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Phosphate Sorption by Active Acid Sulfate Soils of Peninsular Malaysia

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Keywords: phosphate sorption, active acid sulfate, Langmuir II sorption model

ABSTRAK

Data jerapan fosfat daripada empat contoh tanah daripada dua siri tanah Semenanjung Malaysia (Siri Sedu dan Jawa; kedua-duanya Typic Sulfaquepts) telah dijelaskan mengikut model jerapan Langmuir II. Tanah Estet Lim Chin, Estet Raja Muda dan Kuala Linggi mewakili Siri Sedu, manakala tanah daripada Serkat mewakili Siri Jawa. Fosfat terjerap oleh empat tanah tadi berubah mengikut keperluan isoterma jerapan Langmuir II. r^2 bagi tanah Estet Lim Chin dan Raja Muda masing-masing bernilai 0.96 dan 0.95. Jerapan maksima fosfat dan keupayaan penampanan tanah sedu (Estate Lim Chin dan Raja Muda) melebihi daripada tanah Jawa (Serkat) dan tanah sedu (Kuala Linggi). Mengapur tanah sedu (Estet Raja Muda) dan tanah Jawa (Serkat) dengan kadar 1 t ha⁺ telah mengurangkan jerapan fosfat masing-masing sebanyak 3.1 dan 13.1%. Kadar pengapuran melebihi 2 t ha⁺ telah menaikkan keupayaan jerapan P tanah tersebut.

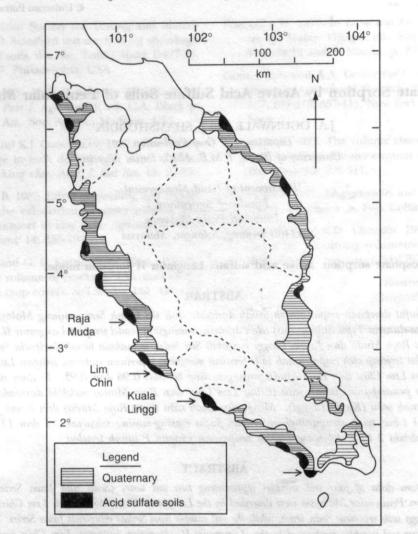
ABSTRACT

Phosphate sorption data of four soil samples representing two soil series (Sedu and Jawa Series; both Typic Sulfaquepts) from Peninsular Malaysia were described by the Langmuir II sorption model. Lim Chin, Raja Muda and Kuala Linggi soils represent Sedu series, while the soil sample from Serkat represents Jawa Series. The phosphate sorbed by the four soil samples conformed to the Langmuir II adsorption isotherm. Lim Chin and Raja Muda estate soils have r^2 values of 0.98 and 0.99, respectively, while Serkat and Kuala Linggi soils have r^2 values of 0.96 and 0.95, respectively. Phosphate adsorption maxima and buffercapacities were higher in the Sedu soils (Lim Chin and Raja Muda Estate) than in Jawa (Serkat) and the Sedu soil (Kuala Linggi). Liming of the Sedu Soil (Raja Muda Estate) and Jawa soil (Serkat) at 1 t ha¹ reduced phosphate sorbed by 3.1 and 13.1 percent, respectively. Rates greater than 2 t ha¹ of lime increased the P sorptive capacities of the soils.

INTRODUCTION

Acid soils of the hot humid tropics generally have small amounts of phosphate available to plants and correspondingly high capacities for phosphate (P) sorption (Weir 1977). Owen (1947) and Zaharah (1979) studied some Malaysian soils and found that they adsorbed different amounts of phosphate from solution. Ahmad (1982) used three adsorption models for P sorption by seven soils from Peninsular Malaysia, whose pH values ranged from 4.0 to 5.0. Ahmad (1982) reported that the Temkin model was useful for soils with high P adsorption capacities while the Freundlich model fits soils with intermediate sorption and langmuir model fits soils with low P adsorption capacity.

