

Temporal Changes in Chemical Properties of Acid Soil Profiles Treated with Magnesium Limestone and Gypsum

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ABSTRACT

Effects of ground magnesium limestone (GML) and gypsum on the properties of Ultisols at two sites, involving a corn groundnut rotation, were studied over 24 months. GML or gypsum was incorporated into the soils of the Bungor and Rengam Series (Typic Paleudults), at the rates of 0, 0.5, 1.0, 2.0, 4.0, and 8.0 t ha⁻¹ to depths of 15 cm (GML and gypsum) and 30 cm (GML). Increases in soil pH and exchangeable Ca and Mg arising from GML application were confined mainly to the zone of incorporation. However, there was a decrease of exchangeable Al at deeper depths. After 15 months, there was a tendency for the pH and exchangeable Ca and Mg on the zone of incorporation to decrease and for the exchangeable Al to increase, effects being the least at the high rates of GML application. There was no significant change in pH or exchangeable Al as a result of gypsum application, but there were increases in exchangeable Ca and extractable SO₄²⁻ in both the zone of incorporation and the subsoil. With time, the exchangeable Ca and extractable SO₄²⁻ in the sub-soils were found to increase, but their concentration in the zone of incorporation decreased. The pH of the soil solution of the control treatment was about 4.0, while Al and Mn concentrations were 150 and 50 µM, respectively. At the GML rate of 2.0 t ha⁻¹ or less, Al in the soil solution was found to exist in the inorganic monomeric form. Meanwhile, the GML application at the rates > 4 t ha⁻¹ could have resulted in complexation of some of Al. In particular, Al³⁺ was the dominant Al species at low pH and liming resulted in a decrease of Al³⁺ species and increase of hydroxyl-Al monomers. GML needed to raise the pH of the soil solution to about 5 was 2.0 t ha⁻¹; this consequently decreased Al and Mn concentrations to a low level. The application of gypsum resulted in a decrease and an increase of Al³⁺ and AlSO₄⁺ activities, respectively.

Keywords: Acid soil, ground magnesium limestone, gypsum, Ultisol

INTRODUCTION

Acid soils (Ultisols and Oxisols) are widespread in Southeast Asia, occupying about 72% of Malaysia, 82% of Thailand, and 43% of Indonesia (IBSRAM, 1985). By far, the most dominant highly weathered soils in Malaysia are the Ultisols. In this country, Ultisols and Oxisols are characterized by high acidity, low effective cation exchange capacity (CEC),

and high aluminium saturation throughout the soil profiles (Tessens and Shamshuddin, 1983).

Foster *et al.* (1980) reported that many of these soils are sufficiently acid that good crops of maize and groundnut could be produced only after application of lime. Liming trials on typical Ultisols (Shamshuddin *et al.*, 1991; Ismail *et al.*, 1993; Sharifuddin *et al.*, 1995) and Oxisols (Shamshuddin *et al.*, 1992) in Malaysia indicate the need of liming for annual crop production.

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Preliminary information indicates that crop production is not good on Ultisols; this limitation may be due to aluminium and manganese toxicities, as well as calcium and magnesium deficiencies in addition to other factors such as deficiencies of phosphorus and micronutrients and water stress arising from subsoil acidity. Therefore, it is important to develop measures to ameliorate the soil acidity to enable sustainable food crop production due to relatively large area of Ultisols in Malaysia and the high potential for food crop production.

Determining the reasons for the amelioration of acid soil infertility by such materials as limestone and gypsum is commonly undertaken by assessment of changes in the solid phase properties of soils following amendment. Additionally, there is the opportunity to understand the process of amelioration through the study of the solution phase properties of soil, particularly in relation to the phytotoxicity of Al, and the availability of Ca and Mg.

Inorganic Al is phytotoxic to roots, and the intensity of toxicity is highly correlated with Al³⁺ activity in the soil solution (Alva *et al.*, 1986a). On the other hand, it is believed that organically-bound Al is non-toxic (Hue *et al.*, 1986). Adams and Hathcock (1984) could not explain observed Al toxicity in the presence of Al species in soil solution, and this was probably because the method used for determination did not discriminate between inorganic monomeric and polymeric Al. Similarly, Wright *et al.* (1987) were unable to estimate phytotoxic Al in the soil solution from the surface using the spectrophotometric method. Kerven *et al.* (1989), however, were able to separate inorganic monomeric from organically-complexed Al using a short-term pyrocatechol violet method.

The field experiments were conducted in Malaysia on two Ultisols to assess the effects of GML and gypsum applications on soil properties and growth of three crops of sweet corn and groundnut grown in rotation. The specific objectives of this study were: (1) to investigate the chemical changes in the solid and solution

phase properties of the soils following GML and gypsum application; and (2) to determine the longevity of liming effects.

MATERIALS AND METHODS

Site Selection and Characterization

Puchong and Chembong were the sites in Peninsular Malaysia selected for the field trials. The soil at Puchong was of the Bungor Series (loamy, siliceous, isohyperthermic, family of Typic Paleudult), whereas the soil at Chembong was of the Rengam Series (clayey, kaolinitic, family of Typic Paleudult). Relevant physico-chemical data of the soil profiles at the two experimental sites are given in Table 1.

The annual rainfall in the vicinity of Puchong is 2369 mm, while evaporation is 1735 mm. At Chembong, the annual rainfall and evaporation are 2314 and 1718 mm, respectively. Monthly evaporation varies little throughout the year at both sites. Such a climate results in the soils at Puchong and Chembong being exposed to strongly leaching environments, especially during the wet months of March, April, May, and October. However, water deficit is experienced in June and July.

Experimental Design

At Puchong, three separate experiments using GML or gypsum were carried out, viz. Experiment 1, in which GML was incorporated to 15 cm depth, Experiment 2 in which GML was incorporated to 30 cm depth and Experiment 3 in which gypsum was incorporated to 15 cm depth. The slope at the experimental area was around 1-2%. The same set of experiments was conducted at Chembong, where the area is flat with a slope of <1%.

The limestone selected for the field experiment was the most common source available in Malaysia and is locally known as ground magnesium limestone (GML) because of its high magnesium content (Table 2). X-ray diffraction analysis (data not shown) showed

TABLE 1
Selected physical and chemical properties of the soils at the Puchong (Bungor Series) and Chembong sites (Rengam series)

Series	Horizon	Depth (cm)	pH (1:1)		Exchangeable cations							Mineral**			
			H ₂ O	1M KCl	Ca	Mg	Na	K	Al	ECEC	CEC*	Organic C (%)	Clay (%)	Major	Minor
Bungor	Ap	0-27	4.91	3.79	1.05	0.30	0.02	0.22	4.02	5.61	13.90	1.95	25	Kn, Gib	Gt, Qtz, Mica
	B21t	27-75	4.76	3.88	0.83	0.18	0.02	0.06	3.98	5.07	9.08	0.80	30		
	B22t	75-125	4.92	3.97	0.81	0.16	<0.01	0.04	3.07	4.08	7.15	0.33	28	Kn, Gib	Gt, Qtz, Mica
	B23t	125-150	5.01	3.98	0.77	0.16	0.02	0.04	3.24	4.23	6.43	0.26	25		
Rengam	Ap	0-20/24	4.83	3.51	1.05	0.17	0.02	0.08	2.68	4.00	8.80	2.13	40	Kn	Gib, Gt, Qtz.
	B1t	20/24-60	4.43	3.49	0.72	0.14	<0.01	0.05	2.83	3.74	7.98	1.21	45		
	B2t	60-98	4.44	3.54	0.69	0.14	<0.01	0.04	2.3	3.17	7.22	0.82	44	Kn	Gib, Gt, Qtz.
	BC	98-150	4.44	3.53	0.79	0.15	0.02	0.03	2.45	3.44	5.75	0.41	35		

* 1 M NH₄OAc
** Kn = kaolinite, Gib = gibbsite, Gt = goethite, Qtz = quartz

that this GML was dominated by dolomite with traces of kaolinite, mica, chlorite, quartz, and goethite. Meanwhile, the contents of calcium and other nutrients in the GML and gypsum are given in Table 2.

