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Study of relationship between zinc fractions and selected soil properties of rice soils

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Abstract
The present study was investigated that Zn fractions and their relationship with soil properties of paddy soils of Coimbatore district, Tamil Nadu. Totally ten Soil samples were collected from Anaimalai and Thondamuthur blocks of Coimbatore district. The results showed that more than 80 per cent of total Zn occurred in residual fraction, while smaller fraction occurred as water soluble plus exchangeable (1.7 %), organically complexed (4.0 %), Fe oxide bound (8.0 %) and Mn oxide (14.5 %) forms. The relative Zn fractions for all the soil samples decreased in the following order: Res > MnOx> AFeOx>Org>WE-Zn. All these four Zn fractions showed no significant and negative correlation with any fractions, except Org. The between organically bound Zn fraction, organic carbon (0.36**) and available Fe (0.56**) was found to be significant and positive. The FeOx bound fraction positively correlated with organic carbon (0.09) and electrical conductivity (0.10**). The MnOx bound fraction was negatively correlated with organic carbon, available Zn and Mn and it was also significant. The residual fractions of zinc was negatively correlated with all soil properties.

Keywords: Rice, Zn fractions, water soluble pus exchangeable

Introduction
Rice is one of the most important food crops and a primary food source for more than one third of world's population (Prasad *et al.*, 2010) [10]. India is the largest rice growing country, while China is the largest producer of rice. In India, rice is grown in an area of 43.90 million hectare with a production of 157.00 million ton with an average productivity of 3.57 tons/ha (Agricultural Statistics, 2016) [2]. In India, Tamil Nadu ranks second in the rice productivity among other states with a cultivated area, production and productivity of 18.28 lakh ha, 5,839 thousand tones and 3190.8 kg ha^{-1}, respectively (Anon, 2014-15) [3]. After nitrogen (N), phosphorus (P) and potassium (K), zinc (Zn) as the most widespread micronutrient deficiency in soils and crops worldwide, resulting in severe yield losses and deterioration in nutritional quality.

Rice is one of the highly sensitive crops to zinc (Zn) deficiency. Zinc availability to rice is strongly related to Zn fractions in the soil. Thus, understanding of the distribution of Zn among various fractions of soils will help to characterise chemistry of Zn in soils and possibly its availability for plant uptake. However, distribution of Zn among various chemical forms may vary significantly in response to changing soil properties (Adhikari and Rattan, 2007) [1]. Paddy fields with different soil moisture regimes bring about numerous changes in the soil physiochemical and electrochemical properties such as pH, Eh, electrical conductivity, $CaCO_3$ content and oxides of Fe and Mn (Soltani *et al.*, 2015) [12]. The effect of soil physical and chemical properties on Zn fractions is well understood and therefore improves the available Zn pools. Thus, the current study was undertaken to determine the Zn fractions and their relationship with some important soil properties of paddy soils.

Materials and methods
Experimental soil
Soil analysis
Totally ten soil samples were collected from Anaimalai and Thondamuthur blocks of Coimbatore district. In each block of Anaimalai and Thondamuthur, five samples were collected from five villages namely Anaimalai (L_1), Periyanai (L_2), Poochamikoil East (L_3), Poochamikoil west (L_4) Indra Nagar (L_5), Thondamuthur (L_6), Nallurvayal (L_7), KTR nagar (L_8), SRP thotam (L_9), Boluvampatti (L_{10}) respectively. The soil samples were air dried, ground and passed through a 2 mm sieve and used for further experiment. The physical and physicochemical properties of the selected soil samples were determined, such as particle size analysis, pH, CEC, OC and DTPA-Zn. Particle size analysis of the soil samples was

determined using the pipette method (Gupta and Dhakshinamurthi (1981) [6]. The soil pH and EC was determined in a 1:2.5 (w:v) soil to water suspension. The organic carbon was measured by Walkley-Blacky, (1934) [14] - wet oxidation method. Available micronutrient was extracted with 0.05 M DTPA – TEA – calcium chloride extractant (pH adjusted to 7.3, Lindsay and Norvell 1978) [9] and analysed for micronutrient concentrations using AAS (GBS Scientific, Australia).

Zinc fractionation

The Zn fractionations were determined using a sequential extraction procedure proposed by Benitez and Dubois (1999) [4] and Chitdeshwari *et al.* (2009) [5] (Table 1) and residual zinc fraction was calculated by arriving the difference of total zinc content and summation of other zinc fractions. 1 g of Soil was weighed into a 50-ml plastic centrifuge tube with individual extracting solutions (Table 1) and shaken in a shaker at room temperature. The supernatant solutions obtained from each successive stage of extraction were centrifuged at 3500 rpm for 15 min, decanted and filtered with Whatman No. 42 filter paper and each fraction was determined operationally. All the samples were extracted in triplicate analysed for their Zn concentration using AAS.

