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Rates of Extraction of Potassium and Aluminium from Five Malaysian Soils by a Cation-exchange Resin

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The rates of release of K and Al from five soils in Peninsular Malaysia pre-treated with mixed chloride solutions of K and Al were determined and found to follow the pseudo-first order kinetics. Plots of $\log(1-K_t/K_\infty)$ *or* $\log(1-Al_t/A_\infty)$ *against time of equilibration,* t, *were found to consist of two distinct sections. The curvilinear section indicates that fraction of cation* (K^+ *or* Al^{3+}) *which is rapidly extracted by the resin, while the linear section reflects a more 'difficultly extractable' fraction which controls the kinetics later. Considering the first-order rate constants for K- and Al-release, it was concluded that the rate constants reflect the chemical characteristics of the soils which are influenced by soil particle size, organic matter content and type of minerals present, but do not provide any clue to the mechanisms controlling the release of the cations.*

The long-term availability of potassium to plants from natural sources can be predicted if the rate and mechanisms of K-release from both primary and clay minerals are established. The kinetics of K-release from natural minerals may be governed by diffusion or the mass action cation-exchange mechanism. In studies on the release of K from primary and clay minerals, most workers proposed that the rate of release is controlled by diffusion and the whole process can be described by a diffusion equation. Rausell-Colom *et al.*[1] showed that the replacement of K in tri-octahedral micas by other cations was a diffusion controlled process while Quirk and Chute[2] found that K-release from Fithian illites at three concentrations of NaCl was controlled by diffusion of interlayer cations to the expanding edges of clay plates. Talibudeen *et al.*[3], using Ca-saturated sulphonated resin to remove K from soils, reported that K-release to the resin involved the simultaneous release of K from the surface of the soil complex, the weathered periphery and the micaceous matrix. Diffusion from the peripheral and matrix regions was suggested as the limiting process controlling the rate of K-release.

Alternatively, Huang *et al.*[4] found that the rate of K-release from K-bearing minerals by the acid dissolution technique conformed to 'first order' kinetics. Smith *et al.*[5,6] showed that the amount of K released by soil samples in sodium tetraphenylboron solutions could be described by a linear relationship between the amount of K replaced and the logarithm of the extraction period. Unlike diffusion-controlled K-release curves, the linearity of the K-release *versus* log *t*(time) curves gives no clue to the process by which soil K is released but has been accepted as a characteristic feature of soils.

The use of H^+-saturated resin to extract K and Al from some Malaysian soils is reported elsewhere[7,8]. Exchangeable K in the soils was rapidly removed by the resin, while the release of the non-exchangeable fraction to the resin was very slow. The cation-exchange resin also showed a very strong preference for Al resulting in the extraction of a large amount of both exchangeable and non-exchangeable Al. In pursuance to the earlier work[7], this paper reports the studies on the rates of release of K and Al from five representative Malaysian soils to the H^+-saturated cation-exchange resin. The possible mechanisms governing the rates of release of K and Al are discussed.

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EXPERIMENTAL

Surface soils (0–15 cm depth) of contrasting physical and chemical properties were collected from five areas under rubber in Peninsular Malaysia *(Table 1)*.. The soils sampled in bulk from either the unmanured plots or in between tree-rows where no fertilisers were applied, were dried in an air-oven at 45°C and passed through a 2 mm roller-sieve. For rate studies involving the cation-exchange resin, the soils were further ground in a ball-mill to pass through a 60-mesh sieve (B.S. sieve).

Rates of Extraction of Potassium and Aluminium from the Soils by H^+-Resin

Ten grammes of soil was packed into a glass column (20 X 3 cm with an adjustable screw-tap at one end) and leached with 300 ml of 1*N* NH_4Cl (adjusted to pH 4.0 with dilute HCl) until the concentration of the effluent remained unchanged. The soil which was converted to the NH_4^+-saturated form was washed with water (till chloride-free) and later leached with mixed chloride solutions of K and Al in a range of equivalent ratios (C_K/C_{Al}) of 1.50:1 to 0.25:1 at a total salt concentration (C_o) of 0.1*N* and intial pH 4.0. Likewise, when 10 ml portions of the effluent showed similar K and Al concentrations as in the influent solutions, the soil was washed chloride-free with 95% alcohol, air-dried and retained for subsequent work.

