

Redox and pH Chemistry and Nutrient Uptake by Rice
in Flooded Oxisols of Sitalung Area of Sumatra, Indonesia

Wm. H. Patrick, Jr., and A. Jugsujinda

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Center for Wetland Resources

Louisiana State University

Baton Rouge, Louisiana 70803-7511, USA

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ABSTRACT

In a laboratory study, the effect of flooding on redox potential (Eh), pH, and the release of nutrient elements was studied in 45 paddy soils collected randomly from the Sitiung Transmigration Area of Sumatra, Indonesia. The soils were clayey, kaolinitic, isohyperthermic family of Typic Haploorthox. Rice (Oryza sativa cv. IR 42) grown on these soils developed physiological disorders associated with flooding. Forty-five rice leaf samples were also collected from the same locations at tillering stage and analyzed for various elements. Eh of the soils sharply decreased and went down to an average value of -217 mV after 60 days of flooding. Soil pH increased from an average of 5.2 to 6.6. Water-soluble and extractable forms of Mn were positively correlated with soil pH but negatively correlated with soil Eh. Extractable Fe was positively correlated with soil pH. After flooding, average value of extractable Fe, Mn, Zn, Cu, Mo, Al, Ca, Mg, P, K and Si concentrations increased, markedly whereas, their water-soluble forms, except Fe, decreased slightly.

Leaf tissue analyses indicated that 51% and 58% of the rice plants suffered Fe and Al toxicity, respectively as their

contents were higher than 300 ppm; a critical content for their toxicity. The rice plant also suffered deficiency of Ca, P, K, Mg, and Si in the ascending order as their contents were below the critical content for deficiency. Al was inversely correlated with extractable forms of Mo, P and K. Ca was significantly correlated with extractable Ca. P was inversely correlated with extractable Al. K was inversely correlated with water-soluble P. Mg was significantly correlated with water-soluble Ca and extractable forms of Ca and Mn. Si was significantly correlated with water-soluble Fe, Cu, Ca, Mg and F and extractable Ca. Relationships between various elements in rice leaf tissues and in soils were established and discussed.

INTRODUCTION

The highly weathered, low fertility, Oxisols and Ultisols soils in the Sitiung area of Sumatra are rapidly being cleared for transmigrant farmers from the over-populated Indonesian islands of Java and Madura. Most of these newly opened areas are being used for growing lowland rice (Oryza sativa cv. IR 36 and IR 42). Rice grown on these flooded soils frequently exhibits poor growth and a leaf discoloration called 'oranging' which develops about two months after transplanting. Grain yields on these affected soils are low. This problem is probably due to physiological disorders caused by nutrient toxicity or deficiency as a result of flooding.

Symptoms of orangeing were earlier recognized in Sri Lanka (Ponnamperuma et al., 1955), and were later observed in flooded rice grown in Llanos Orientales in Colombia (Howeler, 1973). It has been extensively identified in the Philippines, Vietnam, Thailand, Malaysia, India, Sri Lanka, Liberia, Senegal, Colombia, and China, and attributed to a nutritional disorder of flooded rice associated with excess water-soluble Fe which often occurs on strongly acid soils (Jin-Pei and Ponnamperuma, 1984). Ottow et al. (1983) suggested that iron toxicity was due to an insufficient supply of plant nutrients, mainly K, P, Ca and Mg, rather than a high level of active Fe under acid conditions. These hypotheses were later confirmed by Benckiser et al. (1984).

Flooding causes several biological and chemical changes of soil properties that are important to plant nutrition and growth (Redman and Patrick, 1965; Ponnamperuma, 1965; Turner and Patrick, 1968). The effect of decreased soil Eh and associated

changes in soil pH have important implications on phosphate transformations (Mahapatra and Patrick, 1969), on the dissolution of manganese and iron compounds (Gotoh and Patrick, 1972; 1974), and on phosphate sorption and mobilization in acid soil (Holford and Patrick, 1979). Recently, the effect of flooding on reactivity and mobility of K, Ca, Mg, S and trace metal nutrients was reviewed by Reddy and Patrick (1983).

The purpose of this investigation was to elucidate the redox and pH chemistry, and nutrient uptake by lowland rice in problem soils in Sumatra. In particular, our main objective was to quantify the concentration of selected nutrients in the soils using different fractionation procedures, and to establish the relationship between these nutrients and their counterparts in the rice plant. Our goal was to specify the factors responsible for low rice yields and the toxic conditions encountered in these soils.

MATERIALS AND METHODS

Location and Climate.

Sitiung Transmigration area is located about 204 km southeast of Padang, capital city of West Sumatra Province, Sumatra, Indonesia (Figure 1). The area was opened 7 years ago for resettled transmigrant farmers. The land is irrigated and the paddy soils have been used for lowland rice for about 2 years. The climate is that of a tropical rain forest with 7-9 wet months having rainfall over 200 mm/month (September-May) and 2-4 dry months receiving rainfall of about 100 mm/month (June-August). The total annual rainfall for the area is about 2500 mm. Oldemen et al. (1979) classified the climate of the area as B1.

Soils

The soil was classified as clayey, kaolinitic, isohyperthermic family of Typic Haplorthox with a thin 0-12 cm dark brown (10 YR 4/3-3/3). It had a moderately acid reaction, low in P, K, and base saturation. It was high in Fe, Mn and Al saturation and contained a few round Mn concretions. The soil was moderately high in Zn and Cu. Some selected chemical properties of the soil are given in Table 1.

Soil and Plant Sampling.

One part of this study consisted of collecting a number of plant and soil samples at random throughout a field in which symptoms appeared. The idea was to obtain a random distribution of adverse soil conditions that would allow a statistical evaluation to be made of the relationships between the various elements in the soils and their uptake by the rice plant. A total of 45

Table 1. Some chemical properties of top soil layer of Oxisol at Sitiung Transmigration area of Sumatra, Indonesia.

Soil Property	Value	
Sand	31.9	%
Silt	11.9	%
Clay	56.2	%
C	1.72	%
N	0.13	%
C/N	13	
Free Fe ₂ O ₃	3.9	%
Al saturation	69	%
pH (1:1 soil/water ratio)	4.1	
Extractable Ca	0.6	me/100 g
Extractable Mg	0.3	me/100 g
Extractable K	0.2	me/100 g
Extractable Na	0.1	me/100 g
Exchangeable Al	3.1	me/100 g
Exchangeable H	0.2	me/100 g
CEC-soil (NH ₄ OAc)	0.7	me/100 g
Sum of cation	21.5	me/100 g
CEC-clay (NH ₄ OAc)	15.5	me/100 g
Base saturation	14	%

Source: Center for Soil Research (CSR), Bogor, Indonesia.

Sodium Acetate Extractable Fraction. Fifty ml of 1N Na acetate having pH 4.0, was added to the moist soil samples in the centrifuge bottles and shaken for one hour in a mechanical shaker followed by centrifuging on a GSA Rotor at 7000 rpm for 20 minutes. The supernatant liquid was filtered through an 0.45 um membrane filter. The centrifuge bottles containing moist soils were dried in a force draft oven at 105 C for 24 hours for determination of moisture content and oven-dry weight of the soil. The aliquots were acidified with 12N HCl to pH 2 and stored for analysis. Both water-soluble and extractable fractions of selected elements were analyzed on an ICAP.

Soil Incubation.

In order to study the physicochemical changes under flooded soil conditions, the soils were incubated with excess water. Special platinum electrode tubes to be used for soil incubation were constructed by sealing one-half inch piece of 18-gauge platinum wire on both sides near the bottom of 40x138-millimeter Pyrex test tubes (Figure 2).

Before using the test tubes, platinum electrodes were cleaned electrolytically in 1N HCl. This was accomplished by connecting the negative pole of a 12 volt dry cell battery to the platinum electrode and connecting the positive pole to a carbon electrode and allowing hydrogen gas to bubble from the platinum electrodes for three minutes. The performance of the platinum electrodes was checked by immersing the electrode along with the salt bridge which was connected to a calomel electrode in pH 4 and pH 7 buffers. A small amount of quinhydrone was added to the

pH buffers. The reading on the Eh meter in millivolts should be 218 mV (+/-5 mV) for pH 4 buffer and 40.8 mV (+/-5 mV) for pH 7 buffer at 25 C.

