b = coefficient related to the bonding energy of gas to solid surface.

Serious criticisms on the theorical considerations and the validity of the Langmuir equation to soil systems have led to some modifications of the equation (Olsen and Watanabe 1957). The close fit of the Langmuir equation occurs generally at low equilibrium concentration

level, and the adsorption maximum is often exceeded at higher concentration (Harter, 1984; Sanyal and De Datta, 1991; Barrow, 1978). The curved relationship at higher concentrations implies that the bonding energy is not a constant but rather a function of adsorption. That is, there is the rapid reaction of sorbed P into subsurface of crystalline hydrous Fe oxides (Sanyal and De Datta, 1991). The curvilinear isotherm has been ascribed to two straight lines (Syers et al.,1973; Mehadi and Taylor, 1988; Ram et al., 1987). These workers attributed the two straight lines to the existence of two populations of surface sites with widely different affinities for P. The study of P sorption onto kaolinite, gibbsite, and pseudoboehmite shows three distinct regions by the Langmuir equation (Muljadi et al., 1966a, b, c). The first region, highest in free energy of adsorption takes place on the edge of the crystal by a partially reversible reaction. The second region exhibits a lower bond energy while the third region involves electrostatic bonds; both by totally reversible reactions.

The two regions observed in the Langmuir plot were attributed to the variability of bonding energy to a monodentate attachment of P at higher P concentrations, and to bidentate attachment of P at lower P concentrations. The nonuniformity of adsorption sites has led to use of the two surface rather than the standard Langmuir equation (Olsen and Watanabe, 1957). The two-site equation provides meaningful parameters to characterize P behavior in soil and to give a near perfect fit for adsorption isotherm data (Holford et al., 1974; Syers et al., 1973). The form of Langmuir equation for two sites adsorption is as follows:

$$\frac{x}{m} = \frac{V_{m1}b_1c}{(1+b_1c)} + \frac{V_{m2}b_2c}{(1+b_2c)}$$

3.3

The two-site Langmuir equation has the advantage that it defines a limit for P adsorption maximum which meets the Langmuir model criteria (Bohn et al., 1985). This equation has been used to estimate the adsorption capacity of soils for various adsorbates and to estimate P fertilizer requirement.

3-1.1.2. BET

The BET approach often has been used where the adsorption isotherm failed to conform to a single slope Langmuir isotherm (Griffin and Juriak, 1973; Taylor and Ellis, 1978). Multilayer P coverage on a specific site is considered by P adsorption for the BET model in contrast to monolayer coverage by the Langmuir model. The linear adsorption form of the BET equation is expressed as follows:

$$\frac{C}{\frac{x}{m}(C_o - C)} = \frac{1}{V_m b} + \frac{b-1}{V_m b}[\frac{C}{C_o}]$$

3.4

where; C, x/m, and Vm replace b in the Langmuir equation and are related to the bonding energy of the first adsorbed layer only, and C_o is the maximum concentration of P required to cause precipitation of the most likely solid form of P.

3-1.1.3 Freundlich Isotherm

Generally, the empirical Freundlich model fits phosphate sorption data better than the Langmuir and other equations (Polyzopoulos et al., 1985; Ratkowky, 1986). They suggested that the Freundlich isotherm was preferable because of its simplicity of form, realistic assumptions, and ease of derivation. An estimate of adsorption maximum is not provided by the Freundlich isotherm (White and Zelazny, 1986). The Freundlich equation has the following form:

$$\frac{x}{m} = kC^{\frac{1}{n}}$$

3.5

where; x/m is P adsorbed (mg P kg^{-1}), C is the equilibrium concentration of P in solution (mg P L^{-1}), and k and n are constant terms.

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3-1.2 Chemical and Physical soil factors affecting P adsorption

      Changes in P adsorption are influenced by several physicochemical characteristics of soils, i.e., texture, structure, pH, organic matter content, and Fe and Al oxides. Phosphate adsorption by soils varies widely with changes in soil physicochemical properties (Parfitt, 1989; Sanyal and De Datta, 1991). It is important to consider the nature and amount of soil components as well as the valency and concentration of constituent cations to understand P adsorption by soil**.**

3-1.2.1 Clay content

      A strong correlation between P adsorption and clay surface area may be largely due to the association with other soils components such as pH, Fe and Al oxides on particle surfaces, and organic matter (Fox and Kamprath, 1970; Loganathan et al., 1987; Stuaves, 1982; Bennoah and Acquaze, 1989). On tropical soils with low pH, the 1:1 lattice clay increases the number of adsorption sites and, thereby, increases P adsorption. Phosphate adsorption sites occur on kaolinite, gibbsite, goethite and pseudoboechmite (He, 1995; Muljadi et al., 1966a, b, c). They suggested that P adsorption occurs at the edge face of kaolinite involving the OH in kaolinite and hydrated sesquioxides. Kuo and Lotse (1974) attributed P sorption to coordinate covalent bond formation between Al of the oxide surface and O of the phosphate ion.

