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Pedogenetic Forms of Extractable Iron in Selected Soils of Kedah, Malaysia

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The amount of crystalline, amorphous and organo-complexed iron were determined by selective extraction on six pediplain soils. The status of the different iron forms and their usefulness in characterising the morphogenesis of the soils were examined.

The degree of crystallinity is generally high in all the soils. The Oxisols in particular have a constant trend of the active iron ratio indicating homogenised materials. The heterogeneity of the soils is also shown by this ratio but the free iron to clay ratio is a better indicator.

It has been established that iron oxides and hydrous oxides constitute an important component of tropical soils. Most of these oxides are in the form of amorphous and crystalline particles. The dominant source of soil colour has been attributed to the crystalline oxide, hematite[1]. A small fraction of iron also exists in the form of organic complexes. Selective extractions of the various iron fractions have been found to be useful in pedogenetical studies of temperate soils[2,3] and tropical soils[4,5]. Bascomb[6] had shown that a particular method, although specific, can also extract different forms of iron, but despite this limitation, these studies showed that the methods can be utilised to characterise the nature of iron in soils.

This paper attempts to characterise the different forms of iron and their distribution with depth in selected soils from Kedah. In addition, the significance of the iron forms in the morphogenesis of the soils will also be examined.

MATERIALS AND METHODS

Six pediplain soils under rubber were selected. These soils have been characterised in detail in a separate study[7]. The soils are generally acidic with pH (H_2O) ranging from 4.2 to 5.0. The base saturation is 10% and less in the subsoils. The clay mineralogy indicates a typical assemblage of minerals in highly weathered soils. The most dominant mineral is kaolinite followed by aluminous vermiculite and interstratified mica-vermiculite. Gibbsite is another common mineral. Due to the fineness of the iron minerals, they are not readily detected by X-ray diffraction.

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The most important pedological feature in the soils is the occurrence of a stone-line. The locations of the soil profiles and their respective classification according to Soil Taxonomy[8] are presented in *Table 1*.

TABLE 1. LOCATION AND CLASSIFICATION OF THE SELECTED SOILS

Soil series	Location in Kedah, Peninsular Malaysia	Soil classification
Prang	Pinang Tunggal Estate	Tropeptic Haplorthox, clayey, mixed, isohyperthermic
Tandak	Pinang Tunggal Estate	Tropeptic Haplorthox, clayey skeletal, kaolinitic, isohyperthermic
Bungor	Pinang Tunggal Estate	Typic Paleudult, clayey, kaolinitic, isohyperthermic
Chuping	Lim Chow Chong Estate	Orthoxic Tropudult, clayey-skeletal, mixed, isohyperthermic
Tembaga	Felda Bukit Tembaga	Orthoxic Tropudult, fine loamy, siliceous, isohyperthermic
Pokok Sena	Pinang Tunggal Estate	Plinthic Paleudult, clayey-skeletal, mixed, isohyperthermic

Selective extractions involve apportioning of secondary amorphous iron, secondary crystalline iron and organo-iron complex. The iron forms and their corresponding methods of extraction were as follows:

- Fe_d – iron extracted by dithionite-citrate-bicarbonate[9]
- Fe_o – iron extracted by acid ammonium-oxalate[10]
- Fe_p – iron extracted by alkali sodium-pyrophosphate[11].

Fe_d represents the total amount of crystalline, amorphous iron oxides as well as the organo-iron complexes. Amorphous iron is indicated by Fe_o while Fe_p represents the iron complexed by organic matter.

The general outline of the methodology follows that of Mckeague and Day[3] where all the soil samples of less than 150 µm size were employed. Fe_d and Fe_o were determined colourimetrically after digesting the extract with a mixture of sulphuric, perchloric and nitric acids. Fe_p was determined by atomic absorption spectrophotometry and aluminium in the organic complex was determined colourimetrically by the Alizarin Red S method[12].

RESULTS AND DISCUSSION

The pediplain soils are characterised by lithological discontinuities *(Table 2)*. In Chuping and Tembaga profiles, the discontinuities were identified by differences in the clay content while in the rest of the profiles, the occurrence of a stone-line was the indicator. These features show the depositional nature of the soils.

