

Laboratory Studies on the Release of Cations and Anions in Acid Sulfate Soils from Pulau Lumut, Selangor.

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ABSTRAK

Tanah asid sulfat di Semenanjung Malaysia dicirikan oleh pH yang rendah dan Al yang tinggi. Pengurangan ion-ion toksik oleh saliran terkawal adalah disyorkan. Walaubagaimana pun, keasidan potensi masih wujud di dalam tanah oleh sebab lambatnya keluar ion-ion toksik ketika mineral meluluhawa. Satu kajian telah dibuat untuk menentukan pelepasan Al dan ion-ion lain oleh ekstraksi berulang tanah daripada ladang dan oleh penderaman aerobik contoh di makmal. Keputusan menunjukkan Al terlepas berterusan daripada tanah walau pun selepas ekstraksi keenam. Apabila tanah dibiarkan mengalami pengudaraan bebas di dalam keadaan aerobik Al, Mn, Fe, Ca, Mg, K, Na, dan S terkeluar ke dalam tanah oleh pemecahan mineral lempung. Aktiviti ion-ion ini bertambah dengan bererti, mengakibatkan pertambahan pengaliran elektrik larutan tanah. Tambahan lagi, pH larutan tanah turun. Sifat tanah asid sulfat yang biasa dilihat ini mempunyai implikasi yang besar terhadap pengurusan praktiknya.

ABSTRACT

Acid sulfate soils in Peninsular Malaysia are characterized by low pH and high amounts of Al. Alleviation of toxic ions in the soils by controlled drainage is recommended. However, potential acidity remains in the soils due to slow release of toxic ions during mineral weathering. A study was conducted to determine the release of Al and other ions by repetitive extraction of samples from the field and by aerobic incubation of samples in the laboratory. The results showed that Al was released continuously from the soils even after the sixth extraction. When the soils were allowed to undergo free oxidation under aerobic conditions Al, Mn, Fe, Ca, Mg, K, Na and S were released into the soil solutions due to breakdown of clay minerals. Activities of these ions increased significantly, resulting in an increase of electrical conductivity of the soil solution. Additionally, pH of the soil solution dropped. These commonly observed properties of acid sulfate soils have great implications on their management practices.

INTRODUCTION

It is estimated that acid sulfate soils cover an area of approximately 110,000 ha in Peninsular Malaysia (Kanapathy 1973). The sulfuric horizon in these soils is developed from oxidation of pyrite (FeS_2) on exposure to atmosphere by drainage. The soils are characterised by very low pH values (< 3.5) and the presence of yellowish jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) mottles. Conditions conducive for jarosite formation are low pH and strongly oxidising environments (Van Breemen 1982). Although jarosite is very insoluble with $K_{so} = 10^{-98.6}$ (Vlek *et al.* 1974), it can

hydrolyse slowly and change to goethite (Van Breemen 1982). Other minerals found in the clay fraction of acid sulfate soils in Malaysia are kaolinite, mica, smectite and mica-mixed layers (Shamshuddin *et al.* 1986; Auxtero *et al.* 1991) and Al-hydroxy-sulfates such as alunite, basaluminite and jurbanite (Shamshuddin and Auxtero 1991).

Acid sulfate soils in Peninsular Malaysia are almost exclusively found in the coastal plains of the west coast. Under natural conditions, the soils are waterlogged and are often inundated with sea water. When the soils are drained for agricultural