Earlier reports on phosphate sorption by the soils of Peninsular Malaysia (Ahmad 1982; Owen 1947; Zaharah 1979) gave limited information on acid sulfate soils. Acid sulfate soils occupy about 110,000 ha of Peninsular Malaysia (*Fig. 1*). These soils are characterized by low pH (< 3.5) and very high extractable aluminium (Al).



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Fig I. A map of Peninsular Malaysia showing Quaternary deposits and areas where acid sulfate soils are located

The acidity known with acid sulfate soils is due to biological ripening of tidal-marsh soils, and it is not similar to that which results from chemical weathering of rocks in tropical environment. These soils have distinct yellowish jarosite (Kfe₃(SO₄)₂(oh)₆ mottles occurring in either A or B horizon (Auxtero et al. 1991; Carson and Dixon 1983; van Breemen and Harmsen 1975). The presence of pyrite (FeS2) in the soils is common (Poon 1977; Poon and Bloomfield 1977), and it tends to sustain the low pH in the soils (Dent 1986). The liming of acid sulfate soils in Peninsular Malaysia for oil palm production has been reported by Chew et al. (1984). Reports on the effects of liming on the values of P sorbed by soils are variable (Amarasiri and Olsen 1973; Reeve and Sumner 1970; Woodruff and Kamprath 1965). Haynes (1982) and Barrow (1984) showed that variable experimental conditions (lime incubation period, type of background solution, amount of desorbable P in the soil and the pH over which P sorption was measured) account for different results for the effect of liming on P sorption by soils. The source of P salt used for equilibration and the ionic strength of the adsorbate solution (Barrow 1972; Manikandan and Sastry 1984; Naidu *et al.* 1990) affect P sorption by soils.

Acid sulfate soils are not only strongly acidic, a condition that is highly conducive to phosphate sorption, but also contain pyrite which may influence their phosphate sorptive capacities. This paper reports phosphate sorption by two acid sulfate soil series, collected from four different locations, in Peninsular Malaysia as affected by soil chemical properties and lime.

MATERIALS AND METHODS

Surface samples of Sedu and Jawa soils (both Typic Sulfaquepts) were collected from Lim Chin Estate (Sedu series), Raja Muda Estate (Sedu Series), Serkat (Jawa Series) and Kuala Linggi (Sedu Series) (*Fig. 1*). The soil samples were air-dried for 7 d, ground and passed through a 2 mm sieve. Subsamples of each soil were finely ground to pass through 60 mesh sieve and stored for phosphate sorption studies and determinations of iron, aluminium, organic carbon and total phosphorus.

Soil Characterization

Particle-size distribution was determined by the pipette method (Gee and Bauder 1986). Soil extractable acidity was displaced by 1 M KCl by shaking for 1 h and allowing to equilibrate for 12 h. Acidity in the extract was determined titrimetrically with 0.01 M NaOH. Free Al and Fe oxides in the soil were extracted by the dithionite - citrate - bicarbonate (DCB) method (McKeague and Day 1966). A 10 ml aliquot of the DCB extract was digested with 5 ml M HCl and diluted to 100 ml with distilled water. Iron in the digest was analysed colorimetrically by the o-phenanthroline method at a wavelength of 508 nm, and Al by the xylenol orange colorimetric method at a wavelength of 550 nm (Hesse 1971). Short-range order (noncrystalline) Al and Fe in the soils were extracted with acid ammonium oxalate in darkness (McKeague and Day 1966). The extract was digested with 30 percent hydrogen peroxide and nitric acid. Aluminium and Fe in the digest were analysed colorimetrically as above. Pyrite was determined in the soils by the method of Haering et al. (1989). Soil pH was determined in water at a soil: solution ratio of Total phosphorus was determined in 1:1. perchloric acid digest of the 60 mesh - sieved soil (Hesse 1971). Available phosphorus was extracted with Bray - 1 extractant. Both total and available phosphorus were determined with the Murphy and Riley (1962) method at a wavelength of 882 nm.

