

The Characteristics of Iron Concentration in Tropical Paddy Soils with Different Organic Matter Content

Arief Hartono¹, Widiatmaka¹, P. Curmi,² J. Berrier², A Jaffrezic

ABSTRACT

The Characteristics of Iron Concentration in Tropical Paddy Soils with Different Organic Matter Content (A. Hartono, Widiatmaka, P. Curmi, J. Berrier, and A Jaffrezic) : To characterize iron (Fe) concentration in tropical paddy soils with different organic matter content, selected Fe pedological features were collected from two paddy soil profiles in Darmaga, Bogor and two paddy soil profiles from Karawang. Bulk samples and uncovered thin section were subjected to selective dissolution by citrate- bicarbonate (CB) or dithionite citrate-bicarbonate (DCB). Bulk samples analyses showed that Fe-CB increased with increasing organic matter content. On the contrary in samples with less organic matter content, Fe-DCB tended to increase. 336 hours dissolution time was not enough to dissolve all Fe-CB as indicated by the tendency of the curve to increase with time but it was optimum for Fe-DCB. Compared to Fe-total, all samples showed relatively low Fe complexed or adsorbed by organic matter (Fe-CB) (0.5 %-5.53 %) and high Fe oxide amorphous and crystalline (Fe-DCB - Fe-CB) (60.57 %-69.07 %). The uncovered thin section observation showed that there was no Fe dissolution observed in selected coatings and mottles after 150 hours immersion in DCB solution. The XRD analyses showed the presence of goethite and ferrihydrite in the bulk samples. These facts suggested that organic matter will enhance complexation and adsorption of Fe in the formation of Fe pedological features and affected Fe oxide ratio in Fe concentration. These coating and mottle were stable and dominated by Fe oxides partly crystalline as shown by the presence of goethite and ferrihydrite minerals.

Key words: Fe Concentration, Fe Form, Paddy Soil, Pedological Feature

INTRODUCTION

Paddy soils undergo submersion and drying periodically in a year. It enhances reduction and oxidation processes in the soil and changes some chemical, biological and physical properties of the soils (Murase and Kimura, 1997; Tae *et al.*, 1998; Mozammel *et al.*, 2001; Kimura *et al.*, 2002). Reduction and oxidation processes occurring in paddy soils profoundly influence the dynamics of iron in solution as free ion or complexed by ligand existing in the soil such as hydroxides

and organic acids or as solid in the form of amorphous or crystalline minerals (Wang *et al.*, 1993; Jokova *et al.*, 1999). The precipitation of iron and manganese as oxides are typical pedological features existing in hydromorphic soils. Coatings in void, or concretion and diffuse mottles in matrix are the common formation. These pedological features are also can be observed in paddy soils. But so far the mechanism engaged in

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the formation of Mn or Fe concentration in hydromorphic environment are still not well understood.

Selective dissolution technique is one of the ways to study about formation of iron concentration. Citrate-bicarbonate (CB) and dithionite-citrate-bicarbonate (DCB) were introduced by Mehra and Jackson (1960) to selectively dissolve iron concentration. Pagliai and Sequi. (1982) proposed ammonium oxalate to remove iron as amorphous form. Identification of iron concentration using Differential X-ray Diffraction (DXRD) was introduced by Schulze (1981).

By using selective dissolution techniques citrate-bicarbonate (CB) and dithionite-citrate-bicarbonate (DCB) and X-ray Diffraction (XRD), Soulier (1991) and Acebal *et al.* (2000) identified and characterize Fe concentration. By using this dissolution techniques iron concentration can be fractionated into 1) iron complexed by citrate without reduction, 2) amorphous iron forms, and 3) more or less crystallized iron oxide.

Iron concentration in the form of coating, mottle, nodule and concretion can develop in each horizon in soil profile with different environment such as different in organic matter content. The effect of organic matter to the formation Fe concentration is not well evaluated. By evaluating Fe concentration with different organic matter content will give insight into how organic matter affect the formation of Fe concentration. Further, how Fe was immobilized in the form of coating, mottle or concretion in paddy soil. By using CB and DCB selective dissolution techniques the Fe form in the Fe concentration can be determined.

The objectives of this study were to evaluate how organic matter content effect the Fe form in Fe pedological features and its effect to the formation of crystalline Fe oxide

by using selective dissolution citrate-bicarbonate (CB) and dithionite-citrate-bicarbonate (DCB) in bulk samples and in thin section. XRD analyses was used to identify the of Fe oxide crystalline in Fe concentration.

MATERIALS AND METHODS

Samples

Selected samples were collected from two soils profiles of tropical paddy soils developed under volcanic ash parent materials in Darmaga, Bogor and two soils profiles developed under alluvium parent materials in Karawang. Sampling was conducted where the paddy fields were dried and bared. The soil profiles in Darmaga were taken toposequencely. Upslope profile was symbolized as P1D and downslope profile was symbolized with P2D. Two soil profiles from Karawang were taken in flat area and symbolized with P1K and P2K respectively. Soil profiles and selected horizon for bulk samples analyses and thin section observation are presented in Figure 1.