production, as in the case of many parts of the west coast of Peninsular Malaysia, the soils become very acidic. Very often soil pH goes below 3.5, promoting further breakdown of clay minerals in the soils. Si, Al, Fe, Ca, Mg, Na, K and anions are released into soil solution, and later form secondary minerals and/or are lost by leaching. The release of these cations and anions is a function of intensity and length of time of drainage, mineralogy, climate, depth and size of drain and climatic conditions. Auxtero and Shamsuddin (1991) showed that the growth of oil palm seedlings was affected by water regime and Al. Some acid sulfate soils in Malaysia are utilised for cultivation of oil palm (Poon 1977; Poon and Bloomfield 1977), cocoa and coconut (Chew *et al.* 1984) with proper water management practices (Toh and Poon 1982). Reclamation procedures have included applications of inorganic amendments, such as lime (Chew *et al.* 1984) and bunch ash (Yeow *et al.* 1977). Changes in physico-chemical properties of the soils resulting from these reclamation procedures and their effects on the release of cations and anions have not been studied in detail in the past. A study was, therefore, conducted with these specific objectives:

1. To assess the release of Al in acid sulfate soils by repetitive extraction using 1 M KCl
2. To determine changes in the activities of Al^{3+} , Fe^{3+} , Mn^{2+} , Ca^{2+} , Mg^{2+} , K^+ , Na^+ , and SO_4^{2-} in the soil solution as a consequence of aerobic incubation.

MATERIALS AND METHODS

Location and Soil Type

Acid sulfate soils for the study were sampled from Pulau Lumut, which is an island covering an area of approximately 6000 ha, situated off Port Kelang, Selangor, Malaysia. Detailed descriptions of the area, chemical and morphological properties of the soils have already been given by Auxtero *et al.* (1991). The drained part of the island can be divided into cultivated areas (reclaimed > 25 yr) and newly drained areas (drained in 1982). Soil types found on the island, classified according to *Soil Taxonomy* (Soil Survey Staff 1987) are given in Table 1, while Table 2 gives the relevant physico-chemical properties of the soil profiles.

Chemical Analyses

Soils were sampled according to genetic horizons. The samples were air-dried, ground and sieved through a 2 mm sieve. pH (1:2.5) was measured on

TABLE 1
Acid Sulfate Soils in Pulau Lumut Classified
According to Soil Taxonomy (Soil Survey Staff,
1987).

Location	Series	Subgroup
Cultivated areas	Parit Botak	Typic Sulfaquept
	Sedu	Typic Sulfaquept
	Jawa	Sulfic Tropaquept
	Tongkang	Sulfic Tropaquept
Newly drained areas	Sedu (silty a)	Typic Sulfaquept
	Sedu (silty b)	Typic Sulfaquept

the fresh and air-dried samples on suspension of soil in water after 1 h of intermittent shaking and overnight standing. Electrical conductivity (EC) of the air-dried samples was measured in a suspension of soil in water at 1:5 ratio after 1 h of intermittent shaking and overnight standing. CEC was determined by the NH_4OAc method buffered at pH 7 (Chapman 1965). Basic cations were determined from the NH_4OAc extracts; Ca and Mg were determined by atomic absorption spectrophotometry, while Na and K were determined by flame photometry. Al was extracted by 1 M KCl and determined colorimetrically (Barnhisel and Bertsch 1982). Free iron was determined by the method of Mehra and Jackson (1960). Particle size distribution was determined by the pipette method of Gee and Bauder (1982). Water-soluble sulfate was extracted by shaking 10 g soil in 50 ml H_2O for 30 min followed by centrifugation at 2000 RPM. Total sulfur was extracted by the nitric-perchloric acid method (Tabatabai 1982). Sulfur in both extracts was determined by the method of Freney (1986).

Total Analysis

Selected samples were taken for total elemental analysis. For this analysis, soil samples were taken mostly from Ap and Cg horizons. Some elements (Si, Al, Fe, Ca and Mg) were determined in terms of their oxides % by scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDAX).

Repetitive Extraction

A 10 g sample in 50 ml 1 M KCl solution from each horizon of all profiles was shaken for 1 h. The sample was then centrifuged and the supernatant collected. The sample was later subjected to 5 more extractions. Al in each extract was determined.

TABLE 2

Chemical properties of acid sulfate soils from Pulau Lumut, Selangor, Malaysia.