Fe_d is a measure of the total 'free' iron oxides and excludes iron in silicate minerals and oxides such as ilmenite. Crystalline oxides such as goethite and hematite and amorphous iron oxides are components of free iron. The values for Fe_d are generally higher in the lower horizons of all the profiles. The absolute

TABLE 2. FORMS OF EXTRACTABLE IRON IN SOILS

Soil series	Depth (cm)	Horizon	Clay (%)	Fe_d	Fe_o (Fe_2O_3 %)	Fe_p	Al_p (Al_2O_3 %)	Organic carbon (%)
Prang	0–8	Ap	50.9	7.37	0.19	0.87	0.30	2.02
	8–38	B21ox	68.1	7.66	0.17	0.19	0.13	0.86
	38–71	B22ox	65.5	8.27	0.15	0.03	0.06	0.50
	71–97	B23ox	52.9	8.13	0.19	tr	0.04	0.34
	97–147	II B24ox(cnl)	63.8	7.95	0.19	0.05	0.02	0.23
	147–185	II B24ox(cn2)	52.1	9.40	0.18	0.04	0.04	0.16
Tandak	0–3	Apl	70.6	5.74	0.19	1.64	0.61	3.00
	3–15	Ap2	69.2	6.21	0.18	1.25	0.49	1.47
	15–28	B21ox	80.6	6.40	0.16	1.01	0.38	1.04
	28–58	B22ox	74.3	6.36	0.12	0.03	0.06	0.34
	58–109	II B23ox(cn)	81.9	6.37	0.14	0.52	0.21	0.74
	109–132	III B31ox(cn)	52.5	7.95	0.10	0.02	0.04	0.20
Bungor	0–5	Apl	26.9	1.70	0.18	0.61	0.25	1.11
	5–15	Ap2	26.6	1.95	0.20	0.77	0.28	1.05
	15–48	B21t	41.7	2.71	0.18	0.64	0.21	0.43
	48–81	B22t	49.8	3.37	0.10	0.13	0.06	0.33
	81–104	B23t	49.3	3.23	0.09	0.06	0.16	0.25
	104–130	II B24tcn	49.4	4.63	0.12	0.05	0.02	0.20
	130–168	II B3cn	50.4	5.02	0.10	0.01	tr	0.16
Chuping	0–4	Ap	29.2	2.53	0.42	0.77	0.18	1.80
	4–29	B21t	36.0	3.45	0.46	1.00	0.21	0.78
	29–61	II B22tcn	62.6	6.95	0.28	0.84	0.18	0.58
	61–97	III C1	61.7	6.74	0.19	0.10	0.06	0.32
	97–135	III C2	57.7	10.65	0.19	tr	0.06	0.19
Tembaga	0–17	Ap	29.2	2.53	0.42	0.77	0.18	0.84
	17–45	B21t	15.9	1.89	0.31	0.63	0.16	0.33
	45–66	B22t	22.7	2.57	0.24	0.70	0.16	0.25
	66–95	II B23tcn	36.4	6.75	0.12	0.07	0.06	0.23
	95–126	III B31	36.5	7.07	0.08	0.02	0.04	0.17
	126–140	III B32	38.9	6.92	0.09	tr	0.04	0.23
Pokok Sena	0–3	Aplcn	60.7	4.53	0.17	1.35	0.41	2.08
	3–15	Ap2cn	64.2	5.47	0.18	1.41	0.43	1.77
	15–41	B21tcn	85.2	6.38	0.12	1.31	0.51	0.86
	41–76	B22tcn	85.6	6.96	0.10	0.41	0.25	0.50
	76–117	B3cn	82.5	7.39	0.09	0.10	0.09	0.39
	117–168	II Ccn	70.4	9.28	0.09	0.04	0.04	0.26

tr = traces

amounts of Fe_d were highest in the oxisols, Prang and Tandak profiles *(Table 2)*. Fe_p generally attains higher values than Fe_o in the upper horizons but in the lower horizons, the reverse is generally observed. The dominance of Fe_p in the upper parts of the profiles is due to organic matter and this feature is apparent in Tandak and Pokok Sena series where the values are exceptionally high. In the stone-line layer of Tandak series and in the B_{22}tcn horizon of Pokok Sena series, Fe_p is more than Fe_o. This is probably due to the presence of amorphous iron oxides in addition to the iron complexed by organic matter in the pyrophosphate extract[6]. In the case of Tandak series, the stone-line may represent a horizon enriched with organic matter during an earlier phase of pedogenesis. It can be seen that, in the immediate layers, below the Ap horizons in most soils, Fe_p is evidently higher than Fe_o and the magnitude of the difference is comparable to that in the Ap horizons. This is probably due to the downward migration of organic matter which is then fixed and immobilised by Fe in the uppermost B horizon. The values for pyrophosphate-extractable aluminium (Al_p) are given in *Table 2*. Fe_p is generally higher than Al_p and this indicates that iron is more dominant than aluminium in the organic complex.