At each site, the treatments consisted of 0, 0.5, 1.0, 2.0, 4.0, and 8.0 t ha⁻¹ GML or gypsum in a Randomized Complete Block Design (RCBD), with four replications. There was also an absolute control where no basal fertilizer was applied. The size of each experimental

plot was 6.5 m x 4.5 m. The first crop of sweet corn (*Zea mays*) was planted 1 month after the application of GML or gypsum, and this crop was immediately followed by groundnut (*Arachis hypogaea*). This cropping sequence was continued for six cropping seasons, with a total period of 24 months. Basal fertilizers (Table 3) were applied on the basis of past experience and leaf analysis of each crop (data not shown).

TABLE 2
Nutrient concentrations in ground magnesium limestone and gypsum

Element	GML	Gypsum
Ca (%)	18.5	25.1
Mg (%)	6.7	< 0.01
Cu (mg/kg)	17.6	7.2
Fe (mg/kg)	2819	103
Mn (mg/kg)	97	27
Zn (mg/kg)	29	8
P (mg/kg)	1.73	< 0.01

TABLE 3
Nutrient rates for sweet corn and groundnut

Crop sequence	N*	P**	K***	(kg/ha)	
				Ca**	S**
Corn 1	120	100	150	68	7
Groundnut 1	0	0	0	0	0
Corn 2	100	30	50	20	2
Groundnut 2	22	29	56	20	2
Corn 3	120	100	50	68	7
Groundnut 3	22	29	56	20	2

* As urea

** As triple superphosphate

*** As muriate of potash

Sampling and Soil Analysis

At each experimental site, a soil pit was dug and the profile was described and subsequently classified using the soil taxonomy (Soil Survey Staff, 1999). The soils from the pits were sampled according to genetic horizons and the data obtained were used for site characterization (Table 1).

At harvest, corn and groundnut yields were recorded and leaves were sampled. The soil samples in the experimental plots were taken using an auger at 0-15, 15-30, 30-45, and 45-60 cm depths at 1 month after the application of GML or gypsum and subsequently to each corn or groundnut harvest. Five cores were sampled from each plot and bulked, while the soil was air-dried, ground, and passed through a 2 mm sieve.

The pH of the soils from the soil pits was determined in water (1:1) and in 1 M KCl (1:1) for classification purposes, while the pH of the amended soils was determined in water (1:2.5) and in 0.002 M CaCl₂ (1:1) after 1 h of intermittent shaking and 1 day of equilibration. Electrical conductivity (1:5) was determined after 1 h of intermittent shaking and 1 day of equilibration in water. Exchangeable aluminium was extracted by 1 M KCl and determined colorimetrically (Barnhisel and Bertsch, 1982). Organic carbon was estimated using the Walkley and Black method (Nelson and Sommers, 1982). Meanwhile, the cation exchange capacity (CEC) was determined by 1 M NH₄OAc buffered at pH 7 (Chapman, 1965) and by the summation of exchangeable bases and exchangeable aluminium (henceforth referred as ECEC). Charge curves for anions and cations at various pH values were determined using the method of Gillman and Sumner (1987). Sulphate was extracted by 0.008 M Ca(H₂PO₄)₂ (Farina and Channon, 1988) and determined using the turbidimetric method proposed by Freney (1986). The basic exchangeable cations were extracted by 1 M NH₄OAc, calcium and magnesium were determined by atomic absorption spectrophotometer, whereas potassium was determined by flame photometer.

Exchangeable sodium was not determined in all the samples as its amount was found to be negligible (<0.02 cmol_ckg⁻¹), both for the soil pits and for selected amended soils. Texture analysis was carried out using the method of Day (1965). The mineralogical analysis of the clay fraction was determined using the X-ray diffraction analysis.

Soil Solution Extraction and Analysis

Soil samples (topsoil) from Experiment 1 at Puchong at month 1 were rewetted to matrix suction of 10 kPa. After 1 day of incubation, the soil solutions were extracted by centrifuge for 1 h at 2000 rpm. Both the calcium and Mg in the soil solution were determined using the atomic absorption spectrophotometer, while K was determined with the use of flame photometer.

Additional soil samples (topsoil) taken at month 7 were incubated for 1 day at matrix suction for 10 kPa, and the solutions were subsequently extracted by centrifuge for 30 minutes, using fluorocarbon trichlorofluoroethane (Menzies and Bell, 1988). Soil solutions recovered were filtered through 0.22 µm Melipore filters, following which pH and electrical conductivity (EC) were immediately determined on 2 ml sub-samples. Calcium, Al, Mg, Si, Fe, Mn, and S were determined in the remaining solution by inductively coupled plasma atomic emission spectroscopy (ICPAES). Aluminium determined by ICPAES was regarded as the total aluminium (Al_T) in the soil solution.

Inorganic monomeric and organically-complexed Al (at month 7) was separated using the short-term pyrocatechol method proposed by Kerven *et al.* (1989). The activities of the Al species were calculated using the ALMONO computer programme from the University of Queensland, as described by Blamey *et al.* (1983). The soil solution pH, EC, inorganic monomeric Al, Al_T and S were used as inputs from EC.

RESULTS

Physico-Chemical Properties of Untreated Soils

Both the Bungor and Rengam soils were strongly acidic, low in basic cations, but high in exchangeable Al and Al saturation (Table 1), reflecting their occurrence in a strongly leaching environment. The soils were highly weathered, with kaolinite being the dominant mineral in the clay fraction, whereas smaller amounts of gibbsite, goethite, quartz, and mica were also present.

The soils from the experimental sites exhibited pH-dependent charge, reflecting their mineralogy (Fig. 1). For both the surface (0-15 cm) and subsoil (30-45 cm) horizons, CEC_T (Al and Ca absorption) was more than twice CEC_B (Ca absorption) at pH values < 3.5. CEC_B increased rapidly as soil pH increased to about pH 5.5 where CEC_T was equalled to CEC_B . A

small anion exchange capacity (AEC) developed at pH values below 5.5.