Phosphate Sorption Studies

Equilibrium of Non-treated Soils with Phosphate and Adsorbate Solutions

A 1 g soil sample was weighed into each of nine 50 ml capacity vials and 10 ml of 0.04 M KCl was added. Eight tubes received 10 ml, of 5, 10, 15, 20, 22, 25, 28 and 30 ug P g⁻¹ as KH₂PO₄, respectively and these were duplicated. The ninth tube received 10 ml of distilled water and served as control. Two drops of toluene were added to each vial after the pH had been controlled at pH 4.0 with drops of 0.2 M KOH or 0.2 M HCl. Preliminary work indicated that after the second pH adjustment, the soil was well buffered.

The vial was covered with tight screw cap. This gave a soil : adsorbate solution ratio of 1 : 20 and adsorbate solution range of 0 - 15 ug P ml The above adsorbate solution range was used for the soil collected from Kuala Linggi alone. The soil from Serkat (Jawa Series), Lim Chin and Raja Muda Estates (Sedu Series), were treated with adsorbate solution ranges of 0 - 30, 0 - 60 and 0 - 90 ug P ml⁻¹, respectively, with the pH of each equilibration solution adjusted to 4.0 as described above. The ranges were determined by a preliminary stuidy that indicated high P sorptions by these three soils (not shown here). The vials were agitated on an orbital shaker for 1 h at 150 RPM during the first day. Shaking for 30 minutes each day continued for the next five days. The samples were filtered through Whatman No. 42 filter paper during the seventh day and the filtrate analysed for P.

Pre-treatment of Soils before Equilibration with P

The four soil samples were pretreated for the removal of sulfate-S, pyrite-S, aluminium and iron. Sulfate-S was removed by the method outlined by Hearing *et al.* (1989). Exchangeable Al was removed by 1 M KCl solution at a ratio of soil: electrolyte of 1 : 5 and shaking time of 1 minute. Short-range order (non-crystalline) Al and Fe were removed by the acid ammonium oxalate extraction in the dark and shaking time of 4 h (McKeague and Day 1966). Crystalline Al and Fe were removed with dithionite-citrate - bicarbonate (DCB) method of McKeague and Day (1966).

The pretreated soil was washed once with distilled water for sulfate-S and pyrite-S removal, and with 1 M NaCl for oxalate and DCB

treatments. The soils were oven-dried at 30°C for 6 d after pretreatment, ground and sieved to pass through a 60 mesh sieve.

The pretreated Kuala Linggi, Serkat, Lim Chin and Raja Muda Estates soil samples were equilibrated with 10, 20, 50, and 50 ug P g¹, respectively in 0.02 M KCl at pH 4.0 to control the ionic strength. Shaking and filtration were performed as previously described.

Effect of Lime Rates on P Sorption

Twenty g each of Raja Muda Estate and Serkat soil samples were weighed into 100 mL beakers. Five beakers were used for each soil, and into the beakers were weighed 0, 0.005, 0.01, 0.015 and 0.2 g of Ca (OH), respectively, representing 0, 1, 2, 3 and 4 t lime ha¹. Twenty ml of water was added to each beaker and the content stirred vigorously by hand and continuously by mechanical shaker for 1 h. Intermitent stirring continued for another 1 h. The soil samples were allowed to evaporate on a water bath at 300°C for 5 d. The soil samples were then incubated for 42 d at 300°C. The samples were allowed to air-dry for 6 d after incubation, crushed gently and sieved to pass through a 60 mesh sieve. Subsamples of the limed soils and control were used for P equilibration studies as above.

Phosphate Desorbed by 1 M NH₄Cl

Two g each of Raja Muda Estate and Serkat soils were weighed, in duplicates into 50 ml capacity plastic centrifuge tubes. The soils were equilibrated with 15, 20, 25 and 30 tubes were centrifuged at 2500 RPM for 15 minutes and the supernatant decanted. The soil cake was allowed to air dry overnight. The phosphate retained by the soil was extracted with 1 M NH₄Cl solution, using a ratio of 1 : 10 of soil: extractant and a shaking period of 5 minutes after first loosening the cake by use of Vortex Geine mixer. After centrifuging, the supernatant in each case was decanted and filtered through Whatman 42 paper for P determination.