SERIES	HOR*	pH(H ₂ O, 1:2.5)		E.C (1:5) dS/m	Cations						CEC	Sulfur		
		Fresh	Air-dried		Na	K	Mg cmol(+)/kg	Ca	Al	Fe		Clay (%)	Water-sol Total	
Parit	Ap	4.0	3.9	0.08	0.05	0.31	0.17	0.16	2.59	1.25	19.24	35.1	0.01	0.08
Botak	Bj	3.7	3.6	0.09	0.06	0.20	0.29	0.14	2.26	1.95	18.77	56.6	0.14	0.23
Sedu	Bjg	3.4	3.6	0.09	0.13	0.28	1.30	0.41	1.31	3.06	19.66	54.4	0.25	0.63
	Ap	4.0	3.9	0.05	0.06	0.08	0.08	0.28	2.03	1.24	9.99	27.1	0.04	0.14
	Bj	3.7	3.4	0.12	0.11	1.10	1.20	1.26	1.59	2.05	12.55	2.0	0.01	0.52
	Bjg	3.6	3.1	0.45	0.11	0.08	0.24	0.18	2.98	1.89	24.23	37.2	0.33	0.64
	Bjg	3.3	2.9	1.77	0.04	0.04	0.59	0.21	27.10	1.18	26.10	48.7	6.54	0.87
Jawa	Cg	2.9	2.8	3.93	0.07	0.05	5.13	1.35	26.80	1.67	33.12	19.1	11.78	9.64
	Ap	3.4	3.2	0.18	0.06	0.11	0.13	0.18	1.80	1.38	25.48	27.2	0.01	0.18
	Bw	3.4	3.1	0.19	0.08	0.21	0.31	0.20	2.78	1.16	21.32	36.0	0.22	0.11
	Bjg	3.2	3.0	0.59	0.10	0.16	0.57	0.29	31.50	1.45	27.30	30.8	1.13	1.08
Tongkang	Cg	3.1	2.9	1.72	0.04	0.05	5.87	1.53	16.50	1.40	24.02	51.8	6.61	7.61
	Ap	5.3	5.2	0.03	0.10	0.23	5.55	3.73	0.36	1.06	18.88	35.9	0.08	0.05
	Bw	4.1	4.0	0.07	0.13	0.44	3.22	2.92	1.12	1.37	26.00	55.6	0.09	0.07
	Bjg	3.9	3.8	0.09	0.09	0.20	1.58	1.11	5.48	1.22	23.97	26.3	0.15	0.13
Sedu (silty a)	Cg	3.0	2.9	1.36	0.02	0.03	2.53	1.80	9.20	0.99	11.18	21.3	1.13	0.49
	Ap	3.6	3.5	0.63	0.08	0.10	0.10	0.30	2.20	1.50	12.00	31.9	0.28	0.08
	Bj	3.3	3.0	0.91	0.15	0.12	0.25	0.28	1.90	2.20	15.20	37.4	0.71	0.21
Sedu (silty b)	Bg	2.4	2.2	1.83	1.13	1.22	1.45	0.90	4.91	3.06	25.25	42.5	2.11	7.92
	Ap	3.6	3.5	0.30	0.16	0.15	0.18	0.35	3.03	2.26	19.99	17.3	0.26	0.03
	Bw	3.5	3.3	0.94	0.20	0.20	0.28	0.38	2.58	3.05	15.00	18.9	0.76	0.09
	Bjg	3.4	3.2	1.00	0.31	0.24	0.34	0.43	3.98	3.89	24.20	21.3	3.22	0.55
	Cg	3.0	2.9	3.88	1.07	0.35	2.13	1.35	16.50	4.70	28.00	42.5	5.09	1.17

*j denotes jarosite mottles

Accelerated Oxidation

Samples from jarositic layers of Sedu and Jawa series soils were exposed for a period of 12 months. The soils were kept moist by sprinkling water regularly to promote oxidation. Sub-samples were taken every 3 months for the extraction of soil solutions.

