

## RELATIONSHIP BETWEEN EXCHANGEABLE ALUMINUM AND PHOSPHORUS SORPTION PARAMETERS OF INDONESIAN ACID SOILS

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### ABSTRACT

*In acid soils, phosphorus (P) sorption is generally attributed to hydrous oxides of Fe and Aluminum (Al) particularly in tropical soils with low pH. However, reports concerning the role of exchangeable Al in P sorption mechanism are very little. Phosphorus (P) sorption isotherms were studied in fifteen acid upland soils containing different amount of exchangeable Al. P sorption characteristics were satisfactorily described by the Langmuir equation, which was used to determine P sorption maxima and bonding energies, with r values ranging from 0.97 to 0.99. The soils varied widely in their capacities to sorb P. P sorption maxima ranged from 303 to 1429 mg kg<sup>-1</sup> (mean 627 mg kg<sup>-1</sup>) and bonding energies from 0.65 to 8.00 L mg<sup>-1</sup> (mean 2.39 L mg<sup>-1</sup>). Exchangeable Al was found not correlated with P sorption maxima (r = -0.11) but significantly correlated with P bonding energies (r = 0.68\*\*). This was clearly shown by clayey soils from Java and Sumatra but not in sandy soils from Kalimantan. The results suggested that in general, reaction of exchangeable Al with P increased P bonding energy but exchangeable Al was not the main component in P sorption maximum*

**Keywords :** Exchangeable Al, P bonding energy, P sorption maximum

### INTRODUCTION

In acid soils, hydrous oxides of Fe and Al are the main active components in P sorption particularly in tropical soils with low pH. The amount of hydrous oxides of Fe and Al increased P sorption maxima and bonding energy (Sanyal and De Datta, 1991). Other soil characteristics such as pH, clay content, organic matter, exchangeable cations, ionic strength, redox potential, temperature and surface area have been shown to influence P sorption by soils (Mokwunye, 1975; Juo and Fox, 1977; Agbenin and Tiessen, 1994).

Recent studies have revealed more detail information about the active components in P sorption. Dodor and Oya (2000) found that clay, organic matter, Fe<sub>p</sub> (organically bond Fe) and dithionite-citrate-bicarbonate (DCB)-extractable Al (Al<sub>d</sub>) were the active component of P sorption maximum in soil from Okinawa, Japan. In less weathered soils, predictive variables for P sorption models are mostly oxalate-extractable Al and Fe (Al<sub>o</sub> and Fe<sub>o</sub>) (van der Zee and Riemsdijk, 1988; Borggaard *et al.*, 1990; Yuan and Lavkulich, 1994; Beauchemin and Simard, 2000). The overriding influence of Al<sub>o</sub> and Fe<sub>o</sub> on P sorption in less weathered soils has led to the proposition of the ratio of oxalate-extractable P (P<sub>ox</sub>) to Al<sub>o</sub> + Fe<sub>o</sub> as the P saturation index of soils in less weathered (van der Zee and Riemsdijk, 1988; Beauchemin and Simard, 2000; Pautler and Sims, 2000) and acidic soils in Ireland (Maguire *et al.*, 2001), suggesting that concentration of Al<sub>o</sub> and Fe<sub>o</sub> are good estimates of P sorption sites in those soils. Another recent study found that dithionite-citrate-bicarbonate-Al and Fe (Al<sub>d</sub> and Fe<sub>d</sub>) correlated well with P sorption maxima in savanna soils, but not with Al<sub>o</sub> and Fe<sub>o</sub> (Agbenin, 2003).

However, reports concerning the role of exchangeable Al in P sorption parameters are very little. Exchangeable Al was well known correlated with soil pH but its role in P sorption mechanism is not well understood. The objective of this study was to reveal the role of exchangeable Al in P sorption parameters.

