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CORRELATION OF ZINC WITH IRON AND MANGANESE IMMOBILIZED IN SUBSURFACE HORIZONS OF TWO CALCAREOUS RICE SOILS

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The lower four and eight subsurface horizons of the Gujranwala and Satghara soils, respectively were separated by wet sieving into 15-2 mm, 2-0.05 mm (sand) and <0.05 mm (silt and clay) size fractions. Water fractionated material was 66 to 82% silt and clay in the Gujranwala and 88 to 96% in the Satghara. Sand (2-0.05 mm) fraction was 16 to 18% for the Gujranwala and 1 to 8% for the Satghara. The 188-208 cm (deepest) layer in Satghara series was an exception containing 45% of silt and clay and 54% of sand. Nodule fraction (15-2 mm) was 0.4 to 9% of the whole soil in all the horizons. Potassium and ferrous were mostly concentrated into silt and clay size fraction of both the soils. But manganese was more concentrated in coarser (sand and nodule) fractions. There was a significant positive correlation of total zinc concentration with Fe and Mn concentrations in 15-2 mm fracion.

INTRODUCTION

Some of the changes related to zinc nutrition of rice are increased concentrations of HCO_3, Mn and Fe in solution and increased partial pressure of CO_2 and soil pH changes towards neutrality (Ponnamperuma, 1965; Rehmatullah *et al.*, 1976). Increased concentrations of Ca, Mg, HCO_3, Mn and Fe have been observed to antagonize the uptake of Zn by rice plants in solution culture (Forno *et al.*, 1975; Rashid *et al.*, 1976). Nevertheless, ions in solution in saturated soil situation are under continuous gravitational pull to move to lower soil horizons. Sajwan and Lindsay (1986) have hypothesized that Fe in solution diffuses to more oxidized zones in soil and gets precipitated as ferric hydroxide, $Fe_2(OH)_6$, which may depress Zn activity through the precipitation of $ZnFe_2O_4$ or a franklinite-like solid material.

In addition the higher partial pressure of CO_2 and the lower redox potential of flooded rice fields are conducive for precipitation of Mn as $MnCO_3$, MnS, (Ca, Fe, $MnCO_3$) and Mn_3O_4 etc. (Ponnamperuma, 1972; Jenne, 1968). Adsorption, co-precipitation or occlusion of trace metal ions during crystal growth of Fe and Mn oxides can be further accentuated by the precipitation of carbonates under calcareous soil conditions. Carbonaceous concretions containing some Fe and Mn have been reported in subsurface horizons of two important rice growing soils (Gujranwala & Shatghara series) of Pakistan (Rahmatullah *et al.*, 1990). The present paper reports the extent of these concretions in the subsurface horizons and their chemical composition with possible implications on Zn nutrition of flooded rice.

Table 1. Some important properties of the subsurface horizons* involved in this study

Horizon	Depth (cm)	Texture	Colour (Moist) Soil	Colour (Moist) Mottles	pH 1:1	$CaCO_3$ (%)	EC dS/m	CEC me/100 g
Gujranwala series (Fine-loamy mixed hyperthermic Udic Haplustalf)								
Btc1	66-96	SiCL	10YR 3/3	10YR 4/6	8.2	1	0.20	18.8
Btc2	96-130	SiCL	10YR 4/3	7.5YR 4/6	8.2	1	0.21	16.4
Btc3	130-156	SiL	10YR 4/3	5YR 4/4	8.2	1	0.23	15.3
Btc4	156-180	SiL	10YR 4/3	5YR 4/4	8.2	1	0.22	11.2
Satghara series (Fine, mixed, hyperthermic Typic Natrargid)								
2Btcknb1	55-80	SiC	10YR 6/2	7.5YR 4/4	10.0	3	1.87	15.5
2Btcknb2	80-108	SiC	7.5YR 6/4	7.5YR 4/6	9.8	4	1.82	14.0
2Btcknb3	108-128	SiCL	7.5YR 6/4	7.5YR 4/4	9.6	6	1.57	27.7
2Btckb1	128-145	SiL	7.5YR 6/4	7.5YR 5/4	9.2	9	1.34	11.5
2Btckb2	145-158	SiL	10YR 6/3	7.5YR 4/4	9.2	6	1.15	10.7
3BCtck1	158-175	SiL	10YR 6/3	-	8.9	1	0.97	12.1
3BCtck2	175-188	SiL	7.5YR 6/4	7.5YR 4/4	8.6	-	0.81	12.6
3BCtck3	188-208	SiL	10YR 6/3	7.5YR 4/6	8.5	-	0.19	6.7

SiCL = Silty clay loam SiL = Silt loam
SiC = Silty clay

* "Soil Taxonomy and Agrotechnology Transfer", Vol. 1-2, Soil Survey of Pakistan, SMSS-USDA/SCS, Washington, DC.

