

Zinc Transformation in Calcareous Vertisol of Tungabhadra Command*

K. HEMANTH KUMAR AND B. BASAVARAJ

Department of Soil Science and Agricultural Chemistry,
University of Agricultural Sciences, Dharwad-580005,
E-mail : hemanth.agri@gmail.com

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Abstract: Transformation of zinc (Zn) in calcareous vertisol under submergence was carried out at Agriculture College, Dharwad during 2007 under laboratory conditions. Stubbles + ZnSO₄/ZnEDTA, stubbles + FYM, stubbles + ZnSO₄/ZnEDTA + FYM and stubbles were four different treatments imposed for the study. Treatments were replicated five times and laid out in completely randomized design. Results showed that water soluble + exchangeable Zn values were found to decrease during initial period of incubation (0-30 days) but later increased in all the treatments (30-90 days) and higher values were recorded in stubbles + ZnSO₄ / ZnEDTA + FYM. Organically complexed, manganese oxide bound and amorphous sesquioxide bound zinc values increased in all the treatments at 30 days and subsequently decreased. Crystalline bound zinc values were found to decrease (0-90 days) in all the treatments except in ZnSO₄ / ZnEDTA + FYM. Residual and total zinc values were found to increase in all the treatments at 30, 60 and 90 days of incubation.

Key words : Zinc transformation, zinc fractions, calcareous vertisol

Introduction

Wide spread occurrence of Zn deficiency in submerged rice has been reported earlier (Anon., 1977). Zinc is known to occur in a number of chemical forms which differ in solubility and thus availability to plants (Iyengar and Deb, 1977). When a soil is submerged, a number of chemical and electro-chemical changes occur, such as adjustment of soil pH towards neutrality, increase in partial pressure of CO₂, decrease in redox potential, increase in the concentration of Fe and Mn in the soil solution, and decrease in crystallinity of oxides of Fe and Mn etc., Hazra *et al.* (1987) have shown that Zn transformation in submerged soils is very much related to the reduction of Fe₂O₃ and subsequent formation of insoluble hydroxides of iron. The information regarding the transformation of different forms of zinc under submergence in calcareous vertisol of Tungabhadra command is lacking, hence present study was under taken.

Materials and Methods

Incubation studies : A surface soil (0-20 cm) sample at one of the villages of Gangavathi taluk without application of ZnSO₄ / Zn EDTA was used for incubation studies. Four different treatments mentioned below were imposed, replicated five times and laid out in completely randomized design. Required quantity of fertilizers (NPK), stubbles, ZnSO₄ and FYM were weighed as per treatment details and mixed thoroughly to 1 kg of processed soil sample and then filled in each of the plastic container and the water was added, water level maintained at 5 cm level throughout the incubation period. The experiment was incubated at room temperature (25±0.5°C) for 90 days.

T₁ : Fertilizers (NPK) + stubbles + ZnSO₄ / ZnEDTA

T₂ : Fertilizers (NPK) + stubbles + FYM

T₃ : Fertilizers (NPK) + stubbles + ZnSO₄ / ZnEDTA + FYM

T₄ : Fertilizers (NPK) + stubbles (control)

Note : N (120 kg/ha), P (65 kg/ha), K (60 kg/ha), ZnSO₄ (20 kg/ha), stubbles (2 t/ha), FYM (12 t/ha)

The experimental soil was clay in texture with Typic Ustropepts. The initial chemical properties of the soils used for the study indicated that pH, EC, OC and CaCO₃ were 7.38, 0.21 dS m⁻¹, 2.38 g kg⁻¹ and 10.3%, respectively. The soils were there after sequentially extracted for different forms of zinc following Shuman (1985) method after different periods of submergence (30, 60 and 90 days). Water soluble plus exchangeable (WSEX) Zn was extracted with 1M Mg(NO₃)₂ of pH 7.0; organically complexed (OC) Zn with 0.05 M Cu(OAC)₂; manganese oxides (MnOX) bound Zn with 0.1 M NH₂OH.HCl (pH-2), amorphous sesquioxides (AMOX) bound Zn 0.2 M, (NH₄)₂C₂O₄ (pH-3) and crystalline sesquioxides (CRYOX) bound Zn 0.1 M ascorbic acid with acidified ammonium oxalate. The residual Zn was calculated by subtracting the sum of the Zn forms from the total Zn content. Total Zn in the soil was determined by hydrofluoric acid digestion method proposed by Page *et al.*, (1982). Fisher (1960) method of analysis of variance was applied for the analysis of the data and results were interpreted according to the suggestions of Panse and Sukhatme (1967).