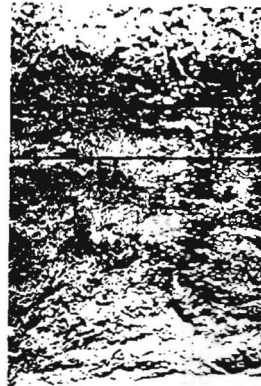
Bulk sample analyses which is to evaluate the kinetic of Fe dissolution of pedological feature of Fe to CB and DCB solution were performed by selecting samples from horizons with different organic matter content from both locations. Kinds of samples evaluated were coating around root in Ap horizons from both locations and mottles in B horizon from Karawang. Besides, matrix from both locations were also selected. Table 1 presents the selected samples and their content of organic matter.

To investigate the pedological features behaviour in respect to their stability same chemical dissolution technique were used on uncovered thin sections with size 110 x 70 mm. Table 2 present the site of samples for thin section.



P1D

Bg3/53-69 cm



P2D

Ap2 /9-20 cm



P1K

Bg1/37-60 cm



P2K

Ap2/30-60 cm

Bg1/60-81 cm

Figure 1. Soil profiles and selected horizon for bulk samples analyses and thin section observation.

Tabel 1. Sample used for bulk analyses

Profil/horizon/depth representatif	Pedological features	C-Organic content (mg/g)
P2D/Apg2/9-20 cm	coating around root	21.1
P2K/Apg2/30-60 cm	coating around root	8.7
P2K/Bg1/60-81 cm	mottle	6.4
P1K/Bg1/37-60 cm	Grey matrix	7.8
P1K/Bg1/37-60 cm	Brown matrix	6.7

Table 2. Samples used for thin section observation

Profil/horizon/depth representatif	Pedological features
P2D/Apg2/9-20 cm	coating around root
P2K/Apg2/30-60 cm	coating around root
P1K/Bg1/37-60 cm	mottle
P2K/Bg1/60-81 cm	mottle

Table 3. Pearson correlation (r) between organic matter content and Fe-CB and Fe-(DCB-CB)

	Fe-CB	Fe-(DCB-CB)
Organic matter content	0.95**	-0.041

** significantly different ($P < 0.01$)

Bulk samples analyses

Pedological features of related horizons were extracted *in situ* to have more concentrated samples. After collecting the sample, modified selective dissolution technique of Mehra and Jackson (1960) according to Jeanroy and Pillon (1989) was performed. Two series of experiment were conducted. One serie was DCB and the other was CB. Two hundred mg of six pedological feature samples were treated by DCB and the other by CB. Each sample of one serie (DCB or CB) were shaken for 1 hour or 2 hours or 6 hours or 48 hours or 336 hours. The solutions obtained after extraction were filtered through micropores filter papers and sent to analyses laboratorium in ARRAS. Total Fe of each pedological feature samples were also analysed.

Uncovered thin section observation

The four thin sections were treated only by DCB solution. Immersion in CB solution was not conducted because no Fe dissolution was observed in soulier (1991) 's experiment. Firstly, they were immersed in DCB in series of time. They were immersed in 1 minute or 10 minutes or 25 minutes or 45 minutes or 1 hour or 48 hours or 150 hours. Dissolution by DCB was continued in a hot water bath (70 °C) if there was no Fe dissolution after 150 hours. Volume of DCB solution were applied that the volume was enough to immerse the thin section (Bullock *et al.*, 1975; soulier, 1991). After the end of immersion, the thin sections were rinsed by ultra pure aquadestilled (twice distillation) water and then observed under optical microscope.

XRD Analyses

XRD analyses was conducted to determine qualitatively Fe oxide crystalline. Samples were derived from bulk samples.

RESULTS AND DISCUSSIONS

Bulk Sample Analysis

The Fe dissolution of the samples are described in kinetic dissolution in time course (Figure 2). Fe-CB showed the amount of Fe complexed or adsorbed by organic matter and Fe-DCB showed the amount of Fe in the form of oxides in crystalline or amorphous, Fe complexed or adsorbed but not Fe in crystalline silicate structure (Jeanroy, 1983). The subtraction between Fe-DCB and Fe-CB (Fe-(DCB-CB)) showed the amount of Fe-oxide amorphous and crystalline.

Figure 2a shows that coating around root in P2D/Apg2/9-20 cm resulted in Fe-CB profoundly higher than the others in each dissolution series (1 hour, 2 hours, 6 hours, 48 hours and 336 hours) (Fig. 2a). It was followed by brown matrix in P1D/Bg3/53-69 cm. Fe-CB of coating around root in P2K/Apg2/30-60 cm, mottles in P2K/Bg1/60-81 cm and grey matrix in P1K/Bg137-60 cm were comparable and the values far below coating around root in P2D/Apg2/9-20 cm. On the contrary Fe-DCB, where coating around root in P2K/Apg2/30-60 cm and mottles in P2K/Bg1/60-81 cm resulted in higher values of Fe-DCB compared with coating around root in P2D/Apg2/9-20 cm and brown matrix in P1D/Bg3/53-69 cm (Figure 2b). Grey matrix in P1K/Bg1/37-60 cm resulted in little amount of Fe-CB and Fe-DCB as well. After 336 hours of dissolution, Fe-CB dissolved ranging from 0.42 to 5.07 mg/g while Fe-DCB dissolved ranging from 32.14 to 65.65 mg/g.