MATERIALS AND METHODS

Undisturbed profile samples for the Gujranwala (Udic Haplustalf) and Satghara (Typic Natrargid) series were obtained from Soil Management Support Services Project of USDA-SCS., Washington, D.C. Nodules occur in lower four and eight surface horizons of the Gujranwala and Satghara series, respectively. Natural ped samples from these horizons were separated into 15-2, 2-0.05 and <0.05 mm size fractions by wet sieving under a fine stream of distilled water. Nodules were the major constituent of 15-2 mm fraction. Sub-samples of 15-2, 2-0.05 and <0.05 mm size fractions for each of the subsurface horizons of the two soils were digested with HF, HNO_3 and HCl for total elemental analyses (Jackson, 1965). Concentrations of K, Fe, Mn, Cu and Zn in the digests were determined using atomic absorption spectrophotometer.

RESULTS

All of the samples were loamy in silty texture (silt loam, silty clay loam, clay), alkaline in pH and calcareous in nature (Table 1). The water fractionated material, mostly silt and clay, was 66 to 82% in the Gujranwala and 88 to 96% in the Satghara. The sand fraction was 16 to 18% for the Gujranwala and 1 to 8% for the Satghara. The deepest layer of Satghara (188-208 cm) containing 45% of silt and clay and 54% sand, was an exception. Most of the nodular fraction (15-2 mm) was less than 9% of the whole soil in all the horizons. Practically, no nodules (15-2 mm fraction) were observed for the upper horizons. It started abruptly at 60 cm depth from surface in both the soils but decreased in lower horizons of the Satghara soil. Morphologically, the 15-2 mm fraction recovered in the two soils was different. The particles were rounded in the Gujranwala series and they were irregularly shaped in the Satghara series (Fig. 1). Nodules were porous and carbonaceous in both the soils. Generally, round black Fe and Mn nodules were found in sand (2-0.05 mm) size fraction.

Table 2. Distribution of different particle size fractions in sub-surface horizons of the Gujranwala series

Horizon No.	Size fraction as % of natural soil		
	15-2 mm	2-0.05 mm	<0.05 mm
1	0.9	16.3	82.9
2	5.7	16.1	78.3
3	3.8	26.0	70.2
4	5.2	28.2	66.6

Total elemental analyses of different size fractions of the Gujranwala and Satghara soils indicated that K and Fe were mostly concentrated into silt and clay (<0.05 mm) size fractions for both the soils (Table 4& 5). The silt and clay size fractions are grouped together. On the other hand, Mn was more concentrated in coarser, i.e. 2-0.05 and 15-2 mm fractions. Similar Fe and Mn distribution among various size fractions has been reported by other investigators (Uzochukwu & Dixon, 1986). Concentration of total Fe and Mn in each of the three fractions did not follow a general trend over different horizons, however, concentrations of both the Fe and Mn tended to increase with depth.

Fig. 1. Morphology of nodules (15-20 mm) found in the two soils

DISCUSSION

Soluble Zn and Cu fertilizers added to soil or that dissolve on flooding for rice cultivation can participate in adsorption on Mn oxides (Jenne, 1968), fixation by soil clay minerals (Rahmatulla *et al.*, 1985) and immobilization by soil microorganisms. Linear correlation coefficients were, therefore, calculated (Table 6) among concentrations of total Fe, Mn, Cu and Zn determined in the nodular (15-2 mm) fractions to identify possible relationships between precipitating Fe and Mn oxides and Zn and Cu in nodules, commonly found in flooded rice soils (Baker *et al.*, 1987). Total Zn concentration in 15-2 mm fraction was significantly correlated with concentrations of total Fe and Mn (Figure 2). Total Cu correlation was only correlated with Mn. Correlation of total Fe concentration with either Mn or Cu was statistically significant. Sajwan and Linsay (1986) have hypothesized a stepwise effect of dissolved Fe on Zn

Table 3. Distribution of different particle size fractions in sub-surface horizons of the Satghara soil.

Horizon No.	Size fraction as % of natural soil		
	15-2 mm	2-0.05 mm	<0.05 mm
1	0.5	2.5	97.0
2	8.2	1.4	90.5
3	7.9	3.2	88.9
4	8.3	3.1	88.7
5	8.0	3.5	88.6
6	1.5	8.2	90.3
7	0.1	3.6	96.3
8	0.4	54.4	45.2

Table 4. Range and mean values of total concentration of some chemical plant nutrient elements in different size fractions of the Gujranwala soil (n = 4)