Chemical Properties of Amended Soils

The trends in pH measured in water and $CaCl_2$ were similar, and only the data for $CaCl_2$ are presented. In general, the pH values measured in water were 0.3 unit greater than those measured in $CaCl_2$. Increases in pH resulting from GML addition were primarily confined to the 0-15 cm depth (Fig. 2). At this depth and at month 3, addition of 2 t ha⁻¹ of GML caused an increase in pH from 4.05 to 4.69, with pH 5.2 being reached at the highest rate of 8 t ha⁻¹ in the Bungor soil. With increasing time beyond month 3, the pH values in the surface tended to decline at the 2 t ha⁻¹ but remained steady at 4 and 8 t ha⁻¹. Similar trends were also observed for the Rengam soil. In Experiment 2, the pH in the topsoil (0-15 cm depth) of Bungor Series applied with 4 and 8

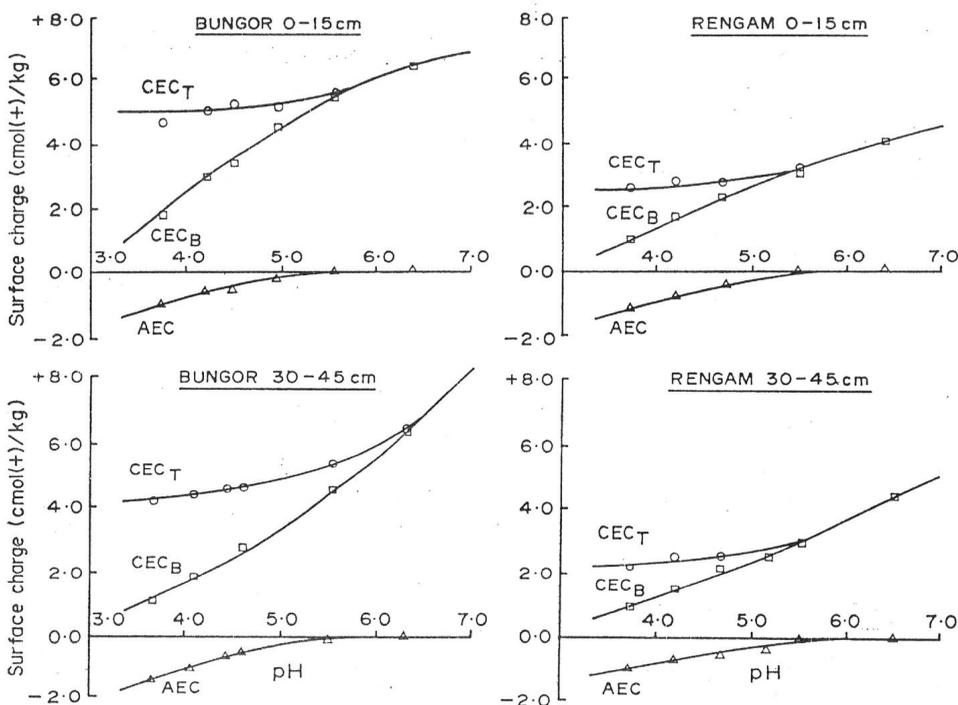


Fig. 1: Changes in CEC and AEC with pH for Bungor and Rengam Series soils

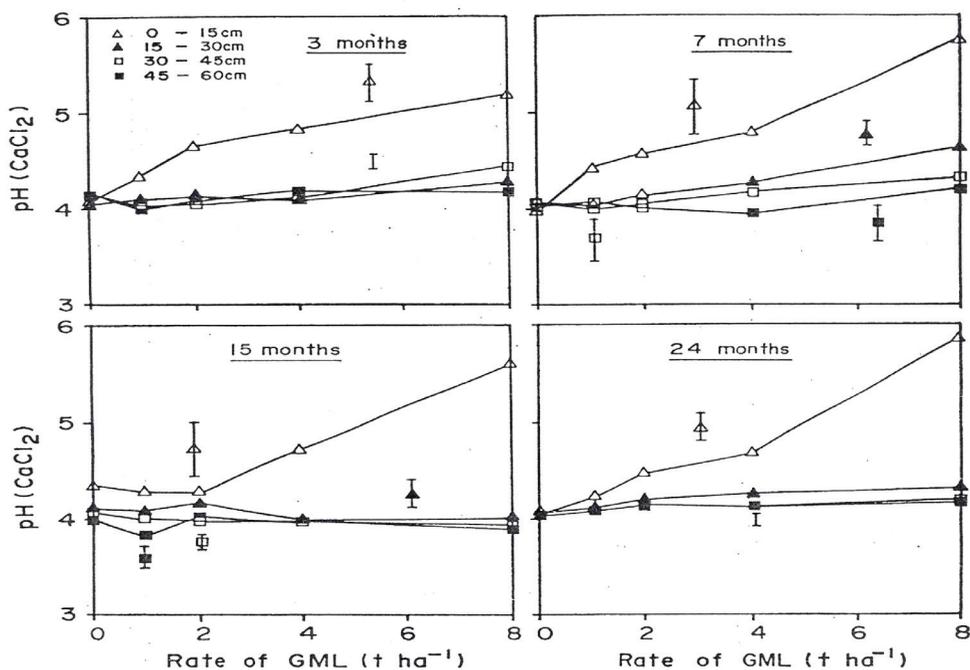


Fig. 2: Soil pH for different horizons of the Bungor soil at months 3, 7, 15 and 24 after application of GML to a depth of 15 cm (Experiment 1). LSD values are for ≤ 0.05

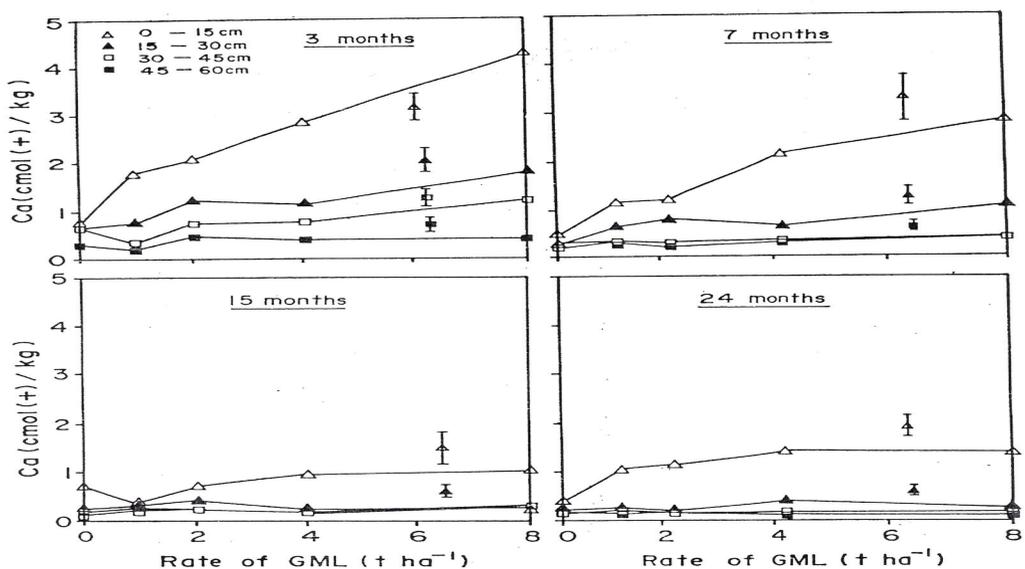


Fig. 3: Exchangeable Ca in different horizons of the Bungor soil at months 3, 7, 15 and 24 after incorporation of GML to a depth of 15 cm (Experiment 1). LSD values are for $P \leq 0.05$