These results showed that organic matter content of the samples affected Fe-complexed or adsorbed and Fe-oxide

amorphous and crystalline distribution of Fe concentration. Fe-CB clearly had relationship with the organic matter content of the sample. Coating around root in P2D/Apg2/9-20 cm with 21.1 mg/g C-organic content resulted in Fe-CB profoundly higher than the others with lower organic matter content. Simple pearson correlation (r) between C-organic content and Fe-CB after 360 hours extraction shows that C-organic content significantly correlated with Fe-CB (r = 0.95) and did not correlated with Fe-(DCB-CB) (r=-0.041) (Table 3).

Organic matter will complex and adsorbe Fe²⁺ and Fe³⁺ (soulier, 1991; Xingkai *et al.*, 1998; Jokova *et al.*, 1999; Yang *et al.*, 2001; Rose *et al.*, 2002) so its present in Fe concentration process will tend to increase Fe-complexed or adsorbed pool and will prevent the formation of Fe oxides pool as amorphous and crystalline. It was indicated by the increase of Fe-CB in this experiment.

This experiment also showed that 336 hours dissolution was not enough to dissolve all Fe-CB. All samples had tendency to have more Fe-CB if dissolution time was increased especially in coating around root in P2D/Apg2/9-20 cm (Fig. 2a). Meanwhile 336 hours dissolution was optimum for dissolving Fe-DCB with indicated by the levelling curve after 336 hours dissolution in all samples (Fig. 2b). It means that Fe dissolution by complexing Fe²⁺ and Fe³⁺ needs more time than reduction processes because citrate in CB must compete with acid organic matter as the other ligand in the soil solution or because Fe complexed in the samples in the form of Fe³⁺ so it was difficult to be complexed by citrate but easier to dissolve by reduction process with dithionite. This is possible because the samples were collected under dry condition (reoxidation) so Fe²⁺ changed to Fe³⁺ (Murase and Kimura, 1997).