3-1.2.2 pH effects

      Major iterations in phosphate chemistry occur from changes in pH. A negative correlation was found between P sorption and pH (Sanyal and De Datta, 1991). Phosphate precipitates with Al and Fe and is adsorbed by Al and Fe oxides in acid soils (Bolan et al., 1988; Mehadi and Taylor, 1988). An increase in pH in acid soils may decrease the concentration of soluble and exchangeable Al and Fe ions which could have adsorbed by phosphate to form insoluble complexes. Sanchez and Uehara (1980) suggested that the decrease in P sorption with an increase in pH reflected higher negativity of surface charge. Nonetheless, at high pH increases in HPO_4^{2-} activity and decreases in $H_2PO_4^-$ activity offset the decrease in electrostatic potential

(Bowden et al., 1980; Barrow, 1984). An additional explanation to rationalize the decrease in P adsorption at higher pH is that Al forms $Al(OH)_3$ and Fe forms $Fe(OH)_3$ and, therefore, little Al and Fe are left to react with P at higher levels of pH (White and Taylor, 1977; Fan, 1993). Higher Ca to Al and Fe ratios lead to formation of insoluble Ca-P as pH increases. The higher concentration of cations on the adsorption sites also increase of P adsorption by decreasing the negative potential on the surface area. (Naidu, 1990; Barrow, 1984).

3-1.2.3 Organic matter

Many investigators suggested that the addition of organic molecules decrease phosphate fixation by soil and, thereby, increase the availability of P (Parfitt, 1977; Yuan, 1980; Sibanda and Young, 1986; Anderegg and Naylor, 1988). The negatively-charged sites in organic matter and P ions can compete for sorption sites on hydrous oxides of Al and Fe. A significant correlation between P sorption and content of both soil organic and Al and free Fe oxides indicated that Al oxide and organic matter play a role in P sorption (Singh and Tabatabai, 1977; Sanyal et al., 1990). Phosphorus retention process by organic matter is similar to that of hydrous oxides and aluminosilicates (Sanyal and De Datta, 1991). The exchange activity involves a substitution of P ions for hydroxyl ions in organic matter. Application of alkaline organic matter increases P sorption by hydrous sesquioxides in acid soils through neutralization of hydrogen (Sanyal et al., 1993). Some data suggested that organic molecules may block sorption sites on Al and Fe oxides, and thereby reduce P sorption (Yuan, 1980; Hue, 1990; Stuanes, 1982).

2-1.2.4 Iron and Aluminum oxides

The capacity of soil to adsorb P is closely related to soil components such as acid ammonium oxalate extractable Fe and Al (i.e., noncrystalline and crystalline oxides of Al, Fe, and Mn). These soil components are directly involved in P adsorption in acid to near neutral soils (Robarge and Corey, 1979). The degree of P adsorption depends on the crystallinity of Fe oxides due to Al substitution for Fe. Overall amorphous Fe oxides adsorb more P than crystalline Fe and

Al hydrous oxides, and also much more than crystalline aluminosilicates and Ca carbonate (Ryden and Pratt, 1980).

Although oxalate extracts Fe and Al from both noncrystalline and poorly crystalline oxides the noncrystalline component has greater surface area and hence, greater P fixation. (Munch and Ottow, 1980; Agbenin, 1995). This poorly crystalline Fe and Al is reported to correlate well with P sorption in soils (Borggaard, 1983; Adams et al. 1987; Logonathan, 1987). Therefore, an extractant that dissolves poorly crystalline Fe and Al could provide a good indication of available P levels in soil (Shahandeh, 1994). Much of the P extracted by dithionite citrate bicarbonate would be in a plant unavailable form.

3-2 MATERIALS AND METHODS

This research was carried out to calculate P adsorption maxima from Langmuir isotherms for determining P fertilizer needs for textually and mineralogically different soils. The soils were obtained from surface and subsurface (A and B) horizons of five soils profiles (Table 3.1). Two mixed horizon soils, mine tailings from the mining process and Starr soil, were used in this study. The average value of selected chemical and physical properties from Ap and Bt horizons are presented in Table 3.2. These soils, which developed from different parent materials, are important for agriculture and cover a wide range of Virginia soils. The classification and parent materials of these soils series are given in Table 3.1. Soil samples were taken from areas without a history of fertilization. The A and B, and mixed horizons of the soil samples were dried, and crushed to pass through a sieve with two mm opening prior to chemical analyses.

