

Changes in Solid Phase Properties of Acid Soils as Affected by Limestone, Gypsum, Palm Oil Mill Effluent and Rock Phosphate Applications

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ABSTRAK

Tanah Ultisol dan Oksisol di Malaysia, yang dicirikan oleh tinggi ketepuan Al, rendah KPK_B dan kekurangan dalam Ca dan/atau Mg, mengandungi kaolinit dan seskuioksida yang tinggi. Faktor ketidaksuburan tanah ini menghadkan pengeluaran tanaman. Satu kajian berpasu telah dijalankan untuk menentukan perubahan sifat kimia di dalam fasal pepejal untuk beberapa tanah Ultisol dan Oksisol di Malaysia yang diakibatkan oleh rawatan batu kapur, gipsum, efluen kilang kelapa sawit dan fosfat batuan. Keputusan kajian menunjukkan cas negatif di atas permukaan lempung tanah yang tidak dirawat bertambah dengan naiknya pH. Rawatan batu kapur, efluen kilang kelapa sawit dan fosfat batuan menaikkan pH, yang mengakibatkan bertambahnya KPK_B. KPK_B di dalam rawatan dengan efluen kilang kelapa sawit ditambahkan lagi oleh kenaikan kekuatan ionik di dalam larutan tanah dan oleh protonatan kumpulan karboksil dan/atau hidroksil di dalam bahan organik. Rawatan dengan efluen kilang kelapa sawit dan batu kapur menyebabkan Ca dan Mg bertukarganti bertambah, manakala Al bertukarganti berkurangan dengan bererti. K bertukarganti didapati berkurangan oleh rawatan gipsum dan batuan fosfat.

ABSTRACT

Ultisols and Oxisols in Malaysia are dominated by kaolinite and sesquioxides, which are characterized by high Al saturation, low ECEC and Ca and/or Mg deficiencies. These acid soil infertility factors are limiting to annual crop production on the soils. A pot experiment was conducted to investigate the chemical changes in solid phase properties of some Malaysian Ultisols and Oxisols affected by limestone, gypsum, palm oil mill effluent and rock phosphate applications. Results obtained showed that the negative charge on the clay surface of the untreated samples increased with an increase in soil pH. Limestone, palm oil mill effluent and rock phosphate applications increased soil pH, resulting in an increase in CEC_B. The CEC_B in the palm oil mill effluent treatment was further increased by an increase in the soil solution ionic strength and by the protonation of carboxyl and/or hydroxyl groups present in the organic matter. Exchangeable Ca and Mg increased, while exchangeable Al decreased significantly after palm oil mill effluent and limestone applications. It was observed that exchangeable K was reduced by gypsum and rock phosphate applications.

INTRODUCTION

Soils of the order Ultisols and Oxisols occupy about 72% of Malaysia (IBSRAM 1985). These soils are acid and highly weathered, with variable-charged minerals such as kaolinite, gibbsite and/or geothite dominating the clay fraction (Tessens and Shamshuddin 1982). The soils also have low cation exchange capacities (CEC), high Al satura-

tion and are deficient in Ca and/or Mg. These acid soil infertility factors are limiting to annual crop production. pH_o (pH at which the net charge on the variable minerals is zero) is affected by the application of soil amendments (Gillman and Sumner 1987). It is important to delineate ameliorants which can be used economically to reduce or remove these acid infertility factors, i.e. increase CEC and Ca and Mg availability and

decrease phytotoxic Al. Potential amendments available in Malaysia include limestone, rock phosphate, gypsum and palm oil mill effluent. Little is known of the ability of these materials to ameliorate acid soil infertility. The objective of this study was to assess the chemical changes in the solid phase properties of samples of some representative Ultisols and Oxisols from Peninsular Malaysia following application of various rates of limestone, gypsum, rock phosphate and palm oil mill effluent. Of particular concern were the changes in charge properties, pH, exchangeable bases and exchangeable Al of the soils.

MATERIALS AND METHODS

Soils

Five soil series which are very widespread in the upland areas of Peninsular Malaysia were selected for the study. The soils were Rengam (Kandiudult), Bungor (Paleudult), Munchong (Hapludox), Katong (Hapludox) and Prang series (Acrudox). Relevant chemical properties of the five soils are given in Table 1. Detailed mineralogy and charge properties of these soils have already been reported (Tessens and Shamshuddin 1982; Tessens and Shamshuddin 1983); major minerals in the clay fraction of the soils were kaolinite, gibbsite and/or goethite. Soil samples for the study were taken from the surface (0-15 cm) and subsoil (30-45 cm).