Filtrates of the samples were analysed for phosphorus with the Murphy and Riley (1962) method at a wavelength of 882 nm. The difference between phosphorus added and that in the equilibrium solution was taken as the phosphate sorbed.

Phosphate Sorption Isotherms

The sorption model used for describing phosphate sorption by the two soil series is the

Langmuir II Isotherm. The equation representing the model is:

Langmuir II: c/q = c/Qm + 1/kQm (Bache and Williams, 1971)

Where q = the quantity of material sorbed by a unit weight of adsorbent (μ g P g⁻¹ soil) c = equilibrium concentration of phospate ion (μ g P ml⁻¹)

Qm = adsorption maximum

 $(\mu g P g^{1})$ and

K = constant which relates to sorption affinity in the equation.

Adsorption maximum was obtained directly by linear regression of P sorbed against P sorbed divided by equilibrium P. The intercept of the line with the ordinate gave a direct measure of adsorption maximum (Qm) for each of the soils with the background electrolyte. The buffering capacities of the soils for P were obtained from the slope of the plot of P sorbed against logarithm of equilibrium P (Arines and Sainz 1987).

RESULTS AND DISCUSSION

Physical and Chemical Properties of the Soils

The four acid sulfate soil samples used for the phosphate sorption study are clayey with clay content ranging from 292 to 705 g kg¹ (Table 1). The pH values are characteristically low, ranging from 3.30 to 4.07. Organic carbon and available phosphorus values are both low (< 1.3%), with least value recorded in the Serkat soil sample (< 0.5%). Total phosphorus values range from 150.3 to 650.3 to 650.8 mg P kg⁻¹. The oil palm at Lim Chin and Raja Muda Estates had received single super phosphate fertilizer treatments at the rates ranging between 160 and 200 kg ha¹ in the previous two years before the soils were sampled (Poon. 1994; personal communication). Oxalate Al values are higher than those of dithionite - citrate bicarbonate (DCB) in the four soils. DCB Fe values are higher than those for oxalate Fe. Total acidity values range from 10.4 to 27.9 cmolc kg¹, accounting for more than 90 percent of the effective cation exchange capacity in the four soil samples. Pyrite-S values ranged from low to fairly high with low values recorded in Kuala Linggi and Serkat soils and fairly high values in Lim Chin and Raja Muda Estates soils.

Soil Series	Silt	Clay g	C _{org}	Pyrite-S	рН	Total Acidity - cmolc kg ¹ ·	Total P	Avail.P	Fe _(ox) * mg	Fe(d)+	Al _(ox)	Al _(d)
Sedu (Lim Chin)	199	705	13.1	3.7	3.76	27.9	597.5	1.7	17309.8	25134.5	247.6	199.0
Sedu (Raja Muda)	302	474	10.9	9.3	4.07	10.4	650.8	1.4	49192.9	57801.7	335.0	125.6
Jawa (Serkat)	203	602	5.0	1.9	3.30	13.4	244.1	0.6	1666.4	33205.2	129.5	62.6
Sedu Kuala Linggi)	410	292	7.6	1.6	3.36	11.8	152.3	0.9	17332.8	37893.9	104.3	77.3
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TABLE 1 General characteristics of the acid sulfate soils used in the study

*ox = acid ammonium oxalate extract +d = dithionite-citrate extract

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Soil Series	Adsorption Maximum	Buffer Capacity	Adsorption Constants (k)*	r2 values
Sedu (Lim Chin)	36.3 (35.7)*	15.7	0.52	0.98
Sedu (Raja Muda)	62.8 (71.4)*	34.1	0.42	0.99
Jawa (Serkat)	13.4 (9.1)*	4.5	-0.70	0.96
Sedu Kuala Linggi)	6.6 (4.8)*	2.1	-1.79	0.95