3.2.2 Soil Analysis

Soil pH was measured in 1:1 soil-to-distilled water ratios after a 1-hour equilibration period. Organic matter content was determined by a chromic acid oxidation method (Walkley-

Black, 1934), and cation exchange capacity by a $MgCl_2$ saturation and $CaCl_2$ displacement procedure (Rich, 1962). Dithionite-citrate bicarbonate (DCB) soluble Al and Fe were extracted by the procedure described by Mehra and Jackson (1960), and exchangeable (1 M KCl) Al was extracted by the Barnishel and Bertsch (1982) technique. Aluminum and Fe in the extractions were determined by inductively-coupled argon plasma spectroscopy and are reported as Al_2O_3 and Fe_2O_3.

3-2.3 Soil test P analysis

The amount of extractable P was determined by the Mehlich 1 (0.05 M HCl and 0.0125 H_2SO_4) extraction method as described by Nelson et al. (1953). Duplicate scoops of soil samples were weighed to facilitate volume to weight conversions. These samples were shaken for 5 minutes on a reciprocating shaker at 180 oscillations, centrifuged and filtered through Whatman no. 42 filter paper. Phosphorus in the filtrates was determined colorimetrically by the molybdate blue ascorbic acid reduction method as described by Murphy and Riley (1962). After color development, absorbance was measured with a Hitachi Model 100-20 spectrophotometer at 880 nm.

3-2.4 Phosphorus adsorption isotherms

Duplicate 3.0 g samples of each soil were equilibrated for 6 days in 100 ml centrifuge tubes with 50 ml of 0.01 M $CaCl_2$ solution and one of nine P concentrations ranging from 0 to 200 μg ml^{-1}. These nine concentrations were equivalent to 0, 1, 5, 10, 15, 25, 50, 100, and 200 μg P ml^{-1} of solution. The tubes were then capped and shaken twice a day for 5 minutes at room temperature (22° C). At the end of the equilibration period soil-solution mixtures were centrifuged at 2000 x g for 5 minutes, supernatant solutions were filtered through Whatman no. 42 filter paper, and P concentration in the filtrates were determined by the method of Murphy and Riley (1962). The concentration differences before and after shaking were assumed to represent the

Table 3-1. Series and Taxonomic Class of soils used in the study.

Soil (Horizon)	Physiographic Region	Taxonomic Class	Parent Material
Vance (A and B)	Piedmont	clayey, kaolinitic, thermic Typic Kanhapludults	Granite (Felsic igneous rock)
Elioak (A and B)	Piedmont	clayey, kaolinitic, mesic Typic Hapludults	Phyllites and mica Schist
Frederick (A and B)	Coastal Plain	clayey, mixed, mesic Typic Paleudults	Limestone (Sedimentary rock)
Kempsville (A and B)	Coastal Plain	fine-loamy, siliceous, thermic Typic Hapludults	Loamy Fluviomarine Sediments
Myatt (A and B)	Coastal Plain	fine-loamy, siliceous, thermic Typic Ochraquults	Loamy Fluviomarine Sediments
Emporia (mine tailings)	Coastal Plain	fine-loamy, siliceous, thermic Typic Udorthents	Loamy Fluviomarine Sediments
Starr (mixed horizons)	Piedmont	fine-loamy, mixed thermic Fluventic Dystrochrepts	Diabase (Mafic igneous rock)

Table 3-2. Selected soil characteristics bearing on P adsorption by the soil under study.

Soil	pH	CEC	Exch. Al	DCB extractable		OM	Clay
				Fe$_2$O$_3$	Al$_2$O$_3$		
		Cmol kg^{-1}	mg kg^{-1}	----------------------%---------------------			
Surface horizons							
Elioak	5.12	8.89	3.7	1.6	0.4	3.4	17.9
Frederick	5.92	8.00	5.1	1.4	0.4	3.1	10.0
Kempsville	5.32	3.32	3.8	0.9	0.4	1.7	7.0
Myatt	5.17	5.00	4.1	0.5	0.4	3.6	12.0
Vance	6.52	6.97	4.3	0.8	0.3	3.0	14.5
Subsoil horizons							
Elioak	4.86	10.36	3.6	6.5	1.4	0.9	57.2
Frederick	5.22	19.00	3.8	3.1	0.7	0.6	43.5
Kempsville	4.86	5.64	3.9	3.5	0.9	0.6	59.7
Myatt	5.42	7.00	3.7	0.8	0.3	0.4	22.0
Vance	5.17	14.08	3.9	4.2	1.1	0.7	32.0
Mixed horizons							
Starr	5.39	-	4.4	17.2	1.3	2.1	40.0
Mine tailings	4.96	5.26	4.6	3.4	0.7	<0.5	20.3

