Phosphorus Sorption Characteristics of Red Soils from Lampung, West- and Central Java

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ABSTRACT

Phosphorus Sorption Characteristics of Red Soils from Lampung, West- and Central Java (S.A. Siradz): Red soil is a common name used to identify any soil showing yellowish to reddish colour, these soils mainly occur in tropical and subtropical regions. The term is frequently used to convey an image of red, infertile, acid soils in the tropics and is associated with tropical and subtropical climates which are characterized by high temperature and humidity. Major soil constraints to crop production may include low pH, low available P and high P fixation capacity, toxicity due to Al and sometimes Mn and Fe, deficiencies of N, Ca, Mg, K, and micronutrients e.g. Mo, Zn and Cu, low CEC and low base saturation, and very low content of weatherable minerals. The aim of this study was to determine the phosphorus sorption characteristics of red soils from Lampung, West Java and Central Java. Soils were sampled at depth of 0-20 cm from minimally disturbed sites after discarding the uppermost few cm consisting of an accumulation of litter. The samples were air-dried, crushed using a ceramic mortar and pestle and then passed through a 0.5 mm stainless steel sieve. Measurements of P sorption were conducted by equilibrating 200 mg of air dry soil (<0.5 mm) in 20 mL 0.2 M KCl containing 0-30 µg PmL^{-1}. P concentrations in filtrate were determined by the molybdate blue method. Phosphorus sorption data for soils were fitted to simple Langmuir and Freundlich isotherm equations and both equations described the data equally well. Langmuir P sorption maximum (x_m) for soil ranged from 719-2747 µg Pg^{-1}, with median values of 1.825 µg Pg^{-1}. There were systematic decreases in the values of Langmuir sorption maximum (x_m) for soils from Lampung > West Java and Central Java. Values of pH(NaF), Al$_d$, and exchangeable Ca were most predictive of P sorption in these soils.

Keywords: Latosols, Langmuir isotherm, Oxisols, P sorption, red soils

INTRODUCTION

Red soils occupy about 29% of arable land in Indonesia and more than 80% of them are on flat to undulating areas where agricultural expansion is most favourable. A major problem of these soils for plant growth is severe to high deficiency of P. Severe deficiency of P and the low eficiency of P fertilization is generally attributed to fixation of P by iron and aluminium oxides *sensu lato.* The iron and aluminium oxides are capable of adsorbing much phosphate on a unit weight basis but are only minor constituents of the soils whereas alumino-silicate clay is a major constituent and may provide an important contribution to P sorption. Further it has been proposed that the mechanism for sorption was the same for the various clay minerals and there are two proposed sorption mechanisms: exchange of phosphate ions with the hydroxyl group linked to the gibbsite layer, and as exchangeable anions which counter a positive charge developed by the adsorption of protons. At low concentrations P was sorbed in accordance with the Langmuir adsorption isotherm for all exchange cations and clay minerals. Clay saturated with divalent ions sorbed more P than clay saturated with monovalent ions.

Because of similarities in the sorption isotherms for alumino-silicates and hydrous oxides, it may be concluded that the adsorption of P was similar for kaolin, gibbsite and pseudoboehmite, differing only in the number of adsorption sites. The adsorption and fixation of phosphate ions onto natural soil kaolin is not fully understood. Most studies on the adsorption of phosphate on kaolin have been carried out using

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macrocrystalline (>1μm) well ordered kaolins of geological origin with the main aim being to investigate mechanisms of adsorption. Little attempt has been made to determine the phosphate adsorption behaviour of soil kaolin and to relate this behaviour to other characteristics of the mineral. Soil kaolin may differ substantially in structure, morphology and composition from mineral kaolin. Similarly there has been little work on P sorption by micro-crystalline iron oxides removed from soil in contrast with the large number of experiments with synthetic iron and aluminium oxides (Dimirkou and Ioannou, 1998). Soil iron oxide commonly differ substantially from most synthetic iron oxides and may exhibit quite different P sorption behaviours. The aim of this study was to determine the phosphorus sorption characteristics of red soils from Lampung, West Java and Central Java, Indonesia.

MATERIALS AND METHODS

Soil sampling sites were on cleared and developed land but from minimally disturbed sites after discarding the uppermost few cm consisting of an accumulation of litter. The samples were air-dried, crushed using a ceramic mortar and pestle and then passed through a 0.5 mm stainless steel sieve. These samples were then divided into 3 parts, one part was used for particle size analysis and for collecting the clay fraction (< 2μm) for mineralogical analysis. One part was for general chemical analysis and P sorption study, and one part for a reserve. Detailed descriptions of soil analysis were presented elsewhere (Siradz, 2000). Some of basic soil properties such as pH, electrical conductivity (EC), and organic C (OC) may summarized in Table 1.