	TABLE 2	
Phosphate adsorption parameters	for two acid sulfate soils of Peninsular Malays	ia

(*) Calculated values from Langmuir II isotherms

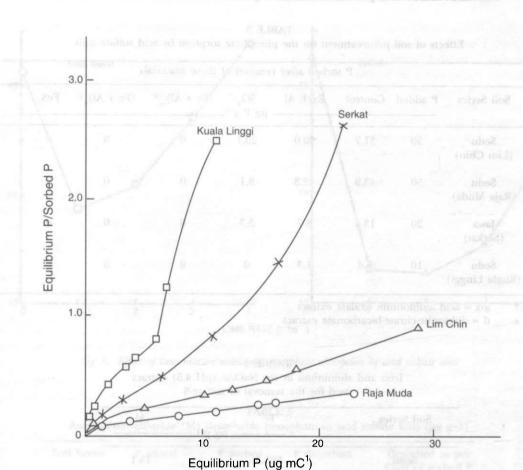
Sorption Isotherms and Adsorption Parameters

The four soil samples varied greatly in their ability to sorb added inorganic phosphate (Table 2). The phosphate sorbed by Lim Chin, Raja Muda Estate soils, Serkat and Kuala Linggi soils conformed to the Langmuir II adsorption isotherm (Fig. 2). The goodness of the Langmuir II model may be assessed by the r² values of the linear regression. Lim Chin and Raja Muda Estate soils both have r² values equal to or greater than 0.98 while Serkat and Kuala Linggi soils have r² values equal to or greater than 0.95 (Table 2). The parabolic relationships of the isotherms for the four soil samples gave r² values of 0.99 for Serkat and Kuala Linggi soils and 0.98 for Lim Chin and Raja Muda Estate soils. This observation is probably due to the fact that energy of adsorption of P by the four soils is not constant. Gunary (1970) suggested that linear relationships imply that the soil adsorbs only a given value of phosphate at monolayer coverage with a uniform bonding energy as exhibited by the Raja Muda Esatate soil (Fig. 2). Curved relationship, by contrast, imply that the soil adsorbs a small value of phosphate firmly and subsequently greater values with lower binding energy. The isotherms of Kuala Linggi, Serkat and Lim Chin are curved (Fig. 2). The curvatures in Langmuir II sorption isotherms could be adduced to the possibility of the migration of sorbed P to sub-surface layers of the adsorbent (Bache and Williams 1971).

The values of buffer capacity and adsorption maxima were higher in both Lim Chin and Raja

Muda Estate soils than in Serkat and Kuala Linggi soils (Table 2). Except for Raja Muda Estate soil, the values of observed adsorption maxima were greater than those calculated from the Langmuir II isotherm, with increases ranging from 1.7 to 47.2 percent. Adsorption maxima values in the Lim Chin and Raja Muda Estate soils were greater than those in both the Serkat and Kuala Linggi soils. This discrepancy could be explained by the higher values of short-range order Al in the former than in the latter two soils (Table 1). It is well established that cations like Fe and Al can hydrolyse to produce hydrous oxide polymers which function as anion exchanger and irreversibly sorb added phosphate (Wilson 1968). It is also known that short-range order hydrous metal oxides of Fe and Al sorb considerably greater values of P than their crystalline counterparts (McLaughlin et al. 1981; Bache 1964). Raja Muda soil had the highest value of buffer capacity followed by those of Lim Chin, Serkat and Kuala Linggi soils, respectively. The differences in the buffer capacity values are likely due to the differences in the total P contents of the soils with values ranging between 152.3 and 650.8 mg P kg¹ (Table 1).

The sorption energy (k) values calculated from the Langmuir II isotherms vary among the soils (Table 2). Although organic carbon value was the least in the Serkat soil among the four soil samples, this reason alone cannot account for the negative k values recorded for Serkat soil.