Element	15-2 mm		2-0.05 mm		<0.05 mm	
	Range	Mean	Range	Mean	Range	Mean
K (%)	0.26-0.44	0.36	0.23-0.49	0.40	0.49-0.65	0.56
Fe (%)	7.86-15.32	10.25	2.17-3.50	2.93	3.80-6.86	5.75
Mn (%)	0.51-1.45	0.94	0.05-1.80	0.51	0.03-0.05	0.04
Cu (ppm)	51.17-115.74	75.78	67.16-76.34	72.73	49.03-84.61	59.84
Zn (mg/g)	0.19-0.30	0.24	0.10-0.23	0.17	0.16-0.25	0.19

Table 5: Range and mean values of total concentration of some chemical plant nutrient elements in different size fractions of the Satghara soil (n = 8)

Element	15-2 mm		2-0.05 mm		<0.05 mm	
	Range	Mean	Range	Mean	Range	Mean
K (%)	0.14-0.44	0.27	0.16-0.47	0.30	0.59-0.81	0.68
Fe (%)	0.94-5.11	2.61	0.60-6.27	3.79	2.46-13.56	8.71
Mn (%)	0.13-1.59	0.60	0.06-1.08	0.32	0.05-0.09	0.06
Cu (ppm)	44.31-147.41	67.59	40.41-157.70	72.13	34.52-124.67	67.10
Zn (mg/g)	0.09-0.20	0.18	0.10-0.39	0.20	0.10-0.24	0.21

Table 6. Linear correlation coefficients among various ion species found in total analysis of nodule (15-2 mm) size fraction (n = 12)

	Fe	Mn	Cu
Mn	0.33	-	-
Cu	-0.04	0.87**	-
Zn	0.58*	0.65*	0.45

* and ** correlation significant at 5 and 1% level of probability, respectively.