Measurements of P sorption were conducted by equilibrating 200 mg of air dry soil (<0.5 mm) in 20 mL 0.2 M KCl containing 0-30 μg PmL^{-1}, A few drops of toluene were added to the tubes to suppress microbial growth. The tubes were sealed with plastic caps and shaken longitudinally for 24 hours at approximately 25°C on a horizontal platform shaker.

After shaking suspensions were centrifuged at 2000 rpm for 15 minutes and the supernatant was filtered through Whatman No 5 filter paper. P concentrations in filtrate were determined by the molybdate blue method.

Sorption studies always face the need to define synthetic parameters that can be used to make quantitative comparisons between soils. The reaction between phosphate and soils in particular has been described mathematically by several adsorption isotherm equations i.e. Langmuir equation (Bolster and Hornberger, 2007; Jiao *et al.*, 2007; Jiao *et al.*, 2008), Freundlich equation (Zhang and Selim, 2007; Bolster and Hornberger, 2007; Jiao *et al.*, 2008), Temkin equation (Anghinoni *et al.*, 1996; Ioannou *et al.*, 1998), and Elovich equation (Dimirkou and Ioannou, 1998) Among these equations the Langmuir and Freundlich equations are the most frequently used to describe the relationship between equilibrium P added and P sorbed by soils and their constituents. Sorption parameters derived from these equations may predict the maximum sorption capacity (x_m) and abundance of adsorption sites (k) for the soils are therefore useful in analysing soil fertility and other management parameters.

The P sorption isotherm data for the soil samples were fitted to the linear form of Langmuir and Freundlich equations, which can be written:

The Langmuir Equation:

$$x = \frac{(ax_m c)}{(1+ac)} \quad ....\text{Equation 1}$$

where: c = concentration of P in equilibrium solution (μg PmL^{-1}), x = amount of P sorbed (μg Pg^{-1} soil), x_m = sorption maximum (μg Pg^{-1} soil), a = coefficient related to bonding energy

Transformation to linear form gives:

$$\frac{c}{x} = \frac{1}{ax_m} + \frac{c}{x_m} \quad ....\text{Equation 2}$$

Table 1. Range and median of pH, EC and OC of Indonesian red soils.

Sample Site	pH (H$_2$O) Range	Med	pH (CaCl$_2$) Range	Med	pH (NaF) Range	Med	EC, mS cm^{-1} Range	Med	OC, g kg^{-1} Range	Med
Lampung	3.83-5.06	4.16	3.83-4.89	4.04	8.16-9.24	8.85	0.06-0.33	0.12	2.6-22.6	7.7
W Java	3.75-5.46	4.36	3.65-5.39	4.24	8.26-9.40	8.93	0.10-0.53	0.22	4.7-27.6	10.5
C Java	4.08-5.48	4.67	4.07-5.44	4.56	8.57-9.13	8.82	0.08-0.54	0.28	5.6-22.4	14.4

A plot of c/x against *c* should give a straight line with slope $1/x_m$ and intercept $1/ax_m$. The major advantage of the Langmuir equation is that the adsorption maximum (x_m) can be calculated.

The Freundlich equation may be written:

$$x = k\ c^b \qquad ....\text{Equation 3}$$

where: x = amount of P sorbed, c = P concentration in equilibrium solution, k and b = constants, where, k is a measure or sorption surface and b relates to the energy of sorption

This equation implies that the energy of adsorption decreases exponentially with increasing saturation of the surface. The equation above can be written in linear form as:

$$\log x = \log k + b \log c \quad ....\text{Equation 4}$$

Plotting log *x* against log c should give a straight line of line with slope *b* and intercept log *k*.