Experimental

Air-dried surface soils (0-15 cm, < 2 mm) from each of the Rengam, Bungor, Munchong, Katong and Prang series were mixed with ground magnesium limestone (henceforth referred to as GML), gypsum, palm oil mill effluent (henceforth re-

ferred to as POME) and rock phosphate as a precursor to a glasshouse trial to assess the response of maize to the various ameliorants. Results of the plant response will be the subject of a subsequent paper. The rates of application were 0, 0.5, 1.0, 2.0, 4.0 and 8.0 t/ha calculated on the basis of lime equivalent. The elemental composition of the GML, gypsum, POME and rock phosphate is given in Table 2. The pot trial involved equilibrating the ameliorants and basal nutrients (180 kg N/ha as urea, 150 kg P/ha as superphosphate and 75 kg K/ha as muriate of potash) for 30 days prior to the growth of maize for 30 days. After harvest, the soils in the pots were air-dried, well mixed and subsampled for laboratory analysis. Each of the four replicates was subsampled.

Soil Analysis

Some of the untreated soil samples were taken to the laboratory for determination of basic chemical properties (Table 1), where pH in water (1:2.5) and CaCl_2 (1:1) were determined after 1 h of intermittent shaking and standing overnight. Basic exchangeable cations were extracted by 1 M NH_4OAc buffered at pH 7; Ca and Mg were determined by atomic absorption spectrophotometry, while K and Na were determined by flame photometry. Al was extracted by 1 M KCl and determined colorimetrically (Barnhisel and Bertsch 1982). Free iron oxide was determined by the method of Mehra and Jackson (1960), while organic carbon was estimated by the Walkley-Black method (Nelson and Sommers 1982). Clay % was determined by the pipette method of Gee and Bauder (1982). ECEC was calculated as the sum of basic exchangeable Al.

TABLE 1
Relevant chemical properties of surface soils (0-15 cm) of
Rengam, Bungor, Munchong, Katong and Prang series.

Series	pH		Exchangeable Cations					ECEC	Al. Sat.	Fe_2O_3	Org. C	Clay
	H_2O	CaCl_2	Ca	Mg	K	Na	Al					
	(1:2.5)	(1:1)	cmol(+)/kg									
Rengam	4.97	4.39	1.05	0.20	0.18	0.03	2.68	4.14	65	1.2	2.13	41
Bungor	4.29	4.09	1.05	0.30	0.22	0.02	4.02	5.16	72	3.6	1.95	25
Munchong	4.68	4.12	0.26	0.17	0.09	0.02	1.76	2.30	77	5.0	1.27	81
Katong	4.87	4.20	0.17	0.17	0.12	0.05	1.32	1.83	72	8.0	2.50	87
Prang	4.39	3.90	0.03	0.05	0.05	0.02	1.58	1.73	91	9.1	1.16	81

TABLE 2
Elemental composition of GML, gypsum, POME and rock phosphate

Material	Elemental Composition							
	N	P	Ca	Mg	Fe	Mn	Cu	Zn
	%		mg/kg					
GML*	nd	1.7x10 ⁶	18.5	6.7	2119	97.3	16.6	29.5
Gypsum	nd	< 1x10 ⁷	25.1	tr	103	26.7	7.2	7.8
POME	1.3	0.44	2.7	1.8	1.2	tr	tr	tr
Rock phosphate	nd	7.29	37.2	0.3	2.0	tr	tr	tr

tr = trace (<0.1)
nd = not determined
* = GML contained 0.4% S

In addition to ECEC, the CEC for the surface and subsoil was determined by Ca adsorption (CEC_B) and by Ca and Al adsorption (CEC_T) as described by Gillman and Summer (1987). AEC was determined by Cl adsorption. On the basis of CEC_T and AEC, the soils were then classified according to the charge categories outlined by Gillman and Sinclair (1987). According to this system a soil is classified as type 2 if both CEC_T and AEC are low, and type 3 if CEC_T is low while AEC is high.

Extraction and Analysis of Soil Solution

The air-dried soils were rewetted to a matrix suction of 10 kPa and the solutions were extracted by centrifugation after 24 h of incubation (Menzies and Bell 1988). pH and electrical conductivity of the soil solution were immediately determined. Ionic strength was estimated from the electrical conductivity (Griffin and Jurinak 1973).

RESULTS AND DISCUSSION

Charge Properties

It was found, generally, that the B horizon of Ultisols had low negative and positive charge, while the highly weathered Oxisols (Acrudox) had low negative and high positive charge. Thus, the soils of Rengam, Bungor and Serdang series (classified as Ultisols) fitted well into the type 2 soil, and the Katong and Prang series soils (classified as Oxisols) fitted into the type 3 soils of the Gillman and Sinclair (1987) classification system. However, Munchong series soil, which is an Oxisol but less weathered than Prang and Katong series, did not fit into the type 3 soil. Instead it fitted into the type 2 soil.