Sixty grams of air-dry soils were weighed, in duplicate, and uniformly mixed with 0.2% ground rice straw before transferring into the electrode tubes. The soils were flooded with an excess of high purity deionized distilled water, and incubated at 30 C. Eh and pH measurements were made within a few minutes after flooding, 24 hours after flooding, and subsequently at daily intervals for 60 days. During the incubation period, the flood water was added to the redox tubes for maintaining a constant water level. Gases, if any, accumulated causing voids were removed by tapping the containers gently by hand on the top of a bench. Eh measurements were made with a Beckman Zeromatic pH meter using the platinum electrode and a saturated calomel half-cell. When making soil Eh measurements the Calomel potential (+245 mV) was added to the meter reading (millivolts). pH measurements of the top 1 cm soil layer were made with the Beckman Zeromatic pH meter using a calibrated combination glass electrode.

Chemical Fractionation of Soils after Flooding.

At the end of incubation, excess flood water was decanted from the redox tubes. The wet soil cores from the incubation tubes were removed insuring that both the oxidized and reduced soil zones were sampled. The samples were immediately transferred to a preweighed centrifuge bottles and weighed to determine water and soil contents. The bottles were immediately purged

with N₂ gas.

Water-Soluble Fraction. Twenty-five ml of oxygen free deionized water was added to the wet soil samples with a hypodermic syringe and the bottles were shaken for 30 minutes in a mechanical shaker. The soil solutions were centrifuged under N₂ atmosphere on a GSA Rotor at 7000 rpm for 20 minutes. The supernatants were filtered through 0.45 µm membrane under an inert atmosphere (Patrick and Henderson, 1980; DeLaune et al 1985). The aliquots were acidified to pH 2 by adding 12N HCl and stored for analysis.

Sodium Acetate Extractable Fraction. One hundred ml of oxygen free 1N sodium acetate (pH 4.0) was added to the residual moist soil from water-soluble fraction with the help of a hypodermic syringe and the centrifuge bottles were purged with nitrogen. The mixture was shaken for 1 hour on a mechanical shaker and centrifuged on a GSA Rotor at 7000 rpm for 20 minutes. The supernatants were filtered through 0.45 µm membrane filter as described earlier. The aliquots were acidified with concentrated hydrochloric acid to pH 2 and stored for analysis. The centrifuge bottles containing moist soils were dried in a forced draft oven at 105 C for 24 hours for determination of moisture content and weight of soil present.

Statistical Analysis.

Simple linear correlation was worked out to establish the relationships between the selected nutrients in the rice leaf tissues and in the soil extracts after incubation.

RESULTS AND DISCUSSION

A.Redox and pH Chemistry of Sitiung Flooded Soil.

1.Changes of soil pH and Eh

At one day of flooding, pH value of the soils ranged from 4.3 to 6.5, with an average value of 5.2 and Eh value ranged from +65 to +605 mV, with an average value of +446 mV (Figure 3). After one day of flooding until one week of flooding, pH of the soils gradually increased and soil Eh sharply decreased. At one week of flooding, pH of the soils increased to an average value of 5.7 and soil Eh decreased to an average value of -86 mV. At two weeks of flooding, average soil pH value increased to 6.3 and average soil Eh decreased to -155 mV. After sixty days of flooding, pH of the soils ranged from 5.9 to 7.3, with an average value of 6.6 and Eh of the soils ranged from -255 to -155 mV, with an average value of -217 mV. The gradual decrease of Eh after one week of flooding was obvious because the soils were quite high in free iron (Table 1). The relatively high redox buffering capacity of the iron system was observed by Patrick (1981) and reported that soils with large amounts of bioreducible iron did not undergo a rapid decrease in redox potential. Several investigators (Ponnamperuma, 1965; Patrick, 1966; Patrick et al., 1973; Gotoh and Patrick, 1974; Morghan and Patrick, 1974) reported that on flooding a soil, pH increased and redox potential decreased from a high value of +500 mV to +100 mV. Almost all of Mn was in the reduced form while a little of ferric Fe had been affected. The oxidized Mn served to maintain the redox potential in the range of +300 mV to +200 mV by accepting elec-

trons from the decomposing organic matter and preventing the redox potential from decreasing to negative values until all of the bioreducible Mn had been converted to the manganous form. Likewise, oxidized Fe maintained Eh in the range of +100 to -100 mV. The buffering effect of Fe was essentially depleted at -150 mV and it was in this range that the facultative anaerobes ceased to function and true anaerobes which reduce sulfate and carbon dioxide took over.

2. Soil pH and Eh Relationship

Relationship between average value of Eh and pH of the soils during the 60-day of flooding is shown in Figure 4. During the first week of flooding (first slope), Eh decreased from +203 mV to -101 mV and the Eh/pH slope was probably controlled by the Mn system. During this period, the slope was -517 mV per pH unit. Correlation coefficient (r) between Eh and pH, during the first week period, was -0.945**. After one week of flooding (second slope), the Eh gradually decreased from -101 to -217 mV through the end of soil incubation period thereby causing the slope to level off. The new Eh/pH slope, -118 mV per pH unit ($r = -0.896^{**}$), was probably controlled by the Fe and SO₄ systems. It was reported that the Eh/pH slope varied from -40 to -140 per pH unit (IRRI, 1963). When the redox potential was controlled by the hydrogen or oxygen system, the Eh/pH slope was -60 mV per pH unit and redox potential measured in soil was a combination of all redox couples present, time of incubation, kind and amount of organic matter as reported by Ponnampetuma (1965). In the present study, the Eh/pH slopes were probably

controlled mainly by Fe and Mn systems, and so it was difficult to establish a particular Eh/pH slope value to describe the relationship between soil Eh and pH. The correlation coefficient between soil fractions and soil Eh and pH parameters is shown in Table 2. At 60 days of flooding, there was a highly significant correlation between soil pH and water-soluble Mn ($r = 0.666^{**}$), and between soil Eh and water-soluble Mn ($r = -0.426^{**}$). A similar correlation was observed for extractable Mn suggesting a relationship between Mn mobility and soil Eh and pH. At the end of 60 days of flooding, however, only extractable Fe was significantly correlated with pH ($r = 0.346^{*}$) (Table 2).

B. Distribution of Elements in Soils and their Relationship with Nutrient Uptake by rice

The distribution of water-soluble and extractable forms of some selected soil elements before and after flooding is shown in Figures 5 and 6. The concentration of elements in the rice plant is shown in Table 3. The correlation coefficient between the various elements in the rice leaf and water-soluble, and extractable forms of nutrient elements in the soils is shown in Tables 4 and 5, respectively. Correlation coefficients showing the relationships between the various elements in the rice leaf are given in Table 6.

B.1. Micro Elements

1. Iron(Fe)

The average concentration, hereafter referred as concentration, of both water-soluble and extractable iron in the soils were low before flooding and influenced by flooding (Figure 5). Extractable Fe was markedly increased whereas water-soluble Fe was only slightly increased after flooding. The decrease in Eh associated with flooding was responsible for the increase in extractable Fe at the expense of water-soluble form (Gotoh and Patrick, 1974). The results suggested that water-soluble iron was largely adsorbed by the exchange and organic sites in the soil, and only a small amount of Fe remained in water-soluble fraction. Water-soluble Fe and the Fe bonded weakly to exchange and organic sites were reported to be more available to the rice plants (Sim and Patrick, 1978).

The chemical composition of the rice leaf showed that Fe

content in the leaf tissues was very high, ranging from 85 to 783 ppm with an average of 334 ppm (Table 3). Yoshida (1981) reported that typical symptoms of Fe toxicity developed in the rice leaf blade containing more than 300 ppm of Fe. In the present study, 51% of the leaf samples analyzed was grouped as having Fe toxicity. Iron concentration in the rice leaf had no significant relationship either with water-soluble Fe or extractable Fe in the soils (Tables 4 and 5). None of the other elements determined in the soils showed any significant relationship with Fe concentration in the rice plant. However, in the rice leaf there was a highly significant correlation between Fe and Zn and Al ($r = 0.523^{**}$ and $r = 0.646^{**}$) (Table 6) thereby suggesting a relationship between Fe, Zn and Al in the leaf tissues.