amount of P that had been sorbed by soils. Averages of duplicate P adsorption data were fitted to the standard Langmuir equation by the nonlinear regression analysis to determine the following sorption parameters:

$$\frac{x}{m} = \frac{V_m bc}{1+bc}$$

3.6

or by the two surfaces model

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

3.7

where; x/m is the quantity of P adsorbed per unit of soil (μg P g soil^{-1}),

b is a constant related to the adsorption energy, and

Vm is the maximum of the monolayer adsorption (μg P g soil^{-1}).

Total adsorption maximum for the two sites model is $Vm_1 + Vm_2$ where the subscripts represent discrete energy sites. The tangential buffer capacity (TCB) was calculated as suggested by Keramidas and Polyzpoulos (1983), i.e., C was substituted for derivative of x/m in the following equation:

$$TCB(C) = \frac{Vm_1 b_1}{(1+b_1 C)^2} + \frac{Vm_2 b_2}{(1+b_2 C)^2}$$

3.8

where Vm_1, Vm_2, b_1 and b_2 were estimated parameters.

3-2.5 Statistic Analysis

Isotherm lines were obtained by nonlinear regression analysis through fitting average P adsorption data to the Langmuir equations. The residual sum of square values of the monolayer

and the two site models were calculated and compared to select the best fit of the observed sorption. Therefore, after selected soils with high adsorption capacity were used for the next study to improve the plant availability of P by poultry litter and compost application. Soil physicochemical properties were correlated with adsorption maxima for the soils. For the nine observations used, r values of 0.67 are significant at the 0.05 probability level and of 0.79 are significant at the 0.01 probability level for these correlations (Gomez and Gomez, 1983).

3-3 RESULTS AND DISCUSSION

3-3.1 P Adsorption Characteristics

The variability in P adsorption (Table 3.3) between surface and subsurface as well as on mixed horizons soil was expected since the soils had wide differences in their physicochemical properties (Table 3.2). These soils have relatively high P sorption capacities as compared with ultisols and oxisols described by Sanchez and Uehara (1980). Phosphate adsorption isotherms constructed with the curvilinear form of the standard Langmuir equation (eq. 3.6) are showed in Figures 3.1, 3.2, and 3.3 for the soils under study.

The isotherms for P adsorption show typical Langmuir characteristics as classified by Sposito (1984), where the amount of P adsorbed increases with the equilibrium solution concentration toward a maximum level of adsorption. These isotherms exhibit a steep and rapid initial phase at low concentration followed by a slower phase at high concentration. Such changes at low concentration have been attributed to the existence of sites with widely different affinities for P adsorption (Munns and Fox, 1976; Parfitt et al. 1989), and the slower phase to a possible migration of sorbed P into crystalline hydrous Fe oxides (Sanyal and De Datta, 1991).

Adsorption isotherm parameters for all the soil studied are shown in Table 3.3. The standard Langmuir equation was used to estimate an adsorption maximum indicative of soil capacity to fix P. The P adsorption maximum by soils varied from 301 to 1144 μg mL^{-1} for

Table 3-3. Phosphorus adsorption parameters as estimated by curvilinear Langmuir adsorption model.

