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Zinc dynamics in lowland rice soil as affected by organic manures and zinc fertilization

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Abstract
Knowledge of zinc distribution in various fractions will help to predict the potential of the soil to supply sufficient zinc for crop production. An incubation study was conducted to assess the distribution of different forms of soil Zn under rice growing soils with zinc solubilizing bacteria, organic manures and zinc fertilization. The soils were incubated at submerged condition for a period of 30 days and destructive sampling was done at intervals *viz.*, 7, 15 and 30 days after incubation. The soil samples were analysed to fractionate Zn into Water soluble, Exchangeable, Organic bound, Carbonate bound, FeOx bound, MnOx bound and Residual forms by sequential extraction. Application of organic manures significantly increased all the Zn fractions. Compared to Vermicompost, FYM increased organic bound, water soluble and exchangeable Zn forms, indicating an increase in bioavailability of soil Zn. Application of $ZnSO_4$ significantly increased the bioavailable Zn (Water soluble, Exchangeable and Organic bound) than the other Zn sources. With progress of incubation time, the water soluble, exchangeable forms significantly declined whereas other forms of Zn (Carbonate bound, FeOx bound, MnOx bound and Residual forms) decreased indicating a significant reduction in Zn phyto availability in soil with time. More than 95 percent of the total Zn content occurred in the relatively inactive and mineral bound residual form, whereas only a small percent occurred in Water soluble, Exchangeable and Organic bound fractions.

Keywords: zinc, lowland rice, manures, zinc fertilization

Introduction
Rice (*Oryza sativa* L.) is one of the most important and valuable cereal crop in the world as well as in India. Micronutrient deficiencies are becoming serious because of escalated nutrient demand from more intensive and exploitative agriculture, coupled with use of high analysis fertilizer and low amount of organic manures. After nitrogen (N), phosphorus (P) and potassium (K), widespread zinc (Zn) deficiency has been found responsible for yield reduction in rice. Indian soils are generally low in zinc (Zn) Zn deficient was found to be a tune of 49 per cent in soils of India (Shukla and Behera, 2011) [10]. Zinc deficiencies also results in the inability of rice plant to support root respiration during flooded conditions (Slaton *et al*., 2005) [11].
Soil Zn is partitioned into different forms that have varying affinities to the various soil constituents *viz*., clay, oxides of Fe, Al, Mn, organic, minerals, many solid components and it is known to occur in a number of chemical forms which differ in solubility and thus availability to plants. These forms include soluble Zn present in soil solution (water soluble), adsorbed on exchange sites (exchangeable), associated with organic matter, co-precipitated as secondary minerals or associated with sesquioxides and as structural part of primary minerals and these different forms control solubility and availability of Zn to plants. Application of soluble Zn fertilizers changes Zn distribution among its various chemical forms (Saffari *et al.* 2009) [8]. Materials other than Zn fertilizers can also change the distribution, as this has been reported for application of organic matters such as compost (clement and Bernal, 2006). These organic materials improve soil fertility and generally increase plant production and can also change heavy metal availability (Almas, Singh and Salbu, 1999) [1]. Keeping this in view, the objectives of this experiment were fixed to study the effect of organic manures and zinc source on distribution of Zn forms in soil, (ii) effect of different incubation time on distribution of Zn in soil.

Materials and Methods
An incubation experiment was carried out in the Department of Soil Science and Agricultural Chemistry, Tamil Nadu Agricultural University,

Coimbatore during (August- 2016) to study the effect of organic manures and zinc sources on different forms of zinc in soil. Bulk samples from the surface horizon (0-15 cm) of a lowland rice soil from Anaimalai block of Coimbatore district were collected, air dried, passed through a 2 mm sieve, and mixed thoroughly. The soil was Anaimalai series (Fine-loamy, mixed, isohyperthermic, noncalcareous, Typic Haplustalf). The physical and physio-chemical 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 (Gee and Bauder, 1987). 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 wet oxidation method (1934). Available micronutrients were extracted with 0.05 M DTPA – TEA – calcium chloride extractant (pH adjusted to 7.3, Lindsay and Norvell 1978) and analysed for micronutrient concentrations using AAS (GBS Scientific, Australia). The results are presented in Table1.