Rates of release of K and Al by the soils to H^+-resin were measured by shaking 2 g soil with 2 g Diaion SK 1B H^+-saturated cation-exchange resin (30–50 mesh) in 15 ml distilled water for various time periods ranging from 15 min to 7 days. At the end of the pre-determined time of shaking, the resin was rapidly separated from the soil by wet sieving (60 mesh sieve). As reported elsewhere[7], the resin was dry-ashed and digested with 20% HNO_3. The digest was filtered, made up to volume and analysed for K and Al. After separating the soil particles from solution by centrifugation K, Al and pH in the soil solution were also determined.

Analysis of Solutions

The amount of K in solution was determined with an EEL flame photometer. The concentration of Al was determined by the 'Aluminon' method of Chenery[9]. The pH of the solution was determined with a Pye Dynacap pH meter set with phthalate buffer (pH 4.0).

RESULTS AND DISCUSSION

The soils were initially converted to the NH_4^+-saturated form and then to the K:Al saturated form by treating with mixed K and Al salt solutions. This pre-treatment was necessary as it ensured that all the soils started from the same initial state of saturation. Since the mean pH value (in 0.01*N* KCl) of the soils was close to 4.0, all equilibrating solutions were adjusted to pH 4.0.

In studies related to the rate of extraction of a cation M^{n+} (K^+ or Al^{3+}) by H^+-resin, two possible mechanisms are proposed. If the rate of extraction of M^{n+} by H^+-resin depends on the concentration of M^{n+} in the soil, the process can be described by first-order kinetics:

$$\log\left(1 - \frac{M_t}{M_\infty}\right) = -\frac{k_m}{2.303}t \qquad \ldots 1$$

where M_t is the amount of M^{n+} extracted at time t

M_∞ is the initial amount in the soil which is extracted when equilibrium is almost attained.

k_m is the apparent rate constant.

A plot of $\log\left(1 - \frac{M_t}{M_\infty}\right)$ against t should be linear and the first-order rate constant, k_m can be calculated from the linear plot.

On the other hand, if the rate of extraction of the cation, M^{n+}, by H^+-resin is controlled by diffusion of the ion out of the lattice or interlayer sites, the whole process can be described by the parabolic rate law formulated by

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TABLE 1. PHYSICAL AND CHEMICAL PROPERTIES OF SURFACE SOILS (< 2 mm)

Soil series	Soil order (parent (material)	pH	Mechanical composition[a] Coarse sand	Fine sand	Silt	Clay	Exchangeable cations[b] (m-equiv./100 g) K	Al	Acid-extractable[c] K (m-equiv./100 g)	Cation exchange capacity (m-equiv./100 g)
Durian	Ultisol (siliceous shale)	3.9	9.9	13.7	31.6	44.8	0.16	6.6	1.76	8.8
Kuantan	Oxisol (basalt)	4.5	5.6	7.3	27.1	60.0	0.11	3.9	0.44	6.9
Munchong	Oxisol (shale)	4.2	6.4	14.7	29.0	49.9	0.13	4.4	0.43	7.3
Rengam	Ultisol (granite)	4.0	38.2	9.5	9.8	42.5	0.09	3.6	0.31	4.2
Selangor	(Inceptisol (mixed marine deposits/ alluvium)	3.8	0.8	9.6	41.1	48.5	0.37	14.9	5.29	15.8

[a]Expressed as percentage on oven-dry basis

[b]K by 1*N* NH_4OAc (pH 7.0) extraction and Al by 1*N* KCl (pH 4.0) extractions

[c]By 6*N* HCl extraction

Eeckman and Laudelout[10]. The parabolic rate law can be written as:

$$\frac{M_t}{M_\infty} = k^{\frac{1}{2}}{}_{m(p)}\sqrt{t} \qquad \ldots 2$$

A plot of M_t/M_∞ against $\sqrt{t}$ should give a linear graph and the parabolic rate constant, $k_{m(p)}$ can be calculated from the gradient of the graph. In this study, M_∞ was taken to be the amount of the cation extracted at seven days when equilibrium was almost attained[7].