Table 1: Zinc sequential fractionation procedures (Benitez and Dubois, 1999 and Chiteshwari *et al*., 2009) [4, 5]

Zn forms	Symbol	Extractants	Soil / Solution ratio (g:mL)	Shaking time (minutes)
Water soluble plus Exchangeable	Ws+Ex-Zn	0.5 M $MgCl_2$ (pH 7.0)	1:10	90
Organically bound Zn	OM-Zn	0.1 M Sodium pyrophosphate	1:10	90
Carbonate bound	Car-Zn	1.0 M Ammonium acetate	1:10	90
Amorphous Fe oxide bound	AFeOx-Zn	1.0 M $HONH_2$.HCl (pH 3.0) prepared in 25 % (v/v) CH_3COOH)	1:20	90
Mn oxidebound	MnOxZn	1.0 M $HONH_2$.HCl (pH 3.0) prepared in 0.5 HCl	1:20	90
Total Zn	Total-Zn	Diacid HNO_3 : $HClO_4$		Digestion with Di acid (HNO_3:$HClO_4$ in the ratio of 5:2)

Results and Discussion

Soil Characteristics

The initial physico-chemical properties of the experimental soils are given in Table 2. The pH of the experimental soils ranged from 6.42 to 7.35 which were near neutral. The soils were free from salinity (0.10 to 0.22 dS m^{-1}). The mechanical composition of all the experimental soils indicated that the soils of different locations belong to different textural classes *viz.*, sandy loam and sandy clay loam. The bulk density and particle density of the soils ranged from 1.26 to 1.46 Mg m^{-3} and 2.33 to 2.56 Mg m^{-3} respectively. The organic carbon was 2.21 to 2.88 g kg^{-1}. The major nutrient status of the soils showed that the available N content of the soils were low in all locations (217 to 232 kg ha^{-1}), the available P and K status of the soils were of high (25.2 to 29.7 and 580 to 624 kg ha^{-1}). However, the content of available micronutrients *viz.*, Cu, Zn, Fe and Mn in soils ranged from 1.14 to 2.34 mg kg^{-1}, 0.80 to 1.44 mg kg^{-1}, 15.52 to 31.00 mg kg^{-1}, and 3.37 to 11.24 mg kg^{-1} respectively. The status of available Fe and Mn was sufficient whereas, the status of available Zn and Cu was found to be in the range of deficient to sufficient range.

Table 2: Soil Characteristics of different locations of rice growing soils of Coimbatore District

Particulars	Location (L_1)	Location (L_2)	Location (L_3)	Location (L_4)	Location (L_5)	Location (L_6)	Location (L_7)	Location (L_8)	Location (L_9)	Location (L_{10})
Sand (%)	48.3	51.2	48.2	56.0	52.2	54.0	47.2	57.6	57.2	55.1
Silt (%)	16.2	18.4	19.0	14.0	12.2	16.2	25.0	11.0	19.0	14.0
Clay (%)	35.0	30.0	32.4	29.6	35.0	29.3	27.2	30.8	23.4	30.2
Textural Class	SCL	SCL	SCL	SCL	SCL	SL	SL	SCL	SCL	SCL
Bulk density (Mg m^{-3})	1.26	1.30	1.29	1.40	1.30	1.34	1.46	1.30	1.34	1.39
Particle density (Mg m^{-3})	2.44	2.43	2.50	2.48	2.55	2.45	2.56	2.42	2.38	2.33
Soil pH	6.27	6.34	6.25	7.26	7.32	7.45	6.5	7.32	7.26	7.05
EC (dS m^{-1})	0.15	0.08	0.10	0.14	0.16	0.22	0.14	0.11	0.14	0.10
Organic carbon (g kg^{-1})	2.88	2.64	3.22	2.61	2.4	2.76	2.35	2.21	2.34	3.04
Available N (kg ha^{-1})	225	217	224	237	220	232	220	217	226	230
Available P (kg ha^{-1})	25.2	26.0	29.7	27.7	26.4	26.6	25.5	26.4	27.4	29.5
Available K (kg ha^{-1})	614	620	624	612	580	610	615	612	620	590
Available Fe (mg kg^{-1})	21.79	30.20	25.42	28.52	31.00	18.79	20.42	17.26	15.52	16.70
Available Zn (mg kg^{-1})	1.15	1.22	1.24	1.07	0.87	0.80	1.08	0.93	0.82	1.34
Available Mn (mg kg^{-1})	11.08	11.24	11.07	8.43	6.42	7.47	11.08	7.25	6.66	3.37
Available Cu (mg kg^{-1})	2.34	1.84	1.80	2.18	1.14	1.94	2.06	2.16	1.68	2.24
Total Zn (mg kg^{-1})	49.95	53.40	56.93	39.47	38.88	54.78	52.85	61.64	69.78	49.95