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Fig 2. Langmuir II sorption isotherms of active acid sulfate soils in Peninsular Malaysia

Effects of soil pre-treatment on P sorption

When exchangeable Al was removed, phosphate sorption was slightly reduced in Lim Chin and Raja Muda Estate soils (Table 3). The reduction in P sorption was more in the Serkat and Kuala I inggi soils with exchangeable Al removal. When sulfate-S was removed, P sorption decreased by 36.6, 81.5, 57.5 and 100 percent for Lim Chin, Raja Muda, Serkat and Kuala Linggi soils, respectively (Table 3). No P sorptions were observed in the four soils after the removal of oxalate Fe and Al, DCB Fe and Al, and pyrite-S (Table 3). The above observations re-affirm the importance of Fe and Al in enhancing the phosphate sorptive capacities of soils in which their oxides are present in large quantities (Wilson 1968; McLaughlin et al. 1981; Ryden et al. 1977; Bache 1964; Weir 1977). The removal of pyrite-S showed similar effects as the oxalate and DCB Fe and Al removal on P sorption by

the four soils. This shows that pyrite-S, to a certain extent, influenced phosphate sorption by these acid sulfate soils. The reduction in phosphate sorption by the soils as a result of sulfate-S removal could be due to the fact that the NaOAc solution used for sulfate-S removal also removed appreciable quantities of Fe and Al (Table 4).

Effects of Lime Rate on Phosphate Sorption

Lime application and incubation of the soils for 42 d gave slight increases in the pH of equilibrium solution. The pH of equilibrium solution of Raja Muda Estate soils were 3.28, 3.29, 3.32, 3.34 and 3.36 for 0, 1, 2, 3, and 4 t of lime, respectively. The pH values for equilibrium solutions of Serkat soil were 2.97, 2.98, 3.03, 3.09 and 3.25 for 0, 1, 2, 3 and 4 t of applied lime, respectively. One t lime ha¹ reduced phosphate sorption by 3.1 and 13.1

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Soil Series	P added	Control	Exch Al		$(Fe + Al)_{ox}^{*}$	$(\mathbf{F}\mathbf{e} + \mathbf{A}\mathbf{I})_{\mathbf{d}}$ +	FeS ₂
Sedu (Lim Chin)	50	31.7	30.0	20.1	0	0	0
Sedu (Raja Muda)	50	43.9	42.3	8.1	0	0	0
Jawa (Serkat)	20	13.4	8.7	5.7	0	0	0
Sedu Kuala Linggi)	10	6.4	1.3	0	0	0	-

E 3	TABLE
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Effects of soil pre-treatment on the phosphate sorption by acid sulfate soils

ox = acid ammonium oxalate extract

d = dithionite-citrate-bicarbonate extract

Soil Series	Fe	Al
A FRANK MARKE	μg g	-1
Sedu (Lim Chin)	503.5	15.1
Sedu (Raja Muda)	605.0	9.1
Jawa (Serkat)	708.7	9.6
Sedu Kuala Linggi)	526.8	5.0

TABLE 4

percent in Raja Muda Estate and Serkat soils, respectively. Phosphate sorption increased with increase in the lime rate, with 4 t lime ha¹ giving rise to 3.7 percent P-sorption. The situation with Serkat soils is slightly different, although followed similar pattern as in Raja Muda Estate soil, in that 2 t lime ha⁻¹ reduced the value of P sorbed by 0.37 percent compared with that sorbed by 1 t lime ha¹ (Fig. 3). The behaviour of these acid sulfate soils with regard to phosphate sorption as affected by liming showed that lime application beyond 2 t ha⁻¹ is not advisable. Increase in P sorption with lime rate

above 2 t ha1 could be attributed to the precipitation of phosphate, probably as insoluble Fe and Al phosphates. The pH of the equilibrium solutions were less than 5.5 to 6.0 believed to be the pH range at which Ca-P compounds could be formed as a result of lime application (Barrow et al. 1980). The effect of lime application at 1 t ha⁻¹ initially induced the displacement of Fe and al into solution and that this probably led to strong reactions of P with Fe and Al to form insoluble compounds. Further increases in lime rate above 1 t ha1 probably led to neutralization of Al3+ and hydroxy-Al as Al-