Rates of Extraction of Potassium and Aluminium by H^+-resin

The amounts of K and Al in the Durian series soil extracted by H^+-resin as a function of time which ranged from 1 h to 45 h are shown in *Figures 1* and *2*, respectively. Similar curves (not shown) were obtained for the other four soils. As can be seen, the maximum amount of K extracted by H^+-resin increased with increasing C_K/C_{Al} values, while for Al, the reverse was obtained. In all the soils, more than 85% of the equilibrium amount of potassium, K_∞ taken up by the resin at seven days was extracted in the initial 10 h compared with about 75% for Al for the same period. The

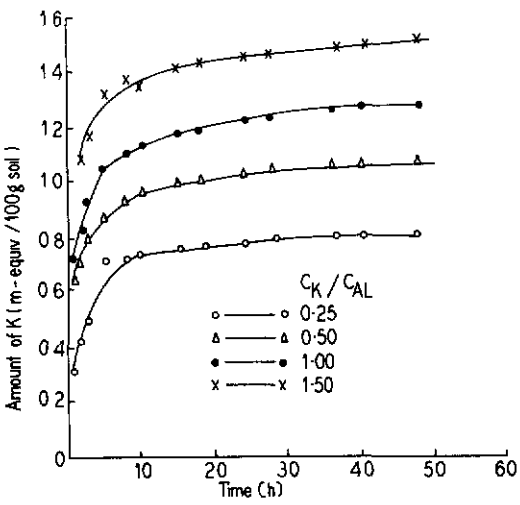


Figure 1. Amount of potassium extracted by H^+-resin as a function of time – Durian series.

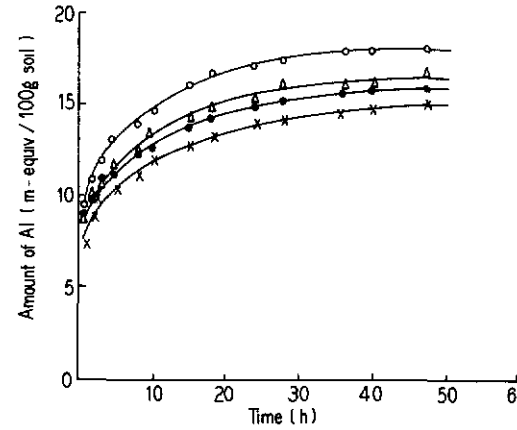


Figure 2. Amount of aluminium extracted by H^+-resin as a function of time – Durian series.

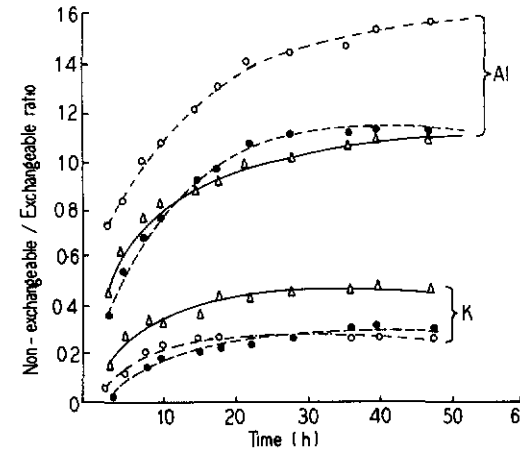


Figure 3. Non-exchangeable/exchangeable ratios against time of equilibration.

change in non-exchangeable/exchangeable ratios (for K and Al) with time is shown in *Figure 3*. In all the three soils, non-exchangeable/exchangeable ratios for Al were higher than non-exchangeable ratios for K, suggesting that non-exchangeable Al was readily extracted by H^+-resin. After 40 h, the amount of non-exchangeable Al extracted appeared to be in excess of the 'inherent' exchangeable Al. This reflects the reactions of H_3^+O on the soils with the consequent release of Al.