### MATERIALS AND METHODS

**Soil samples.** Surface horizon from 15 acid upland soils from Sumatra, Java and Kalimantan were collected.

**Methods of soil analyses.** Soil samples were air-dried and crushed to pass through a 2-mm sieve. Selected chemical and physical properties were analysed. Soil pH was measured in a 1:1.5 (w/v) water solution using a pH-meter. Clay content was determined by the pipet method. Organic C in soil was measured with a NC analyzer (Sumigraph NC analyzer NC-800-13 N, Sumika Chem. Anal. Service). Available P was obtained by Bray-1 (Bray and Kurtz, 1945) with absorbance at 693 nm determined using a UV-VIS spectrophotometer (UV-1200, Shimadzu Corporation, Japan). Cation exchange capacity (CEC) was obtained by 1 M NH<sub>4</sub>OAc pH 7.0 extraction. Exchangeable Al was extracted with 1 M KCl.

Phosphorus sorption data were obtained using the procedure described by Fox and Kamprath (1970). Duplicate of 3 g soil samples (< 2 mm) from each of the 30 samples were equilibrated in 30 mL of 0.01 M CaCl<sub>2</sub> containing various P concentration (0 mg L<sup>-1</sup> – 100 mg L<sup>-1</sup>) as KH<sub>2</sub>PO<sub>4</sub> for 6 days at 25° C. Two drops of toluene were added to suppress microbial activity, and the suspension shaken for 30 minutes twice daily. At the end of the equilibrating period, the soil suspensions were centrifuged

and filtered. P in the supernatant solution was determined by the procedure of Murphy and Riley (1962). The amount of P sorbed by the soils was calculated as the difference between the amount of P added and the amount remaining in solution.

The P sorption data were fitted to the linear form of the Langmuir equation as described below to determine the maximum sorption capacity and bonding energy.

$$C/x/m = C/b + 1/Kb$$

Where, C = the equilibrium concentration of P in the soil solution; x/m = the quantity of P sorbed per unit mass of sorbent, b = P sorption maximum, K = a constant related to the bonding energy of sorption.

**Statistical analyses.** Simple correlation analyses were applied. SYSTAT 8.0 was used for the analyses (SPSS Inc., 1998).

## RESULTS AND DISCUSSION

### Soil Characteristics

Selected chemical and physical properties of the soils are given in Table 1. Soil pH ranged from 4.04 to 5.61. The clay content ranged from 14.8 to 88.6%. Sandy soils from Kalimantan mostly showed low clay contents (<40 %). Organic C ranged from 1.10 to 5.39%. Exchangeable Al ranged from not detectable (nd) to 23.1 cmol kg<sup>-1</sup>. The highest value of exchangeable Al was shown by the soil sample from Gajrug. Exchangeable Al of some soils from

Java (e.g. Karang Pandan and Pringsurat) and from Sumatra (e.g. PD 1, PD 2 and Kota Bumi) were not detectable. All soil samples from Kalimantan contained exchangeable Al. Available P (as measured by Bray-1) ranged from 0.90 to 47.9 mg kg<sup>-1</sup>. The values of Bray-1-P were relatively low except those from Teluk Dalam (Kalimantan). This is probably a consequence of low P fertilization levels, since most of the land is used for subsistence. CEC ranged from 5.74 to 40.3 cmol kg<sup>-1</sup>. The highest values of CEC were shown by soil samples from Gajrug. CEC seemed to increase with increasing amounts of clay. Soils from Kalimantan showed very low CEC values (mostly were below 5 cmol kg<sup>-1</sup>).

### Phosphorus Sorption Parameters

Langmuir P sorption maxima, bonding energies and r values for the Langmuir equation are presented in Table 2. The P sorption data were satisfactorily described by the Langmuir equation with correlation coefficients ranging from 0.97 to 0.99 even in high P concentration range. This agrees with the results reported by Dodor and Oya (2000) but not with those reported by Vo *et al.* (1996) and Henry and Smith (2002), who suggest the equation can simulate only in a limited range of equilibrium P concentration. The P sorption maxima varied among the soils, ranging from 303 to 1429 mg kg<sup>-1</sup> with a mean of 627 mg kg<sup>-1</sup> and standard deviation 324 mg kg<sup>-1</sup>. Bonding energies also varied ranging from 0.64 to 9.00 L mg<sup>-1</sup> with a mean of 2.82 L mg<sup>-1</sup> and standard deviation 2.39 L mg<sup>-1</sup>.