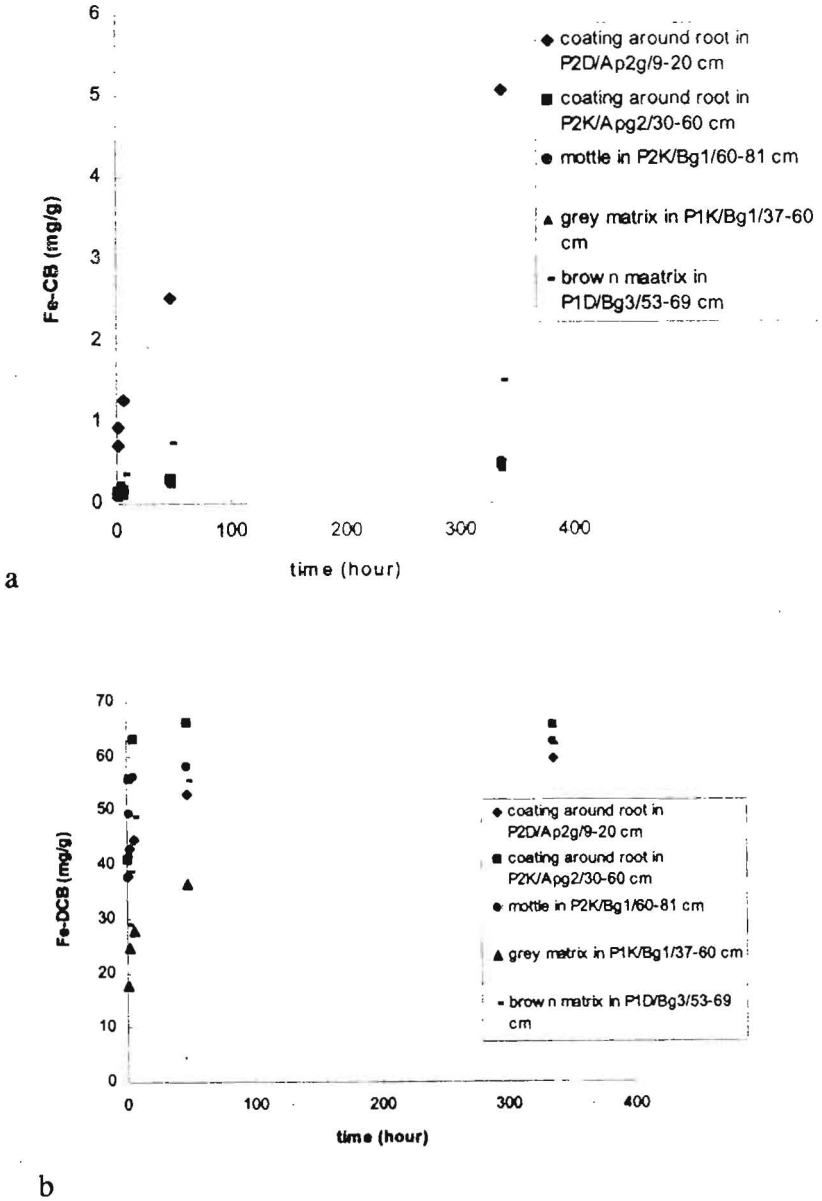


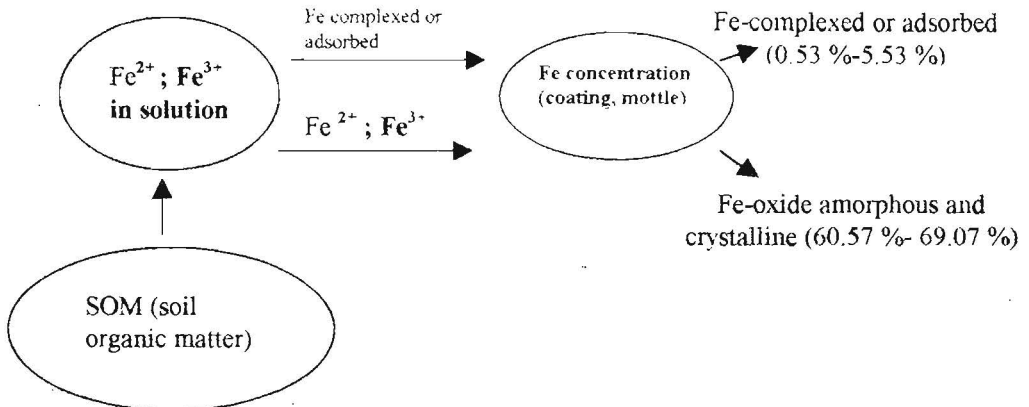
Figure 2. Kinetics Fe Dissolution Curve Obtained by CB and DCB.

The distribution of Fe oxides as amorphous and crystalline pool was shown in Fig. 3. After 336 hours dissolution, Fe oxide as amorphous or crystalline in the samples ranged between 31.72 mg/g to 65.18 mg/g.

Fe-total of the samples are presented in Table 4. Fe-total of all samples were relatively comparable except grey matrix in P1K/Bg1/37-60 cm. The highest Fe-total was brown matrix in P1D/Bg3/53-69 cm (99.70 mg/g) and the least was grey matrix in P1K/Bg1/37-60 cm (53.60 mg/g). It is clearly explained why PK/B/matrix resulted in little amount of Fe-CB and Fe-DCB. Kinetics Fe dissolution curve by CB and DCB compared to Fe-total are shown in Fig. 4. It is shown that Fe-CB dissolved after 336 h compared to Fe-total ranged between 0.53 % (grey matrix in P1K/Bg1/37-60 cm) to 5.53 % (coating around root in P2D/Apg2/9-

20 cm) (Fig. 4a) while Fe-DCB dissolved after 336 h ranged between 61.10 % (grey matrix in P1K/Bg1/37-60 cm) to 74.60 % (mottles in P2K/Bg1/60-81 cm) (Fig. 4b). From these Figures it is shown that not all Fe dissolved by these solutions. This was because that DCB could not extract Fe in crystalline silicate structure (Jeanroy, 1983). This experiment showed that Fe complexed by organic matter pool occupied small portion of the Fe concentration in the samples and It was shown that all samples were dominated by Fe oxides as amorphous and crystalline which occupied 60.57 % to 69.07 %.

The formation mechanism of Fe concentration involving Fe in solution and soil organic matter in these selected samples could be proposed as scheme below.



Tabel 4. Fe-total of the samples.

Profil/horizon/depth representatif	Pedological features	Fe-total (mg/g)
P2D/Apg2/9-20 cm	coating around root in Ap horizon	21.1
P2K/Apg2/30-60 cm	coating around root in Ap horizon	8.7
P2K/Bg1/60-81 cm	mottlé	6.4
P1K/Bg1/37-60 cm	Grey matrix	7.8
P1K/Bg1/37-60 cm	Brown matrix	6.7