RESULTS AND DISCUSSION

Characteristics of Phosphate Sorption Isotherms

To illustrate the results of this study, P in equilibrium solution has been plotted against P sorbed. All soil samples showed strong P sorption. The overall shapes of isotherm curve for each samples were remarkably similar despite the great differences in the amount of P sorbed at a particular P concentration in solution. Each isotherm was characterized by a large increase in the amount of P sorbed for equilibrium solution (concentration range of 0 to approximately 1.0 µg PmL^{-1}). The P sorbed in

this concentration range is generally attributed to chemisorption involving ligand exchange between phosphate and OH at the surface of soil particles (Bhatti *et al*., 1998). The P sorption isotherm presented correspond to 24 hrs of equilibriation but continuing sorption would have occurred for longer equilibriation times (Barrow *et al*., 1998). There is much evidence, most recently from Strauss *et al*. (1997), that the continuing slow reaction is caused by diffusion of ions from the surface of the adsorbing particle into its interior. Because of the high affinity and non linear sorption behavior of phosphate for reactive surfaces of metal (hydro)oxides, it is considered that phosphate diffusion always associated with sorption. The sorption mechanism is assumed to involve the formation of surface coating of metal phosphate at the expense of underlying metal(hydro)oxide and includes adsorption on the walls of the inner pores of porous particles or an intermediate situation (Lookman *et al*., 1994). Since phosphate ions are negatively charged, there is a semi permanent increase in negative charge and therefore a decrease in the electric potential of the reacting soil particle (Barrow *et al*., 1998).

Fitting adsorption data to the adsorption equations was carried out by plotting the data in the transformed linear forms of the adsorption equations. The goodness of fit was assessed by simple linear regression coefficients calculated for the linear transforms. Plotting the adsorption data of all soils in the linear form of the Langmuir and Freundlich equations resulted in similar and highly significant relationships between P in equilibrium solution and P sorbed by soil. Typical plots of the P sorption data for sample from
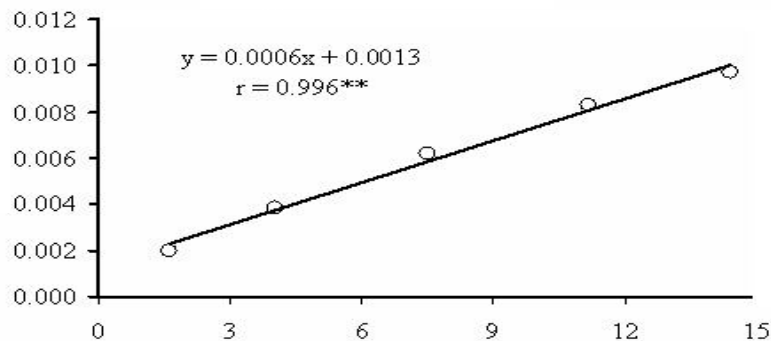

Figure 1. Typical curves for soil P adsorption plotted as Langmuir isotherms for sample A5 from Lampung.
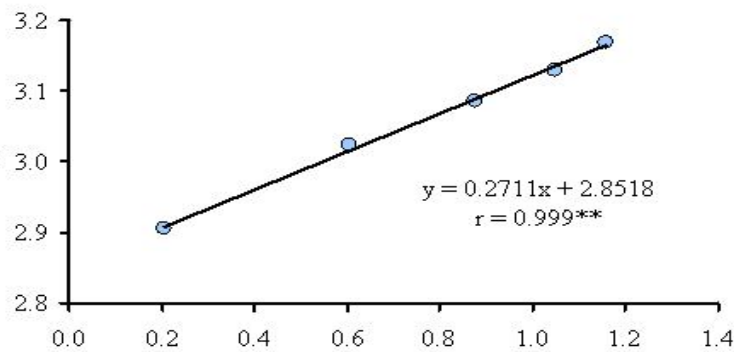
Figure 2. Typical curves for soil P adsorption plotted as Freundlich isotherms sample
A5 from Lampung

Lampung following Langmuir and Freundlich equations are presented in Figure 1 and Figure 2.

There are a wide range of values of the Langmuir maximum sorption capacity for soils. However, the sorption parameters were similar for soils from Lampung and West Java. For this group of soils the median value of sorption parameter x_m is about 2.000 µg Pg^{-1} soil. For soils from Central Java the value of x_m is about 1.500 µg Pg^{-1} soil. Similarly, the value of k derived from Freundlich equation which is indicative of the number of sorption sites was about 1.000 unit for soils from Lampung and West Java and about 500 unit for sample from Central Java (Table 2).

Table 2. Range, mean and median values of the Langmuir maximum sorption capacity (x_m) and sorption site energy constant (k) for soils.