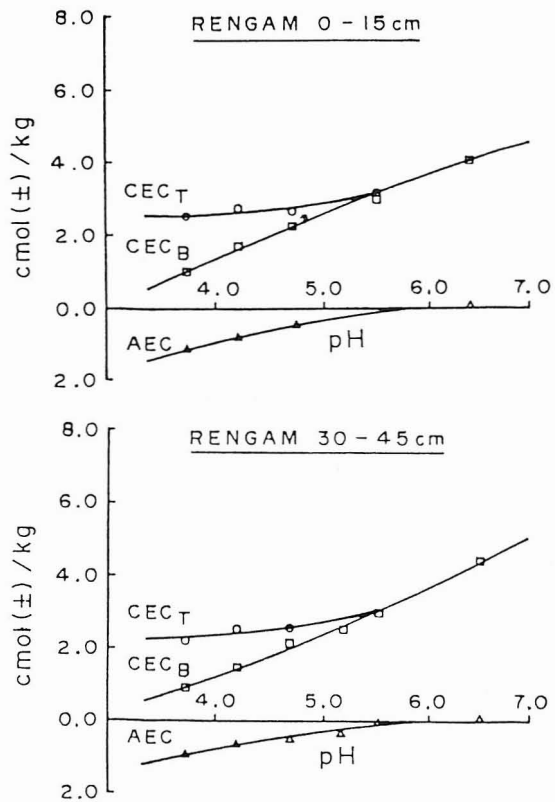


Fig. 1: Changes in CEC and AEC with increasing pH in the soil of Rengam series

Fig. 1 shows changes in charge properties (untreated samples) with a change in soil pH in the Rengam series soil. In this soil, where the clay fraction was found to be dominantly kaolinite, the negative charge was low at soil pH (4.39) (Table 1). CEC_B in the soil at pH of 4.0 was about 1.5 cmol(+)/kg, while CEC_T was 2.5 cmol(+)/kg.

When soil pH was raised from 4.0 to 5.5, CEC_B increased two-fold. At pH of 5.5, CEC_T equalled CEC_B and Al adsorption was zero. The charge properties of the subsoil were observed to be similar to those of the topsoil.

In the Munchong series soil (Fig. 2A), changes in charge properties (untreated samples) with changing pH were similar to those of Rengam series. In the Prang series, however, iron oxide was very high (Table 1), resulting in the presence of high amounts of positive charge (Tessens and Shamsuddin 1982). Although the amounts of iron oxides are high in the soil (Table 1), the positive charge was lower than the negative charge at pH of 4.0 (Fig. 2B). This is attributed to the

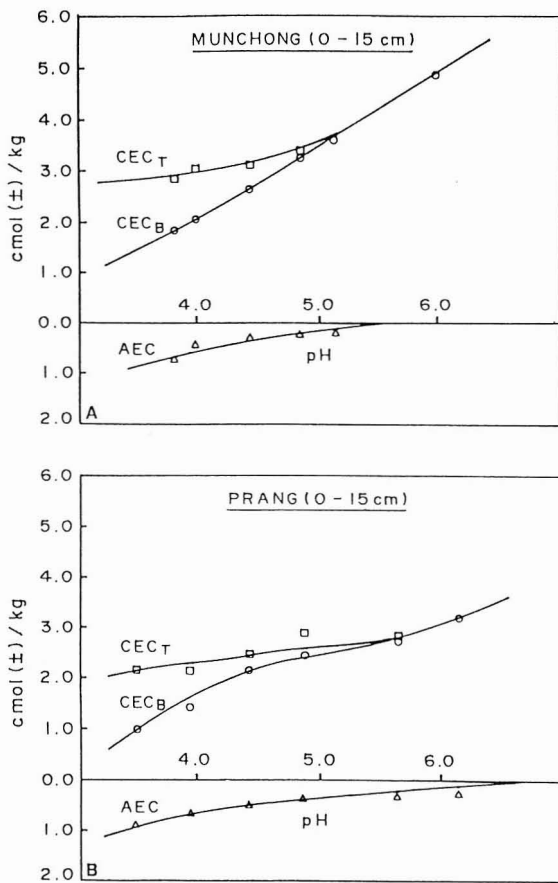


Fig 2: Changes in CEC and AEC with increasing pH in the Munchong (A) and Prang (B) series.

presence of organic matter in the Ap horizon. In the B horizon, however, the soil was reported to have net positive charge (Tessens and Shamsuddin 1982), and some of the positive charges were permanent in nature (Tessens and Zayyah 1982).