The effects of flooding of soils on the availability of Fe to rice plants have been well documented by many workers. Jugsujinda (1975), and Jugsujinda and Patrick (1977) found that uptake of Fe by the rice plant was markedly increased under anaerobic conditions at pH 7 and below. Schwab and Lindsey (1983a) demonstrated that Fe uptake by the rice plant was related to the concentration of Fe^{2+} in solution. Ottow et al. (1983) showed that leaves affected by Fe toxicity revealed low or deficient amounts of K and P and often of Zn and sometimes of Ca and Mg. They concluded that Fe toxicity was due to a multiple nutritional soil stress (insufficient supply of K, P, Ca and Mg) rather than to a high level of active Fe under acid conditions. This conclusion was later confirmed by Benckier et al. (1984).

2. Manganese (Mn)

The concentration of both water-soluble and extractable Mn was also low before flooding (Figure 5). Flooding for 60 days caused a marked increase in extractable Mn in the soils. Water-soluble Mn, however, decreased suggesting that some of water-soluble Mn was adsorbed by exchange and organic sites after flooding. The weakly adsorbed Mn at the exchange sites may become easily available to the rice plant. The increase in extractable Mn in the soil after flooding indicated increased Mn solubility and availability to the rice plants. In our earlier studies, Jugsujinda (1975), Jugsujinda and Patrick (1977) observed that Mn uptake by rice was higher under anaerobic conditions than under aerobic conditions. Schwab and Linsey (1983b) further observed that Mn uptake by rice increased with increasing Mn $2+$ activity in soil solution in controlled redox suspensions. Mn transformations in flooded soils have been examined by a number of workers (Clark et al., 1957; Turner and Patrick, 1968; Gotoh and Patrick, 1972).

The content of Mn in the leaf ranged from 115 to 3339 ppm with an average of 1367 ppm (Table 3). The average content of leaf Mn was well below the critical level for Mn toxicity. The critical content for Mn toxicity is 7000 ppm for rice shoot as reported by Yoshida (1981). In many cases, high Mn content in rice tissue is frequently associated with high yield possibly indicating that high Mn content in the soil is associated with various favorable soil conditions. The low level of Mn obtained in this study might indicate unfavorable soil conditions.

There was a significant correlation between leaf Mn and water-soluble forms of Mn, Ca and Mg in the soils ($r = 0.367^*$, 0.384^* and 0.303^* , respectively) (Table 4), and between leaf Mn and extractable forms of Mn and Ca in the soils ($r = 0.326^*$ and 0.496^{**}) (Table 5). The results obtained are consistent with the results reported by Schwab and Lindsey (1983b).

It was interesting to note that Mn of leaf was significantly correlated with Ca, Mo and Si of the leaf (Table 6).

3. Zinc (Zn)

The results showed that more Zn in the soils was recovered in extractable form than in water-soluble form (Figure 5). However, the concentration of Zn in water-soluble form was higher before flooding than after flooding the soils. This indicated that submergence resulted in decrease in the concentration of Zn in the soil solution. These results were in agreement with the findings of other workers (Forno et al. 1975; Reddy and Patrick 1977b; Sim and Patrick 1978; Gambrell et al. 1980).

The high recovery of extractable form of Zn in the soils before flooding (oxidized condition) was attributed to the release of adsorbed and coprecipitated Zn in the colloidal hydrous oxide in the soil. The importance of the adsorption and coprecipitation processes in regulating zinc availability has been reported by Kinniburgh et al. (1976); Kalbasi et al. (1978) and Shuman (1978) as cited by Gambrell et al. (1980).

Under reducing conditions, on the other hand, Zn was complexed by organic matter and also got adsorbed on exchange and organic sites (Sim and Patrick, 1978). In our study, the redox potential of the soil after two weeks to 60 days of flooding was recorded to be as low as -200 mV and at this Eh value, Zn might have been precipitated as ZnS. It has been reported that at Eh -150 mV, metals formed sparingly soluble precipitates with sulfide which were not available to the rice plants (Cornell and Patrick (1968). This suggested that the solubility of Zn was decreased by reduction because of its bonding on exchange and organic sites, and also precipitation with sulfide. This decreased the mobility of Zn and lessened its possibility of

reaching the toxic levels under flooded conditions (Sim and Patrick, 1978). However, temperature played an important role in regulating the amount of Zn complexed with organic acids and thereby controlled its release for plant uptake. Yoshida (1981) reported that organic acids in submerged soil accumulated small quantities of Zn at high temperature followed by fast decomposition.

The content of Zn in the rice leaf tissues ranged from 11 to 44 ppm, with an average of 30 ppm (Table 3). This content of Zn was well above the critical content of 10 ppm for Zn deficiency and also quite below the critical level of 1500 ppm for Zn toxicity in the rice shoot (Yoshida, 1981). A significant relationship between soil Zn and leaf Zn was recorded. Extractable Zn in the soils was inversely related to Zn uptake by the rice plant ($r = -0.429^{**}$) (Table 5). The results suggested that Zn uptake was low when extractable Zn was high and vice versa. Extractable Zn was not absorbed by the rice plant and had to be solubilized into water-soluble form for its uptake. Leaf Zn was also inversely related to Mn, Mo, Al, P, K and Si in the leaf.

Another interesting relationship was observed between leaf Zn and leaf Fe. There was a significant correlation between Zn and Fe in the leaf tissues ($r = 0.523^{**}$) (Table 6). These results were consistent with the results obtained in our earlier studies which indicated that Fe or Mn did not interfere with the uptake of Zn (Jugsujinda and Patrick, 1977).

4. Copper (Cu)

A large amount of water-soluble Cu, about three folds higher than extractable form, was recovered in the soils before flooding (Figure 5). After flooding, the trend was reversed as water-soluble Cu was lower than extractable form.

The data on Cu content of rice leaf tissue ranged from 0.8 to 16 ppm, with an average content of 7 ppm (Table 3). This concentration was in the normal range of Cu i.e. 6-30 ppm for rice straw as reported by Yoshida (1981). Leaf Cu was inversely correlated with water-soluble P ($r = -0.315^*$) (Table 4) and extractable Si ($r = -0.402^{**}$) (Table 5).

A significant correlation coefficient between leaf Cu and P and K in the leaf tissue was established with r values of 0.304* and 0.330* (Table 6).

5. Molybdenum (Mo)

A larger amount of water-soluble Mo was released in the soils before flooding than after flooding (Figure 5). Irrespective of the moisture regimes, a small amount of extractable Mo was recovered. This was attributed to sorption of both water-soluble and extractable Mo under reducing soil conditions. Reddy and Patrick (1983) reported that micronutrients such as Zn, Cu, Mo, Co, and B were not readily involved in soil oxidation-reduction reactions but their solubility and mobility were affected by poor aeration. However, soil reduction helped to solubilize trace elements specifically adsorbed onto the oxides and hydroxides of Fe $3+$ and Mn $4+$.

The Mo content in the rice leaf tissue ranged from 0.25 to 2.10 ppm with an average value of 1.12 ppm (Table 3). Ishizuka and Tanaka (1962) reported that in water culture, rice did not show deficiency symptoms of Mo when its content in the leaf tissue was 0.04 ppm. However, the rice plant developed typical symptoms of Mo toxicity at 4 ppm in the leaf. In the present study, the concentration of Mo in the rice leaf tissues was above the deficient level and below the toxic level, therefore, considered adequate for plant growth.

In the rice leaf, Mo was positively correlated with Ca and Si with r values of 0.469** and 0.331*, respectively (Table 6).

6. Aluminum(Al)

The concentration of both water-soluble and extractable Al was slightly decreased after flooding the soils (Figure 5). Although Al is not affected by oxidation-reduction reactions, increase in soil pH after flooding may be responsible for low concentration of Al in water-soluble as well as extractable forms.