Extraction of Soil Solution and Chemical Speciation

Air-dried soil samples from the accelerated oxidation experiment were rewetted with distilled water to a matrix suction of 10 kPa (field capacity). Soil solutions were extracted after 1 day of equilibration, following the recommendation of Menzies and Bell (1988), by centrifuge for 2 h at 2000 RPM. The solutions were then filtered through 0.22 μm Millipores. pH and EC were immediately determined on a 2 ml sub-sample. The rest of the soil solutions were kept for the determination of Na, K, Ca, Mg, Fe, Mn, Cl, S, P and Al by inductively coupled plasma atomic emission spectroscopy (ICPAES). The GEOCHEM computer program of Sposito and Mattigod (1980), which was modified by Chaney (1987), was used to speciate metals and ligands in the soil solution. Input consisted of an estimate of ionic strength of the soil solution based on EC (Griffin and Jurinak 1973), metal concentrations (Na, K, Mg, Ca, Mn, Fe, Al), ligand concentrations (P, S, Cl) and pH of soil solution.

RESULTS AND DISCUSSION*Soil Properties*

Chemical, mineralogical and morphological properties of the soils at Pulau Lumut, Selangor have been described elsewhere (Auxtero *et al.* 1991; Shamshuddin and Auxtero 1991). The soils are morphologically variable in nature, with grey colours reflecting the poor drainage conditions. The clay fraction is dominated by kaolinite, mica and smectite, with minor amounts of halloysite, gibbsite and mica-mixed layers (Auxtero *et al.* 1991). Jarosite was observed in voids and/or root channels where oxido-reduction normally takes place.

Table 3 gives the total elemental composition of Ap and Cg horizons of soils in the cultivated areas. Note that only SiO_2 , Al_2O_3 , Fe_2O_3 , CaO and MgO are given here; it is seen that SiO_2 is the major element in the composition of the soils, followed by Al_2O_3 . Under very acid conditions, Si is stable, and thus does not go into solution. On the other hand, Al and Fe dissolve readily at low pH. Once in solution Al and Fe hydrolyse, resulting in the production of protons.

TABLE 3
Total chemical composition of soils in the cultivated areas.

Series	Hor	Composition (%)				
		SiO_2	Al_2O_3	Fe_2O_3	CaO	Mg
Parit Botak	Ap	69.79	19.89	3.19	0.71	1.41
	Bjg	39.16	11.19	44.20	0.63	0.30
Sedu	Ap	82.10	8.62	1.85	1.19	0.60
	Cg	75.20	15.68	2.63	0.86	1.00
Jawa	Ap	81.96	9.97	1.34	1.41	0.68
	Cg	71.20	18.53	2.65	0.97	1.10
Tongkang	Ap	77.21	13.21	3.60	0.64	< 0.1
	Cg	57.25	10.40	10.25	0.66	< 0.1

Extractability of Al

Aluminium in the sub-soils extracted by 1 M KCl was very high. The Cg horizons of Sedu, Jawa, Tongkang and Sedu silty type series contained 26.80, 16.50, 9.20 and 16.50 cmol (+)/kg soil, respectively (Table 2). The abundance of Al in the soils is associated with the oxidation of pyrite and the subsequent lowering of the soil pH, which then breaks down clay minerals and releases Al. In all horizons, Al saturation in the soils is very high, a condition unfavourable for growth of most crops. Aluminium is reported to adversely affect the growth performance of oil palm grown in acid sulfate soils (Poon 1977; Poon and Bloomfield 1977).

The quantity of Al extracted six times by 1 M KCl is shown in Fig. 1. It was observed that the quantity of Al removed after the sixth extraction was low; the amount being lower in the Ap (Fig. 1A) than the jarositic layer (Fig. 1B). Nevertheless, Al was still being extracted at the sixth extraction, indicating the high buffering capacity of the soils, especially in the jarositic layer. Under field conditions, Al is expected to be continuously released into the soil solution when Al in the soil solution is lost by leaching. However, a long span of time would be required before Al is removed completely from the soils by this mechanism.