The ratio of oxalate-extractable iron to dithionite-extractable iron (Fe_o/Fe_d) has been used by several workers as an indication of the relative proportions of amorphous and crystalline iron oxides[2,3]. This ratio is also termed as the 'active iron ratio' and is related to the degree of crystallinity or ageing of the iron oxides. The active iron ratio decreases with depth *(Table 3)* and this indicates a high degree of ageing in the subsoils while in the topsoils there are higher proportions of amorphous oxides. The proportion of amorphous iron oxides in the topsoils ranges from 13% to 20% in Chuping and Tembaga profiles to 3% in Prang and Tandak series. The degree of crystallinity is considered to be highest in the latter two profiles and suggest these profiles to be the most weathered. Inspection of active iron ratios also provides some indication of the iron-bearing minerals present[13]. Magnetite is absent in all profiles since it has an extremely high ratio in the range of 12 to 17. Hematite is expected to be present in the topsoils of Tembaga and Chuping series soils. Prang, Tandak and Pokok Sena series show values close to goethite mineralogy. Mineralogical implications of the active iron ratio relate to dominance of types of minerals. Ratios which are of the same magnitude as that of pure mineral as given by Gamble and Daniels[13] imply that this particular mineral is dominant *(Table 3)*. Based on this, the intermediate ratios in the top horizons of Bungor series can be interpreted as indicating mixed hematite-goethite mineralogy.

The constant Fe_d/clay ratio usually denotes co-migration of clay and Fe oxides. Changes in magnitude of this

TABLE 3. ACTIVE IRON RATIOS OF IRON OXIDE MINERALS AND QUARTZ[a]

Mineral	Fe_o/Fe_d
Magnetite	12.18–16.69
Hematite	0.16–0.20
Goethite	0.04–0.05
Quartz	0.02

[a]Taken from Gamble and Daniels[13]

ratio indicate heterogeneity of the soil parent materials. This feature is evident in all the profiles *(Table 4, Figure 1).* Except for Pokok Sena series, the increase in the ratio coincides with the stone-line layers. In the case of Pokok Sena profile, the increase in the ratio occurs in the lowest horizon. Where the trend of the constant ratio ceases, a lithological discontinuity exists in the profile. The higher amount of Fe oxides in the horizons below the discontinuity is probably due to silicate weathering and possible accumulation of Fe by lateral movement from adjacent substratum and also due to partial weathering of the laterite nodules. In the topsoils of Bungor, Chuping, Tembaga and Pokok Sena profiles, the ratio is somewhat lower in magnitude compared to the other horizons. This discrepancy can be attributed to the surface wash of a relatively higher amount of Fe than clay particles. This phenomenon is considered to take place during the later stage of profile development. In the Tandak and Prang series, this feature is not evident since the iron oxides are in a state of higher degree of crystallinity as shown by the smooth trend of the rather low values of the active iron ratio.

CONCLUSION

The rather constant trend of the active iron ratio in Prang and Tandak series indicates homogenised materials which are characteristic of Oxisols. The low values of the ratio imply that the dominant iron form is crystalline. The degree of crystallinity in general is also high in the other soils and this is a reflection of the weathering regime under humid tropical conditions. The active iron ratio in Pokok Sena series is comparable to the Oxisols and this feature serves as an additional parameter in the identification of this profile as an intergrade to Oxisols. Progressive release of iron is evident in the upper horizons of Bungor series even though this part of the profile is homogenous. This phenomenon is better expressed in Chuping and Tembaga series where younger deposits are encountered at shallower depths. In both of these profiles, the trend of the active iron ratio partly coincides with depositional breaks. However, the free iron to clay ratio is shown to be a more effective indicator of lithological discontinuities.