The content of Al in the leaf tissues ranged from 68.3 to 1656 ppm with an average value of 380 ppm. This content was higher than the critical content of 300 ppm for Al toxicity in the rice shoot as reported by Yoshida (1981) and 58% of leaf samples analyzed showed Al toxicity symptoms. In spite of high soil pH, high uptake of Al by the rice plant may be associated with some other factors in the Sitiung soils.

The content of Al in the leaf was inversely related to extractable Mo, P and K in the soils giving r values of -0.302^* , -0.294^* , and -0.292^* , respectively (Table 5). A positive relationship was observed between leaf Al and leaf Fe ($r = 0.646^{**}$) (Table 6).

B.2. Macro Elements

1. Calcium (Ca)

The concentration of extractable Ca after flooding the soils was slightly higher than before flooding while water-soluble form of Ca was slightly lower after flooding (Figure 6). Apparently, flooding had little effect on the distribution and solubility of Ca. This was expected because Ca did not undergo oxidation-reduction reaction like Fe and Mn. Reddy and Patrick (1983) reported, however, that reduction of insoluble iron and manganese to soluble forms displaced other cations from the exchange complex to the solution.

The content of Ca in the rice leaf tissue ranged from 0.14 to 1.0% with an average of 0.45% (Table 2). It was reported that the rice plant showing Fe toxicity had 0.2% Ca content in the leaves which was critical content of Ca deficiency in the rice leaf (Ottow et al., 1983). The soils under study were low in Ca, however, supply of Ca was adequate for rice growth as reflected by average Ca content in the leaves. However, 2% of the rice leaf samples analyzed showed Ca deficiency symptoms. Ca displaced from the exchange complex and Ca content in irrigation water might have supplied Ca requirement of the rice plant. This was supported by the data of field experiments in the Sitiung Area which indicated that the natural supply of Ca was adequate for rice growth because it did not response to lime application (Jugsujinda et al. 1985).

Leaf Ca was significantly correlated with extractable Ca in the soil with r value of 0.487** (Tables 5). Within the leaf tissue, Ca was significantly correlated with Mn, Mo, Si, and

inversely correlated with K (Table 6).

2. Magnesium (Mg)

The solubility and distribution of Mg in the soils were affected slightly by water regimes. High amounts of water-soluble form of Mg was recorded before flooding than after flooding. Further, flooding of the soils had a notable effect on extractable form of Mg; more amount was recovered after flooding than before flooding. These results are different from the findings of Reddy and Patrick (1983) who reported that flooding had a similar effect on the solubility and distribution of Mg and Ca.

The content of Mg in the leaf tissue ranged from 0.04 to 0.19% with an average value of 0.11%. Ottow et al. (1983) and Yoshida (1981) reported that the critical content for deficiency of Mg in the rice leaf was 0.1%. In our study, 33% of the leaf samples analyzed were deficient in Mg (Table 3).

Leaf Mg was significantly correlated with water-soluble and extractable forms of Ca, and with extractable Mn with r values of 0.417**, 0.312* and 0.321*, respectively (Table 4 and 5).

3. Phosphorus (P)

The concentration of water-soluble and extractable P was not affected under aerobic conditions. After flooding, the concentration of extractable P was increased markedly, and was about 10-fold higher than water-soluble P (Figure 6). It is well known that P did not undergo oxidation-reduction reactions in flooded soils but these reactions did have a marked indirect effect on its reactivity (Reddy and Patrick, 1983). They further reported that most of the changes in reactivity of P as a result of anaerobic conditions was associated with the Fe chemistry of the soil. The decrease in water-soluble P in the Sitiung soils after flooding may be explained by adsorption-desorption processes which controlled its concentration in soil solution. Patrick and Khalid (1974) reported that in Crowley silt loam soil more P was adsorbed under reduced conditions than under oxidized conditions when P concentration in the soil solution was high. This pattern was reversed at high solution P concentration. They explained that the differences in the behavior of phosphate under oxidized and reduced conditions was attributed to the changes brought about in ferric oxyhydroxide by soil reduction.

The content of P in the rice leaf tissues ranged from 0.03 to 0.2% with an average of 0.14% (Table 2). The critical content of P in the rice leaf blade for its deficiency is 0.1% as reported by Yoshida (1981). Ottow et al. (1983) observed that P content of rice leaves with clear symptoms of Fe toxicity ranged from 0.1 - 0.2% which was inadequate for rice requirement. In the present study, the average P content in the leaf tissues was low and 13% of the rice plant samples collected from the

Sitiung area were grouped as deficient.

Leaf P was inversely correlated with extractable Al
($r = -0.305^*$) (Table 5), and significantly correlated with leaf Cu
($r = 0.304^*$) (Table 6).

4. Potassium(K)

Before flooding, the concentration of water-soluble K was considerably higher than extractable form of K. After flooding, however, the concentration of water-soluble K was decreased by seven-fold as compared to extractable form (Figure 6). The decrease in water-soluble K and increase in extractable form of K in the soils after flooding may be due to the release of K from the exchange sites. Reddy and Patrick (1983) reported that although potassium was not involved in oxidation-reduction reactions the release of large amounts of Fe $^{2+}$, Mn $^{2+}$, and NH $_4^+$ in soils with low O $_2$ resulted in displacement of K $^+$ ions from the exchange complexes to the soil solution.

The content of K in the rice leaf tissues ranged from 0.52 to 1.88% with an average of 1.36%. The critical content of K deficiency in rice blade was reported to be 1.0% (Yoshida, 1981). In our study, the average content of K was slightly above the critical content of K deficiency, and only 16% of the rice leaf samples were classed as deficient in K.

Leaf K was inversely correlated with water-soluble form P with r value of -0.345* (Table 5). In the leaf tissue, K was positively correlated with Cu (r = 0.330*) and inversely correlated with Ca (r = -0.445**) (Table 6).

5. Silicon(Si)

The soil water regimes had no influence on the amount of water-soluble Si in the soils. However, extractable form of Si was greatly increased after flooding compared to no flooding (Figure 6). In general, flooding increased the solubility of Si. Unpublished data from IRRI also confirmed that the solubility of silica (SiO_2) was increased after submergence and marked differences in soluble SiO_2 content were observed among soils before and after flooding (Ponnamperuma, 1965). Precipitation of iron caused a decrease in SiO_2 concentration, and the reduction of ferri-silica complexes liberated silica. Therefore, reversible changes in solubility of silica appeared to be associated with oxidation-reduction of iron (Ponnamperuma, 1965). It has also been reported that the readily soluble Si in soil is either adsorbed on exchange sites or combined with amorphous aluminum and ferrous hydroxide (Imaizumi and Yoshida, 1956; and McKealogue and Cline, 1963) as cited by Yoshida (1981).

The content of Si in the leaf tissues ranged from 12.2 to 529 ppm (0.001 to 0.05%) with an average value of 228 ppm (0.02%). Yoshida (1981) reported that the application of silicates in the field was beneficial for rice growth when silica content of straw was below 11%. However, in solution culture the addition of silicon had little effect on vegetative growth when silica content in the leaves was 0.07% (Yoshida et al., 1959 as cited by Yoshida, 1981). Further, Tanaka and Park (1966) as cited by Yoshida(1981) found that the application of Si had no effect on rice growth and yield when its content in green leaves

was above 1.25% These reports indicated that the content of Si in the leaf samples under investigation was low, and all the rice leaf samples were categorized as deficient thereby suggesting that silica application could prove beneficial to rice grown in the wetland soils of Sitiung, Sumatra. In the present study, silica was extracted with concentrated HNO₃ which might have caused low extraction of Si as compared to HF method. Low extraction of Si by HNO₃ was perhaps the reason indicating deficiency of Si in the rice plant samples under the present study.

A positive relationship existed between leaf Si and several other water-soluble elements in the soil, e.g., Fe, Cu, Ca, Mg and P with r values of 0.405**, 0.385*, 0.483**, 0.508** and 0.543**, respectively (Table 4). Also, a relationship between leaf Si and extractable Ca was observed ($r = 0.519^{**}$) (Table 5). Positive correlation coefficients between leaf Si and other elements, i.e., Mn, Ca and Mo in the leaf tissues were observed (Table 6).