| Soil	Adsorption maximum				Binding energy constant		
	One-site	Two sites			Langmuir	Two sites Langmuir	
		Vm_1	Vm_2	Total		b_1	b_2
	------------------$\mu g\ g^{-1}$-----------------						
Surface horizons							
Elioak	833	170.5	747.1	917.6	0.084	6.23	0.035
Frederick	487	48.5	438.6	487.1	0.068	0.07	0.060
Kempsville	301	19.5	284.9	304.4	0.176	1.27	0.140
Myatt	395	200.3	248.5	448.8	0.120	0.35	0.025
Vance	531	165.0	437.8	602.8	0.142	1.89	0.039
Subsoil horizons							
Elioak	1336	339.7	1070.5	1410.2	0.310	7.41	0.120
Frederick	507	253.0	266.5	519.5	0.300	0.61	0.129
Kempsville	813	381.9	588.5	970.4	0.480	3.40	0.040
Myatt	400	237.0	327.7	564.7	0.350	1.23	0.010
Vance	1144	317.0	1068.3	1385.3	0.080	4.47	0.020
Mixed horizons							
Mine tailings	878	393.5	715.3	1098.8	0.340	2.87	0.020
Starr	1491	79.4	1445.0	1525.4	0.110	1.12	0.090
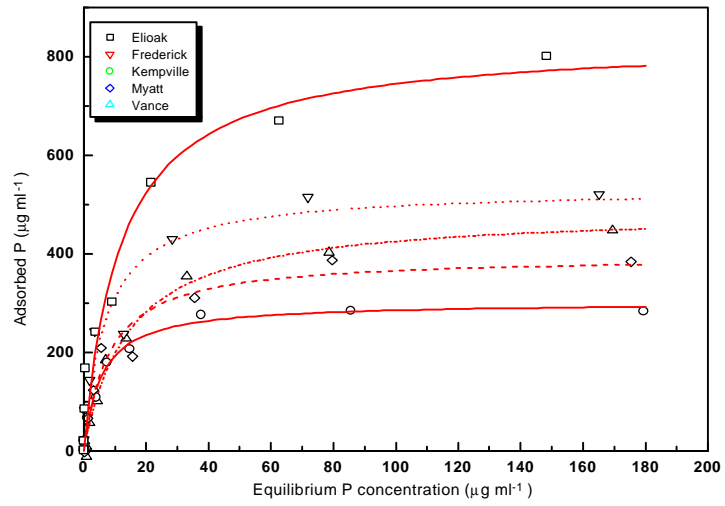
Fig. 3-1. Phosphorus adsorption isotherms for five surface soils.
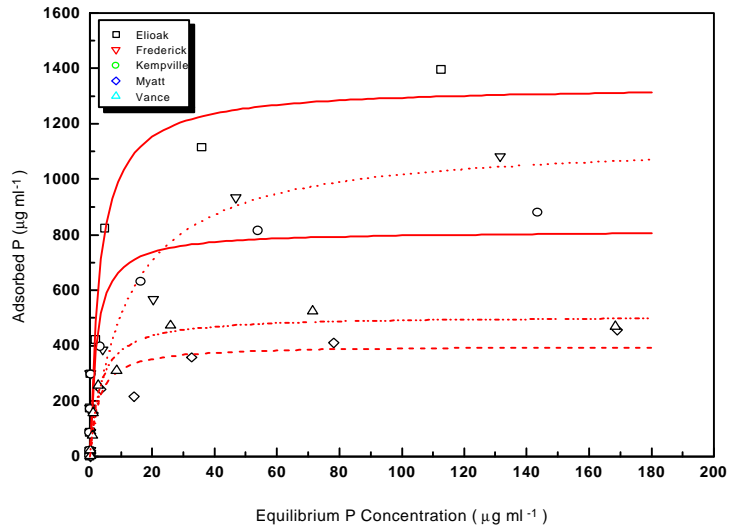

Fig. 3-2. Phosphorus adsorption isotherms for five subsoils.
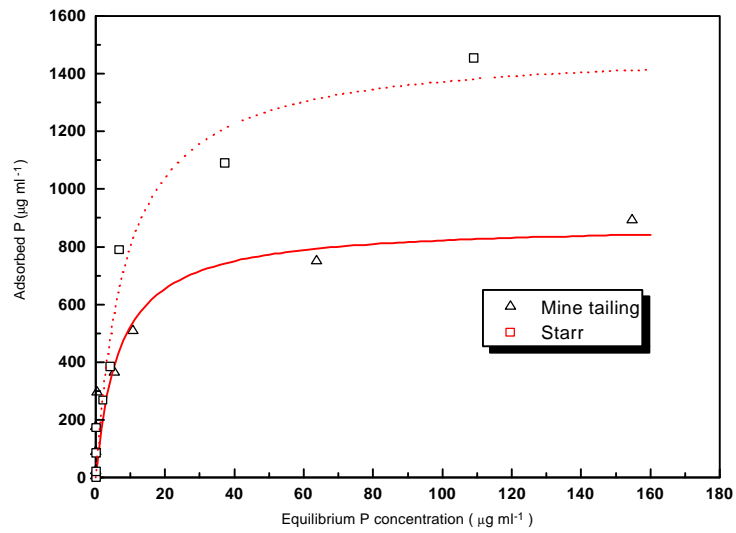
38

