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Potassium quantity and intensity variations of soils under anaerobic condition in relation to their mineralogical properties

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Key words: potassium, quantity-intensity (Q/I) relationship, anaerobic, mineralogical properties

Abstrak

Dua jenis tanah yang mengandungi ciri mineralogi yang berbeza, telah direndam dalam keadaan anaerobik dan perubahan kuantiti dan intensiti K dengan masa, telah dikesan sehingga 45 hari. Tanah siri Selangor yang banyak mengandungi liat 2:1 menunjukkan kapasiti penukaran K ($\triangle K_E$) yang tinggi, dibandingkan dengan tanah siri Sendong yang mengandungi liat 2:1 yang sedikit. Apabila 'penurunan' bermula, perubahan kuantiti dan intensiti K menunjukkan bahawa cas negatif telah terdedah apabila kompleks Fe-permukaan larut. Ini meninggikan kapasiti penukaran K yang ditunjukkan oleh peningkatan $\triangle K_{Eo}$ dan pengurangan CR_{Ks}. Keadaan anaerobik yang berpanjangan boleh 'menurunkan' Fe^{3+} yang di dalam 'lattice octahedral' kepada Fe^{2+}. Pengagihan semula cas negatif di dalam 'lattice' liat 2:1 boleh meninggikan daya pengikatan K dengan proses runtuhan lapisan (layer collapse) atau penyerapan pada tempat-tempat bertenaga lebih tinggi di permukaan liat. Ini ditunjukkan oleh pengurangan nilai-nilai CR_{Ks} dan $\triangle K_{Eo}$. Dengan keadaan anaerobik yang lebih lama, pembentukan polimer Fe dan Al-hidroksida di antara lapisan-lapisan 'lattice' liat dijangka dapat melepaskan lebih banyak K ke tempat-tempat penukaran (yang ditunjukkan oleh pembalikan anjakan garisan-garisan kuantiti-intensiti dengan peningkatan CR_{Ks} dan $\triangle K_{Eo}$).

Abstract

Two soils with different mineralogical characteristics were subjected to anaerobic condition and their quantity-intensity variations were monitored with time up to 45 days. Selangor series with an appreciable amount of 2:1 clays showed higher capacity for exchangeable K ($\triangle K_E$) as compared with Sendong series which had only very small amount of 2:1 clay. At the onset of reduction the quantity-intensity variation indicated that negative charges were exposed when Fe-surface complex dissolved. This increased the exchange capacity for K as shown by the increase in $\triangle K_{Eo}$ and decrease in CR_{Ks}. Longer anaerobic condition could reduce the octahedral Fe^{3+} to Fe^{2+}. The redistribution of negative charges in the layer lattices of the 2:1 clays could enhance the fixation of K by layer collapse or adsorption of K on higher energy sites on the clay surfaces. This is indicated by the decrease in CR_{Ks} and $\triangle K_{Eo}$ values. With further reduction, Fe or Al hydroxides

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polymers could form in the interlayer position of the clays which released more K to the exchangeable sites (indicated by the reversal of the shift of the quantity-intensity curves with the increase in CR_{Ks} and $\triangle K_{Eo}$).

Introduction

Potassium is not directly affected by a decrease in the oxidation-reduction potential when a soil becomes anaerobic; and only the oxidation state of +1 is important for this element in aqueous or soil environment (Lindsay 1979). K fixation was enhanced by the reduction of octahedral ferric iron in smectites and soil clays (Chen et al. 1987). The reduction of the octahedral Fe^{3+} to Fe^{2+} caused some Na-saturated smectites to partially or completely collapse due to the increase in the net negative charge of the clay minerals (Stucki, Low et al. 1984). K fixation is caused by the entrapment of K^+ ions between collapsed layers. Thus when a soil is subjected to anaerobic condition by submergence, the process of K fixation could occur depending on the mineral contents of the soil, which in turn affect the distribution of K in the solid and liquid phases of the soil. Ponnamperuma (1965) reported that flooding a soil increased the K^+ concentration in the soil solution as a result of an exchange reaction due to increase in Fe^{2+} and Mn^{2+}. Kadrekar and Kibe (1976) studied the fixation and release of K in soils by wetting to moisture equivalent and found a fixing capacity of 0.06 to 0.9 $cmol_c$/kg soil and a K release ranging from 12.8% to 26.7% of the initial exchangeable K during 180 days. Nevertheless information on the variation in a soil K distribution as affected by a change in redox condition and mineral content, is scarce if not non-existent.