Table 1. Some Chemical and Physical Properties of the Soils Used

Location	Soil order *	Depth (cm)	pH H <sub>2</sub> O (1:1.5)	Organic C (%)	Clay	CEC (cmol kg <sup>-1</sup> )	Exch. Al (cmol kg <sup>-1</sup> )	Bray 1-P (mg kg <sup>-1</sup> )
<b>Java</b>								
Darmaga	Inceptisols	0-13	4.37	2.22	70.0	18.1	4.21	2.91
Gajrug	Ultisols	0-14	4.24	2.52	65.1	40.3	23.10	5.65
Tegal Garu	Ultisols	0-15	4.34	1.56	65.5	13.8	2.70	2.91
Karang Pandan	Alfisols	0-10	4.77	1.29	67.4	13.1	nd	3.30
Pringsurat	Alfisols	0-9	4.56	1.10	88.6	13.3	nd	0.90
<b>Sumatra</b>								
PD1	Ultisols	0-14	5.61	5.39	55.5	21.1	nd	1.19
PD 2	Ultisols	0-27	4.64	1.82	23.7	8.83	nd	7.18
Kota Bumi	Alfisols	0-20	4.34	1.70	36.7	7.57	nd	2.24
Rimbo Bujang	Ultisols	0-4	4.04	2.09	46.2	9.31	1.64	7.15
Sitiung	Ultisols	0-14	4.42	1.94	66.3	17.0	5.02	4.73
<b>Kalimantan</b>								
Sebuluh	Ultisols	0-9	4.12	1.08	28.7	12.2	3.01	9.22
Kota Bangun	Ultisols	0-4	4.51	1.36	14.8	5.7	1.21	12.30
SM-BP	Ultisols	0-11	4.60	1.73	16.1	6.7	1.22	10.30
SM 1	Ultisols	0-10	4.66	1.81	31.3	11.7	0.83	6.86
Teluk Dalam	Ultisols	0-9	4.37	0.95	30.0	8.8	1.62	47.90

\*Soil Survey Staff (1998); nd: not detectable

Table 2. Equilibrium Langmuir Sorption Maxima (b), Bonding Energies (K), and r Value at 25 °C

Location	Soil order	Depth	Sorption maximum (b)	Bonding energy (K)	r
		(cm)	(mg P kg <sup>-1</sup> )	(L mg <sup>-1</sup> )	
<b>Java</b>					
Darmaga	Inceptisols	0-13	526	6.33	0.99
Gajrug	Ultisols	0-14	625	8.00	0.98
Tegal Garu	Ultisols	0-15	557	3.60	0.98
Karang Pandan	Alfisols	0-10	1111	3.00	0.99
Pringsurat	Alfisols	0-9	1111	4.50	0.99
<b>Sumatra</b>					
PD1	Ultisols	0-14	1429	3.50	0.99
PD 2	Ultisols	0-27	435	1.64	0.99
Kota Bumi	Alfisols	0-20	526	1.19	0.97
Rimbo Bujang	Ultisols	0-4	417	0.86	0.99
Sitiung	Ultisols	0-14	588	5.67	0.99
<b>Kalimantan</b>					
Sebuluh	Ultisols	0-9	400	0.64	0.97
Kota Bangun	Ultisols	0-4	303	0.65	0.99
SM-BP	Ultisols	0-11	500	0.95	0.95
SM 1	Ultisols	0-10	455	0.92	0.99
Teluk Dalam	Ultisols	0-9	417	0.80	0.99
Mean			627	2.82	
SD			324	2.39	