Cumulative Al in the soils removed by 1 M KCl after six extractions was plotted against extraction number. A hyperbolic relationship was obtained between cumulative Al and extraction number. An example of such a curve is given in Fig. 2 for Sedu series soil. A similar trend was found for all the soils

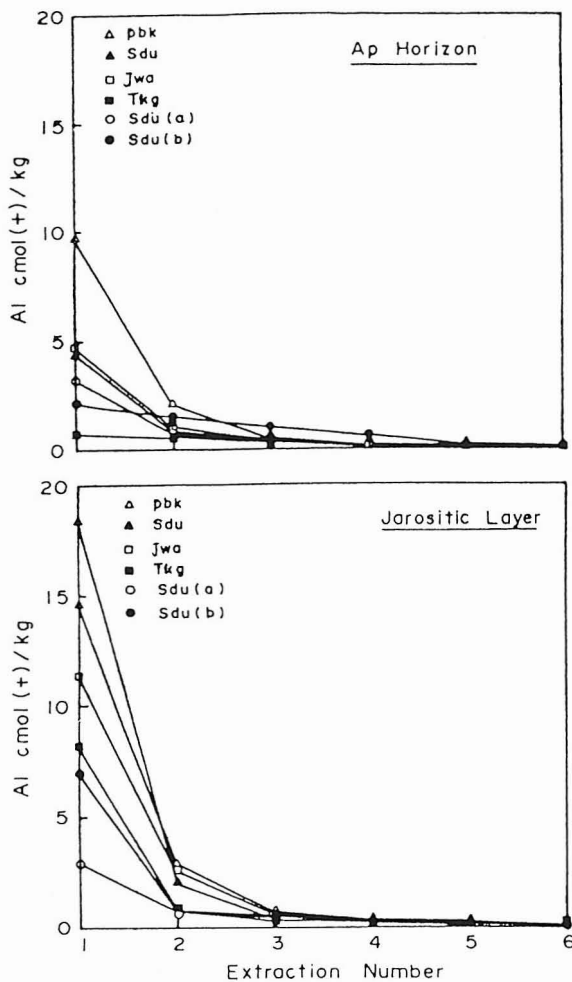


Fig. 1: Amounts of Al extracted by 1M KCl against extraction number in soils from Ap and jarositic layer.

under study. After the fourth extraction, the increment in Al removed was linearly related to extraction number, indicating a constant removal rate of Al. A similar observation was reported by Oates and Kamprath (1983). They suggested that a constant rate of removal of Al with repeated extraction represented non-exchangeable Al. Sivasubramaniam and Talibudeen (1972) proposed that exchangeable Al can be estimated by extrapolating the last points on the cumulative curve to zero extraction. Aluminium value obtained by this procedure conformed very well with the sum of Al removed after 2 extractions (Fig. 2).

Soil Oxidation in Artificially Aerated Samples
pH and Electrical Conductivity. Changes in soil solution chemical properties of Jawa series undergoing accelerated oxidation are shown in Fig. 3. A similar

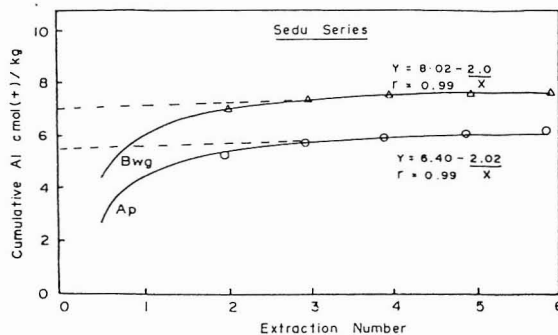


Fig. 2: Cumulative Al extracted by 1M KCl from Ap and Bwg horizons of Sedu series.