Mathews and Beckett (1962) presented a technique for describing the distribution of K on solid and liquid phases i.e. the relationship between exchangeable and soil solution K which they called the quantity-intensity (Q/I) relationship of K in a soil. The quantity factor represents the change in exchangeable K of the soil ($\triangle K_E$) while the intensity factor is the ratio of K to the square root of Ca plus Mg in the soil solution (CR_K). This paper aims at evaluating the variation of the empirical K quantity and intensity relationships of soils with different mineralogical properties and understanding the mechanisms of fixation and release processes of K due to anaerobic condition.

Materials and methods

Soils

The soils used in this study were sampled from two rice growing areas: Tanjong Karang (Selangor series – Aeric Tropaquept) and Kelantan (Sendong series – Typic Tropaquent). Selangor series is derived from marine alluvium while Sendong series is derived from riverine alluvium. The soils were air dried, pounded and passed through 2-mm sieve. Some chemical and physical properties of the soils are given in *Table 1*.

Table 1. Some chemical and physical properties of the soils studied

Soil series	Soil depth (cm)	pH	Exchangeable cations by 1*N* NH_4 OA_C				OM (%)	N (%)	Sand (%)	Silt (%)	Clay (%)
			K*	Ca*	Mg*	CEC*					
Selangor	0–15	5.7	0.5	8.0	14.6	39.2	5.6	0.3	4.5	42.5	45.0
Sendong	0–15	4.3	0.1	0.4	0.8	13.5	5.0	0.2	1.3	33.4	59.2

*Unit in $cmol_c$/kg

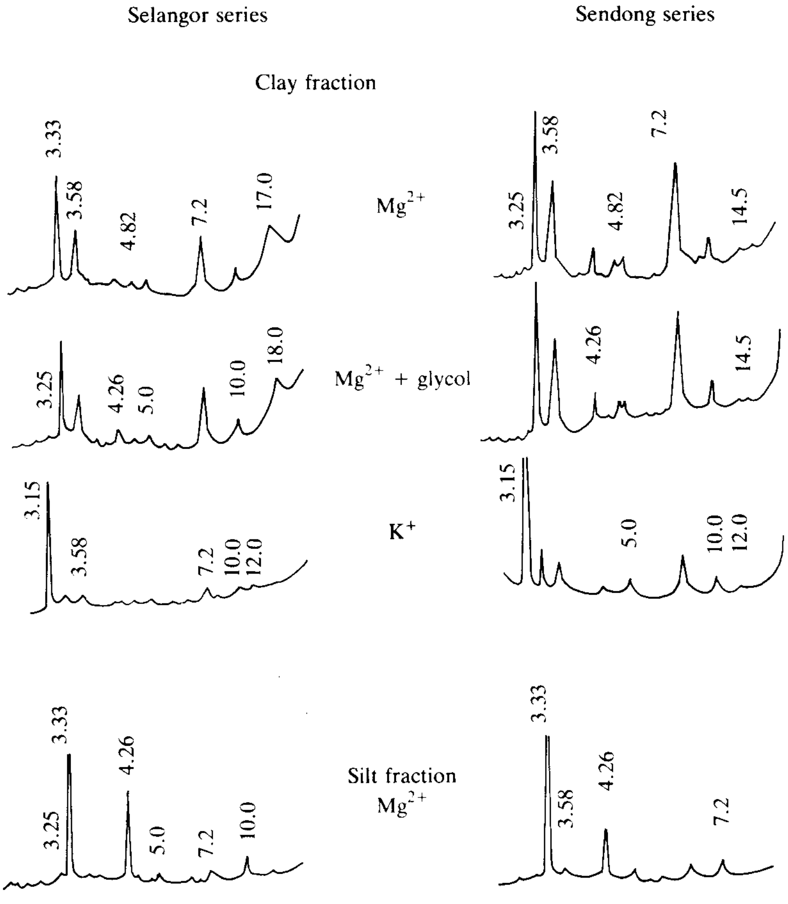

Figure 1. X-ray diffractograms of Selangor and Sendong series (numbers indicate spacing in Å)