TABLE 2. AMOUNT OF POTASSIUM AND ALUMINIUM EXTRACTED FROM POTASSIUM; ALUMINIUM SATURATED SOILS BY H^+-SATURATED RESIN AFTER SEVEN DAYS' EQUILIBRATION

Soil series	Equilibrating solution (C_K/C_{Al})	Resin K	Resin Al	Non-exchangeable cations K[b] (m-equiv./100 g soil)	Non-exchangeable cations Al[c] (m-equiv./100 g soil)	Soil solution[a] pH	Soil solution[a] K (m-equiv./litre)	Soil solution[a] Al
Durian	0.25	0.853	18.31	0.229	9.61	2.65–2.45	< 0.038	< 0.031
	0.50	1.125	16.87	0.263	8.56			
	1.00	1.318	16.25	0.268	8.40			
	1.50	1.548	15.57	0.273	7.72			
Kuantan	0.25	0.404	13.38	0.083	6.57	3.20–3.05	< 0.019	< 0.031
	0.50	0.421	12.65	0.079	6.41			
	1.00	0.696	12.48	0.085	6.22			
	1.50	0.743	12.24	0.091	5.98			
Munchong	0.25	0.481	10.25	0.117	4.23	3.02–2.80	< 0.021	< 0.031
	0.50	0.650	11.15	0.123	4.46			
	1.00	0.834	10.39	0.126	4.09			
	1.50	0.867	10.30	0.131	4.10			
Rengam	0.25	0.350	10.68	0.072	6.33	3.56–2.93	< 0.024	< 0.086
	0.50	0.447	10.38	0.093	6.25			
	1.00	0.529	10.47	0.110	6.18			
	1.50	0.553	10.19	0.121	6.07			
Selangor	0.25	1.986	30.81	0.635	15.68	2.46–2.31	< 0.056	< 0.120
	0.50	2.291	29.93	0.641	15.43			
	1.00	2.867	30.44	0.649	15.33			
	1.50	3.013	29.61	0.668	15.20			

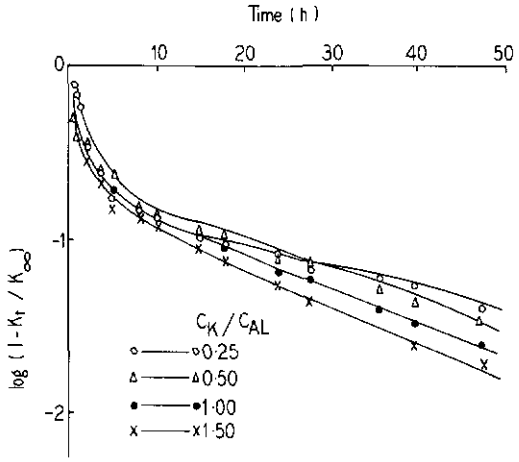
[a] Range of pH, K and Al concentrations in soil solutions (15 min – 7 days)

[b] Difference between K extracted by H^+-resin and exchangeable K by 1*N* NH_4 OAc

[c] Difference between Al extracted by H^+-resin and exchangeable Al by 1*N* KCl

Applying the parabolic rate law *(Equation 2)* formulated by Eeckman and Laudelout[10] to the rates of extraction of K and Al in the soils by H^+-resin, it seems that under the conditions the experiments were carried out, there was no linear relationship between K_t/K_∞ or Al_t/Al_∞ and $\sqrt{t}$ for all the soils, indicating that the process was not controlled by diffusion of K or Al out of the lattice or interlayer position onto the surface. The maximum concentration of K in the equilibrium solution *(Table 2)* was 0.06 m-equiv./litre, reflecting the capacity of the resin to maintain low K values in solution. Rausell-Colom *et al.*[1] found that K concentration up to 1.0 m-equiv./litre had no retardation effect on the diffusion process. Thus, in this experiment, K in the equilibrium solution had no influence on the exchange of interlayer or lattice K with H_3^+O ion.

The first-order mechanism described by *Equation 1* was tested. In *Figures 4* and *5*, only plots of $\log(1 - M_t/M_\infty)$ against t for the Durian and Munchong series soils are shown. Generally, the curves for the extraction of K and Al are made up of two distinct sections, suggesting that there



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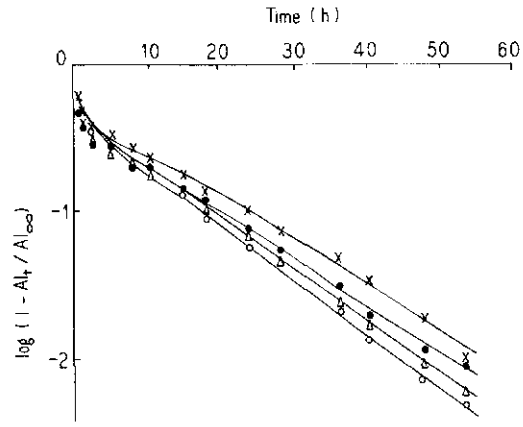