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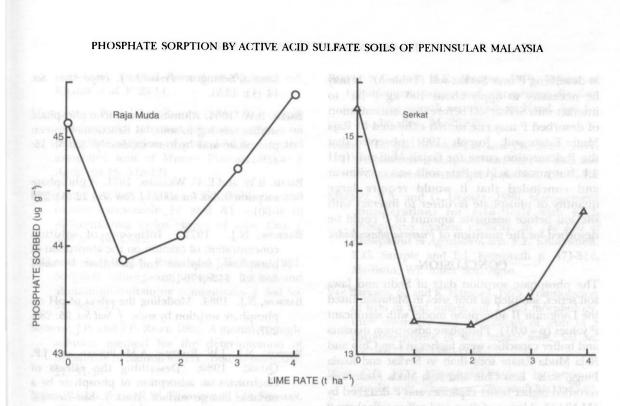


Fig 3. Effect of lime rate on maximum phosphate absorption by acid sulfate soils

Soil Series	P added	P sorbed	P desorbed	Desorbed as per Cent of sorbed H
	the provest	allon a		
Sedu	15	14.49	5.97	41.2
(Raja Muda)	20	14.55	7.80	53.6
	25	17.59	11.83	67.2
	30	27.02	12.48	46.2
Jawa	15	11.66	1.42	12.22
(Serkat)	20	13.43	1.81	13.5
	25	14.44	3.11	21.5
	30	8.13	3.89	47.8

TABLE 5Ammonium chloride (M) desorbable phosphate in acid sulfate soils (µg g-1)

hydroxide precipitates which led to the increase in the number of P sorption sites, thereby reflecting increases in maximum P sorbed (Sanchez and Uehara 1980 Fig. 3).

Phosphate Desorbed by M1NH4Cl

The percent P desorbed by 1 M NH4Cl increased with values of added P up to 25 μ g P g⁻¹ for the Raja Muda Estate soil, and then declined (Table 5). The percent P desorbed by 1M NH₄Cl increased with values of added P in Serkat soil (Table 5). Raja Muda Estate soil has received initial dressing with super phosphate, at the rates which ranged between 160 to 200 kg ha⁺ in the previous two years before sampling, whereas Serkat samples had not received such fertilizer application. It seems that the P desorbed is closely related to the initial quantity of total P present in the soil. The phosphate desorption data clearly showed the superiority of Raja Muda at desorbing P over Serkat soil (Table 5). It may be necessary to apply about 100 kg P ha⁻¹ to interact with Serkat soil before the concentration of desorbed P may rise to that exhibited by Raja Muda Estate soil. Joseph (1991) observed that the P desorption curve for Gajah Mati soil (pH 4.1, but not an acid sulfate soil) was curvilinear and concluded that it would require large quantity of phosphate fertilizer to interact with the soil before adequate amount of P could be desorbed for the nutrition of *Puereria phaseoloides*.

CONCLUSION

The phosphate sorption data of Sedu and Jawa soil series, sampled at four sites in Malaysia, fitted the Langmuir II adsorption model with significant r^2 values (p = 0.01). Phosphate adsorption maxima and buffer capacities were higher in Lim Chin and Raja Muda Estate soils than in Serkat and Kuala Linggi soils. Lim Chin and Raja Muda Estate soils recorded higher buffer capacities and P desorbed by 1M NH,Cl. Liming of these acid sulfate soils above 2 t hal increased their P sorptive capacities. The P sorptive characteristics of Kuala Linggi soil are different from those of Lim Chin and Raja Muda Estate soils because Kuala Linggi soil sorbs less P. The phosphate sorption parameters (adsorption maximum, buffer capacity and Langmuir II k) indicate that Kuala Linggi soil may not belong to Sedu series with Lim Chin and Raja Muda Estate soils.

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