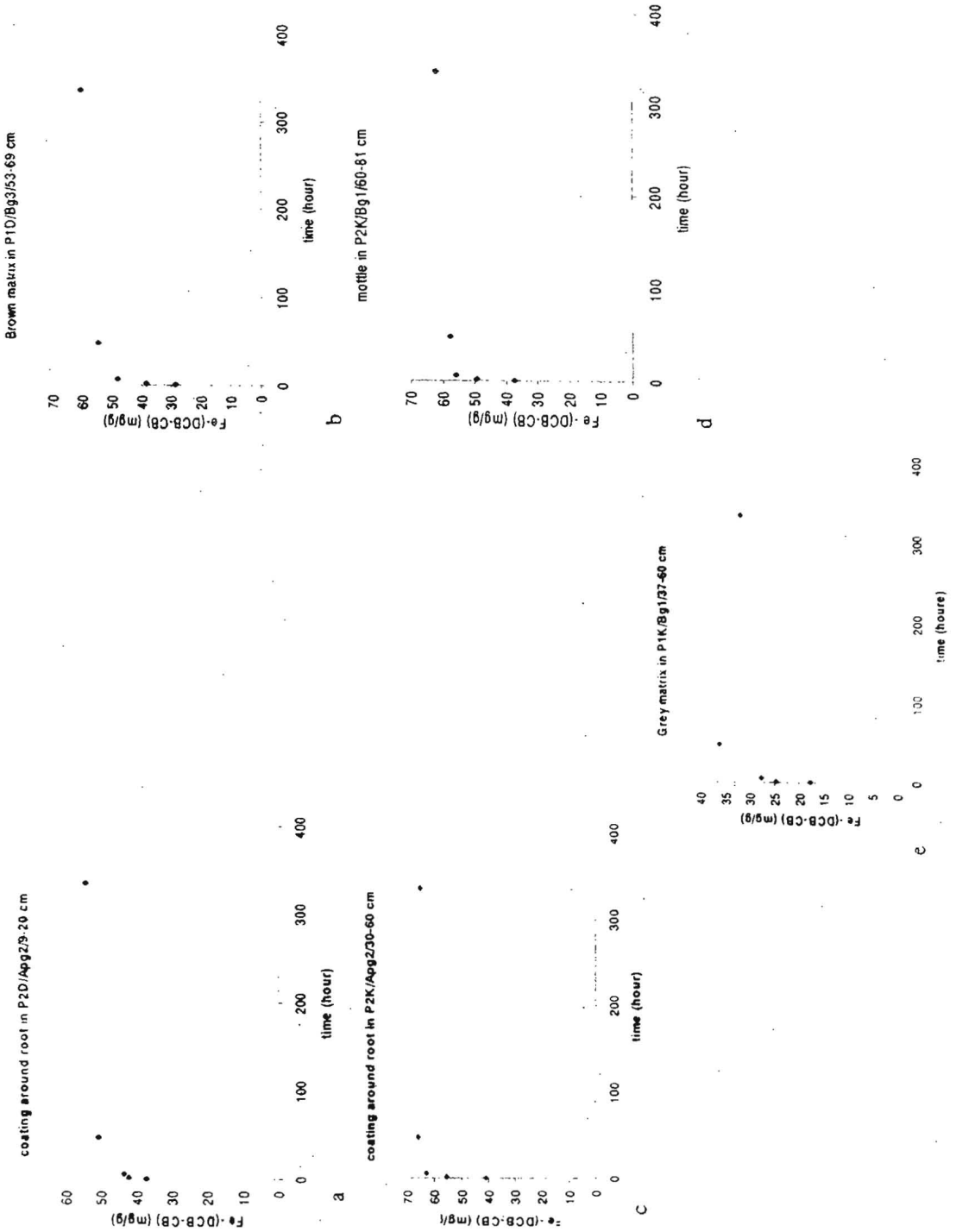
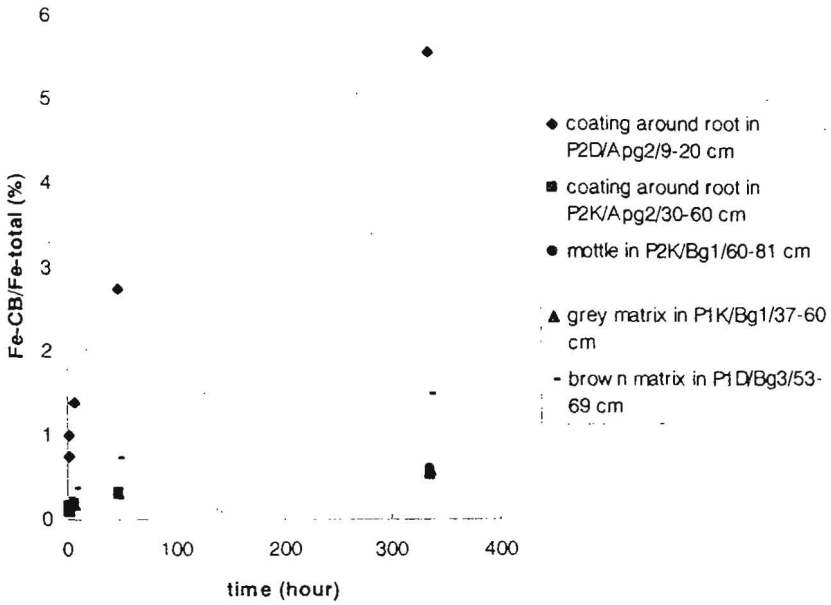
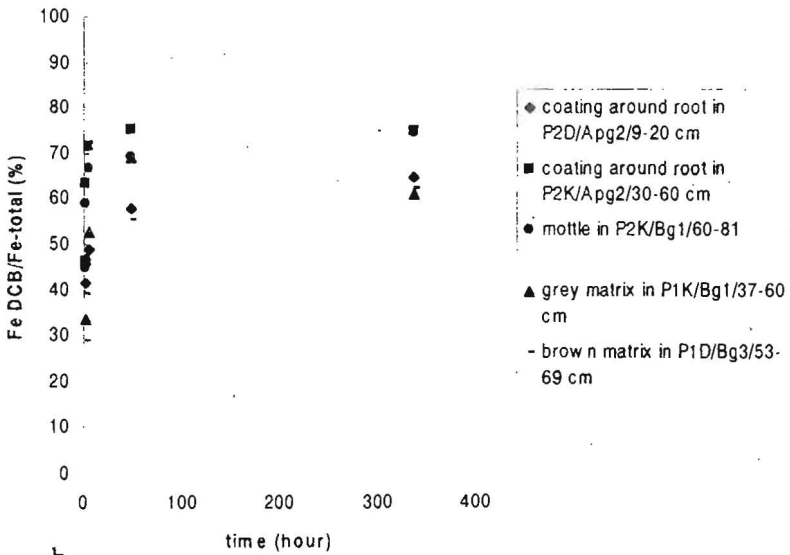


Figure 3. Kinetic Fe-DCB - Fe-CB curve



a



b

Figure 4. Kinetics Fe Dissolution Curve by CB and DCB compared to Fe-total

That proposed mechanism pointed out that soil organic matter is determining factor for Fe concentration like coating or mottle to contain amorphous or crystalline form.

The small amount of Fe complexed or adsorbed by organic matter in the samples indicated that reduction and oxidation process occurring in these paddy field have been lasting for long periode which enhanced the formation of Fe oxide amorphous and crystalline.