Mineral identification

X-ray diffraction analyses were done on the clay and silt fractions of the soils which had been treated with Mg^{2+}($MgOAc$, $MgNO_3$ and $MgCl_2$ in sequence), Mg^{2+} + glycol and K^+ ($KOAc$, KNO_3 and KCl in sequence). The silt fraction was Mg saturated only.

Quantity-intensity relations

Quantity-intensity relations of the soils were determined by a method similar to that introduced by Beckett (1964). Ten sets of duplicated 5 g soil samples for both soil types were placed in bottles containing 50 mL K solution. The solutions were made up in 0.01*M* $CaCl_2$ and the concentration of K ranging from 0 to 40 µg/mL. The samples were subjected to anaerobic condition by displacing the air with oxygen-free nitrogen and sealing the bottles. Solution from the first set of samples were filtered off after 1 h shaking. The remaining nine sets of samples were placed in an incubator at 30 °C and agitated every 24 h. The solutions of one set were filtered off subsequently at 5-day intervals up to 45 days. The solutions were analysed for K, Ca and Mg. The change in exchangeable K ($\triangle K_E$) in cmol$_c$/kg was calculated using the formula:

$\triangle K_E$ = [K]original – [K]equilibrium 1

and the concentration ratio:

$CR_K = [K]/\surd([Ca]+[Mg])$ 2

where all concentrations were expressed as moles/L in the equilibrium solution.

Table 2. Minerals present in the soils studied and their theoretical CEC values

Mineral type	Selangor Soil	Sendong soil	CEC ($cmol_c/kg$)*
Silica oxides	Quartz[1]	Quartz[1]	–
Aluminium oxides	Gibbsite[3]	Gibbsite[3]	–
Tectosilicates	Feldsfars[3]	Feldsfars[3]	–
2:1 Phyllosilicates	Micas[2]	Micas[2]	–
1:1 Phyllosilicates	Kaolinite[1]	Kaolinite[1]	5
2:1 Phyllosilicates	Smectites[1]	-np-	105
2:1 Phyllosilicates	-np-	Vermiculites[3]	160
2:1:1 Phyllosilicates	Chlorite[3]	Chlorite[3]	Variable

*Source: Alexiades and Jackson (1966)
np = not present
Expected quantity 1 = abundant
2 = little
3 = very little

The concentration ratios (CR_K) were plotted against ΔK_E to obtain the quantity/intensity curves.

Results

Mineralogical composition

Diffractograms for clay and silt fractions of the two soils are shown in *Figure 1*. The common minerals found in both soils are quartz, kaolinite, micas, feldsfars and gibbsite. The obvious difference between the two soils is the existence of smectites (variable basal spacing 2:1 phyllosilicates) in the Selangor soil, which is indicated by the strong reflection at 18 Å after treating the samples with Mg^{2+} + glycol. This mineral is not found in Sendong soil. In the latter, however, there is an indication of the presence of small amount or poorly crystallized vermiculite (stable basal spacing 2:1 phyllosilicates), as shown by the weak reflection at about 14–15 Å after treating the sample with Mg^{2+} and Mg^{2+} + glycol. There are also weak reflections at about 12 Å after the clay fraction of both soils was treated with K^+ This might indicate the interstratification of phyllosilicates, e.g. chlorite-smectites in Selangor soil and chlorite-vermiculite in Sendong soil. The strong reflection at 3.15 Å of the clay fraction of both soils after treating with K^+ is probably an interference due to KCl impurities.