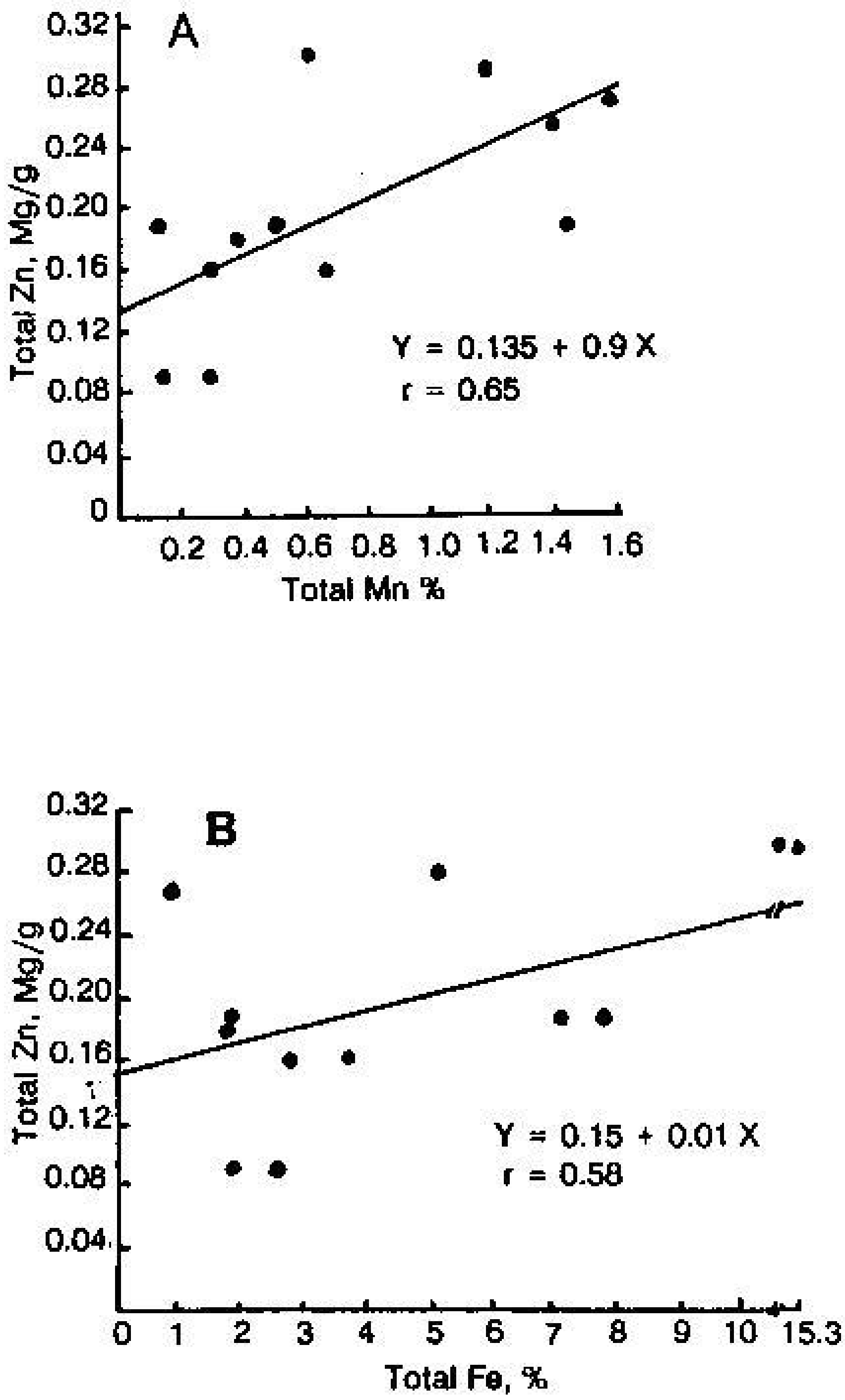

Fig. 2. Relation of total zinc with manganese (A) and iron (B) concentrations in 15-2 mm size fraction.

solubility in reduced rice soil condition. Parallel to this precipitating Mn minerals in marine environment have been observed to show scavenging properties (Burns & Burns, 1977; Jenne, 1968). According to Ponnamperuma (1972) little is known about the mineralogy of manganese in submerged soils. A research on the following precipitates may be fruitful: $MnCO_3$, (Ca, Fe, Mn) CO_3, MnS, Mn_3O_4, (Mn_3O_4, Fe_3O_4) and $Mn_3(PO_4)_2$. Both Fe and Mn have been found precipitating in soil profiles in fields continuously under flooded rice cropping system (Moormann & van Breemen, 1978). Precipitating species of both Fe and Mn have been observed as inactivating several metal cations e.g. Co, Li, Pb, Zn, Cu and Ni (Talor & McKenzie, 1966) of which Zn is important for flooded rice. The growing crystal of Fe and Mn oxides in subsurface horizons can be a sink for Zn in such soils. Study of release-retention behaviour of these solid particles for Zn and Cu would be helpful in the management of such soils.

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REFERENCES

Anonymous. 1986. Soil taxonomy and agrotechnology transfer. Vol 1& 2. Soil Survey of Pakistan. SMSS-USDA/SCS., Washington, DC.

Baker, W.H., L.R. Hossner and F.T. Turner. 1987. Calcite solubility in a flooded rice environment. Agron. Abst., p. 166.

Burns, R.G. and V.M. Burns. 1977. The mineralogy and crystal chemistry of deep sea manganese nodules - A polymetallic resource of the twenty-first century. Phil. Trans. Roy. Soc., London A, 286: 283-301.

Forno, D.A., S.' Yoshida and C.J. Asher. 1975. Zinc deficiency in rice. I: Soil factors associated with the deficiency. Plant Soil, 42: 537-550.

Jackson, M.L. 1965. Soil Chemical Analysis. Prentice-Hall, Inc., N.J., USA.

Jenne, E.A. 1968. Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and water: The significant role of hydrous Mn and Fe oxides. Adv. Chem. Series, 73: 337-387.

Moormann, F.R. and N. van Breemen. 1978. Rice, Soil, Water, Land. Int. Rice. Res. Inst., Los Banos, Philippines. pp: 53-106.

Ponnamperuma, F.N. 1972. The chemistry of submerged soils. Adv. Agron. 24: 29-96.

Ponnamperoma, F.N. 1965. Dynamic aspects of flooded soils. In mineral nutrition of rice. Int. Rice Res. Inst., Los Banos, Manila, Philippines. pp: 295-328.

Rahmatullah, J.B. Dixon and D.C. Golden, 1990. Manganese-containing nodules in two calcareous rice soils of Pakistan. In: "Soil Micromorphology" (L.A. Douglas ed.). Elsevier Sci. Pub., Amesterdam, The Netherlands. pp: 387-394.

Rahmatullah, M.I. Bajwa and G.R. Sandhu, 1985. Fixation of zinc by some rice soil clays under upland conditions. Commun. Soil Sci. Plant Analysis, 16: 615-620.

Rahmatullah, F. M. Chaudhry and A. Rashid. 1976. Micronutrient availability to cereals from calcareous soils. II. Effect of flooding on electrochemical properties of soils. Plant Soil. 45: 411-420.

Rashid, A., F.M. Chaudhry and M. Sharif. 1976. Micronutrient availability to cereals from calcareous soils. III. Zinc absorption by rice and its inhibition by important ions of submerged soils. Plant Soil. 45: 613-623.

Sajwan, K.S. and W.L. Lindsay. 1986. Effects of redox on zinc deficiency in paddy rice. Soil Sci. Soc. Am. J. 50: 1264-1269.

Taylor, R.M. and R.M. McKenzie. 1966. The association of trace elements with manganese minerals in Australian soils. Aust. J. Soil Res. 4: 29-39.

Uzochukwu, G.A. and J.B. Dixon, 1986. Manganese oxide minerals in nodules of two soils of Texas and Alabama. Soil Sci. Soc. Am. J. 50: 1358-1363.