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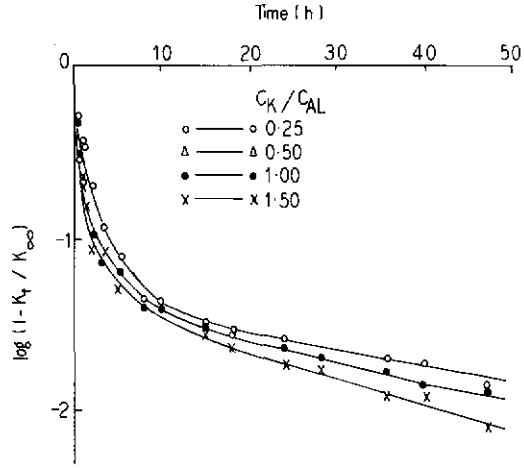
Figure 4. Plot of log $(1-K_t/K_\infty)$ and log $(1-Al_t/Al_\infty)$ against time of equilibration – Durian series.



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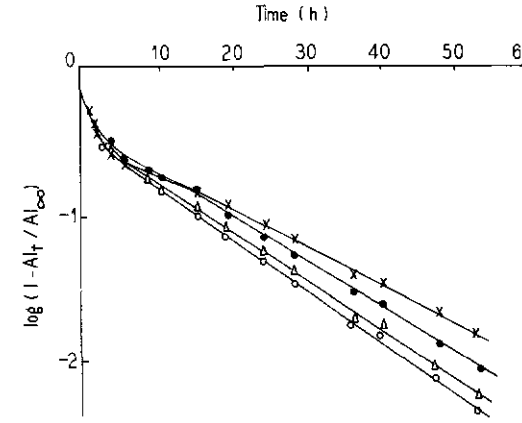

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Figure 5. Plot of log $(1-K_t/K_\infty)$ and log $(1-Al_t - Al_\infty)$ against time of equilibration – Munchong series.

are two portions of K or Al extracted by H^+-resin. The curvilinear section indicates that fraction of cation (K^+ or Al^{3+}) which is rapidly extracted by the resin, while the linear section reflects a more 'difficultly extractable' fraction which controls the kinetics later. For K, the curves were linear after 10 h of rapid extraction when more than 85% of the equilibrium amount (K_∞), was extracted during the period. As for Al, the linear relationship was obtained only after 5 h when more than 65% of Al_∞ was removed by the resin.

Based on the above observations, the extraction of K or Al by H^+-resin can be envisaged to involve two elementary consecutive reactions. The first is an exchange reaction which can be presented by

$$M - clay + H^+\text{-resin} = H^+\text{-clay} + M - resin \quad ... 3$$

where the cation M is initially on the exchange phase or released from interlayer space or clay lattice to the adsorbed phase. The second reaction is a slow decomposition represented by:

$$H^+\text{-clay} \rightarrow M - clay \quad ... 4$$

in which a lattice cation, M, is released from the lattice into the exchange complex of the clay. This slow decomposition of H^+-clay determines the rate of the overall reaction.

The significance of the rate-determining reaction *(Equation 4)* can be assessed by considering the first-order rate constants for K and Al which were calculated from the slopes of the straight-line graphs exemplified by *Figures 4* and *5* for Durian and Munchong series soils. With higher C_K/C_{Al} values, the rate of extraction of K increased, while that of Al decreased *(Table 3)*. The rate constants for K in all the soils varied from 0.81×10^{-2} to 4.89×10^{-2} per hour. Since all the soils contain mainly kaolinite[11], this range of values is relatively higher than the range, 1.46×10^{-2} to 7.67×10^{-5} per hour, for the release of K by 1*N* HNO_3 dissolution of Also, Eeckman and Landelout[10] observed that first-order decomposition of clay lattice occurred micaceous minerals determined by Huang *et al.*[4] at acid concentration above 0.5*N*. Under the conditions in which 2 g soil is in contact with 2 g H^+-resin (9.70 m-equiv. H^+), it is unlikely, that the first-order rate constants in *Table 3* are for the reaction described by *Equation 4*. However, from the large amount of non-exchangeable Al extracted by the resin, decomposition of clay lattice is possible, but this cannot be regarded as the dominant reaction.