The Uncovered thin section observation

Thin section observation was used to evaluate the stability of Fe concentration. Fe dissolution to DCB of selected pedological features were observed. The results showed that there was no Fe dissolution observed in selected pedological features when they were immersed in DCB solution. It was shown that there was no Fe dissolution in all samples after 150 h immersion. There was no changes observed for examples at coating around root in P2D/Apg/9-20 cm (Fig. 5a,b) and at mottle in P1K/Bg1/37-60 cm (Figure 5c and d). Probably Fe dissolution occurred but it was too small amount to be observed through the picture.

Different results were obtained where dissolution by DCB was conducted in a hot water bath (70 ° C) for 15 minutes. By this method some dissolutions of Fe were observed in some pedological features. Representatives figure is mottle in P1K/Bg1/37-60 cm (Figure 6). But Fe dissolution by DCB in a hot water bath (70° C) for 15 minutes did not occur in coating around root. for intances in P2D/Apg/9-20 cm (Fig. is not shown). This result showed that the selected Fe concentration were stable and confirmed the bulk analyses results that the Fe pedological features in these paddy

soils were dominated Fe oxide amorphous and crystalline.

XRD analyses

Bulk samples analyses and thin section observation showed that Fe concentration in selected pedological features were dominated by Fe oxides amorphous or crystalline. XRD analyses was performed to evaluate qualitatively the kinds of Fe oxide minerals in the samples.

By using characterisation of goethite and ferrihydrite proposed by Brindley and Brown (1980), XRD analyses showed clearly that Fe concentration in some pedological features was goethite and probably ferrihydrite. Mottles from P2K/Bg1/60-81 cm before treated by CB and DCB showed the presence of goethite and probably ferrihydrite and collapsed after extracted by DCB for 336 h (Fig. 7). The presence of goethite and ferrihydrite were also found in coating around root in Ap horizon from P2D/APG2/9-20 cm before treatments and also collapsed after extracted by DCB for 336 h (Fig. 8).

The presence of goethite and ferrihydrite in coatings around root and mottles showed that some Fe concentration in these pedological features have already developed to crystalline mineral.

CONCLUSIONS

Organic matter content affected the Fe distribution in the formation of Fe concentration like in coating and mottles. Fe complexed or adsorbed pool will increase with increasing organic matter content. The increased Fe complexed or adsorbed pool decreased Fe oxide pool ratio in Fe concentration.