The minerals present in the soils studied with their respective cation-exchange capacity are listed in *Table 2*. The mineralogical composition of the soils studied was well correlated with the nature of their parent materials. The presence of smectites in the Selangor soil is explained by the marine alluvium parent materials. This mineral might be transported from other regions or synthesized under marine or brackish environment. The absence of smectites in the Sendong soil is explained by the riverine alluvium parent materials, as there is no source of this mineral inland as well as the environment is not conducive for the mineral formation. The presence of the small amount of vermiculite in this soil probably indicates an intermediate stage in the transformation of chlorite or micas to kaolinite.

Quantity-intensity relations

The variations of K quantity-intensity relationship of Selangor and Sendong soils during the period of anaerobic condition are shown in *Figure 2*. It can be seen that Selangor soil had a greater capacity, as indicated by the greater slopes of the quantity-intensity curves, than Sendong soil. The size of the capacity factor is an important determinant of K availability. Both soils showed a similar trend of shifts

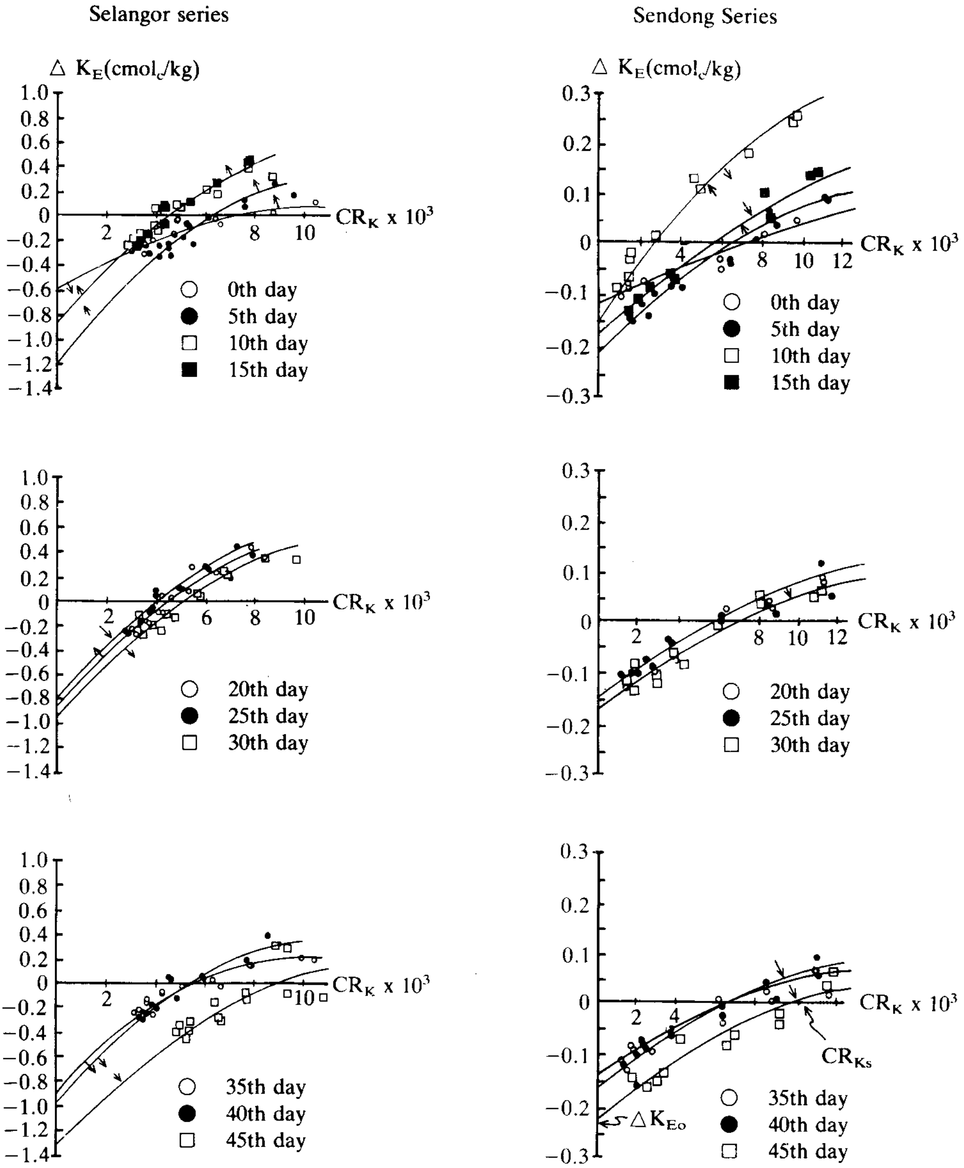

Figure 2. Changes of the quantity/intensity relationship of K in the soils studied after a period of anaerobic condition; arrows indicate the directions of the shifts of the quantity/intensity curves

of the curves with time. For Selangor soil the shift resulted in a big change in the exchangeable K (ΔK_{Eo}) which can be determined by extrapolating the curves to the vertical axis (at $CR_K = 0$). Considering the position of the curves, the shift from 0 to 5 days increased the ΔK_{Eo}. After 5 days up to 25 days K_{Eo} decreased and