trend was also observed in Sedu Series soil. After six months of oxidation, the pH of the soil solution of Jawa series decreased from 3.3 to 3.1 (Fig. 3A). The pH decreased further to 2.9 after another six months of oxidation. The decrease in pH with time was due mainly to the release of acidity by the continued oxidation of pyritic materials and partly from the hydrolysis of acidic cations such as Al and Fe. There could also be some acidity from the hydrolysis of jarosite, although jarosite itself is known to be quite insoluble (Vlek *et. al.* 1974).

EC increased steadily from 1.33 dS/m to 3.78 dS/m in Jawa series in 12 months as shown in Fig. 3A. In Sedu series, EC increased from 0.85 dS/m to 4.86 dS/m (data not shown). A significant increase in EC within a comparatively short span of time suggests that jarositic layers of acid sulfate soils should not be drained completely and that the drainage canals should be kept shallow. A drop in pH and an increase in EC are expected to take place in the dry months of June to July. An increase in the ionic strength arising from an increase in EC results in an increase in Al³⁺ activity (Bruce *et al.* 1989).

Iron and Manganese. Fig. 3A shows changes in the activities of Fe and Mn in the soil solution of Jawa series undergoing oxidation. The calculated activities of Fe increased sixteenfold in 12 months, while those of Mn increased sixfold. In the fresh sample of Jawa series, Mn activity was only 3.3 μM. At 12 months, the activity had gone up to 20.3 μM. These increases in activities of Mn and Fe could be detrimental to oil palm growth. Similar increases in the activity of Fe and Mn in the soil solution of the Sedu series were noted (data not shown).

Basic Cations. Magnesium and K in the soil solution were very high in Jawa series, consisting of about 95% of basic cations in the soil solution. This

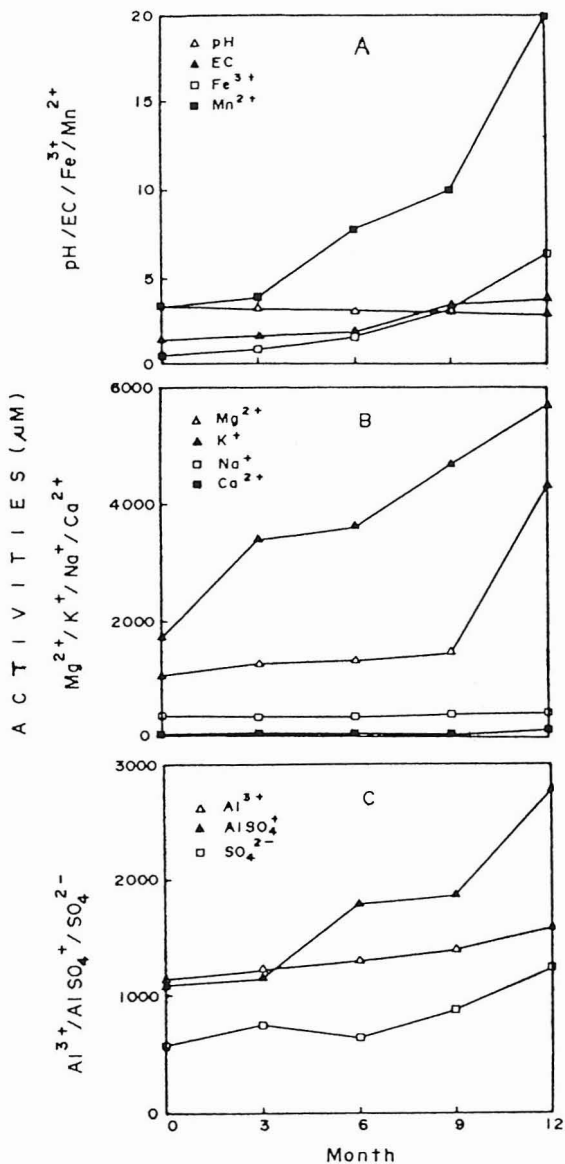


Fig. 3: pH, EC and activities of cations and anions in soil solution of Jawa series.