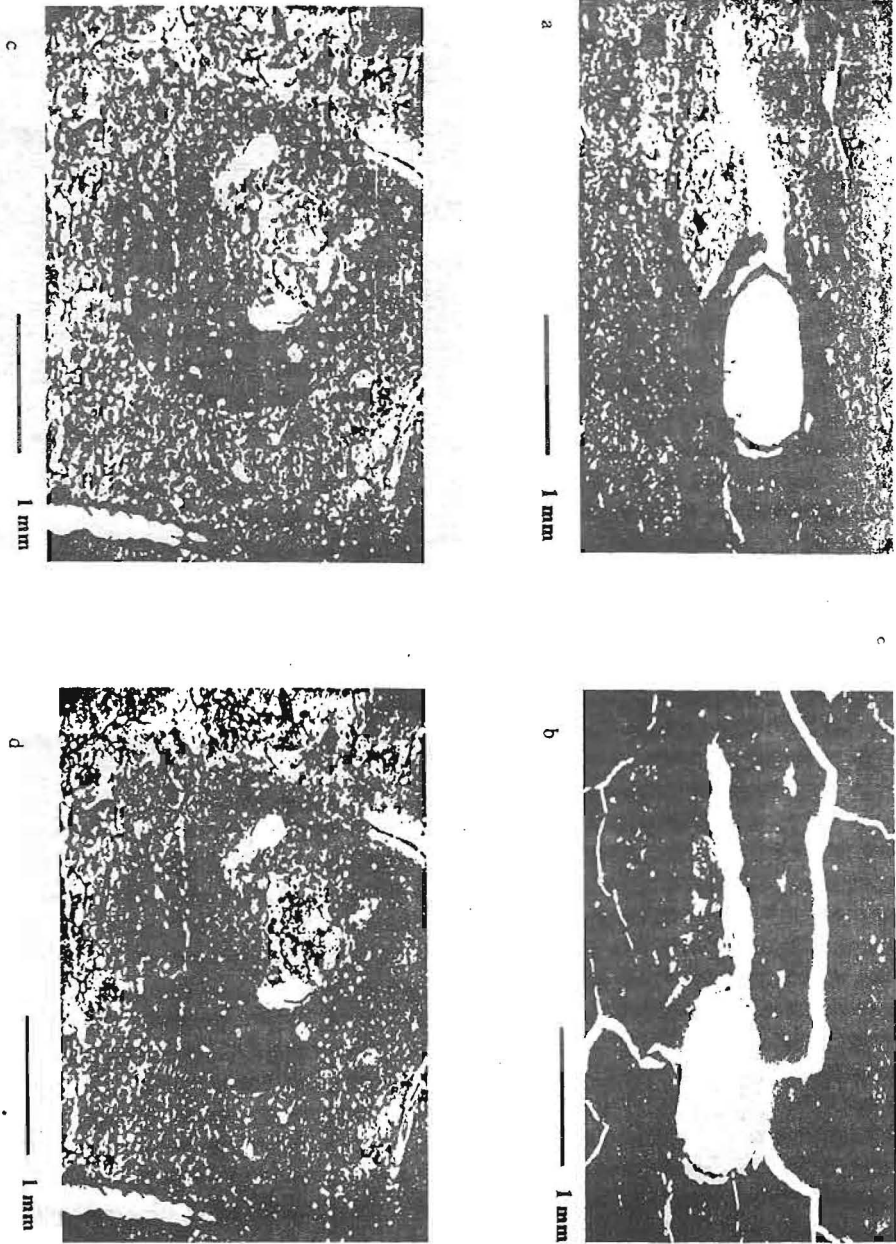
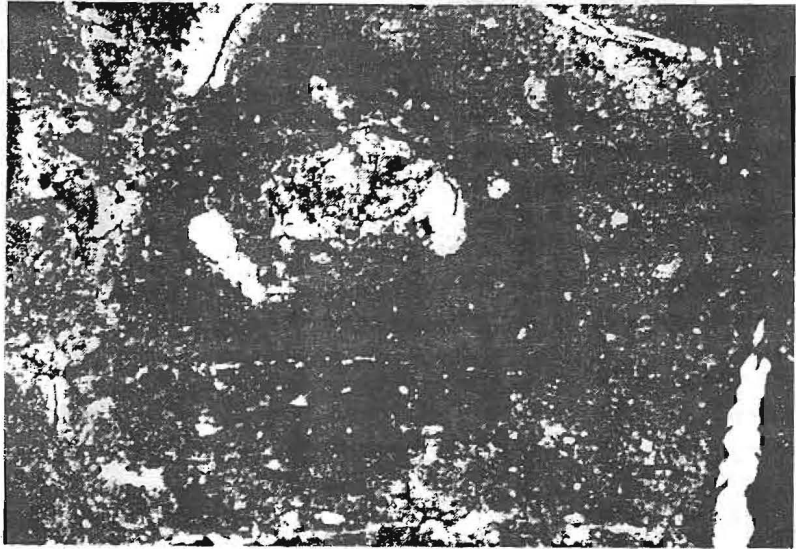
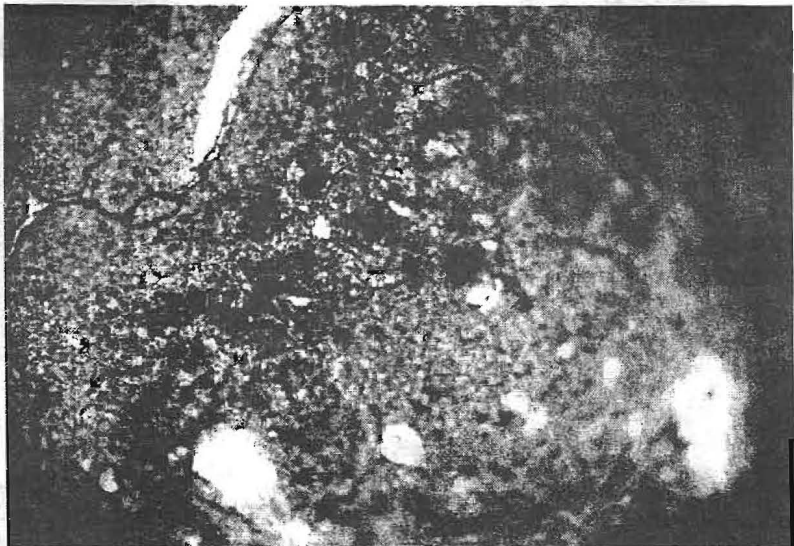


Figure 5. Coating around root in thin section located in P2D/Apg/9-20 cm before DCB treatment (a); after 150 h immersion in DCB solution (b) and mottle in P1K/BG1/37-60 cm before treatment (c); after 150 h immersion in DCB solution (d).



a

1 mm



b

1 mm

Figure 6. Mottle in P1K/BG1/37-60 cm before treatment (a); immersed in DCB solution in heated water for 15 minutes (b)