increased again thereafter. For Sendong soil the shift resulted in a comparatively smaller change in ΔK_{Eo}, and the reversion of the shift took place after 10 days only as compared to 25 days in Selangor soil. The shift also resulted in changes in the soil solution K quantified by CR_{Ks} which could be estimated from the

Table 3. Estimated CR_{Ks} and $\triangle K_{Eo}$ values of the soil studied, with time

Time	Selangor series		Sendong series	
(days)	CR_{Ks} x 10^3 $(mol/L)^{0.5}$	$\triangle K_{Eo}$ (cmol$_c$)/kg)	CR_{Ks} x 10^3 $(mol/L)^{0.5}$	$\triangle K_{Eo}$ (cmol$_c$/kg)
0	8.0	0.60	7.5	0.11
5	6.5	1.20	6.3	0.23
10	4.8	0.90	2.5	0.15
15	4.8	0.90	5.5	0.18
20	4.6	0.90	5.5	0.15
25	4.3	0.80	6.0	0.15
30	5.2	0.95	7.0	0.20
35	5.5	0.90	7.0	0.16
40	5.2	1.00	7.0	0.16
45	8.5	1.30	10.0	0.23

intercept of the curves on the horizontal axis when there were no net adsorptions on the clay surfaces. For Selangor soil CR_{Ks} decreased from 0.0080 to 0.0043 up to 25 days of anaerobic condition and increased again to 0.0085 at 45 days. For Sendong soil the CR_{Ks} decreased from 0.0075 to 0.0025 at 10 days of anaerobic condition but subsequently increased to 0.01 at 45 days. The values of estimated $\triangle K_{Eo}$ and CR_{Ks} are listed in *Table 3.*

Discussion

The contribution of mineral types *(Table 2)* to the behaviour of K in solution and on solid surfaces and the capacity of the minerals to hold K, is distinctly shown in *Figure 2.* From *Table 2* it can be deduced that the cation-exchange capacity of Selangor soil which could affect K distribution in liquid and solid phases was mainly contributed by smectite and organic matter *(Table 1).* The cation-exchange capacity of Sendong soil should be contributed mainly by organic matter with minor contribution by vermiculite which is present in small proportion.