Fig. 3-3. Langmuir isotherm for phosphate adsorption by Starr and Mine tailing soils.
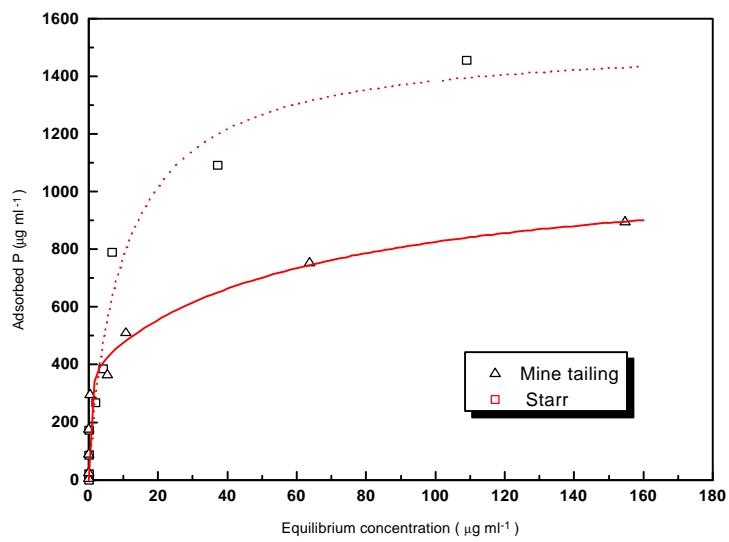

Fig. 3-4. Two site Langmuir isotherms for phosphate adsorption by Starr and Mine tailing soils.

A and B horizons. For the mix horizons, the P adsorption maximum is 878 μg mL^{-1} for the mine tailings and 1491 μg mL^{-1} for the Starr. The highest rate of P adsorption by surface soil was found for Elioak which had the highest Fe oxide and high Al oxide. By contrast, the lowest amounts of adsorbed P were observed for Kempsville and Myatt which contained relatively low amounts of Fe oxide. Among the subsurface soil sample Elioak, Starr, and Vance had the highest amount of P adsorption while Myatt and Frederick had the lowest. The lowest maximum adsorption value for Myatt soil is not a surprising result considering the low Fe_2O_3 and Al_2O_3 contents in this soil. The high adsorption maxima for the Elioak, Starr, and Vance soils may be due to high Al and Fe oxides, and also to high clay content which offer an increase in surface area for phosphate adsorption (Fox and Kamprath, 1970; Woodruff and Kamprath, 1965).

The bonding energy like the adsorption maxima tended to increase with soil depth (Table 3.3). However binding energies appear poorly related to the adsorption maximum. Mubiru and Karathanasis (1994) suggested that the binding energy can be better related to the amount of adsorbed P rather than P adsorption maximum. Since the initial rapid phase of P adsorption results from the reaction of P with Al and Fe oxides, the larger portion of the binding energy can be attributed to the sites associated with Al and Fe oxides (Agbenin, 1995). Furthermore, the lower binding energy occurred when the reactive site is saturated with native P (Agbenin, 1994). Consequently, there is a better fit for the P adsorption at a low energy.