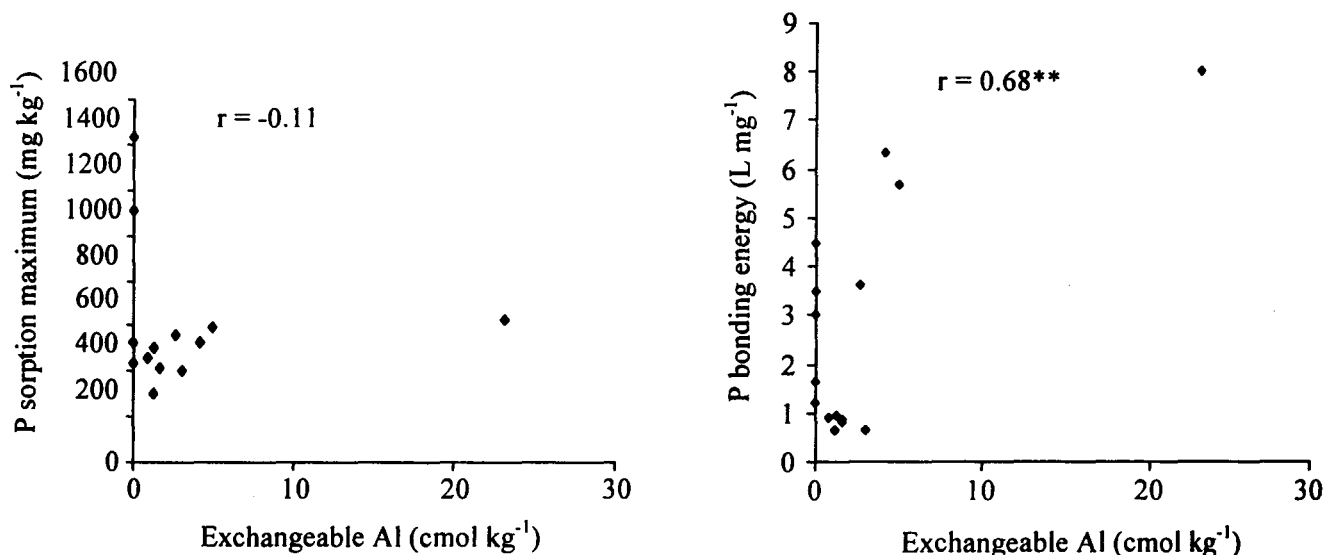


Figure 1. Correlation between Exchangeable Al and P Sorption Parameter

Some soils from Java and Sumatera (e.g. Karang Pandan, Pringsurat, Darmaga, Gajrug, Tegal Garu, Sitiung and PD1) exhibited higher sorption capacities (526 to 1429 mg kg<sup>-1</sup>) and higher bonding energies (3 to 8 L mg<sup>-1</sup>) in contrast to the soils from Kalimantan which have P sorption maxima ranging from 303 to 500 mg kg<sup>-1</sup> and bonding energies ranging from 0.64 to 0.95 L mg<sup>-1</sup>. Low P sorption

maxima and bonding energies were also found in soils from PD2, Kotabumi and Rimbo Bujang. These soils contain quartz and the clay content is similar to those from Kalimantan. In general, high sorption values are probably due to the high clay content of the soils which offer a large specific surface area for P sorption (Uehara and Gillman, 1981).