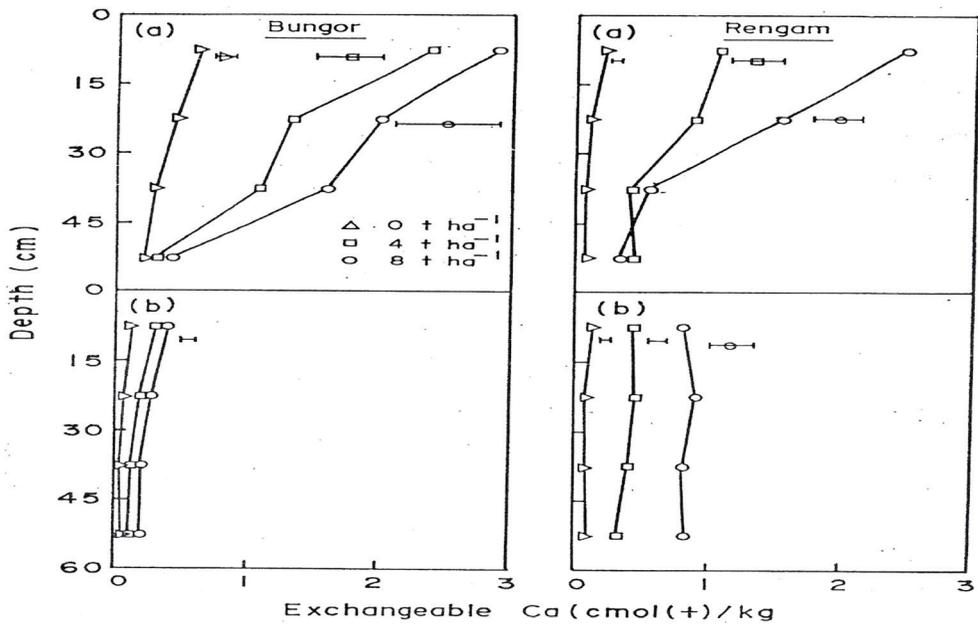


Fig. 4: Exchangeable Ca in different horizons of the Bungor and Rengam soils at (a) 7 months and (b) 24 months after incorporation of gypsum to 15 cm. LSD values are for $P \leq 0.05$

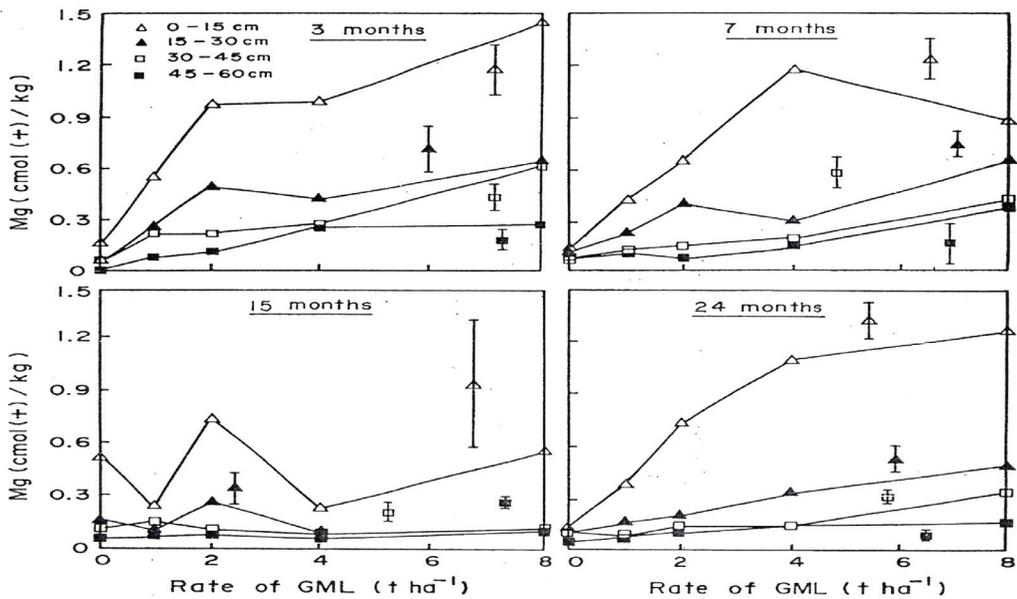


Fig. 5: Exchangeable Mg in different horizons of the Bungor soil 3, 7, 15 and 24 months after incorporation of GML to a depth of 15 cm (Experiment 1). LSD values are for $P \leq 0.05$

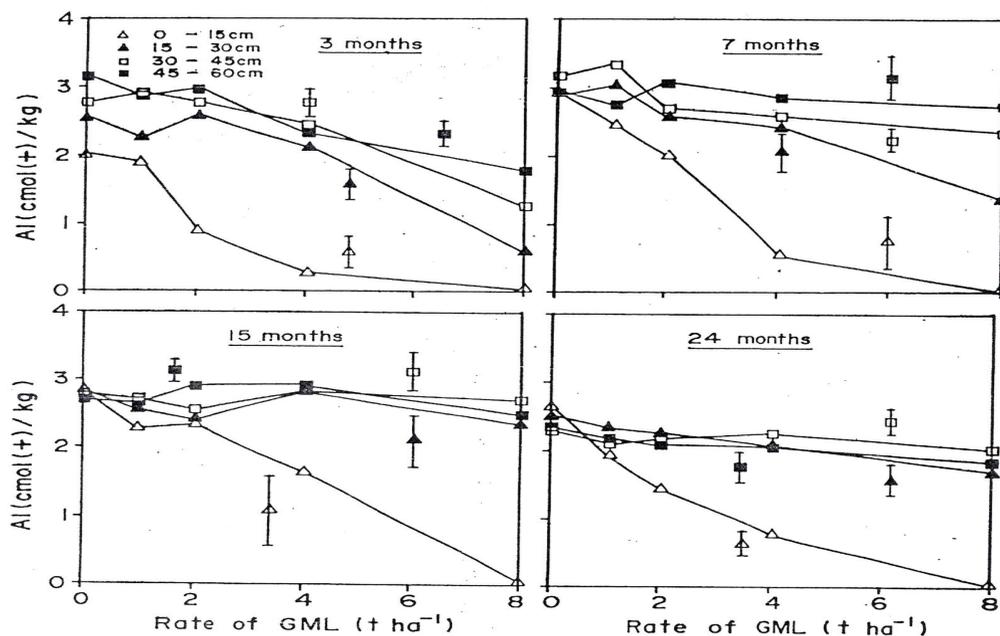


Fig. 6: Exchangeable Al in different horizons of the Bungor soil 3, 7, 15 and 24 months after incorporation of GML to a depth of 15 cm (Experiment 1). LSD values are for $P \leq 0.05$