Immediately after anaerobic condition set in before 5 days CR_{Ks} decreased from 8.0 x 10^{-3} to 6.0 x 10^{-3} $(mol/L)^{0.5}$ and from 7.5 x 10^{-3} to 6.3 x 10^{-3} $(mol/L)^{0.5}$ while $\triangle K_{Eo}$ increased from 0.6 to 1.2 cmol$_c$/kg soil and from 0.11 to 0.23 cmol$_c$/kg soil, for Selangor and Sendong soil respectively. This would mean an increase of about 167% of the buffer capacity for Selangor soil and about 148% for Sendong soil, assuming linear relationship between CR_K and $\triangle K_E$. This is thought to be a result of the dissolution of the polymeric inner-sphere Fe- surface complex (Sposito 1984) or coatings of ferric hydroxide caused by the reduction of Fe^{3+} to Fe^{2+}. Several evidence indicate that soils may have coatings of hydrous oxides on the clay minerals and dissolution studies also suggest that hydrous iron oxides may be present on vermiculite particles (Greenland and Mott 1978). There is also evidence for coatings of iron oxides and finely divided clay minerals on larger clay particles in Australian soils (Fordham and Norrish 1979). Iron oxide coatings precipitated onto kaolinite, illite and bentonite clays under suitable laboratory conditions, lead to an increased net positive charge on the clay surface and a change in surface properties (Rengasamy and Oades 1977; Greenland and Mott 1978; Kavanagh and Quirk 1978). The change of Fe^{2+} concentration in soil solution due to anaerobic condition was shown by many workers such as Ponnamperuma et al. (1967) and Patrick and Reddy (1978). The dissolution of Fe-surface complex could expose many negative charges and hence the increase in cation-exchange sites. This in turn changed the distribution of K in solution and on the surface which resulted in the change in the slope of the quantity-intensity curves *(Figure 2)* from 0 to 5 days. This result also indicates that the surface affinity for K was greater than for Fe^{2+} as one might have thought that the higher concentration of Fe^{2+} in the soil solution would displace most of the K from the exchange sites.

One interesting feature that can be seen in *Figure 2* is the shift of the quantity-intensity curves in more or less parallel sequences after 5 days, which reflect the changes of the distribution of exchangeable K and solution K after the soil became anaerobic. The shift towards decreasing CR_{Ks} and $\triangle K_{Eo}$ in both soils is a strong indication that K fixation by the K-fixing minerals such as smectite and vermiculite had occurred, or at least higher energy sites had been involved in the exchange reactions. With longer period of anaerobic condition the Fe^{3+} situated in the octahedral layer of smectites, vermiculites or chlorite especially those at the edges of the minerals, could be reduced to Fe^{2+} When octahedral Fe^{3+} in a clay lattice is reduced, the negative charge of its unit cell is increased (Stucki, Golden et al. 1984; Stucki, Low et al. 1984). It is reasonable to believe that the increase in negative charge increases the coulombic attraction between the silicate layers and the interlayer cations and thus lowers the energy of the layers in the collapsed state relative to that in the expanded state. The magnitude of K fixation is therefore dependent on the amount of 2:1 clay present in the soil. This is reflected by the difference in clay types in Selangor and Sendong soils *(Table 2)*.

The increase in Fe^{2+} concentration coupled with redox and pH changes could enhance the formation of Fe(II)Fe(III) oxides or hydroxides (Lindsay 1979). These oxides or hydroxides could displace the K in the non-exchangeable or high energy sites and thus K became more exchangeable. It is also possible that the exchangeable Al displaced by Fe^{2+} and K^+ during earlier anaerobic period, also coupled by the rise in pH, could be transformed into polymers and become interlayered in the 2:1 clay minerals as in the process of chloritization (Brinkman 1970). These processes could release K from interlayer lattice to exchangeable K, and are reflected by the reversal of the parallel shifts of the quantity-intensity curves after 25 days by Selangor soil and 10 days by Sendong soil, with the increase of $\triangle K_{Eo}$ and CR_{Ks}. In Sendong the amount of K release was relatively smaller than in Selangor soil. The difference in the period before shift reversal and the magnitude of K release are indicative of the amount and type of minerals that exist in the soils. It is also possible that the rate processes of fixation and release of K, could occur at the same time, at different sites of interlayer lattices and clay types; but in the early stages of anaerobic condition the rate of K release was outweighed by the rate of K fixation while in the later stages of anaerobic condition the rate of K release was more important than the rate of K fixation.