Sampling Area		x_m (µg Pg^{-1})	k
All Sample	Range	719-2747	388-1569
	Mean	1871	955
	Median	1825	923
Lampung	Range	1451-2748	388-1569
	Mean	1968	1045
	Median	2023	1085
West Java	Range	1748-2710	752-1783
	Mean	2075	1099
	Median	2004	966
Central Java	Range	719-1960	422-1051
	Mean	1495	656
	Median	1503	549

Compared to some published data the present data for P sorption by Indonesian Red soils indicate moderate levels of P sorption. Fontes (1988) reported an average value of 4482 µg Pg^{-1} for x_m of Brazilian Oxisols derived from sandstone, clay stone, mafic rock and schist. On the other hand Syarif (1990) found the x_m value for Andosols from Indonesia was 4.510 µg Pg^{-1}. Clearly there is a large diversity of x_m values both within and between soil types (Table 3).

Phosphate Sorption and Soil Properties

The contents of iron and aluminium oxides/oxyhydroxides are often considered as a major causes of the high P retention capacity of tropical soils. Microcrystalline, poorly ordered oxide minerals may be present which would have a larger sorption capacity than well crystalline forms. Some workers proposed that amorphous Fe and Al compounds (determined as oxalate soluble Fe and Al) governed the sorption capacity of Red soils (Owusu-Bennoah *et al.*, 1997; Vanderhove *et al.*, 1998). In contrast with these authors, in this study it has been found that Al$_d$ (dithionite-citrate-bicarbonate soluble Al) was a superior indicator (r = +0.549**) (Figure 3) of P sorption capacity.

A strong correlation between Al$_d$ and P sorption by soil has been reported by several workers (Tsadilas *et al.*, 1996). Much of Al$_d$ may be present in Al substituted iron oxides (Siradz, 2000).

Fe$_d$ showed a positive relationship with x_m but the relationship is less significant than for Al$_d$. However, since there is a strong relationship between Al$_d$ and Fe$_d$ (Siradz, 2000) and the amounts of Fe$_d$ in

Table 3. A comparison of Langmuir maximum sorption capacity (x_m) for soils reported by other workers

| Soil	x_m, µg Pg^{-1}	References
Andosols, Indonesia	4510	Syarif, 1990
Oxisols, Brazil	4482	Fontes, 1988
Oxisols, Jonggol-Indonesia	3302	Prasetyo and Gilkes, 1994
Yellow Podzolic, Western Australia	2132	Singh and Gilkes, 1991
Red earth, Western Australia	1321	Singh and Gilkes, 1991
Calcareous soils, Morocco	808	Amrani *et al.*, 1999
Red yellow Latosols, Brazil	805	Pereira and Defaria, 1998
Present study	2000	
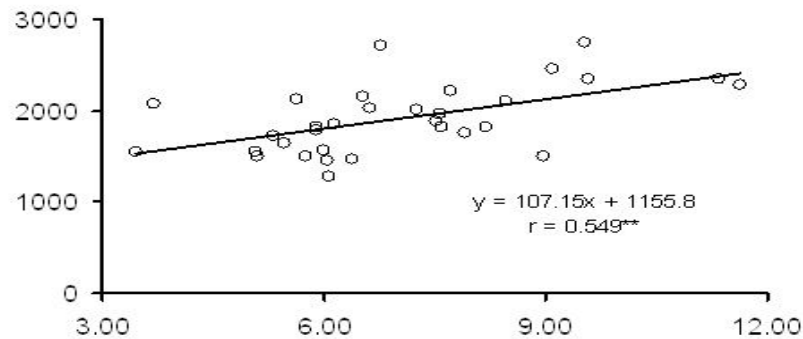
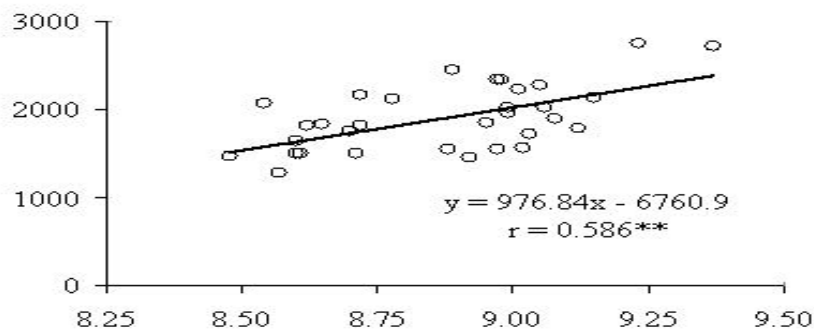Figure 3. Relationship of Langmuir sorption maximum (xm) with Al$_d$.