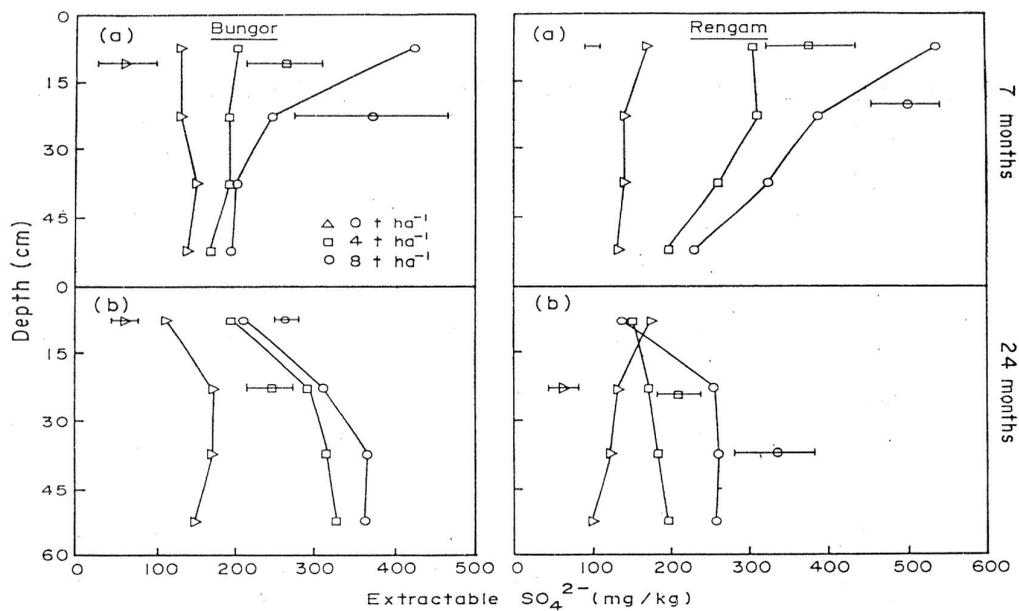


Fig. 7: Extractable SO_4^{2-} in different horizons of the Bungor and Rengam soils at (a) 7 months and (b) 24 months after incorporation of gypsum to 15 cm. LSD values are for $P \leq 0.05$.

t GML ha⁻¹ was 5.4 and 6.3, respectively. The corresponding pH in the Rengam soil was 5.8 and 6.2. As for both the experimental sites, the application of gypsum had little or no effect on soil pH, either with depth or over time.

When GML was applied, the changes in EC were small (data not presented). For the Bungor and Rengam soils, the application of the highest rate of GML (8 t ha⁻¹) to the 0-15 cm layer increased EC from 0.12 to 0.20 dS m⁻¹ and 0.11 to 0.17 dS m⁻¹, respectively after 3 months. Meanwhile, after 15 months, the EC values dropped to 0.05 and 0.09 dS m⁻¹, respectively. There was an increase in EC for both soils as a result of gypsum application, especially at the high rates of application.

Increases in exchangeable Ca in the GML experiments in Bungor soil at 3 and 7 months after application were largely confined to the zone of incorporation; the data for Experiment 1 (0-15 cm incorporation) are shown in Fig. 3. At the end of the third crop (15 months after the application of GML), the amount of exchangeable Ca in the treated soils was found to decline to a level similar to that of the control (Fig. 3). At Chembong, exchangeable Ca was high in the plots supplied with 4 and 8 t GML ha⁻¹. Generally, Ca in the topsoil at GML of 2 t

ha⁻¹ rate decreased to the level of the control at month 24. In both soils, however, there was no evidence of Ca movement in horizons beyond the depth of incorporation. The incorporation of gypsum in the surface 15 cm of Bungor and Rengam soils increased exchangeable Ca in the short-term, and this effect extended to the 15 to 30 cm layer in the Rengam soil and to the 30 to 45 cm layer in the Bungor soil (Fig. 4). After 24 months, however, there was little difference observed in the levels of exchangeable Ca in the horizons, but the levels at the 4 and 8 t ha⁻¹ rates of gypsum were higher than in the untreated soil, particularly in the case of the Rengam soil.

In the Bungor soil, exchangeable Mg significantly increased in the 0-15 cm layer, following the incorporation of GML to that depth; this effect, first recorded at month 3, persisted at month 24 (Fig. 5). There was a trend towards a slight increase in exchangeable Mg in the sub-soils layers, particularly at the highest rates of GML application. Similar results were also observed for the Rengam soil.

Exchangeable K in the topsoil (Experiment 1) of both the Rengam and Bungor soils at month 3 ranged from 0.1 to 0.5 cmol_ckg⁻¹, with an average value of 0.2 cmol_ckg⁻¹. In the sub-soils of both soils, exchangeable K

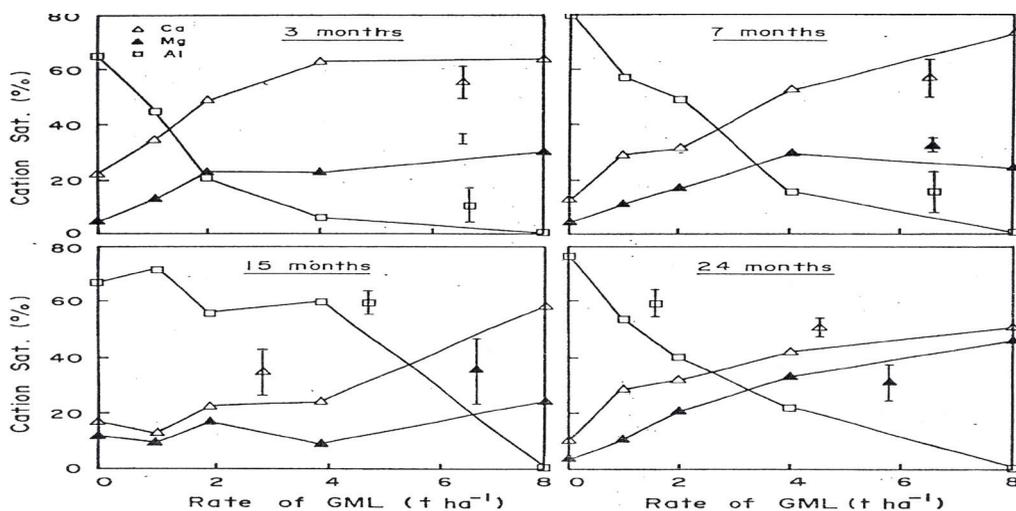


Fig. 8: Ca, Mg and Al saturations in the surface 15 cm of the Bungor soil at 3, 7, 15 and 24 months after incorporation of GML to a depth of 15 cm (Experiment 1). LSD values are for $P \leq 0.05$

was $< 0.1 \text{ cmol}_c\text{kg}^{-1}$. Exchangeable K in the topsoil of both soils at month 7 was $< 0.1 \text{ cmol}_c\text{kg}^{-1}$. Meanwhile, exchangeable K at month 7 (groundnut) was lower than at month 3 (corn) because the soils were not fertilized for groundnut (Table 3). At months 15 and 24, exchangeable K in the topsoil was $0.1\text{-}0.2 \text{ cmol}_c\text{kg}^{-1}$. Generally, it was observed that neither GML nor gypsum significantly affected the amount of exchangeable K in the soils.