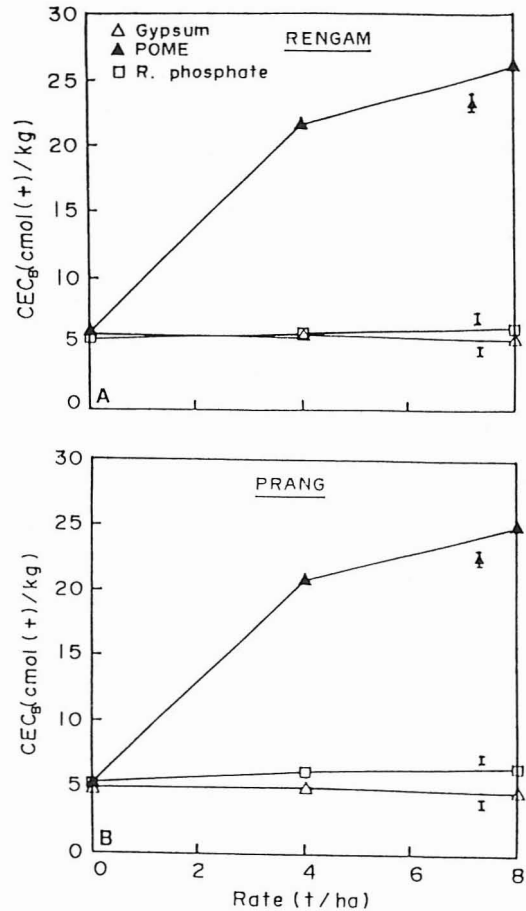


Fig 3: Effect of gypsum, POME and rock phosphate applications on CEC_B of Rengam and Prang series soils. LSD values are for $P < 0.05$.

The effects of POME, gypsum and rock phosphate applications on the CEC_B of the soils of Rengam and Prang series are depicted in Fig. 3. It was observed that POME increased CEC_B , while gypsum and rock phosphate did not have a significant effect on CEC_B . It will be shown later (Fig. 4) that POME increased pH, which then increased CEC_B as suggested in Fig. 2.

Soil pH

Effects of GML. Soil pH ($CaCl_2$) increased steadily with an increasing rate of GML application (Fig. 4) with a maximum pH of 6.3 being achieved at the highest rate of application (Prang series soil). In the Oxisols (Munchong and Prang), the highest pH values achieved were above 6.0, attributed

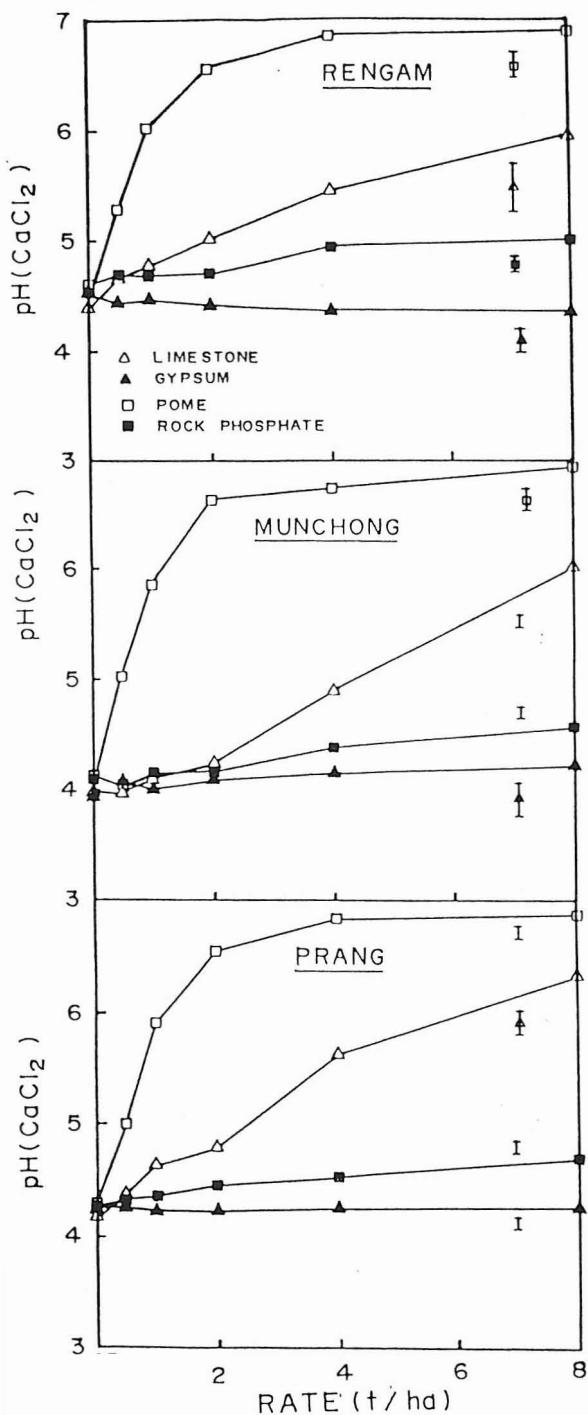


Fig 4: Effects of limestone, gypsum, POME and rock phosphate applications on soil pH (CaCl₂). LSD values are for P < 0.05.

to the lower amount of exchangeable Al values in the Oxisols (Table 1). The oxides which control the buffering action of the Oxisols (Shamshuddin 1989) are active only at high pH. As depicted clearly in Figs. 1 and 2, increasing the soil pH by

lime application resulted in an increase of negative charge in the soils. For instance, an increase in the soil pH from 4.4 to 5.0 increased CEC_B in the topsoil of Rengam series from 1.8 to 2.5 cmol(+)/kg (Fig. 1). Thus, liming increases Ca adsorption on to the soils with variable-charged minerals by an increase in CEC_B. This explains the retention of Ca in the zone of incorporation of limed soils (Pavan *et al.* 1984; Manrique 1987). The effects of GML on pH and CEC_B of Katong and Bungor series were similar to those of Prang and Rengam series, respectively (data not presented).