Smith *et al.*[5,6] found a linear relationship between K released and logarithm of extraction time in soil materials and further showed that this linear relationship could be derived from the assemblage of a number of curvilinear relationships, each characteristic of a particular mineral and size class. Munn *et al.*[12] further showed that the linear relationships derived by Smith *et al.*[5,6] were significantly related to the first-order kinetics approach, *viz.* log(cumulative K released) *versus* time. Consequently, the curves presented in *Figures 4* and *5* could be accounted for by the exchange reaction *(Equation 3)*. Essentially, there are two fractions of cations extracted by H^+-resin. The first fraction is loosely held by the soil and can be extracted within 10 hours. The other fraction is more strongly adsorbed and can be displaced by H_3^+O ion very slowly. The rate constants given in *Table 3* represent the combined effects of various particle sizes and types of minerals in the soils on the release of K and Al to H^+-resin. The rate constants provide a criteria for soil comparisons, but they give no clue to the mechanisms controlling the rate of release of K or Al to the resin.

The rate constants for the release of K for each of the treatments increased in the order: Rengam < Kuantan < Selangor < Munchong < Durian, while the non-exchangeable K values *(Table 2)* followed the order: Selangor > Durian > Munchong > Rengam ~ Kuantan. It is apparent that Selangor series soil which contained appreciable amounts of expanding 2:1

TABLE 3. RATE CONSTANTS FOR THE RELEASE OF POTASSIUM AND ALUMINIUM FROM THE SOILS TO H^+-RESIN

Soil series	Rate constants (10^{-2} hour^{-1})							
	K (C_K/C_{Al})				Al (C_K/C_{Al})			
	0.25	0.50	1.0	1.5	0.25	0.50	1.0	1.5
Durian	2.58	3.17	4.46	4.89	8.78	8.06	7.48	6.77
Kuantan	1.15	–	–	1.58	8.20	–	7.77	6.91
Munchong	2.02	–	2.73	3.45	8.20	7.82	6.71	5.76
Rengam	0.81	–	–	1.00	3.25	–	3.20	3.00
Selangor	0.88	0.94	1.56	1.62	2.50	2.20	1.62	1.50

TABLE 4. LINEAR CORRELATIONS BETWEEN RATE CONSTANTS AND SPECIFIC SURFACE AREAS OF THE SOILS

Rate constant	Regression equation	Correlation coefficient (r)
First-order	$k_K = 2.046 + 0.003S$	0.053^{NS}
	$k_{Al} = 8.453 + 0.062S$	$0.600^{P} < 0.02$

NS = not significant
S = specific surface area

type minerals (mainly montmorillonite) and organic matter would show stronger K-adsorption or K-fixation than the Durian series soil which contained more illite in its clay fraction and thus released K at a slower rate. Kuantan and Rengam series soils which contained mainly kaolinite and no 2:1 type mineral in their clay fraction were easily depleted of K in the initial 10 h and thus displayed slower K-release.

In studies related to surface-area determinations[8], it was found that the rate constants for the release of Al to H^+-resin were linearly correlated with the apparent specific surface areas of the soils determined by adsorption of cetyl pyridinium bromide from solution *(Table 4)*. The good correlations between the rate constants for Al and specific surface areas suggested that release of Al was closely associated with the magnitude of the exposed surfaces of the soil particles. An increase in surface area favoured attack by H_3^+O and thus resulted in a large amount of Al being released.

CONCLUSION

Rate studies showed that most of the soils in Peninsular Malaysia have low to very low K-retention capacities and the exchangeable-K fraction could be rapidly depleted. Considering these factors, the choice of fertilisers, the timing and frequency of application should receive closer attention. Preferably, the use of slow-release fertilisers which could minimise leaching loss and maintain a constant supply of K should be investigated. In addition, the presence of large amounts of exchangeable and non-exchangeable Al which compete with cations like K ang Mg merits further studies.

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