The trends in exchangeable Al following GML incorporation were similar for the soils at both sites and both depths of incorporation, whereas only data for the 15 cm incorporation for the Bungor soil at Puchong are presented (Fig. 6). At month 3, the exchangeable Al in the zone of incorporation was reduced to one-half of its original value after the application of 2 t ha^{-1} of GML and to zero at the highest application rate. There was also a trend towards a reduction in exchangeable Al in the sub-surface layers at month 3, this effect being significant ($P < 0.05$) at the 8 t ha^{-1} application rate (Fig. 6). Beyond month 3, the exchangeable Al levels began to rise, but at month 24, a significant depression in exchangeable Al below the untreated soil was still evident for the GML rates beyond 2 t ha^{-1} . In the topsoil of Rengam Series (Experiment 1), at month 3, exchangeable Al became zero due to the application of 4 t GML ha^{-1} , and the values started to increase after 15 months. In Experiment 2, similar trends were observed in both the Bungor and Rengam soil series. In particular, there was no significant change in exchangeable Al in soils at both Puchong and Chembong sites with the addition of gypsum, even at the rate of 8 t ha^{-1} . However, Al saturation in the soils was decreased due to the increase in exchangeable Ca supplied by gypsum.

A progressive downward movement of SO_4^{2-} in the soils amended with gypsum was observed (Fig. 7). The increase in SO_4^{2-} at month 7 was mostly marked in the 0-30 cm zone. At month 24, the SO_4^{2-} levels in the surface layers of the amended soils were shown to decline, whereas the downward movement of this nutrient resulted in an increase in its levels right through the deepest layer sampled (45-60 cm) (Fig. 7).

Changes in Al saturation in the surface of 15 cm for the Bungor soil, when GML was incorporated to 15 cm, are given in Fig. 8. Similar trends were also observed for the Rengam soil. The application of GML at 2 t ha^{-1} was sufficient to decrease Al saturation from $>60\%$ to $<20\%$ at month 3. After 7 months, however, the Al saturation was found to increase to $>40\%$. The buffering effect of the soil also resulted in increases in Al saturation at other GML rates, although the 8 t ha^{-1} rate was sufficient to keep the level close to zero, even after month 24.

Calcium saturation in the surface of the untreated Bungor soil was 22% at month 3, and this was increased to $> 60\%$ at the GML application of 4 t ha^{-1} (Fig. 8). With increasing length of time, the saturation of Ca in the surface of the amended soil tended to decrease with time. Magnesium saturation followed similar trends to those recorded for the Ca saturation (Fig. 8).

Chemical Properties of Soil Solution

The concentration of calcium in the topsoil of Bungor Series (Experiment 1) at month 1 was increased from 1247 to $4077 \mu\text{M}$ due to the application of 8 t GML ha^{-1} (Fig. 9). Meanwhile, the concentration of calcium in the sample applied with 2 t GML ha^{-1} was $2705 \mu\text{M}$. There was a significant drop in the concentration of Ca in the soil solution with depth (Fig. 10). The concentration of calcium in the soil solution of the nil treatment below 45 cm depth was only $309 \mu\text{M}$, while the concentration of Ca in the subsoil slightly increased with the increasing rate of GML application. At month 7, the concentration of Ca in the soil solution ranged from 2900 to $4758 \mu\text{M}$, without any significant difference between the different treatments.

Fig. 9 depicts the changes in the concentration of Mg in the soil solution of Bungor topsoil (Experiment 1) with the increasing rate of GML application. The concentration of magnesium was found to increase from 655 to $1396 \mu\text{M}$, and this resulted from the application of 2 t GML ha^{-1} . Meanwhile, the concentration of magnesium in the sample treated with 8 t GML ha^{-1} was $3300 \mu\text{M}$. It was observed that the concentration of

Mg was higher in the top than in the subsoil, even in the nil treatment. The progressive increase in the GML rate was followed by a concomitant increase in the concentration of Mg in the subsoil (Figure 10). At month 7, a three-fold increase in the concentration of Mg was due to application of 8 t GML ha⁻¹ was observed.

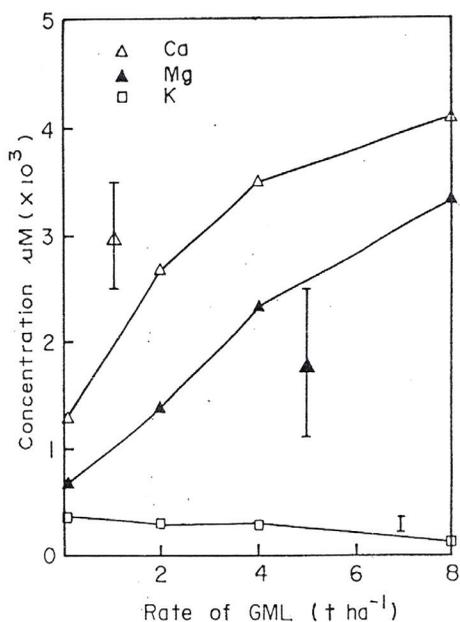


Fig. 9: Ca, Mg and K concentrations in the soil solution from topsoil of Bungor soil in Experiment 1 at month 1 after GML application. LSD values are for P ≤ 0.05

Some of the Ca and Mg released from the dissolution of GML replaced K in the exchange complex. Most of the replaced K might have remained in the soil solution, while some found their ways into the soil profile via leaching. As such, the concentration of K in the soil solution decreased with the increasing rate of GML application (Fig. 9). It was observed that the K concentration in the soil solution decreased from 345 to 121 μM due to the application of 8 t GML ha⁻¹.

Other elements determined in the soil solutions from Experiment 1 at Puchong and Chembong sites at month 7 were Al, Fe, Mn

and Si. Mitscherlich equations were fitted to the regressions of Al, Fe and Mn concentrations in both soils with pH data. It was found that the concentrations of Al, Fe and Mn were highly correlated with pH of the soil solution. This implies that the availability of Al, Fe and Mn to plant decreases with an increase in soil solution pH. Soil solution pH was raised to about 5 due to the application of GML at 2 t ha⁻¹ (Table 4). At pH5, the concentration of Al was reduced to < 25 μM, while the concentration of Mn was decreased to < 15 μM. Soluble Mn decreased much more slowly as pH increased than soluble Al, similar to what had been reported by Hue *et al.* (1987). Apparently, the concentration of iron was also reduced by the application of 2 t GML ha⁻¹. There was a general decrease of Si concentration with an increase in pH. Curtin and Smilie (1983) reported a similar reduction in the concentration of Si by liming.