Effect of Gypsum. There was a drop in pH as a result of gypsum application, although the change was not significant (Fig. 4). There could also be a drop in pH_o due to specific adsorption of SO₄⁻² on the mineral surfaces (Mott 1981). Specific adsorption of SO₄⁻² on the mineral surfaces of the Oxisol can cause an increase in negative charge (Zhang *et al.* 1989; Marcano-Martinez and McBride 1989). A plot of CEC_B against rate of gypsum application (Fig. 3B) did not show any significant increase in CEC_B by an application of up to 8 t gypsum/ha.

There was an increase in the soil solution ionic strength as a result of gypsum application (data not presented). An increase in the ionic strength can also increase negative charge of the variable-charged minerals (Uehara and Gillman 1981). Again this is not manifested clearly in Fig. 3A, B, i.e. there was no significant effect.

Effects of POME. POME application at the rate of 0.5 t/ha increased soil pH from 4.3 to 5.0 in Prang series (Fig. 4) while in the Rengam series the corresponding pH increase was from 4.4 to 5.3. An increase in soil pH by POME application seen in Fig. 4 resulted in an increase of CEC_B. POME itself had provided some negative charges (Shamshuddin *et al.* 1987) and these additional charges were increased further by the protonation of carboxyl and/or hydroxyl groups in the POME when the soil pH was increased. POME application may result in a decrease of pH_o (Shamshuddin *et al.* 1987) which, in turn, increases negative charge (Uehara and Gillman 1981). Charge increases in the soil by these mechanisms were not significant. Fig. 3 shows that CEC_B increased five-fold by the application of 8 t POME/ha.

It was observed that POME application increased soil solution ionic strength (data not presented). An increase in soil strength also resulted in an increase of negative charge on the soil surface (Uehara and Gillman 1981). This explains the different observation with gypsum application.

Effects of Rock Phosphate. It was observed that the pH of the five soils treated with rock phosphate (8 t/ha) increased about 0.2 unit above that of the nil treatment (Fig. 4). However, the corresponding pH increase in the soil solution was much higher, about 1.5 units in the Prang and 0.5 unit in the Rengam series (data not presented). There could be a slight decrease of pH_o due to the specific adsorption of phosphate (Wann and Uehara 1978). An increase in the soil pH and a decrease in the pH_o resulted in an increase of negative charge on the mineral surfaces (Fig. 3). Naidu *et al.* (1990) reported that adsorption of P on the mineral surfaces reduced positive charge at low pH and increased negative charge at high pH.

Exchangeable Ca and Ca Saturation

The exchangeable Al was higher in the untreated Ultisols (Bungor, Rengam) than in the Oxisols (Munchong, Katong, Prang) (Table 1). The effects of GML, gypsum, POME and rock phosphate applications on these two soil types would then be different. Fig. 5 depicts changes in the exchangeable Al with increasing rates of GML, gypsum, POME and rock phosphate applications. There was a clear decrease in exchangeable Al in the GML and POME treatment as a result of an increase in the soil pH (Fig. 4). Exchangeable Al was reduced to a minimal level by an application of 0.5 t POME/ha. Exchangeable Al in the soil of the POME-treated samples was mostly precipitated as $Al(OH)_3$ when pH was increased above 5.5, while the rest of the Al could have been chelated by the organic matter. Oates and Kamprath (1983) reported that most of the Al chelated by organic matter could not be extracted by 1M KCl.

Exchangeable Al in the Ultisol (Rengam series) was not affected by gypsum application, but in the Oxisols (Munchong and Prang series) there was a significant drop in exchangeable Al with an increasing rate of gypsum application (Fig. 5). Exchangeable Al in Oxisols was replaced by Ca coming from dissolution of gypsum. Since pH did not change significantly after gypsum application (Fig. 4), Al could not be precipitated as $Al(OH)_3$, but may have precipitated as insoluble Al-hydroxy-sulfate minerals as suggested by Alva *et al.* (1988).