observation was also true for the soil solution of Sedu series. The activities of these cations increased significantly as a result of oxidation for a period of 12 months. In the Jawa series, Mg activity increased fourfold, while K activity increased threefold (Fig. 3B). Some of the K and Mg in the soil solution were derived from the weathering of mica-mixed layers and Mg-bearing minerals like smectites. This was promoted by an increase in soil acidity and the subsequent lowering of pH. Clay minerals break down faster under low pH than under high pH. The presence of high K and Mg activities in the soil solution may help promote

good plant growth, provided that toxic cations, such as Al and Mn, are alleviated. There was a slight increase in Ca and Na activities.

Aluminium and sulfate. Al³⁺ activity in Jawa series was very high (Fig. 3C). There was a slight increase in Al activity in response to a decrease in soil solution pH (Fig. 3A). The increase in Al³⁺ activity was partly due to an increase in the ionic strength of the soil solution (Bruce *et al.* 1989). SO₄²⁻ activity increased twofold in 12 months. Lindsay (1979) reported that Al³⁺ and SO₄²⁻ in solution will react instantly to form Al(SO₄)⁺. In this study, a threefold increase in Al(SO₄)⁺ activity was noted within the study period. After 12 months of oxidation, activity of Al(SO₄)⁺ in Jawa series was 2770 μm. Monomeric Al species, such as Al³⁺ and Al(SO₄)⁺, are the major Al species in the soil solution.

Management Implications. Acid sulfate soils at Pulau Lumut should be managed taking into account the chemical properties of the soils and factors influencing the growth performance of crops such as oil palm. Removal of water using a system of drainage (Toh and Poon 1982), which keeps the water table level above the pyritic layer may be good for Sulfaquepts (Jawa and Tongkang series), but may not be suitable for Sulfaquepts (Sedu series). For Sulfaquepts, once flooding is introduced Al, Mn and other toxic ions are released and brought to the surface, causing injury to plants. The presence of high amounts of cations and anions in the soil solution of the surface soils increases EC to a high level, which may also affect crop growth. The deleterious effect of EC on oil palm seedlings grown on acid sulfate soils of Pulau Lumut in pot experiments has been shown in an earlier paper (Auxtero and Shamsuddin 1991).

A suitable system of drainage is required to allow the removal of excess water, especially during the rainy months. Since the concentrations of Al and sulfate are high in the water from drainage canals and soil pits (Shamsuddin and Auxtero, 1991), regular flushing of this water into the main drain is advocated.

During the dry months the level of the water table in the soils recedes. This condition promotes the drying up of the soils in the island, resulting in a further oxidation of pyritic materials and subsequent release of sulfate and acidic cations (Auxtero *et al.* 1991). A drastic drop in pH of the soil results in an increase in the activities of Al and

Mn. This may happen in the case of Sulfaquepts (Sedu series and Sedu silty). Removal of the excess ions by leaching is not advocated because of the slow process of mineral weathering and subsequent release of ions.

CONCLUSION

One of the major elements in the composition of acid sulfate soils in Pulau Lumut is Al. This Al is released by the breakdown of clay minerals during drainage, being promoted by low pH. As the release is slow, removal of this toxic ion by leaching is not practical. If these acid sulfate soils are allowed to freely oxidize, other ions are released, whereby activities of Al^{3+} , Mn^{2+} , Fe^{3+} , Ca^{2+} , Mg^{2+} , K^+ , Na^+ and SO_4^{2-} in the soils solution increase. pH of the soil solution drops and EC increases, causing injury to crops such as oil palm. The soils should be managed such that the excess water is removed and Al kept low, while keeping the pyritic layer under reduced conditions.

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