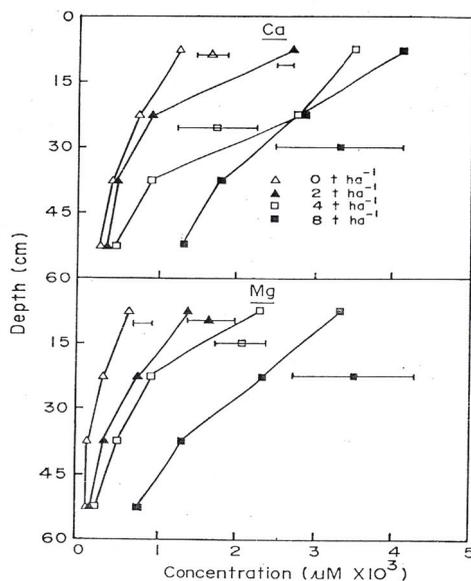


Fig. 10: Changes in the soil solution Ca and Mg with depth in Bungor soil 1 month after GML application. LSD values are at P ≤ 0.05

At month 7, the concentration of sulphate (Experiment 1) in the soil solution from the topsoil of both Bungor and Rengam soils increased with the increasing rate of GML

TABLE 4
Effects of GML application on pH and the amount of inorganic Al in the soil solution of Bungor and Rengam soils in Experiment 1 (0-15 cm depth)

Rate of GML (t ha ⁻¹)	pH	Al _{inorg}	Al _{org}	Al _{inorg} /Al _T
		------%-----		
Bungor Series				
0	3.91	134	0	100
0.5	4.22	96	0	100
1.0	4.75	34	0	100
2.0	4.93	17	0	100
4.0	5.37	5.4	2.1	72
8.0	6.11	0.5	3.2	13
Rengam Series				
0	4.01	199	0	100
0.5	4.22	110	0	100
1.0	4.33	112	0	100
2.0	4.51	76	0	100
4.0	5.90	5.5	3.1	62
8.0	6.15	1.6	2.4	40

application. The concentration of sulphate in the soil solutions of Bungor and Rengam soils, treated with 8 t GML ha⁻¹, was 1604 and 878 µM, respectively. The increase in the concentration of sulphate was probably due to the exchange of adsorbed sulphate by hydroxyl on the exchange sites and the reduction in AEC with increasing pH.

At month 7, the soil solutions extracted from the soils of Bungor and Rengam Series were very clear, suggesting that little or no carboxylic and/or fulvic acids were present. Hence, Al in the soil solution was expected to be present mostly in the inorganic monomeric form. The amounts of inorganic and organically-complexed Al, as determined by the short-term (60 second) pyrocatechol violet method of Kerven *et al.* (1989), are given in Table 4.

Total aluminium (Al_T) was also measured using the pyrocatechol violet method after 20 minutes reaction, which could be used as a check. It was found that if Al measured by PCV, 20 minutes reaction was less than that measured by ICPAES, whereas some Al in the solution was found to be complexed with organic materials. These were the cases for the samples treated with 4.0 t GML ha⁻¹ or more (Table 4). It was also noted that the samples treated with 2 t GML ha⁻¹ or less contained 100% inorganic monomeric Al. The samples treated with 4 t GML ha⁻¹ or more contained low concentration of Al, and as such Al was no longer present at the level toxic to crop growth.

The ratio of Al reacted in 60 s (PCV) to the Al reacted in 20 minutes was determined. It was found that whenever this ratio exceeded

0.85, the Al in the soil solution was estimated to be 100% inorganic monomeric. This simple procedure can be used as a test to determine the soil solution which contained organically-complexed Al.

The percentage of Al complexation increased with the increase in pH, and this finding is in agreement with that reported by Curtin and Smillie (1983). The organically-complexed Al is known to be non-phytotoxic (Hue *et al.*, 1986). This, thus, limits alleviates Al toxicity in three ways: 1) it decreases Al concentration in the soil solution; 2) it reduces Al toxicity by increasing Ca and Mg in the solution (Besso and Bell, 1992); and 3) it promotes complexation of Al by organic matter, thereby reducing the concentration of inorganic monomeric Al. Curtin and Smillie (1986) believe that an increase in the organically-complexed Al after liming was associated to the solubilization of organic matter.

Major Al species in the control or nil treatment was Al^{3+} (Table 5). When soil solution pH was increased due to GML application, both Al^{3+} and $AlSO_4^+$ activities were found to decrease, while hydroxyl-Al monomer activity increased. At the GML rate of 1.0 t ha^{-1} or higher, $Al(OH)_2^+$ became the major Al species. A similar observation had already been made by Pavan *et al.* (1982). At the GML rate of 4.0 t ha^{-1} or higher, Al^{3+} and $AlSO_4^+$ species were either absent or very small.

Al^{3+} and $AlSO_4^+$ ions were the major Al species in the gypsum treated samples at month 7 (Table 5). The next major species was $Al(OH)_2^+$. The soil solutions which contained very high activities of $AlSO_4^+$ were also found to contain high concentrations of SO_4^{2-} and Ca, suggesting the presence of high amounts of gypsum in the soil samples. Therefore, the application of gypsum was observed to have brought about a reduction of Al^{3+} and an increase of $AlSO_4^+$ activities.

DISCUSSION

Solid Phase Properties

Both soils at Puchong (Bungor Series) and Chembong (Rengam Series) were strongly acidic and highly weathered with kaolinite being the dominant mineral, although the Bungor Series soil contained some mica (Table 1). The presence of the latter resulted in the Bungor soil having a higher CEC than the Rengam soil; additionally, it contained higher exchangeable Al in spite of having a higher pH than the Rengam soil. The buffering capacity of highly weathered soils depends upon the amount of exchangeable Al and proportion of kaolinite in the clay fraction (Shamshuddin and Tessens, 1983); this, in turn, would be expected to affect the longevity of liming effects.

The presence of high amounts of kaolinite and some goethite in the clay fraction resulted in an increase in negative charge on the clay surfaces when soil pH was raised by the GML application. This is similar to the finding reported by Shamshuddin and Ismail (1995). Meanwhile, negative charge was increased by two-fold when soil pH was raised to 6.0 (*Fig. 1*). The progressive increase in the soil pH, due to increasing rate of liming, was mainly observed in the surface soil (*Fig. 2*). This observation helps to explain the retention of Ca released by GML in 0-15 cm zone (*Fig. 3*). On the other hand, the application of gypsum resulted in insignificant increase of pH and negative charge on the clay surfaces. Some of the Ca in the gypsum experiment were in excess of the soil exchange capacity and thus moved deeper into the soil profile, as shown in *Fig. 4*.

At month 24, most of the extractable SO_4^{2-} in the gypsum experiment was found below 45 cm depth. Exchangeable Ca in the surface and subsoil was reduced to the level of the control (*Fig. 4*), while most of the Ca provided by gypsum had probably moved deeper into the profile or lost via leaching. There was, therefore,

a greater mobility of gypsum compared with GML. Thus, gypsum is a good source of Ca to alleviate Ca deficiency.

Bruce *et al.* (1989) reported that critical Ca saturation for soybean was 11%. It is evident that Ca is sufficient in the topsoil of the two soil series undertaken in the present study. Ca saturation was 22% in the nil treatment at Puchong site at month 3 (*Fig. 8*). Nonetheless, this value became lower at the subsequent sampling time. Generally, Ca saturation exceeded 20% in the amended topsoil with > 1 t GML ha⁻¹.

Magnesium saturation of 10-15% is regarded as sufficient for crop growth (Eckert, 1987). In the nil treatment of Experiment 1 (Puchong), Mg saturation was <10% (*Fig. 8*). Meanwhile, exchangeable Mg was <0.15 cmol_ckg⁻¹ in the

subsoil, a level considered as critical for the growth of corn and groundnut (Tropsoils, 1984). Data presented in *Fig. 5* and *9* suggest that at least 1 t GML ha⁻¹ is needed to increase exchangeable Mg and Mg saturation to >0.15 cmol_ckg⁻¹ and >10%, respectively in these soils.