SUMMARY AND CONCLUSIONS

This study was carried out to investigate the effect of flooding on the release of water-soluble and extractable forms of elements in soils, and also to establish relationship of nutrients with their counterparts in the leaf tissues. Forty-five soils and an equal number of rice leaf samples were collected randomly from the Sitiung Transmigration Area of Sumatra, Indonesia. The results indicated that the solubility and distribution of nutrient elements in the soils were markedly affected by flooding. Flooding caused dramatic changes in oxidation-reduction potential (Eh), pH, and the release of water-soluble and extractable forms of nutrient elements. Further, the Eh of the soils sharply decreased and went down to an average value of -217 mV after 60 days of flooding. Soil pH increased from an average of 5.2 to 6.6. After flooding, average concentration of extractable Fe, Mn, Al, Cu, Zn, Ca, Mg, P, K, and Si was higher than average water-soluble form. Water-soluble and extractable forms of Mn were significantly correlated with soil pH but inversely correlated with soil Eh. The extractable Fe was significantly correlated with soil pH.

Leaf tissue analyses indicated that the rice plants suffered Fe and Al toxicity as their contents were more than 300 ppm; a critical level for their toxicity. The rice plants also suffered deficiency of Ca, P, K, Mg, and Si in the ascending order as their contents were below the critical content for deficiency. P was inversely correlated with extractable Al. Mg was significantly correlated with water-soluble Ca and extractable forms of Ca and Mn. K was inversely correlated with

water-soluble form of P. Si was significantly correlated with water-soluble P, Fe, Ca, Mg, P and Cu and extractable Ca. Some nutrients showed either toxicity or deficiency levels in the rice leaf tissues. Fe and Al toxicities were probably the major cause of 'oranging' symptoms. Other factors which might be responsible for yield depression were the deficiencies of Ca, P, K, Mg, and Si caused by low soil Eh thereby resulting in their precipitation with amorphous Fe oxyhydroxides ($\text{Fe}(\text{OH})_3$).

It is well documented that redox potential and pH are the principal factors influencing the mobilization and immobilization of nutrient elements in flooded soils and their availability to rice plants. It is, therefore, important to differentiate the extent of problem caused either by redox potential and pH induced toxicity or nutrient deficiencies which may be aggravated by toxic soil conditions. A system for growing plants under controlled redox potential - pH conditions will be employed in the subsequent studies to isolate the factors for yield depression under toxic conditions prevailing in these soils. Further, another laboratory study is needed to determine the solubility of elements with different fractionation schemes after flooding the soils and also to determine their content recorded under different combinations of pH-redox conditions. This will help to overcome both deficiency and toxicity nutritional problems of the soils before successful growing of rice in the Sitiung area.

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List of captions used in the Tables and Figures of a manuscript entitled "Redox and pH Chemistry and Nutrient Uptake by Rice in Flooded Oxisols of Sitiung Area of Sumatra".

Table 1. Some chemical properties of top soil layer of Sitiung Transmigration area of Sumatra.

Table 2. Correlation coefficient showing the association between water-soluble and extractable elements and pH-Eh parameters at 60 days after flooding.

Table 3. Contents of various elements in the rice leaf.

Table 4. Correlation coefficient showing the association between water-soluble soil elements and elements in the rice leaf.

Table 5. Correlation coefficient showing the association between extractable soil elements and elements in the rice leaf.

Table 6. Correlation coefficient showing the association between the various elements in the rice leaf.

Fig. 1. Location of soil and rice plant samples in Sitiung Transmigration Area of Sumatra, Indonesia.

Fig. 2. Redox tube used for incubation study under flooded soil conditions.

Fig. 3. Effect of flooding on soil Eh and pH.

Fig. 4. Relationship between soil Eh and pH in flooded soil.

Fig. 5. Distribution of water-soluble and extractable forms of some selected micro elements in soils.

Fig. 6. Distribution of water-soluble and extractable forms of some selected macro elements in soils.

Table 1. Some chemical properties of top soil layer at the sampling site on Sitiung Transmigration area of Sumatra, Indonesia.

Soil Property	Value	
pH (1:1 soil/water ratio)	4.5	
C/N ratio	12	
Extractable P2O5	38	mg/100 g
Extractable K2O	15	mg/100 g
Exchangeable Ca	0.3	cmol(+)kg ⁻¹
Exchangeable Mg	0.1	cmol(+)kg ⁻¹
Exchangeable K	0.1	cmol(+)kg ⁻¹
Exchangeable Na	0.1	cmol(+)kg ⁻¹
Exchangeable H	0.99	cmol(+)kg ⁻¹
Exchangeable Al	1.52	cmol(+)kg ⁻¹
Base saturation	2	%
Al saturation	85	%
Free Fe2O3	0.63	%
Total Mn	294.3	mg/100g
Total Cu	0.41	mg/100g
Total Zn	0.72	mg/100g

Source: Center for Soil Research (CSR), bogor, Indonesia (unpublished data).

Table 2. Correlation coefficient showing the association between water-soluble and extractable elements and pH-Eh parameters at 60 days after flooding. \$

Water-soluble	pH	Eh	Extractable	pH	Eh
Micro element					
Fe	ns	ns	Fe	0.346*	ns
Mn	0.666**	-0.426**	Mn	0.692**	-0.429**
Zn	0.478**	0.513**	Zn	0.478**	ns
Cu	-0.531**	ns	Cu	0.397*	ns
Mo	ns	ns	Mo	0.587*	ns
Al	0.384*	0.332*	Al	0.310*	ns
Macro element					
Ca	0.456**	-0.505**	Ca	0.516**	-0.488**
Mg	0.330*	ns	Mg	ns	ns
P	ns	ns	P	0.588**	ns
K	0.300*	0.332*	K	0.543**	ns
Si	ns	ns	Si	0.616**	-0.291*

n=45

*,** Sinificance at the 5 and 1% levels of probability, respectively.
ns = non-significance.

Table 3. Contents of various elements in the rice leaf.

Element	Minimum	Maximum	Average	% of Sample showing Deficiency (D) or Toxicity (T) #

Micro element (ppm)				
Fe	85.00	783.00	334.00	(T) 51%
Mn	115.00	3339.00	1367.00	-
Zn	11.00	44.00	30.00	-
Cu	0.75	16.14	7.00	-
Mo	0.25	2.10	1.12	-
Al	68.30	1656.00	380.00	(T) 58%
Macro element (%)				
Ca	0.14	1.00	0.45	(D) 02%
Mg	0.04	0.19	0.11	(D) 33%
P	0.03	0.22	0.14	(D) 13%
K	0.52	1.88	1.36	(D) 16%
Si	.00	0.05	0.02	(D) 100%

As quoted by Yoshida (1981).

Table 4. Correlation coefficient showing the association between water soluble soil elements and elements in the leaf.

Water-soluble element in soils	Element in the rice leaf					
	Mn	Zn	Cu	Si	Mg	K
Micro element						
Fe	ns	ns	ns	0.405**	ns	ns
Mn	0.367*	ns	ns	ns	ns	ns
Zn	ns	ns	ns	ns	ns	ns
Cu	ns	ns	ns	0.385*	ns	ns
Mo	ns	ns	ns	ns	ns	ns
Al	ns	0.317*	ns	ns	ns	ns
Macro element						
Ca	0.384*	ns	ns	0.483**	0.417**	ns
Mg	0.303*	ns	ns	0.508**	ns	ns
P	ns	ns	-0.315*	0.543**	ns	-0.345*
K	ns	-0.315*	ns	ns	ns	ns
Si	ns	ns	ns	ns	ns	ns

n=44

*,** Significance at the 5 and 1% levels of probability, respectively.
ns = non-significance.

Table 5. Correlation coefficient showing the association between extractable soil elements and elements in the rice leaf.