In the rock phosphate experiment, a drop in exchangeable Al can be partly accounted for by the precipitation of Al as $Al(OH)_3$ due to an increase in soil pH. Rock phosphate dissolved slowly, resulting in a slight increase in pH (Fig.4). The newly available P most probably reacted with the

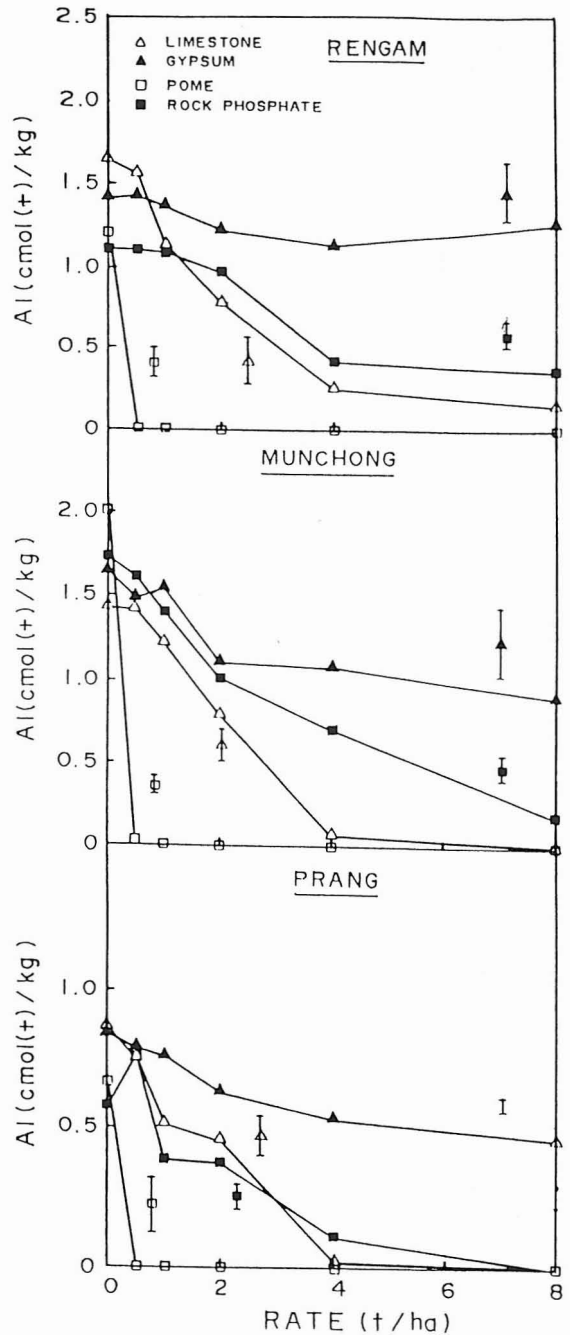


Fig 5: Effects of limestone, gypsum, POME and rock phosphate applications on exchangeable Al in Rengam, Munchong and Prang series soils. LSD values are for P < 0.05.

Al in the soil solution to form insoluble Al-phosphate, which further reduced exchangeable Al in the soil.

Aluminium saturation needs to be reduced to about 30% (Friesen *et al.* 1982; Tropsoils 1984). In order to lower Al saturation to this value 2 t GML/ha or 4 t rock phosphate/ha are needed

(data not shown). However, it needed only 0.5 t POME/ha to reduce Al saturation to this level.

Exchangeable Ca and Ca Saturation

Exchangeable Ca in the Oxisols was very low (Table 1), thus liming is necessary to increase Ca in these soils. Fig. 6 shows that there were steady increases in exchangeable Ca with increasing rate of GML or gypsum application. It was observed that more exchangeable Ca was found in the gypsum treatments than in the GML treatments in both Rengam and Munchong series, reflecting the greater solubility of gypsum as compared to limestone. However, this was not the case for the soil of Prang series, where exchangeable Ca was higher in the GML than in the gypsum treatment.

There was a significant increase in exchangeable Ca in the POME treatments of Rengam series (Fig. 6), reflecting the presence of high amounts of Ca in the POME (Table 2). Application of POME at the rate of 8 t/ha increased exchangeable Ca in the soil of Rengam series from 0.25 to 7.11 cmol(+)/kg. There were smaller increases in exchangeable Ca in the Oxisols (Munchong and Prang series) as compared to the Ultisol (Rengam).

Rock phosphate contains a high amount of Ca (Table 2), but it is not readily available due to low solubility. A period of time is needed before rock phosphate dissolves completely. It was observed that there was a significant increase in exchangeable Ca with an increasing rate of rock phosphate application (Fig. 6). The increase in exchangeable Ca was higher in the Munchong series than either Prang or Rengam series (Fig. 6) because of the lower soil solution pH in Munchong (data not shown) than in the Prang or Rengam series. Rock phosphate dissolves faster under more acid conditions.

Calcium saturation in the nil treatment of the soils of Rengam, Munchong and Prang series is > 10% (data not shown). In general, it needs 0.5 t GML/gypsum/POME/ha to raise Ca saturation to about 20%. In the case of rock phosphate, it needs about 2 t/ha to bring Ca saturation to this level. Calcium saturation of 11% is considered critical for soybean growth (Bruce *et al.* 1989).