Meanwhile, the application of gypsum resulted in an increase of EC. The highest EC was obtained for the topsoil of Bungor soil (Experiment 1) at month 3 due to the application of 8 t gypsum ha⁻¹, with a value of 0.89 dS m⁻¹. The calculated ionic strength (Griffin and Jurinak, 1973) was 11.6 mM and, at this value, the activity of Al³⁺ predicted by the equation of Bruce *et al.* (1989) was about 1.3 μM.

Friesen *et al.* (1980) reported that corn shoot yield declined at 28% Al saturation, while an expert system, Tropsoils (1984) believed

TABLE 5
Changes in activities of Al species affected by GML and gypsum application in Bungor soil in Experiment 1(0-15 cm depth)

Rate of GML (t ha ⁻¹)	pH	Al species				
		Al ³⁺	Al(OH) ²⁺	Al(OH) ₂ ⁺	Al(OH) ₃	AlSO ₄ ⁺
-----μM-----						
GML						
0	3.91	55.4	3.3	4.8	0	3.9
0.5	4.22	28.6	4.6	15.7	0.1	5.4
1.0	4.75	11.2	2.0	7.4	0	1.9
2.0	4.93	1.2	0.7	11.3	0.5	0.5
4.0	5.37	0.5	0.4	7.5	0.2	0.2
8.0	6.11	0	0	0.3	0.1	0
Gypsum						
0	4.30		4.7	19.0	0.1	14.5
0.5	4.22		3.1	10.7	0.1	251.6
1.0	4.25		2.7	9.8	0.1	8.1
2.0	4.66		3.3	31.0	0.5	105.7
4.0	4.26		6.6	24.6	0.1	105.9
8.0	4.55		5.1	36.6	0.4	43.8

that respective Al saturations for corn and groundnut grown on acid tropical soils were 30 and 40%. Data presented in *Fig. 8* suggest that $> 2 \text{ t GML ha}^{-1}$ is needed to reduce topsoil Al saturation to $< 40\%$. In the untreated soils or those amended with gypsum, Al saturation was $> 30\%$. Sharifuddin *et al.* (1995) reported that maximal corn yield was obtained on an Ultisol > 2 years after 2 t GML ha^{-1} had been applied.

Solution Phase Properties

The pH of the soil solution was found to increase with the rising rate of GML application, whereby the application of 8 t GML ha^{-1} resulted in an increase of pH from 4.0 to about 6 (Table 4). The pH of the soil solution was linearly correlated ($R^2 = 0.848$) with pH (CaCl₂), implying that pH (1:1) 0.002 M CaCl₂ could be used as an estimate of soil pH under field conditions. This is possible because the ionic strength of a 0.002 M CaCl₂ solution was near to the ionic strength of the soil solution extracted from a common tropical soil. Therefore, the application of gypsum did not affect the pH of the soil solution significantly (Table 5). Meanwhile, no significant decrease in pH was observed, even at the gypsum rate of 8 t ha^{-1} .

The pH of the soil solution in the nil treatment was about 4.0 (Table 4). At this pH value, the concentrations of Al and Mn in the soil solution were 150 and $50 \mu\text{M}$, respectively. In a solution culture study, Blamey *et al.* (1983) found that soybean root elongation was reduced severely when the Al concentration exceeded $10 \mu\text{M}$. Therefore, the pH of the Bungor and Rengam soils has to be raised by liming in order to bring down the concentrations of Al and Mn to the level suitable for crop production.

Increasing soil pH resulted in an increase of CEC_T (or CEC_B) of the Bungor and Rengam soils, and that the CEC_T was higher in the Bungor than in the Rengam soil. At the GML application of 8 t ha^{-1} , the pH was raised to 6.11 in the soil solution of the Bungor Series (Table 4). As such, more Ca would be retained than at lower pH. In addition, Ca is more tightly held to the mineral surfaces than either Mg or K. Thus, there would

have been more Ca in the soil solution of the Bungor soil at month 7 than that presented in *Fig. 3* had it not been for this reaction.

In a study using Ultisols of Nigeria, Friesen *et al.* (1980) found that corn shoot yield declined at a soil solution Al concentration of $148 \mu\text{M}$. Referring to data presented in Table 4, it was observed that the soil solution pH of Bungor and Rengam in the control treatment was 3.9 and 4.0, respectively. The available data indicated that at the soil solution of about 4, the concentration of Al was about $150 \mu\text{M}$. Thus, corn grown on these soils without liming would be subjected to Al toxicity. Al³⁺ activity in the soil solution from the Bungor soil treated with 1 t GML ha^{-1} or less was $> 10 \mu\text{M}$ (Table 5). In the gypsum experiment, Al³⁺ activity was generally $> 10 \mu\text{M}$. The growth of soybean is affected by the presence of Al³⁺ activity at $4 \mu\text{M}$ (Bruce *et al.*, 1988). Al toxicity is alleviated by the presence of SO₄²⁻, as shown by the improvement of barley seedlings root elongation (Cameron *et al.*, 1986). Release of SO₄²⁻ into the soil solution by the GML application would be expected to partly reduce Al toxicity by this mechanism.

An increase in the concentration of Ca, in the soil solution of soil applied with GML (*Fig. 9 and 10*) and/or gypsum, would have some effects on Al toxicity. Mitigation of Al toxicity by Ca had been reported by Alva *et al.* (1986a, b). AlSO₄⁺ is known to be less toxic than Al³⁺ and in an increase of AlSO₄⁺, and this, to a limited extent, would alleviate Al toxicity in the soil. The alleviation of Al toxicity by gypsum application in the acid soils of United States had been reported by Summer *et al.* (1986).

CONCLUSIONS

The data presented in this study provide a clear evidence of the benefits of liming acid soils. Ameliorative effects shown by high pH and low exchangeable Al in the zone applied with GML lasted more than 2 years at the rate of 2 t GML ha^{-1} or higher. Meanwhile, the increases in pH and exchangeable Ca, arising from the GML application, were confined mainly to the zone of incorporation (0-15 cm). However, a

reduction in exchangeable Al was observed at 15-30 cm depth. The application of gypsum did not result in a significant change in soil pH and exchangeable Al, but Ca and extractable SO_4^{2-} moved deeper into the profile. The application of gypsum was found to increase EC, which in turn, increased ionic strength that might increase Al^{3+} activity in the soil solution.

Under natural conditions, soil solution pH was about 4.0, at which the concentrations of Al and Mn in the soil solution were about 150 μM and 50 μM , respectively. Thus, liming is needed to bring down the concentrations of Al and Mn to an acceptable level for crop production. The application of ground magnesium limestone at the rate of 2 t ha^{-1} increased soil solution pH to about 5, which would precipitate out most Al^{3+} ions. The corresponding concentrations of Al and Mn at that pH were < 25 μM and < 15 μM . Meanwhile, Al^{3+} was the major Al species at low pH. Therefore, increasing the pH by applying GML resulted in an increase of hydroxyl-Al monomers, especially $\text{Al}(\text{OH})^{2+}$. The application of gypsum decreased Al^{3+} and increased AlSO_4^+ , and hence, gypsum application, to a limited extent, would be expected to alleviate Al toxicity.

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