Experimental data were fitted to the two-sites Langmuir equation (Fig 3.4, 3.5, and 3.6). Isotherms for all soils show the same behavior for the two-sites and the monolayer Langmuir models, i.e, slope changes occur at high phosphate ion concentrations. The differences between these two models are difficult to detect graphically. Nevertheless, the considerable improvement in goodness of fit of two-site over one site model is shown by a comparison of their residual sums of squares (Table 3.4). Overall the magnitude of error in the two-site model is relatively small but is consistent as compared with the one site model. The better fit of a two-site Langmuir model as compared with the monolayer model may be attributed to multilayer P adsorption rather than monolayer adsorption (Syers et al. 1973; Ram et al., 1987; Mehadi and Taylor, 1988; Kuo 1988).
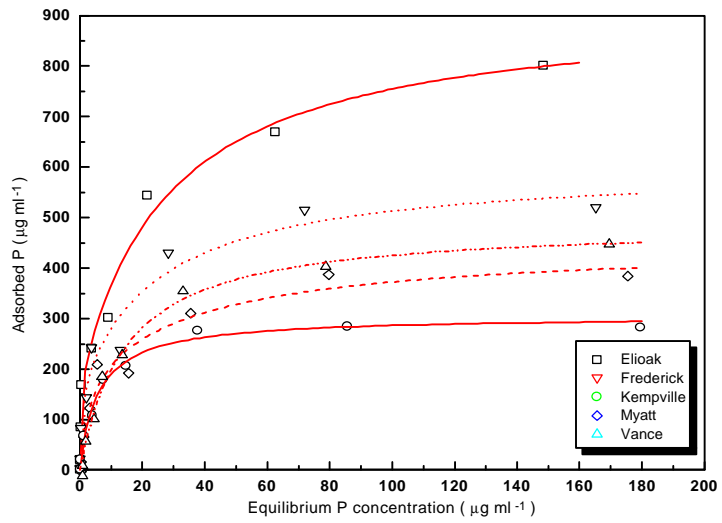
Fig. 3-5. Two site Langmuir isotherms for phosphorus adsorption by five surfaces soils.
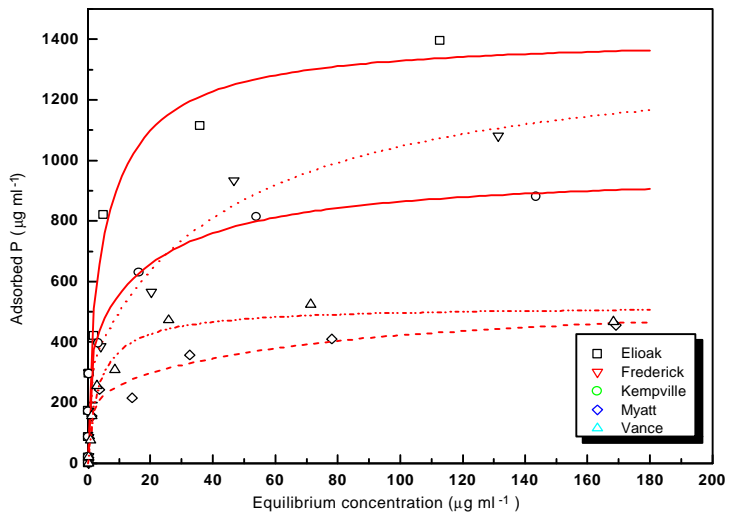

Fig. 3-6. Two site Langmuir isotherms for phosphorus adsorption by five subsoils.

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Table 3-4. Residual sums of squares of one site and two sites Langmuir.

Soil samples	Residual sums of square x 10^2	
	Langmuir - one site	Two sites Langmuir
Soil Surfaces (A)		
Elioak	333.6	78.2
Frederick	31.1	38.8
Kempsville	12.6	10.7
Myatt	84.2	60.4
Vance	213.8	112.3
Subsoils (B)		
Elioak	1012.5	526.4
Frederick	83.6	77.7
Kempsville	673.4	140.8
Myatt	225.4	94.5
Vance	1417.8	515.3
Mixed horizons		
Mine tailings	1679.3	537.8
Starr	1237.4	1157.2

The b_1 and b_2 represent the free binding energy constant of the two sites Langmuir model. Their values vary considerably within each soil group (Table 3.3). The b_1 coefficient contributes more for the adsorption of P at the initial phase of adsorption and the b_2 which is a low energy consuming process, accounts for the slower P adsorption phase.

3-3.2 Soil Properties Affecting P Adsorption

Phosphorus adsorption maxima have been correlated with various physical, chemical, and mineralogical properties (Fox and Kamprath, 1970; Syers et al., 1973; Loganathan et al., 1987). A large range of P adsorption maxima were obtained on Starr, Vance, and Elioak soils which likewise contained high amount of clay (Table 3.3). The P adsorption maximum was highly correlated with the amount of clay in A horizon ($r^2 = 0.82$), but weakly correlated with clay in B horizons ($r^2 = 0.42$). These results agree with those of Fox and Kamprath (1970), Syers et al. (1973), and Loganathan et al. (1973), but disagree with the results of Ayodele and Agboela (1983) who did not find a relationship between P adsorption maximum and clay content. Saunders (1965) reported on intercorrelation within the adsorption parameters, and suggested that the clay contribution to P adsorption could be through its coating with extractable components such as Al and Fe oxides. These coatings are characterized by a large surface area for P fixation (Sanyal and De Datta, 1991).

Dithionite citrate bicarbonate extractable Fe and Al data are presented as Fe_2O_3 and Al_2O_3 data for the seven soils studied are presented in Table 3.2. The DCB extractable Fe and Al contents in all the subsoils were more than double that in the surface soils, and correlated with the P adsorption in the subsoils ($r^2 = 0.70$, and 0.89, respectively). The coefficient of correlations of P adsorption maximum with soil surface are lower for both Al ($r^2 < 0.50$) and Fe ($r^2 = 0.51$). Extractable Al was also found highly correlated to the P adsorption in the B horizon soils, ($r^2 = 0.92$) but the r^2 value obtained in A horizon was much lower ($r^2 = 0.17$). This close relationship between extractable Al and P adsorption for B horizon soil agrees with the results of Juo and Fox (1977). Singh and Tabatabai (1977) found that Al oxides were more reactive with P

than equivalent amounts of Fe oxides, which together with the high Al_2O_3 content (Table 3.2) may partially explain the high P fixing capacity in the subsoils.