Extractable element in soils	Element in the rice leaf							
	Mn	Zn	Cu	Al	Ca	Mg	Si	P
Micro element								
Fe	ns	ns	ns	ns	ns	ns	ns	ns
Mn	0.326*	-0.310*	ns	ns	ns	0.321*	ns	ns
Zn	ns	-0.429**	ns	ns	ns	ns	ns	ns
Cu	ns	ns	ns	ns	ns	ns	ns	ns
Mo	ns	-0.331*	ns	-0.302*	ns	ns	ns	ns
Al	ns	-0.330*	ns	ns	ns	ns	ns	-0.305*
Macro element								
Ca	0.496**	ns	ns	ns	0.487**	0.312*	0.519**	ns
Mg	ns	ns	ns	ns	ns	ns	ns	ns
P	ns	-0.367*	ns	-0.294*	ns	ns	ns	ns
K	ns	-0.292*	ns	-0.292*	ns	ns	ns	ns
Si	ns	-0.407**	-0.402**	ns	ns	ns	ns	ns

n=45

*,** Significance at the 5 and 1% levels of probability, respectively.
ns = non-significance.

Table 6. Correlation coefficient showing the association between the various elements in the rice leaf.

Element in the rice leaf	Element in the rice leaf										
	Fe	Mn	Zn	Cu	Mo	Al	Ca	Mg	P	K	Si
Micro element											
Fe	1.000										
Mn	ns	1.000									
Zn	0.523**	ns	1.000								
Cu	ns	ns	ns	1.000							
Mo	ns	0.432**	ns	ns	1.000						
Al	0.646**	ns	ns	ns	ns	1.000					
Macro element											
Ca	ns	0.627**	ns	ns	0.469**	ns	1.000				
Mg	ns	ns	ns	ns	ns	ns	ns	1.000			
P	ns	ns	ns	0.304*	ns	ns	ns	ns	1.000		
K	ns	ns	ns	0.330*	ns	ns	-0.445**	ns	ns	1.000	
Si	ns	0.511**	ns	ns	0.331*	ns	0.448**	ns	ns	ns	1.000

n=45

*,** Significance at the 5 and 1% levels of probability, respectively.
ns = non-significance.

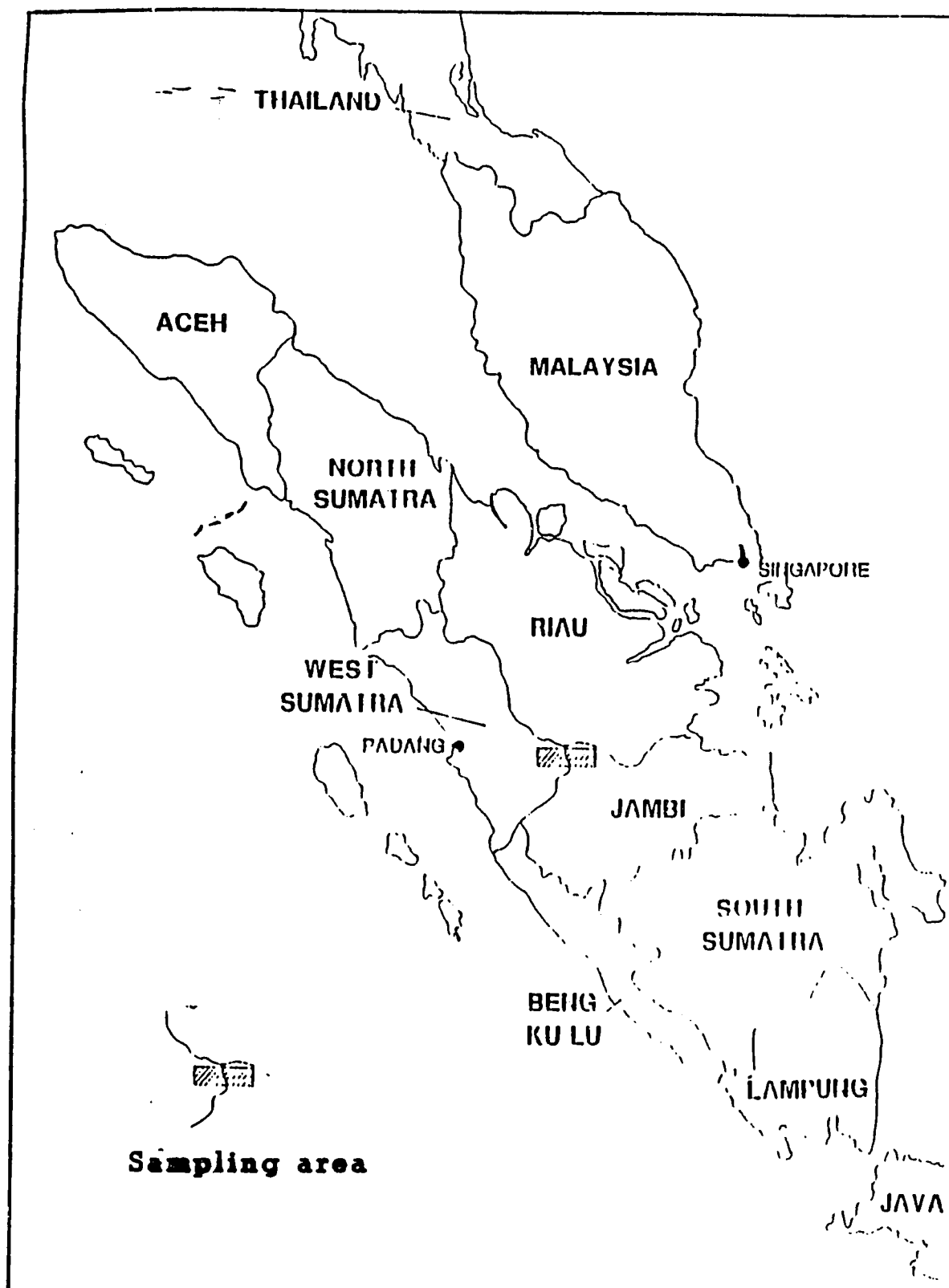
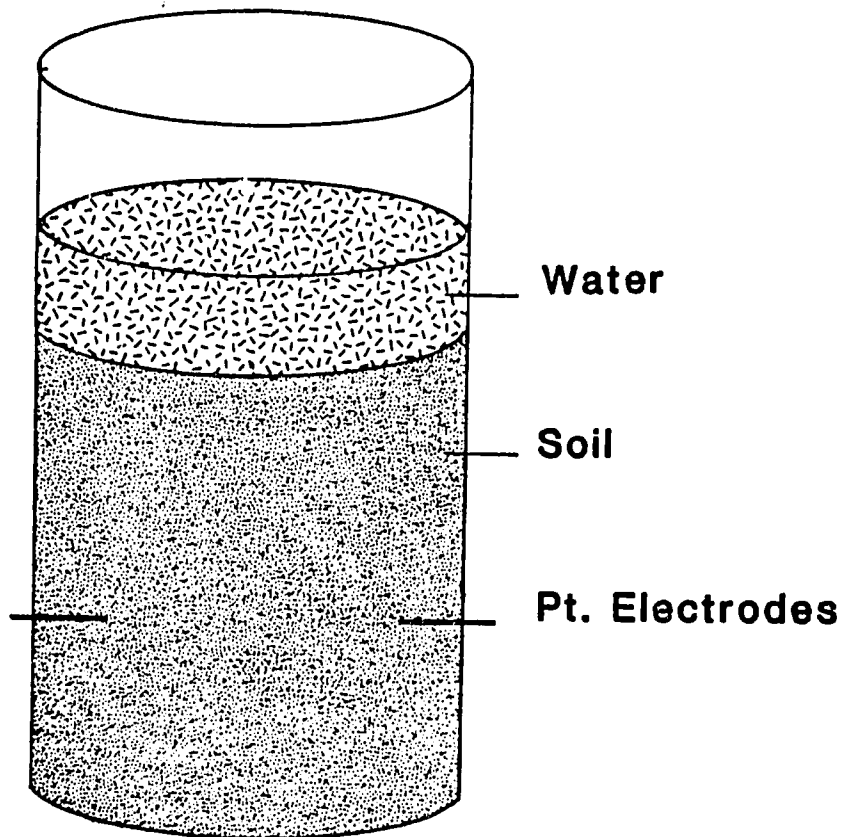


Fig. 1. Location of soil and rice plant samples in Sitiung Transmigration area of Sumatra, Indonesia.