Zn fractions

The relative Zn fractions for all the soil samples decreased in the following order: Res > MnOx> FeOx>Org>WE-Zn (Table 2). Considering all soil samples (n=10), the residual fractions as the largest part of total Zn ranged from 66 to 83 per cent, whereas the WE as the smallest portion varied between 1.05 and 2.08 per cent of the total Zn. (Tabassum *et al.*, 2014; Soltani *et al.*, 2015 and Worachart *et al.*, 2017) [11, 12, 16]. The Zn fraction WE-Zn is thought to be a vital fraction as this fraction considered fairly mobile thus readily available to plants (Worachart *et al.*, 2017) [16]. The organically complexed, which is known to play a significant role in zinc nutrition of lowland rice (Mandal and Mandal, 1987) [7] was found to vary from 1.40 - 2.11 mg kg^{-1} followed by AFeOx (2.61 - 4.42 mg kg^{-1}) and MnOx (4.52 - 7.06 mg kg^{-1}). The total Zn of the selected paddy soils ranged from 38.88 to 69.78 mg kg^{-1}. Shetty *et al.* (2001) [13] studied the distribution of Zn among different fractions. They also reported that water soluble plus exchangeable forms vary in the range of 0.14 to 0.32 mg kg^{-1} with the lowest contribution (0.32 to 0.74 %) to total Zn and residual fractions contributed highest to total Zn (86.68 to 91.64 %). The higher content of amorphous sesquioxide bound Zn and Manganese oxide bound Zn could be attributed to greater ability of amorphous sesquioxide to adsorb Zn because of their high specific surface area. Similar finding were reported by Wijebandara *et al.* (2011) [15]

Table 3: Zn fractions in rice growing soils of Coimbatore District

Locations	L_1	L_2	L_3	L_4	L_5	L_6	L_7	L_8	L_9	L_{10}
Water Soluble + Exchangeable	0.86	0.56	0.95	0.82	0.68	0.73	0.88	0.82	0.77	0.67
Organically bound	1.84	2.11	1.89	1.75	1.48	1.66	1.58	1.56	1.45	1.40
Fe oxide bound	2.61	3.24	4.42	2.78	3.16	4.40	4.30	3.99	3.09	3.42
Mn oxide bound	4.59	5.53	4.78	5.24	5.63	7.06	5.74	6.24	4.54	4.52
Residual Zn	37.86	39.93	43.01	27.16	25.71	38.83	38.37	46.81	57.59	38.10
Total Zn (mg kg^{-1})	49.95	53.4	56.93	39.47	38.88	54.78	52.85	61.64	69.78	49.95

Zn fractions and soil Properties

Results (Table 4) showed that the amount of Zn in water soluble plus exchangeable zinc was not significant and negatively correlated with soil pH. The negative correlation of different forms of Zn with pH might be due to the fact that at higher pH, higher oxides of Zn will be formed and zinc bound in these forms does not come into solutions easily (Kumar *et al.,* 2010) [8] The pH of the soil had no significant and negative correlation with any fractions, except Org. The organically bound fraction was found to be significant and positively correlated with organic carbon (0.36**) and available Fe (0.56**) (Soltani *et al.,* 2015) [12]. The AFeOx bound fraction positively correlated with organic carbon (0.09) and electrical conductivity (0.10**) (Hazra *et al.,* 1987) [7]. The MnOx bound fraction highly significant and negatively correlated with organic carbon (-0.39**), available Zn (-0.55**) and Mn (0.11**). The residual fraction was significant and negatively correlated with all the soil properties. Overall, it is suggested that the distribution of Zn among various chemical forms may vary significantly in response to changing soil properties.

Table 4: Simple correlation relationships between soil properties and Zn fractions

Zn Fractions/Soil Properties	Water Soluble + Exchangeable	Organically bound	Fe oxide bound	Mn oxide bound	Residual Zn
Soil pH	-0.26	-0.68**	-0.02	0.42	-0.06
EC (dSm^{-1})	0.10**	-0.30	0.11**	0.52**	-0.21**
Organic carbon (g kg^{-1})	0.14	0.36**	0.09	-0.39**	-0.13
Clay (%)	0.02	0.28	-0.19*	-0.03	-0.61**
Available Fe (mg kg^{-1})	-0.23	0.57**	-0.29**	0.01**	-0.70**
Available Zn (mg kg^{-1})	0.02	0.40*	-0.09*	-0.55**	-0.16*
Available Mn (mg kg^{-1})	0.294	0.807*	0.09*	-0.11**	-0.200*

** and * denote significance at 0.01 and 0.05 probability levels, respectively.

Conclusion

On the basis of the results, it can be concluded that the distribution of native soil Zn in rice fields depend on the soil characters. Zinc fractions in the selected soils mainly distributed in the order of Res > MnOx> AFeOx>Org>WE-Zn. Zinc is mostly occurred in residual followed by MnOx fractions. The water soluble plus exchangeable and organic bound fractions occurred in smaller quantity than the other Zn fractions. The pH, OC and clay content were the most important factors in controlling the distribution of native Zn soils. The study suggested that the bioavailability of zinc was affected by different soil properties and which might be enhanced proper and soil management practices which control the precipitation of zinc in soil.

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