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TABLE 4. ACTIVE IRON RATIO AND Fe_d/CLAY RATIO IN SOILS

Soil series	Depth (cm)	Fe_o/Fe_d	Fe_d/clay
Prang	0–8	0.03	0.11
	8–38	0.02	0.11
	38–71	0.02	0.11
	71–97	0.02	0.10
	97–147	0.02	0.13
	147–185	0.02	0.18
Tandak	0–3	0.03	0.08
	3–15	0.03	0.08
	15–28	0.02	0.08
	28–58	0.02	0.08
	58–109	0.02	0.08
	109–132	0.01	0.15
Bungor	0–5	0.10	0.05
	5–15	0.10	0.06
	15–48	0.07	0.06
	48–81	0.03	0.06
	81–104	0.03	0.06
	104–130	0.03	0.09
	130–168	0.02	0.10
Chuping	0–4	0.17	0.06
	4–29	0.13	0.08
	29–61	0.04	0.11
	61–97	0.03	0.11
	97–135	0.02	0.16
Tembaga	0–17	0.20	0.06
	17–45	0.16	0.10
	45–66	0.10	0.09
	66–95	0.02	0.19
	95–126	0.01	0.19
	126–140	0.01	0.18
Pokok Sena	0–3	0.04	0.08
	3–15	0.03	0.09
	15–41	0.02	0.08
	41–76	0.01	0.08
	76–117	0.01	0.09
	117–168	0.01	0.13

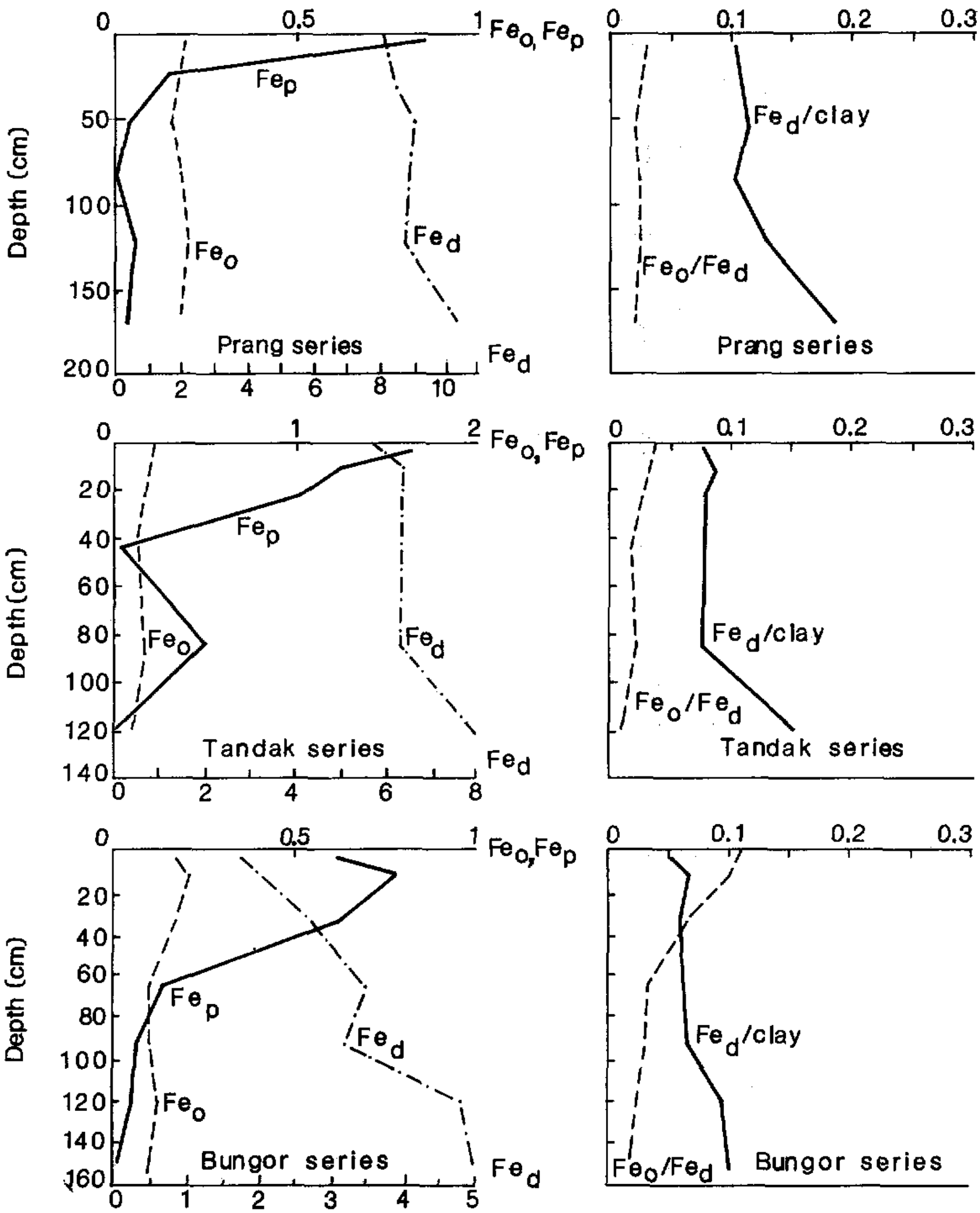

Figure 1. Distribution of iron forms (Fe_d = dithionite-extraction, Fe_p = pyrophosphate-extraction and Fe_o = oxalate-extraction) and their derived functions with depth.