SPECIFICATION:

outer dia. = 44mm

inner dia. = 40 mm

height = 138 mm

Pt. height from bottom = 25 mm

Pt. extend outside tube = 5 mm

Pt. extend inside tube = 5 mm

Fig. 2. Redox tube used for incubation study under flooded soil conditions.

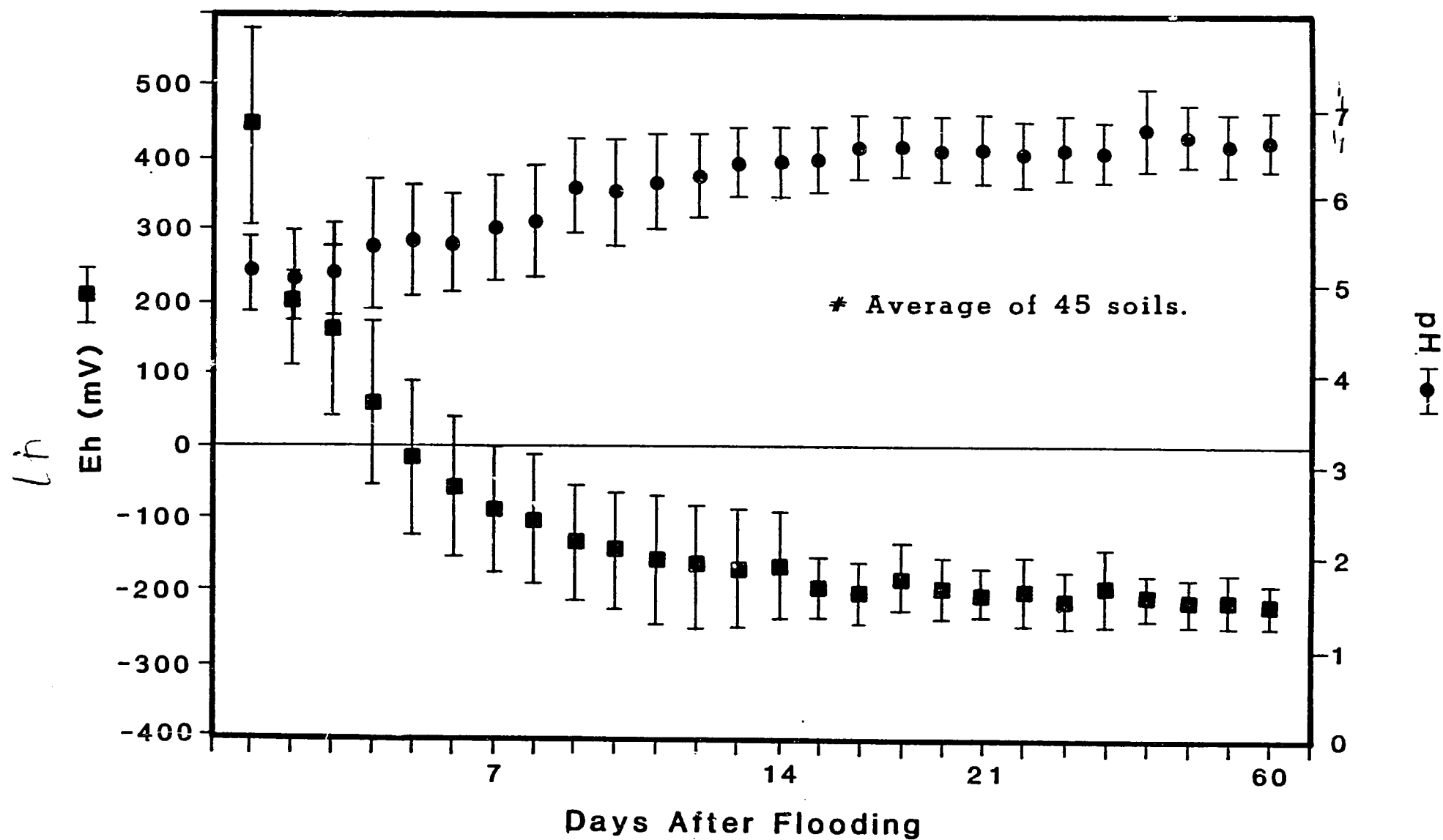
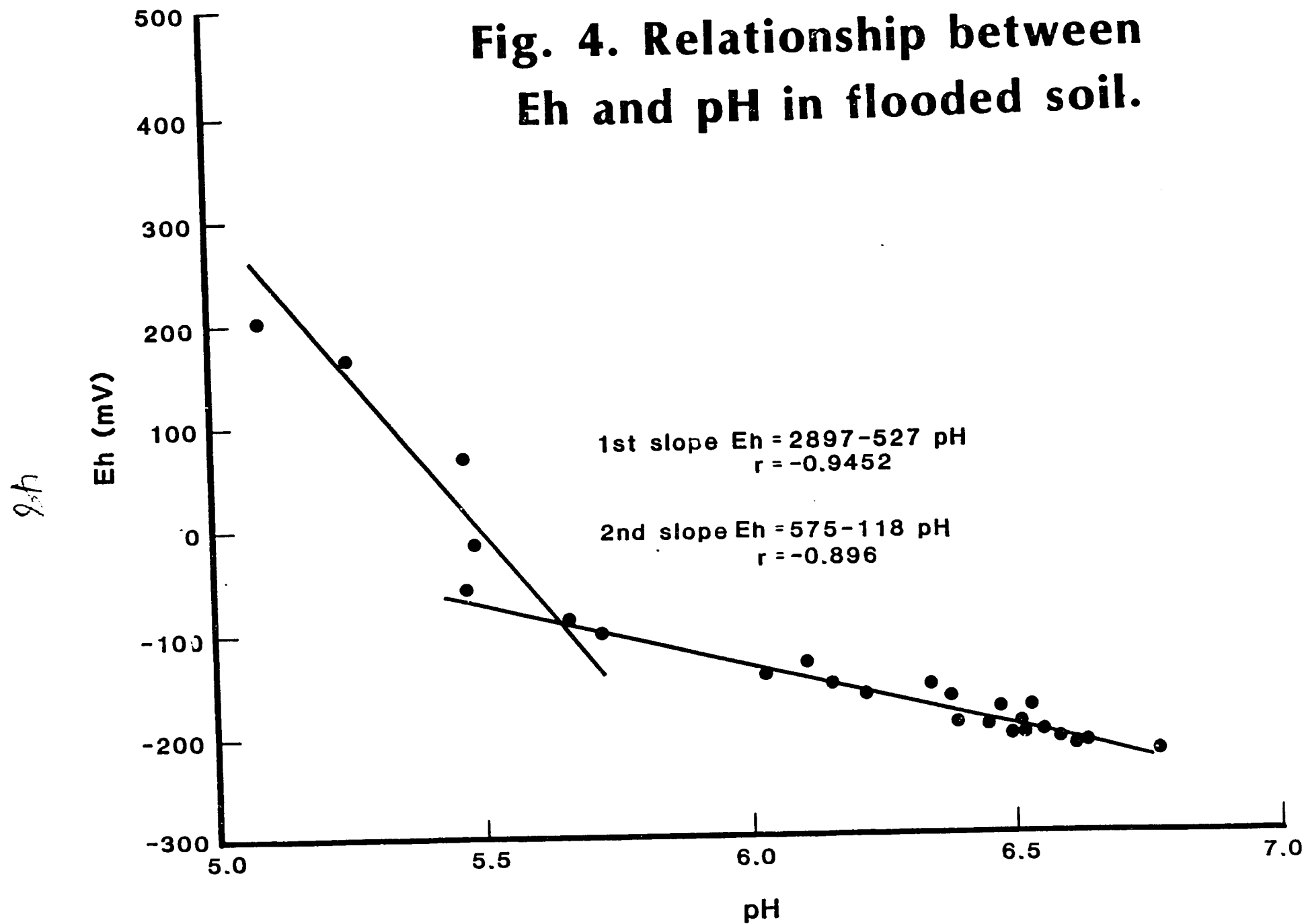