Exchangeable Mg and Mg Saturation

Fig. 7 summarizes changes in exchangeable Mg resulting from application of GML and POME in the soils of Rengam and Prang series. GML application increased exchangeable Mg in the soils of Rengam and Prang series significantly. This in-

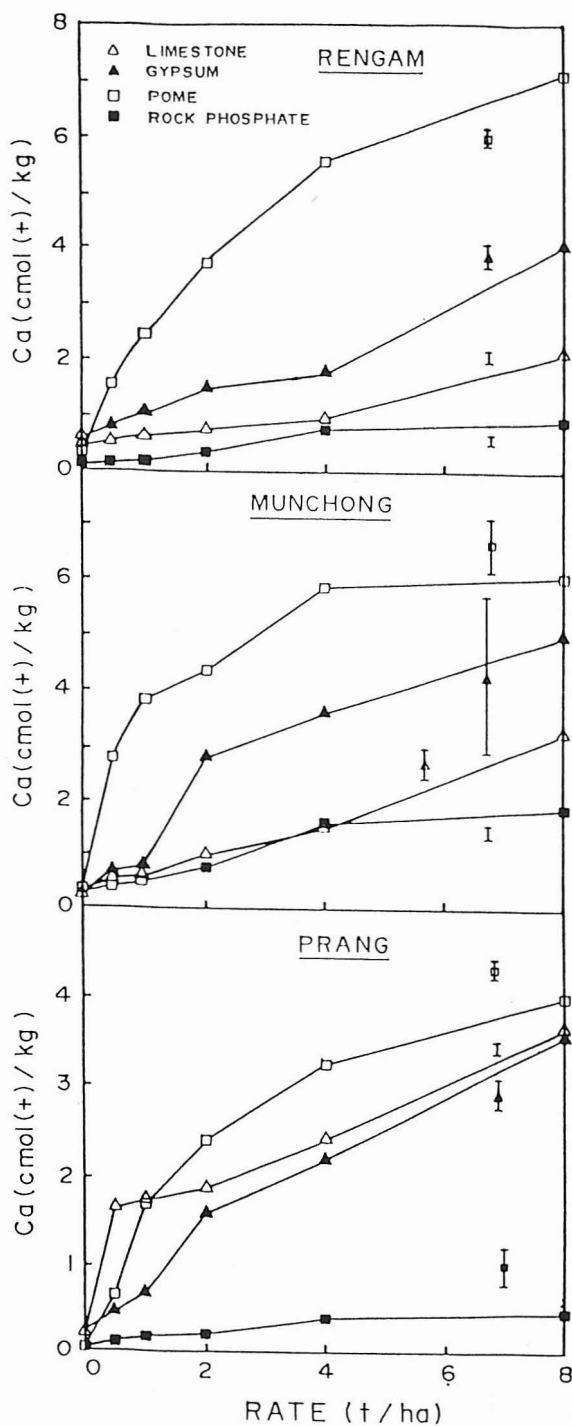


Fig 6: Effects of limestone, gypsum, POME and rock phosphate applications on exchangeable Ca in Rengam, Munchong and Prang series soils. LSD values are for P < 0.05.

crease would be expected to alleviate Mg deficiency in the highly weathered soils. An increase in exchangeable Mg was even higher in the soils treated with POME. This provides an indication of the ready availability of Mg when POME is incor-

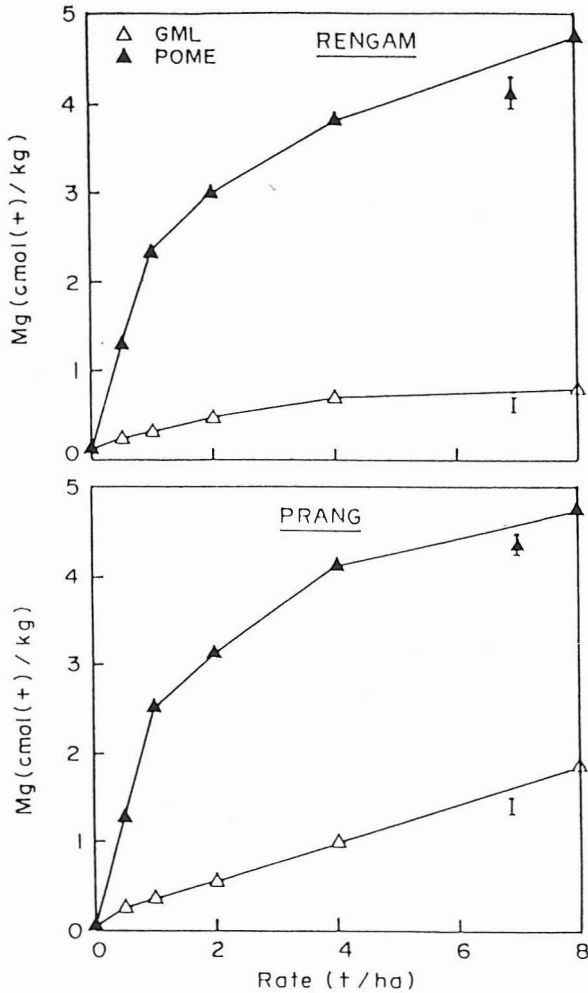


Fig 7: Effects of limestone and POME applications on exchangeable Mg in Rengam and Prang series soils. LSD values are for $P < 0.05$.

porated into the soils. For instance, application of 2 t POME/ha increased exchangeable Mg in Prang series from 0.05 to 4.6 cmol(+)/kg.