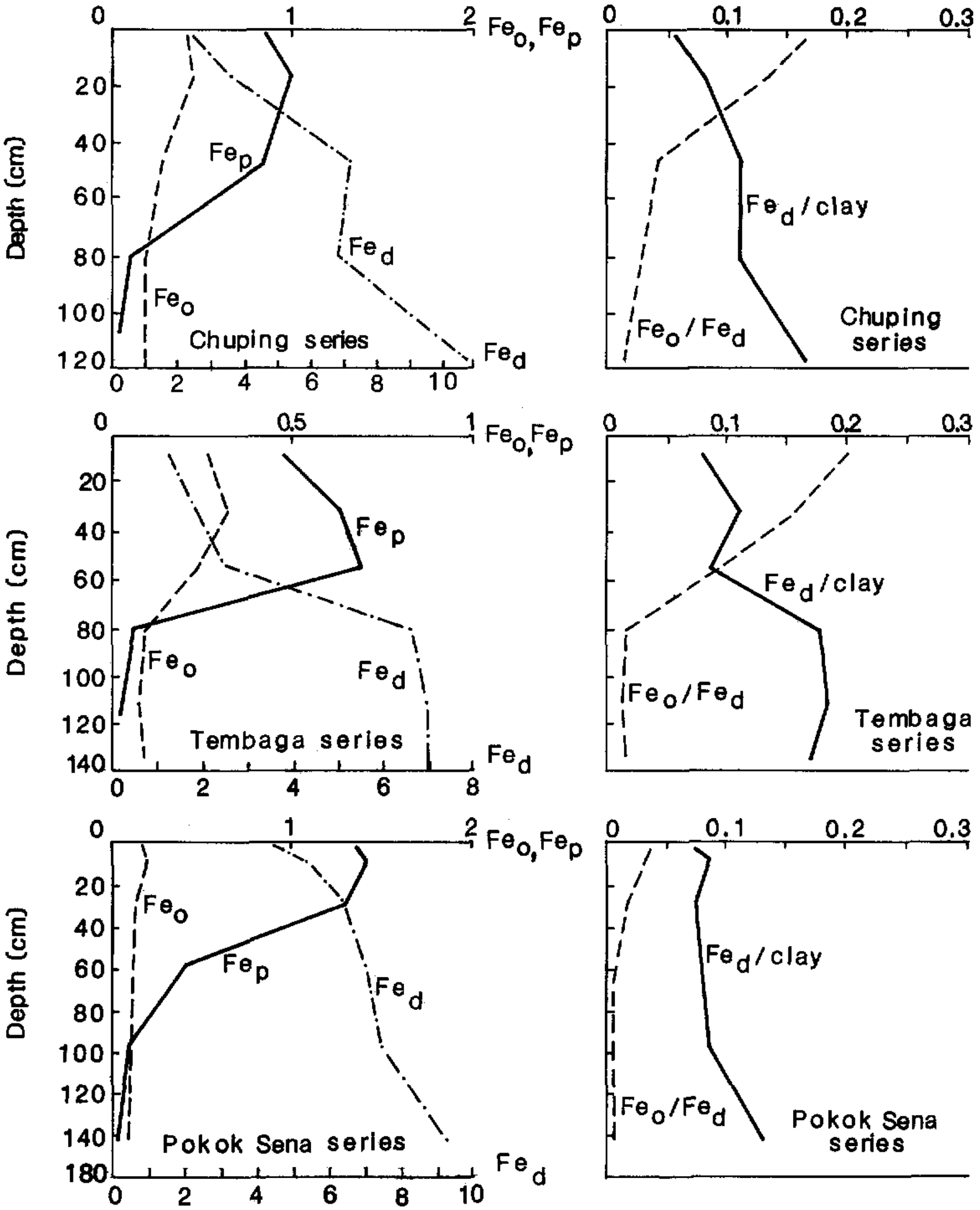

Figure 1. Distribution of iron forms (Fe_d = dithionite-extraction, Fe_p = pyrophosphate-extraction and Fe_o = oxalate-extraction) and their derived functions with depth (contd.).

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