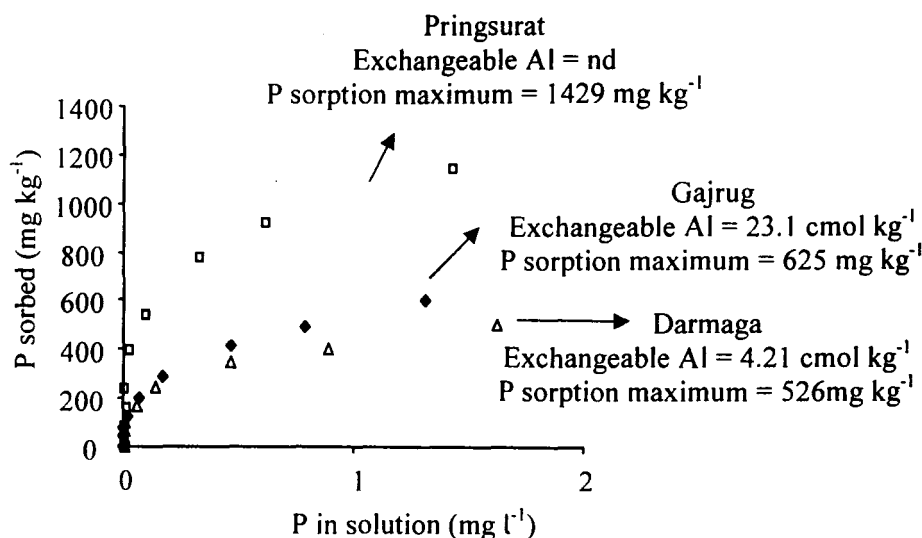


Figure 2. P Sorption Isotherm at 25°C of Soils with Different Level of Exchangeable Al

### Correlation between Exchangeable Al with P Sorption Parameter

Correlation between exchangeable Al with P sorption maxima and bonding energies is presented in Fig. 1. It is shown that exchangeable Al was not correlated with P sorption maxima ( $r=-0.11$ ) but significantly ( $P<0.01$ ) correlated with P bonding energies ( $r=0.68^{**}$ ). It means that there was no significant correlation between exchangeable Al and P sorption maxima despite it is being considered as active component of P sorption mechanisms (Iyamuremye *et al.*, 1996).

This finding agrees with Nanzyo *et al.* (1995) who reported that  $H_2PO_4^-$  is more reactive with Al-humus and ferrihydrite than with exchangeable Al. In addition, Nanzyo *et al.* (1995) observed that when  $10 \text{ mg P l}^{-1}$  of  $KH_2PO_4$  was added to soils, no significant correlation was obtained between the exchangeable Al contents and the decrease in phosphate sorption due to removal of exchangeable Al. Fig. 2 shows clearly that soil from Gajrug with very high exchangeable Al ( $23.1 \text{ cmol kg}^{-1}$ ) had much lower P sorption maximum than that of soil from Pringsurat with no exchangeable Al and comparable P sorption maximum with soil from Darmaga with lower exchangeable Al ( $4.21 \text{ cmol kg}^{-1}$ ).

Unlike in P sorption maxima, exchangeable Al was very significantly correlated with P bonding energies (Fig. 1). It means that exchangeable Al increases P bonding energy. This finding indicated that reaction between exchangeable Al and  $H_2PO_4^-$  (precipitation) will give high bonding energy. This phenomenon was clearly shown by clayey soils from Java and Sumatra (Table 1 and 2) where soils with high exchangeable Al showed high bonding energy. For example, soil from Gajrug with exchangeable Al  $23.14 \text{ cmol kg}^{-1}$  showed the highest value of bonding energy ( $8.00 \text{ L mg}^{-1}$ ). However this phenomenon was not performed by sandy soils from Kalimantan. This is probably because the clay content of these soils was very low (< 35 %). The clay content was significantly correlated with hydrous oxide of Fe and Al. Soils with high clay

content had high hydrous oxide of Fe and Al (Dodor and Oya, 2000). These sandy soils with low clay content resulted in low P sorption maxima and bonding energy, therefore the effect of exchangeable Al was not clearly shown by these sandy soils.

### CONCLUSIONS

The soils varied widely in their capacity to sorb P. The langmuir equation provided a good fit to P sorption data with r values ranged from 0.97 to 0.99 in soils studied. The P sorption maxima ranged from 303 to  $1429 \text{ mg kg}^{-1}$  with a mean of  $627 \text{ mg kg}^{-1}$  and standard deviation  $324 \text{ mg kg}^{-1}$ . Bonding energies also varied ranging from 0.64 to  $9.00 \text{ L mg}^{-1}$  with a mean of  $2.82 \text{ L mg}^{-1}$  and standard deviation  $2.39 \text{ L mg}^{-1}$ .

It was found that exchangeable Al was not correlated with P sorption maxima but significantly correlated with P bonding energies. It suggested that exchangeable Al was not the main component in P sorption maximum. Exchangeable Al increased P bonding energy when it precipitated P in the soil solution.

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