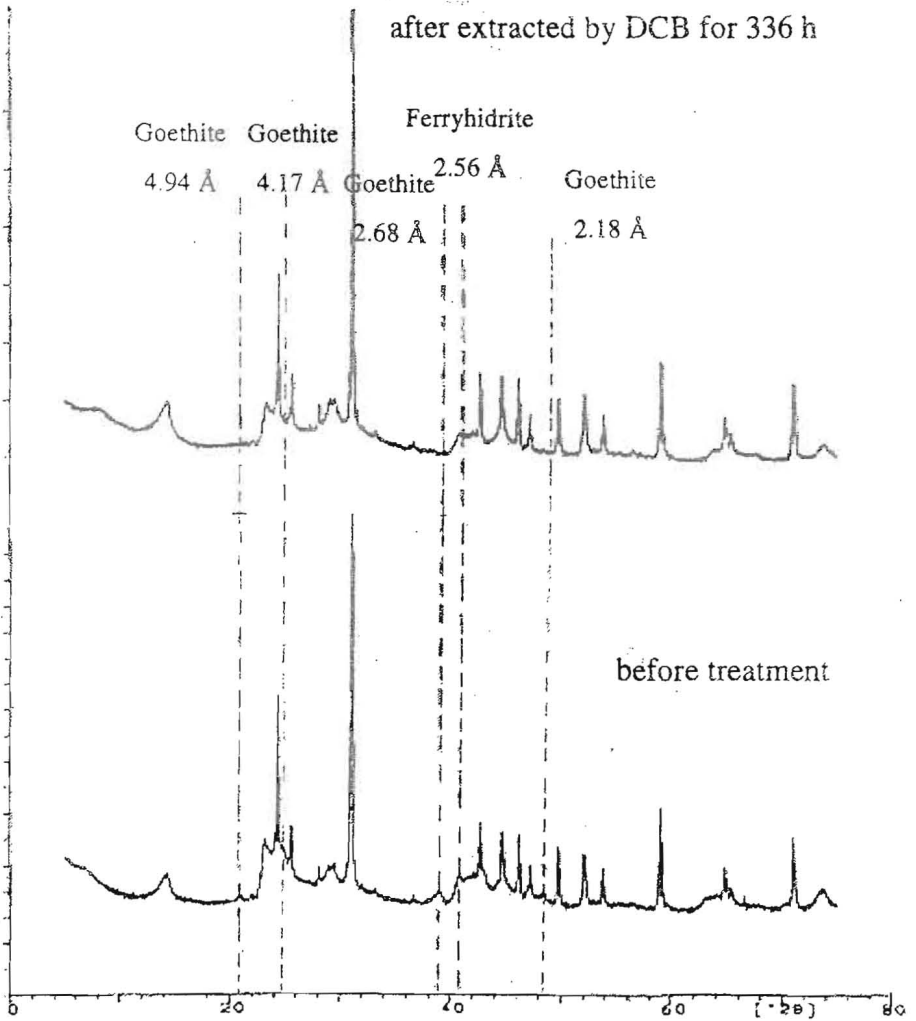


Figure 7. XRD analyses of mottles from P2K/Bg1/60-81 cm before treatment and after extracted by DCB for 336 h.

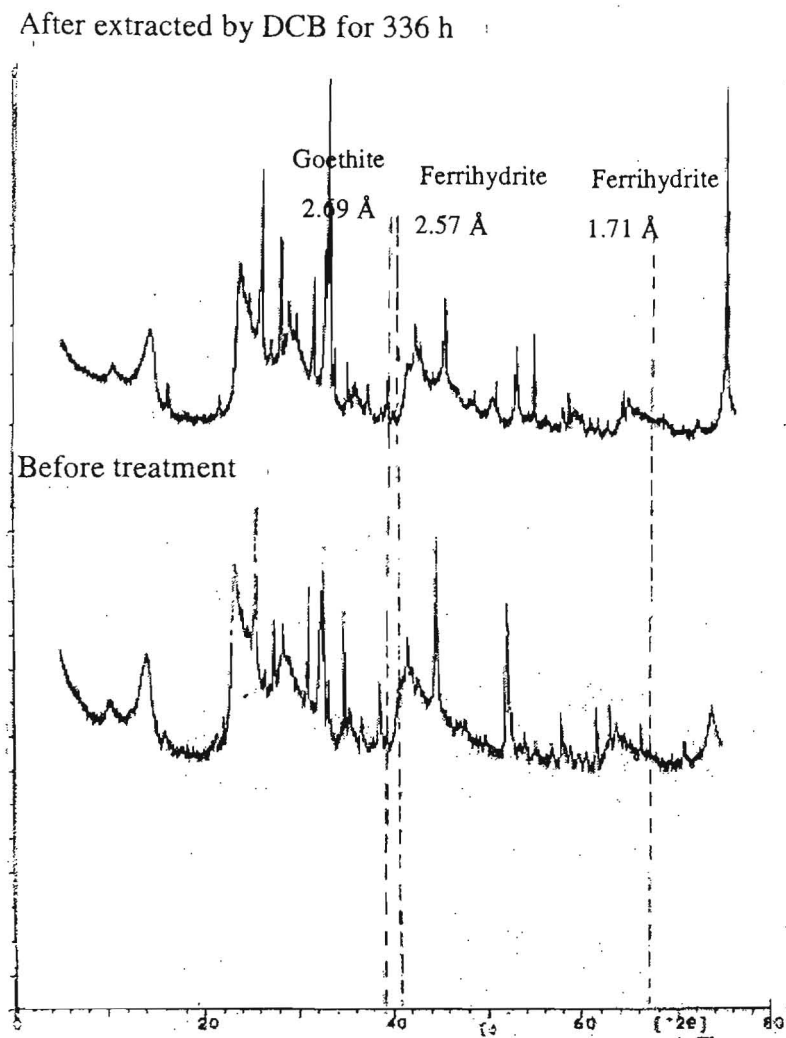


Figure 8. XRD analyses of coating around root from P2D/Agp2/9-20 cm before treatment and after extracted by DCB for 336 h.

336 h dissolution time was not enough to dissolve all Fe-CB as indicated by the tendency of the curve to increase but it was optimum for Fe-DCB. Compared to Fe-total, in all samples Fe complexed or adsorbed was very small amount (0.5 % - 5.53 %) while Fe oxide amorphous and crystalline was relatively high amount (60.57 %- 69.07 %).

The stability of Fe concentration in selected pedological features were very high and containing goethite and ferrihydrite. The presence of goethite and ferrihydrite in selected pedological features indicated that some Fe concentration has developed to crystalline Fe oxides.

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