Conclusion

The behaviour of K in Selangor and Sendong soils under anaerobic condition can be explained by the relationships between quantity-intensity variations and the mineral contents of the soils. It was shown that three mechanisms could take place and influenced K distribution on the solid and liquid phases when the soils were subjected to anaerobic condition:

- The dissolution of inner-sphere Fe-surface complex exposing negative charges which increased the exchangeable K ($\triangle K_{Eo}$) and decreased the soil solution K as indicated by (CR_{Ks})
- The reduction of octahedral Fe^{3+} to Fe^{2+} which induced the development of layer negative charges and enhanced K fixation by the increased

coulombic attraction between silicate layers and the interlayer K

- The release of K from the nonexchangeable sites by the replacement of the interlayer K by the Fe or Al hydroxide polymers.

These findings can have practical implications to the behaviour of fertilizer K applied to lowland-rice fields during rice growing periods. It is suggested that the relative merits of K fertilization at different periods after submergence or choosing the appropriate transplanting time so that the rice plant could use K at its best time of availability, should be reexamined.

References

Alexiades, C. A. and Jackson, M. L. (1966). Quantitative clay mineralogical analysis of soils and sediments. *Clays Clay Miner.* ***13***: 35–52

Beckett, P. H. T. (1964). Studies on soil potassium II 'Immediate' Q/I relations of labile potassium in the soil. *J. Soil Sci.* ***15***: 1–8

Brinkman, R. (1970). Ferrolysis, a hydromorphic soil forming process. *Geoderma* ***3***: 199–206

Chen, S. Z., Low, P. F. and Roth, C. B. (1987). Relation between potassium fixation and the oxidation state of octahedral iron. *J. Am. Soc. Soil Sci.* ***51***: 82–6

Fordham, A. N. and Norrish, K. (1979). Electron microprobe and electron microscope studies of soil clay particles. *Aust. J. Soil Res.* ***17***: 283–306

Greenland, D. J. and Mott, C. J. B. (1978). Surfaces of soil particles. In *The chemistry of soil constituents* (Greenland, D. J. and Hayes, M. H. B., ed.) p. 321–53. Chichester: John Wiley & Sons

Kadrekar, S. B. and Kibe, M. M. (1976). Release of soil potassium on wetting and drying. *J. Indian Soc. Soil. Sci.* ***21***: 161–6

Kavanagh and Quirk, J. P. (1978). The adsorption of polycatconic Fe (III) species on Na-illite. *Geoderma* ***21***: 225–38

Lindsay, W. L. (1979). *Chemical equilibria in soils* New York: John Wiley and Son

Mathews, B. C. and Beckett, P. H. T. (1962). A new procedure for studying the release and fixation of K ions on soils. *J. agric. Sci.* ***58***: 59–64

Patrick Jr., W. H. and Reddy, C. N. (1978). Chemical changes in rice soils. In *Soils and rice* p. 361–79. Los Banos: IRRI

Ponnamperuma, F. N. (1965). *Dynamic aspects of flooded soils and the nutrition of rice plants* Baltimore, Maryland: John Hopkins Press

Ponnamperuma, F. N., Tianco, E. M. and Loy, T. (1967). Redox equilibria in flooded soils. I. The iron hydroxide systems. *Soil Sci.* ***103***: 374–82

Rengasamy, P. and Oades, J. M. (1977). Interaction of monomeric and polymeric species of metal ions with clay surfaces. I. Adsorption of iron (III) species. *Aust. J. Soil Res.* ***15***: 221–33

Sposito, G. (1984). *The surface chemistry of soils* Oxford: Oxford University Press

Stucki, J. W., Golden, D. C. and Roth, C. B. (1984). Effects of reduction and reoxidation on structural iron on the surface charge and dissolution of dioctahedral smectites. *Clays Clay Miner.* ***32***: 350–6

Stucki, J. W., Low, F., Roth, C. B. and Golden, D. C. (1984). Effects of oxidation state of octahedral iron on clay swelling. *Clays Clay Miner.* ***32***: 357–62

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