Table 1: Selected characteristics of the studied soil

Property	Values
Soil texture	Sandy Clay Loam
Sand (%)	57.3
Silt (%)	19.0
Clay (%)	23.7
Organic carbon (g kg^{-1})	2.34
CEC (c mol(p+)kg^{-1})	16.4
pH	7.19
EC (d S m^{-1})	0.14
DTPA Zn (mg kg^{-1})	0.82
Total Zn (mg kg^{-1})	69.78

The experiment was laid out in Factorial Completely Randomized Design with three replications. Experimental units were polyethylene pots, each containing 100 gram soil. Treatments consisted of four zinc sources (No Zn, ZnO @ equivalent to Zn in $ZnSO_4$, $ZnSO_4$ @ 25 kg ha^{-1} and Zn-EDTA @ 5 kg ha^{-1}) and three different organic manures (No manure, Farm Yard Manure @ 12.5 t ha^{-1} and Vermicompost @ 5 t ha^{-1}). Enough deionised water was added to bring submerged condition and the pots were covered with lid with few holes to prevent evaporation while allowing exchange of gases. At the end of each incubation time, samples were air dried and analysed to determinate chemical forms of zinc. The physico-chemical characteristics of the organic manures used for conducting the experiment is presented in Table 2.

Table 2: Characteristics of Organic Manures

Characteristics	Farm Yard Manure	Vermicompost
pH	7.11	7.42
EC (dSm^{-1})	0.40	3.6
Organic Carbon (%)	13.5	26.2
N (%)	0.65	1.82
P (%)	0.39	0.95
K (%)	1.25	0.84
Zn (mg kg^{-1})	85.0	77.0

Fractionation Procedure

Zn fractions in soil samples were estimated by subjecting surface soils to fractionation using different extractants. In this method, a 5 g soil sample is sequentially extracted as outlined in Table 3. The Zn forms thus determined, are reported as water soluble (WS-Zn), exchangeable (Ex-Zn), Organic bound (OM-Zn), Fe oxide (FeOx-Zn), Mn Oxide bound Zn (MnOx-Zn) and residual Zn. Residual Zn was determined by calculating the difference between the total and sum of all fractions (Benitez and Dubois, 1999; Chitdeshwari *et al.*, 2009) [2, 3].

Table 3: Sequential extraction procedure used for the fractionation of soil Zn (Benitez and Dubois, 1999; Chitdeshwari *et al.*, 2009) [2, 3].

Zn forms	Symbol	Extractants	Soil /Solution ratio (g:mL)	Shaking time (minutes)
Water Soluble	Ws-Zn	Water	1:10	120
Exchangeable	Ex-Zn	0.5 M $MgCl_2$ (pH 7.0)	1:10	90
Organically bound	OM-Zn	0.1 M Sodium pyrophosphate	1:10	90
Carbonate bound	Car-Zn	1.0 M Ammonium acetate	1:10	90
Fe oxide bound	FeOx-Zn	1.0 M $HONH_2$.HCl (pH 3.0) prepared in 25 % (v/v) CH_3COOH)	1:20	90
Mn oxide bound	MnOx-Zn	1.0 M $HONH_2$.HCl (pH 3.0) prepared in 0.5 HCl)	1:20	90

Table 4: Organic manures and Zn fertilizers on the different Zn Fractions (mg kg^{-1}) (each value is the mean of three replications)