Gypsum and rock phosphate did not contain significant amounts of Mg (Table 2). Their applications had very little effect on exchangeable Mg (data not shown). In fact exchangeable Mg in these treatments was slightly reduced. This was due to the replacement of exchangeable Mg by Ca from the dissolution of the gypsum or rock phosphate.

Generally, crops need 10 - 15% Mg saturation (Eckert 1987). It was observed that liming the soils at 1 t/ha increased Mg saturation to > 10% (data not shown). POME contains a high concentration of Mg, hence, 0.5 t/ha is sufficient to raise Mg saturation > 10%.

Exchangeable K

A change in exchangeable K with increasing rates of GML, gypsum, POME and rock phosphate applications is depicted in Fig. 8. It is seen that there was a drop in exchangeable K in the soils treated with gypsum and rock phosphate in all the three soils. An increase in exchangeable Ca in the samples treated with gypsum and rock phosphate might have replaced exchangeable K on the exchange complex, resulting in a decrease in exchangeable K in the soil. GML and POME

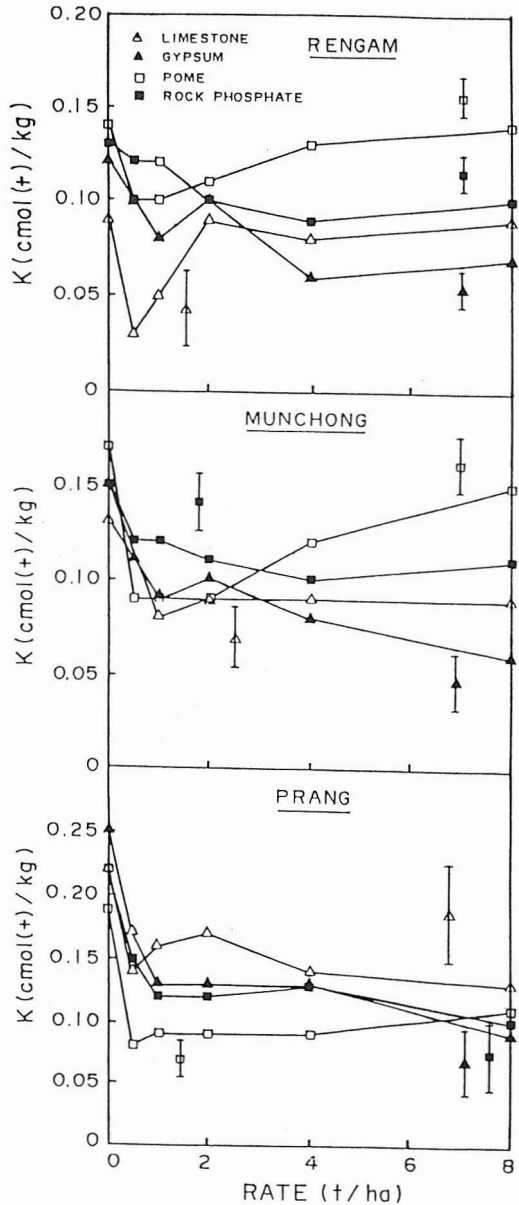


Fig 8: Effects of limestone, gypsum, POME and rock phosphate applications on exchangeable K in Rengam, Munchong and Prang series soils. LSD values are for $P < 0.05$

applications did not seem to affect the amount of exchangeable K in the 3 soils under discussion.

Exchangeable Na

Soils of Rengam, Munchong and Prang series were highly weathered, existing under strongly leaching environments. As such, the soils contained low amounts of exchangeable Na, with a value of 0.03 cmol(+)/kg or less (Table 1). As a result of the treatment, regardless of the type of amendments, exchangeable Na had increased ten-fold. There was no difference in exchangeable Na in the soils between treatments or rate of application.

CONCLUSION

Constraints for annual crop production on acid soils of Malaysia can be overcome by proper management practices, which include applications of GML, gypsum, POME and rock phosphate at a suitable rate and time. Soil pH increased and exchangeable Al decreased when GML, POME and rock phosphate were incorporated into the soils. Ca, Mg and other nutrients were made available when these amendments dissolved. Gypsum application reduced exchangeable K in the soils. Gypsum and POME application increased soil solution ionic strength. An increase in ionic strength coupled with an increase in soil pH resulted in an increase of negative charge on the mineral surfaces, leading to a decrease in leaching losses of cations in the soils.

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