Figure 4. Relationship between x_m and pH(NaF)

soils are about 8-10 fold those of Al$_d$, Fe$_d$ may play a more important role in the overall P sorption by the Indonesian Red soil for present study. Positive relationship between P sorption and Fe$_d$ have been identified by many workers (Careira and Lajtha, 1997; Bonifacio and Barberis, 1999).

P sorption maximum (x_m)(Figure 4) and the sorption site coefficient (k) are positively and significantly correlated to pH (NaF). Gilkes and Hughes (1994) suggested that pH (NaF) would provide an accurate and convenient estimate of potential P sorption by soils since NaF solution releases surface

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hydroxyl from poorly ordered compounds which correspond to the oxalate soluble Al fraction. For this study a strong positive relationship exists between P sorption capacity and Al_d which is considered to be free Al in crystalline oxides in soil. This indicates that NaF solution released OH not only from poorly ordered but also from well ordered Al compounds.

Further results of this study indicates that there was a negative and much less significant relationship (r = -0.333*) exists between P sorption maximum and pH(CaCl$_2$). pH(CaCl$_2$) has been considered to be a measure of exchange acidity which measured Al^{3+} in addition to H^+. The negative relationship between x_m and pH shows that sorption decreases with increasing soil pH. This can be partly explained by the decrease in positive charge of hydroxy-surfaces with increasing pH, namely the disappearance of $-H_2O^+$ ligands that have very strong affinity for phosphate. The negative relationship between P sorption and pH is consistent with the findings of other workers (Ioannou *et al.*, 1994; Zhang *et al.*, 1996).

P sorption parameters x_m were also negatively and very strongly correlated with exchangeable Ca (r=-0.529**), base saturation (r=-0.702**) and electrical conductivity (EC)(r=-0.416*). However, these properties are not independent variables since there are strong interrelationships between BS, EC and exchangeable Ca (Siradz, 2000).

Organic C is known to affect P sorption in several ways, the net effects of which can be positive, negative or nil. The most positive effects have often been attributed to the inhibition of oxide crystallization by organic molecules, which contribute to an increase in the proportion of Fe_o and Al_o. At low pH, phosphate can be adsorbed by protonated amino-groups. Adverse effects of organic matter on P sorption are considered to be mostly due to the competition of organic anions with phosphate for adsorption sites (Afif *et al.*, 1995; Violante *et al.*, 1996).

In this study, the sorption parameter *k* is negatively related to organic C. In view of the mechanisms mentioned earlier, this observation suggests that the dominant effects of organic carbon in the soils is to provide organic compounds that compete with phosphate for sorption sites on mineral surfaces. A negative relationship between total organic C content and P sorption has also been reported by Ngachie (1996) and Silva *et al.* (1997).

In Table 1, it can be seen that median values of x_m of soils systematically decreased in the order Lampung > West Java > Central Java. This trend can be explained as a consequence of the negative relationships of x_m with soil pH, organic C, exchangeable Ca and base saturation, all of these soil properties follow the reverse order Lampung < West Java < Central Java.

CONCLUSIONS

The shapes of isotherm curve for each samples were remarkably similar despite the great differences in the amount of P sorbed at a particular P concentration in solution. Each isotherm was characterized by a large increase in the amount of P sorbed for equilibrium solution (concentration range of 0 to approximately 1.0 μg PmL^{-1}). The P sorbed in this concentration range is generally attributed to chemisorptions involving ligand exchange between phosphate and OH at the surface of soil particles

P sorption data for soils were fitted to simple Langmuir and Freundlich isotherm equations and both equations described the data equally well. Langmuir P sorption maximum (x_m) for soil ranged from 719-2747, with median values of 1.825 μg Pg^{-1}. The dimensionless Freundlich parameter k which is believed to indicate the abundance of sorption sites ranged from 388-1569. There were systematic decreases in the values of Langmuir sorption maximum (x_m) for soils from Lampung > West Java and Central Java. This trend is likely to be related to the inverse relationships of P sorption with pH and organic matter which is a consequence of climatic factors e.g. different rainfall in these sampling areas. Values of pH (NaF), Al_d, and exchangeable Ca were most predictive of P sorption in these soils. It has been long recognized that pH (NaF) is useful in predicting P sorption by Andept and lateritic soils of Western Australia (Gilkes and Hughes, 1994) but it appear its use may be extended to Red soils of Indonesia.

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