DAI		Water soluble Zn				Exchangeable Zn				Organically Bound Zn			
		M1	M2	M3	Mean	M1	M2	M3	Mean	M1	M2	M3	Mean
7	Zn1	0.045	0.078	0.073	0.065	0.82	1.07	1.10	1.00	1.78	2.18	2.00	1.99
	Zn2	0.064	0.097	0.090	0.084	1.15	1.43	1.36	1.31	2.30	2.47	2.37	2.38
	Zn3	0.108	0.133	0.126	0.122	1.32	1.55	1.50	1.46	2.42	2.55	2.47	2.48
	Zn4	0.081	0.107	0.101	0.096	1.30	1.38	1.47	1.38	2.30	2.52	2.36	2.39
	Mean	0.075	0.104	0.098	0.092	1.15	1.36	1.36	1.29	2.20	2.43	2.30	2.31
15	Zn1	0.042	0.084	0.076	0.067	1.12	1.40	1.27	1.26	2.06	2.25	2.17	2.16
	Zn2	0.067	0.102	0.095	0.088	1.30	1.52	1.47	1.43	2.37	2.77	2.58	2.57
	Zn3	0.110	0.139	0.129	0.126	1.47	1.58	1.53	1.53	2.53	3.10	2.72	2.78
	Zn4	0.083	0.115	0.107	0.102	1.44	1.53	1.47	1.48	2.43	2.82	2.67	2.64
	Mean	0.076	0.110	0.102	0.096	1.33	1.51	1.44	1.43	2.35	2.74	2.54	2.54
30	Zn1	0.037	0.079	0.071	0.062	1.02	1.12	1.17	1.10	1.85	2.36	2.23	2.15
	Zn2	0.062	0.097	0.090	0.083	1.28	1.32	1.30	1.30	2.28	2.90	2.84	2.67
	Zn3	0.105	0.134	0.124	0.121	1.32	1.45	1.44	1.40	2.57	3.32	2.90	2.93
	Zn4	0.078	0.110	0.102	0.097	1.30	1.38	1.38	1.35	2.40	2.73	2.65	2.59
	Mean	0.071	0.105	0.097	0.091	1.23	1.32	1.32	1.29	2.28	2.83	2.66	2.59
		SEd		CD (0.05)		SEd		CD (0.05)		SEd		CD (0.05)	
	Zn	0.0006		0.0012**		0.008		0.017**		0.018		0.036**	

	M	0.0005	0.0010**	0.007	0.014**	0.015	0.032**
	T	0.0005	0.0010**	0.008	0.014**	0.016	0.031**
	ZnxM	0.0010	0.0020**	0.015	0.029**	0.032	0.064**
	MxT	0.0009	0.0018**	0.013	0.026**	0.027	0.055**
	ZnxT	0.0010	0.015**	0.017	0.030**	0.031	0.064**
	ZnxMxT	0.0018	NS	0.026	0.052**	0.054	0.110**

DAI: Days after incubation; M1: No manure; M2:Farm Yard Manure, M3: Vermicompost; Zn1: No Zn; Zn2: ZnO; Zn3: ZnSO4; Zn4:Zn-EDTA

		M1	**M2**	**M3**	**Mean**	**M1**	**M2**	**M3**	**Mean**	**M1**	**M2**	**M3**	**Mean**
7	Zn1	2.29	2.78	3.20	2.76	2.96	2.83	2.92	2.90	4.02	3.85	3.90	3.92
	Zn2	2.46	3.22	3.91	3.20	3.25	2.95	3.10	3.10	4.30	4.14	4.20	4.21
	Zn3	2.73	3.36	3.74	3.28	3.36	3.15	3.22	3.24	4.54	4.37	4.33	4.41
	Zn4	2.38	2.57	3.12	2.69	3.32	3.00	3.18	3.17	4.42	4.28	4.30	4.33
	Mean	2.47	2.98	3.49	2.98	3.22	2.98	3.11	3.10	4.32	4.16	4.18	4.22
15	Zn1	2.22	2.73	3.15	2.70	3.12	2.95	3.05	3.04	4.20	3.35	3.45	3.67
	Zn2	2.39	3.17	3.86	3.14	3.35	3.09	3.20	3.21	4.37	3.69	3.80	3.95
	Zn3	2.66	3.31	3.69	3.22	3.52	3.37	3.33	3.41	4.60	4.07	4.03	4.23
	Zn4	2.31	3.26	3.34	2.97	3.32	3.28	3.30	3.30	4.48	3.78	3.80	4.02
	Mean	2.40	3.12	3.51	3.01	3.33	3.17	3.22	3.24	4.41	3.72	3.77	3.97
30	Zn1	2.10	2.66	3.13	2.63	3.37	3.20	3.30	3.29	4.32	3.42	3.56	3.77
	Zn2	2.28	3.11	3.85	3.08	3.60	3.34	3.45	3.46	4.41	3.76	3.93	4.03
	Zn3	2.49	3.26	3.69	3.15	3.77	3.62	3.58	3.66	4.65	4.14	4.17	4.32
	Zn4	2.18	3.14	3.27	2.86	3.57	3.46	3.50	3.51	4.52	3.85	4.10	4.16
	Mean	2.26	3.04	3.49	2.93	3.58	3.41	3.46	3.48	4.48	3.79	3.94	4.07
		SEd		**CD (0.05)**		**SEd**		**CD (0.05)**		**SEd**		**CD (0.05)**	
	Zn	0.019		0.038**		0.020		0.040**		0.029		0.058**	
	M	0.017		0.033**		0.018		0.035**		0.025		0.050**	
	T	0.016		0.032**		0.016		0.034**		0.024		0.049**	
	ZnxM	0.033		0.066**		0.035		0.070**		0.050		NS	
	MxT	0.029		0.057**		0.030		NS		0.044		0.088**	
	ZnxT	0.033		0.066**		0.035		NS		0.050		0.101*	
	ZnxMxT	0.058		0.115**		0.061		NS		0.088		NS	