Because soil samples were taken from two different horizons, the organic matter amount and composition probably differs in the subsurface as compared to surface soils under the study. Some researchers found negative correlation between organic matter content and P adsorption (Saunders, 1965; Kafkafi et al., 1988), i.e, opposite to the lack of an affect in this study (r^2=0.06). Organic matter functions by either sorbing P or blocking the site associated with P sorption (Fox, 1981) which partially explains why the soil surfaces with a higher organic matter content had less P fixation than the subsoils in this study (Table 3.2). The mine tailings has a low organic matter content due to mixing of horizon during the mining process. Hence, there would be little negative interaction with organic matter that would decrease P adsorption in the mine tailings.

The surface and subsurface soils differed widely in organic matter, oxides, and layer silicate contents (Table 3.2). Soil pH interacts with organic matter, oxides, and layer silicates to change P adsorption. The wide variation in contents of soil components would mask pH effects on P adsorption and would cause a low correlation between pH and P adsorption as occurred in this study.

3-3.3 Phosphorus requirement

The use of P adsorption curves for P fertilization that leads to optimum plant growth has been reported by Juo and Fox (1977), Fox and Kamprath (1970), and Roy and De Datta (1985). A value of 0.2 mg P kg^{-1} in soil solution was suggested by Berkwith (1964) for normal growth of a wide range of crops . The average values of P sorbed to maintain a soil solution concentration of 0.2 mg P kg^{-1} are given on Table 3.5 for the soils under study. The surface horizons required relatively small amounts of P to attain 0.2 mg P kg^{-1} in the equilibrium solution as compared with the subsoils and mixed horizons soils. Previously described soils properties may have contributed to low the P sorption in some of the soils. The P requirement was relatively high for the Elioak,

Table 3-5. Phosphorus adsorbed by soils at 0.2 ppm and phosphorus requirement in each group of soil.

Soil	P adsorbed at 0.2 ppm	P requirements
	----------μg g^{-1}---------	--------kg ha^{-1}--------
Surfaces Soils		
Elioak	102.1	224.6
Frederick	7.1	15.6
Kempsville	19.8	43.6
Myatt	9.8	21.6
Vance	30.0	60.0
Subsoils		
Elioak	277.9	611.4
Frederick	28.3	62.3
Kempsville	151.5	333.3
Myatt	40.0	80.0
Vance	288.7	635.1
Mixed horizons		
Mine tailings	140.3	308.7
Starr	119.6	263.1

Kempsville, and Vance subsoils, and for the Starr and mine tailings. These soils contain relatively high amounts of clay and Al and Fe oxides and low amounts of organic matter, which leads to high P fixation capacity.

3-4 CONCLUSION

The results of this study indicate that the two sites Langmuir model provides a better fit for the P sorption on these soils than the single site Langmuir model. From the observed adsorption capacities, soils used in this experiment can be divided into three groups. First, soils with high P sorption capacities are soils developed in the Piedmont region. The adsorption maximum for Elioak was 917.6 μg P g^{-1} for the surface soil and, 1410.2 μg P g^{-1} for the subsoil and for Vance was 602.8 μg P g^{-1} for the surface horizon and 1385.3 μg P g^{-1} for the subsoil. The second group of soils developed in the Coastal Plain region had a low P adsorption maximum as compared with the first group of soil. Those are: Kempsville soil with P adsorption maximum of 304.4 and 970.4 μg P g^{-1} for surface and subsoil, Myatt soil with P adsorption maximum of 448.8 and 564.7 μg P g^{-1} for surface and subsoil, and Frederick soil with P adsorption maximum of 487.1 and 519.5 μg P g^{-1} for surface and subsoil, respectively. The third group of soils comprises mixed horizons soils, Starr and mine tailings with high adsorption maximum of 1525.4 and 1098.8 μg P g^{-1}, respectively. The difference in P adsorption capacities between these soils were more likely correlated to the soil physicochemical properties of each soil. Increased organic matter reduced P sorption, which suggests an increase P sorption capacity in highly eroded soils. This result was observed on mine tailing due to reduced organic matter and Al and Fe oxides in the surface horizon. Consequently application of an organic amendment high in soluble P or limestone would be expected to increase P availability in these soils.

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