Fig. 3. Effect of flooding on soil Eh and pH.#

**Fig. 4. Relationship between
Eh and pH in flooded soil.**



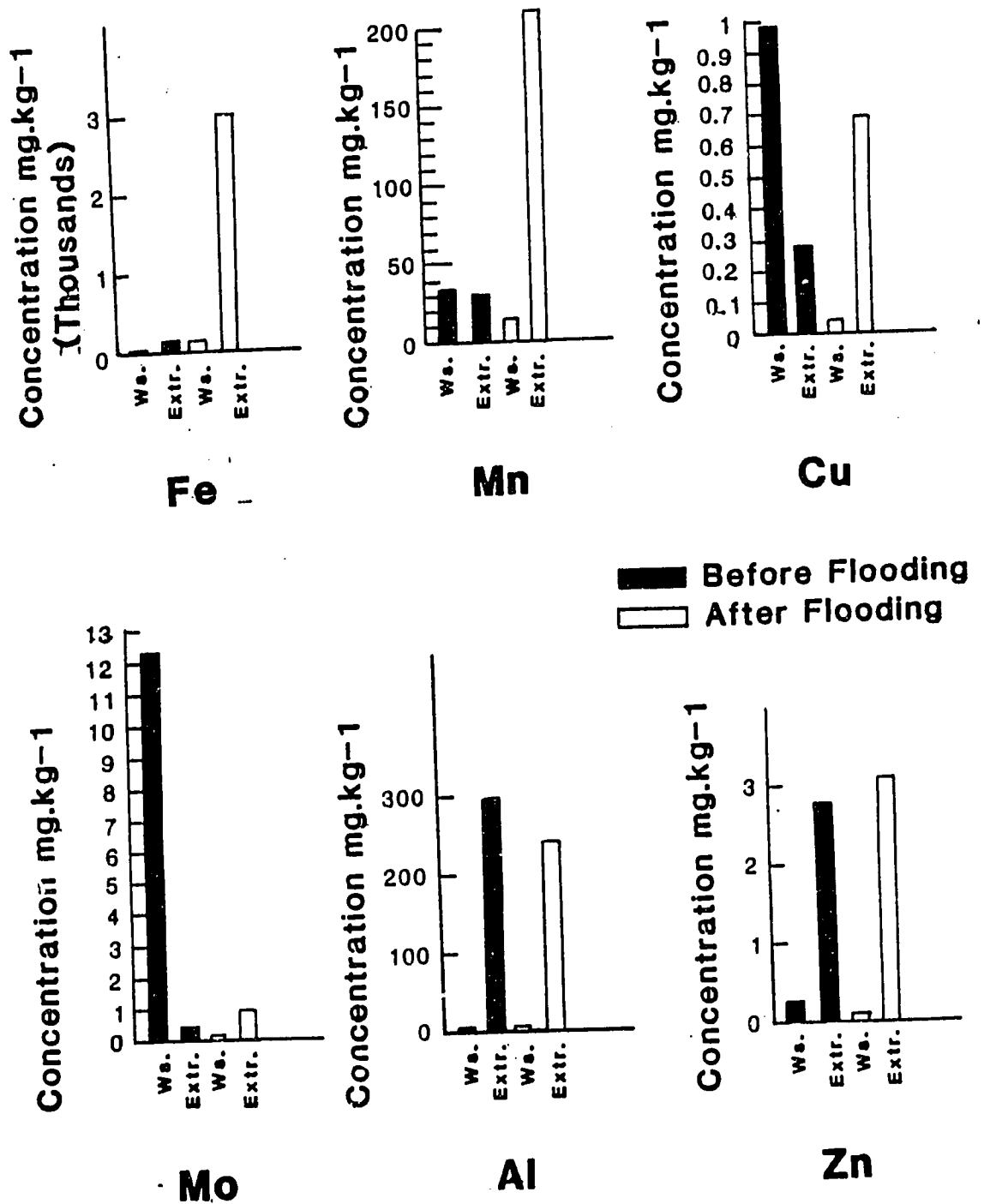


Fig. 5. Distribution of water-soluble and extractable forms of some selected micro elements in soils.

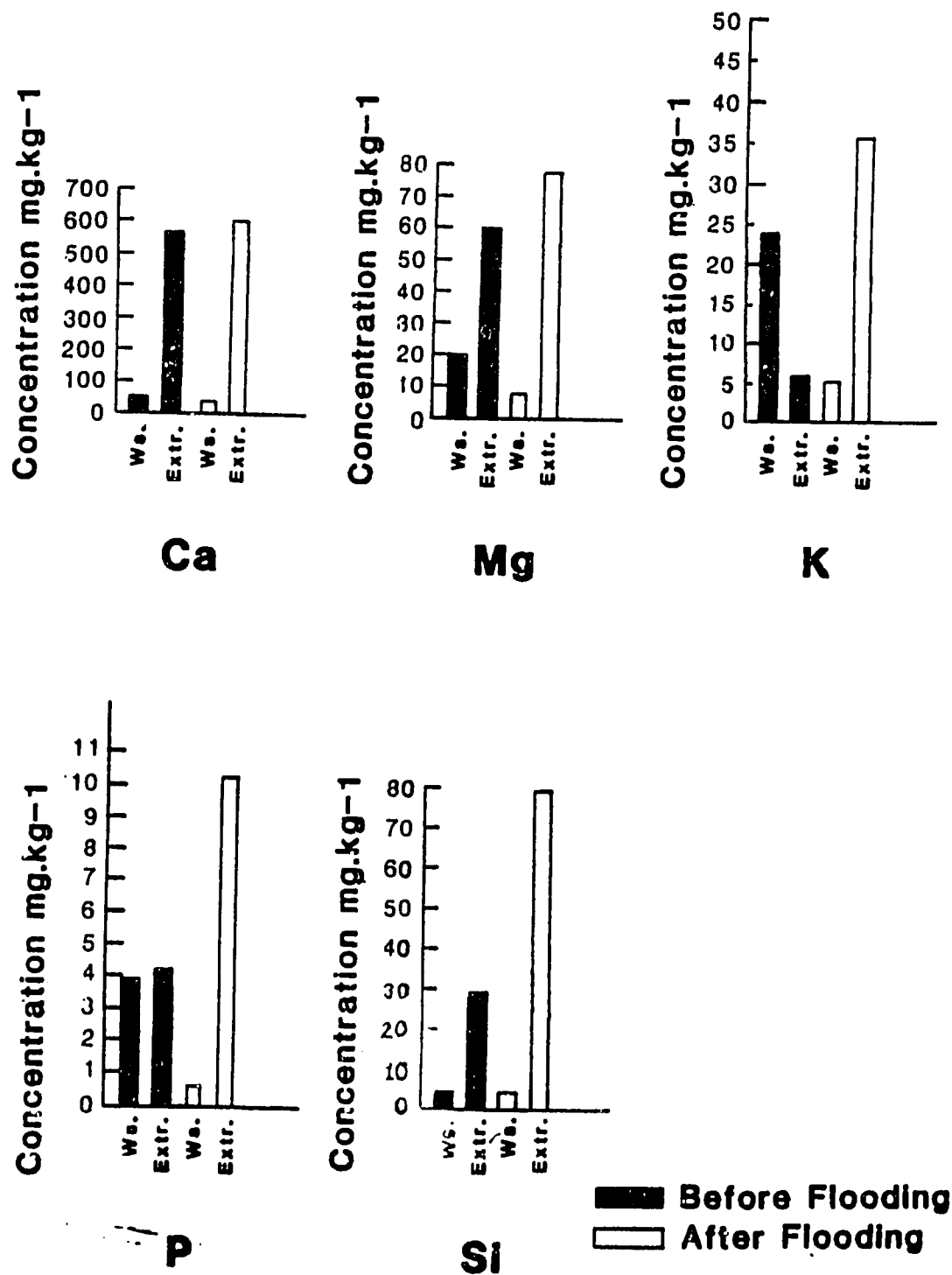


Fig. 6. Distribution of water-soluble and extractable forms of some selected macro elements in soils.