DAI: Days after incubation; M1: No manure; M2: Farm Yard Manure, M3: Vermicompost; Zn1: No Zn; Zn2: ZnO; Zn3: $ZnSO_4$; Zn4:Zn-EDTA

DAI		**Res-Zn**				**Total-Zn**			
		M1	**M2**	**M3**	**Mean**	**M1**	**M2**	**M3**	**Mean**
7	Zn1	61.75	62.77	61.40	61.97	73.4	75.4	74.4	74.4
	Zn2	61.34	62.42	60.77	61.51	74.6	76.3	75.5	75.5
	Zn3	62.22	63.77	62.45	62.81	76.3	78.5	77.5	77.4
	Zn4	60.71	62.73	61.52	61.65	74.2	77.1	76.0	75.8
	Mean	61.51	62.92	61.54	61.99	74.6	76.8	75.9	75.8
15	Zn1	60.26	62.83	61.45	61.51	72.9	75.5	74.6	74.3
	Zn2	62.37	64.02	62.10	62.83	76.1	78.3	77.1	77.2
	Zn3	63.58	65.29	63.88	64.25	78.3	80.8	79.3	79.5
	Zn4	61.27	63.44	61.88	62.20	75.2	78.1	76.5	76.6
	Mean	61.87	63.90	62.33	62.70	75.6	78.2	76.9	76.9
30	Zn1	59.86	62.57	61.07	61.17	72.7	75.5	74.6	74.2
	Zn2	61.82	63.70	61.61	62.38	75.8	78.3	77.1	77.1
	Zn3	63.03	64.82	63.39	63.75	78.1	80.8	79.3	79.4
	Zn4	60.78	63.25	61.36	61.80	75.0	78.0	76.4	76.5
	Mean	61.37	63.59	61.86	62.27	75.4	78.2	76.8	76.8
		SEd		**CD (0.05)**		**SEd**		**CD (0.05)**	
	Zn	0.38		0.76		0.53		1.05	
	M	0.33		0.66		0.46		0.91	
	T	0.33		NS		0.46		1.21	
	ZnxM	0.66		NS		0.91		NS	
	MxT	0.57		NS		0.79		NS	
	ZnxT	0.66		NS		0.91		NS	
	ZnxMxT	1.14		NS		1.58		NS	

DAI: Days after incubation; M1: No manure; M2: Farm Yard Manure, M3: Vermicompost; Zn1: No Zn; Zn2: ZnO; Zn3: $ZnSO_4$; Zn4:Zn-EDTA

Results and Discussion

It was evident from the data presented in Table 4, that the distribution of Zn in soils were significantly affected by Zn fertilizer and organic manure application found in the order of WS < Ex < OM <Car< FeOX < MnOX < Res Zn. FYM treated soil have the higher amount of phytoavailable Zn than the Vermicompost treated soil and control. Comparing the two sources of organic manures, farmyard manure showed its superiority over other manure which might be due to the increased availability of native and applied Zn by the formation of organometallic complexes (Udayasooriyan, 1988) [13]. Among different chemical fractions of Zn, the water soluble fraction (WS) exhibited lower values ranging 0.065 to 0.126 mg kg^{-1}. Also observed that the highest value of Zn content was associated with residual fraction followed by Fe oxide fraction oxide while the lowest was with water soluble and exchangeable fractions. Both the residual Zn and oxide bound Zn are considered as the stable fractions while the exchangeable Zn and water soluble Zn are more soluble and immediately available to plants (Saffari *et al.* 2009) [8]. At 30 days after incubation, the release pattern of water soluble fraction recorded a decrease with period of submergence which might be due to the precipitation of applied Zn as hydroxides and carbonates besides its adsorption on the surface of amorphous sesquioxides (Prasad *et al*., 1996) [7]. The exchangeable Zn fractions also varied from 1.00 – 1.53 mg kg^{-1}. Shetty *et al.* (2001) studied the distribution of Zn among different fractions and reported that water soluble + exchangeable forms the lowest value in the range of 0.14-0.32 mg kg^{-1}. Similarly, the Zn content in water soluble, exchangeable Zn fractions increased with the application of $ZnSO_4$ followed by Zn-EDTA.

The organic bound fraction increased with time period in the range of 1.99 – 2.93 mg kg^{-1} which might be due to the application of organic manures. Similarly, the Zn content in organic bound fractions increased with the application of $ZnSO_4$ followed by Zn-EDTA. Chitdeshwari and Krishnasamy (2005) [4] studied the transformation of Zn and Zn enriched organic manures in rice. They reported that higher amount of applied Zn was recovered as occluded Zn followed by organically bound and complexed-Zn in rice soil. Sunil Kumar (2017) [12] observed that high content of Zn as organic fraction as evidenced in the present investigation also which might be due high organic carbon build up in soil due to FYM additions.

Carbonate bound Zn also increased with time period in the range of 2.76 – 3.28 mg kg^{-1}. The Phyto availability of Car-Zn is much less than the soluble plus exchangeable or organic forms, but it could be used by the subsequent crops. Therefore, the carbonate form is a reserved form of Zn that is potentially available to plants (Yasrebi *et al.* 1994) [14]. The FeOx bound fraction and MnOx bound fraction increased with time period in the range of 2.90 – 3.66 mg kg^{-1} and 3.92 -4.41 mg kg^{-1} respectively. Similarly, the Zn content in FeOx and MnOX fractions increased with the application of $ZnSO_4$ and decreased with application of Zn-EDTA showed that the reduction in Zn availability was possibly due to the slow transformation of Zn from loosely bound fractions such as exchangeable fraction to strongly bound fractions such as Fe-Mn oxide.

In Farm Yard Manure and Vermicompost–treated soil, there is an increase in WS, Ex, Car, OM-Zn forms as compared to these fractions in the control soil. However, the MnOx, FeOx and Res Zn form decreased as compared to the control in FYM and Vermicompost treated soil. The greatest increase in WS, Ex and OM-Zn fractions were associated with Farm Yard Manure–treated soil samples. Fresh organic wastes, such as animal manures, are rich in soluble organic compounds, which can increase the solubility of metals shortly after addition to soil (Almas, Singh, and Salbu 1999) [1].

Conclusions

In untreated soil, Zn was mainly found in residual and Carbonate fractions. Application of Zn fertilizers increased all chemical forms of soil Zn. A marked portion of applied Zn was converted to Carbonate bound Zn, which is potentially available for crops. Application of organic manures to the soil increased all the chemical forms except MnOx-Zn; the highest increase occurred in OM-Zn fractions. This suggests that Zn bioavailability in soil increased following the application of organic materials. The concentration of Ws-Zn, Ex-Zn and OM-Zn were more in FYM treated soil than vermicompost treated soils. Likewise, the Zn Phyto availability was more in $ZnSO_4$ > Zn-EDTA > ZnO. The available Zn status of soil increased significantly with the levels of Zn amongst the organic manures in the order of FYM> Vermicompost and Zn fertilization in the order of $ZnSO_4$>Zn-EDTA>ZnO. According to current study, $ZnSO_4$ with Farm Yard Manure can be recommended as excellent fertilizer practice in rice soils.

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