Results and Discussion

The different Zn fractions at the start of incubation were 0.41, 1.82, 2.92, 3.25, 3.60, 273, 285 mg per kg for water soluble + exchangeable zinc, organically complexed zinc, manganese sesquioxide zinc, amorphous sesquioxide zinc, crystalline bound zinc, residual zinc and total zinc, respectively. Water soluble plus exchangeable Zinc : The amount of WSEX-Zn varied from 0.2 to 0.31, 0.23 to 0.34 and 0.25 to 0.36 mg kg⁻¹ in T₄ and T₃ treatments respectively at 30, 60 and 90 days of incubation (Table 1 and Fig. 1). WSEX -Zn content decreased

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significantly with time of incubation and attained the values which were below critical level at 30 days of incubation, followed by marginal increase after submergence of 60 and 90 days due to combined incorporation of ZnSO_4 and FYM. The decrease might be due to the precipitation of soluble Zn as hydroxide and carbonates (Brar and Sekhon, 1976), its adsorption on the surface of manganese oxides and amorphous sesquioxides (Hazra *et al.*, 1987). Organic matter application under submergence resulted in the decrease in WSEX-Zn. The conditions prevailing under this situation are favourable for microbial immobilization and formation of ZnCO_3 and $\text{Zn}(\text{CO}_3)_2\text{OH}_2$ (Brar and Sekhon, 1976) and adsorption of Zn on the surface of organic complexes due to low Eh values (Sims and Patrick, 1978).

Organically complexed Zinc: The amount of OC-Zn ranged from 1.85 to 2.49, 1.86 to 2.46 and 1.83 to 2.74 mg kg^{-1} in T_4 and T_3 treatments respectively at 30, 60 and 90 days of incubation (Table 1 and Fig. 2). OC-Zn showed an increase in all the treatments after submergence, attained a peak value at 30 days of submergence and thereafter showed a declining trend. Addition of FYM alone brought about marginal change in the content of OC-Zn. On the other hand, combined application of FYM along with ZnSO_4 increased the content of OC-Zn. The increase is possibly due to the release of Zn bound by crystalline sesquioxide on their reduction under submerged condition and its subsequent chelation by organic compound resulting from anaerobic decomposition of soil organic matter. The declined trend towards latter period might be due to the decrease in stability of Zn organic complexes at the lower E^h of the soils attained at the prolonged submergence (Reddy and Patrick, 1977).

Manganese sesquioxide bound zinc: The amount of MnOX-Zn were in the range 2.88 to 3.47, 2.74 to 3.38 and 2.75 to 3.40 mg kg^{-1} in T_4 and T_3 treatments respectively at 30, 60 and 90 days of incubation (Table 1 and Fig. 3).

MnOX-Zn recorded an increase in all the treatments at 30 days of submergence and declined thereafter. Application of ZnSO_4 alone or combined application of ZnSO_4 along with FYM increased the manganese sesquioxide bound zinc in soil during all the stages of incubation. Mandal (1961) and Ponnamperna (1972) observed that under anaerobic condition some amount of higher oxides of manganese are converted to lower valent compounds, which are diffused to the oxic region

and gets re-oxidised to form manganic hydroxide having large specific surface area and hence high adsorption capacity. The Zn released from other bound forms might have held by manganic hydroxide resulting in an increased content of manganese sesquioxide bound form of zinc. The increase in MnOX-Zn may also be attributed to the reduction in some crystalline form of iron oxides upon submergence as reported by Willet (1979) and thus releasing some amount of occluded zinc for its subsequent adsorption on the hydrous oxide form. The decreasing MnOX-Zn might be due to the decreased redox potential of soils which caused the reduction of freshly formed manganic hydroxide resulting in the release of adsorbed zinc.

Amorphous sesquioxide bound zinc: The amount of AMOX-Zn varied from 3.04 to 4.19, 2.92 to 4.13 and 2.94 to 4.16 mg kg^{-1} in T_4 and T_3 treatments respectively at 30, 60 and 90 days of incubation (Table 1 and Fig. 4). AMOX-Zn increased in all the treatments at 30 days of submergence and thereafter showed a decreasing trend. Application of ZnSO_4 and FYM alone or in combination increased the AMOX-Zn during all the stages of incubation. The increase might be due to the fact that under the reduction condition in submerged soils there is an increase in the formation of hydrated oxides of Fe and Mn (Hazra *et al.*, 1987) the freshly formed compound of which possess larger surface area and hence have strong adsorption capacity. The water soluble Zn already present in the soil or released from the other forms might have adsorbed on the surface of these freshly formed hydroxides.

Crystalline bound zinc: The amount of CRYOX-Zn varied from 3.01 to 4.15, 2.95 to 4.08 and 2.94 to 4.06 mg kg^{-1} in T_4 and T_3 treatments respectively at 30, 60 and 90 days of incubation (Table 1 and Fig. 5). CRYOX-Zn decreased in all the treatments from the initial value of 3.60 mg kg^{-1} after submergence at all the periods of incubation except T_3 and the maximum decrease was noticed in 90 days after incubation in the control treatments (2.94 mg kg^{-1}). The decrease might be due to reason that under reduced condition in submerged soils, some of the crystalline sesquioxides might have undergone transformation to an amorphous form resulting in the release of a part of the Zn occluded by the former and it's subsequent by a sorption latter (Hazra *et al.*, 1987)

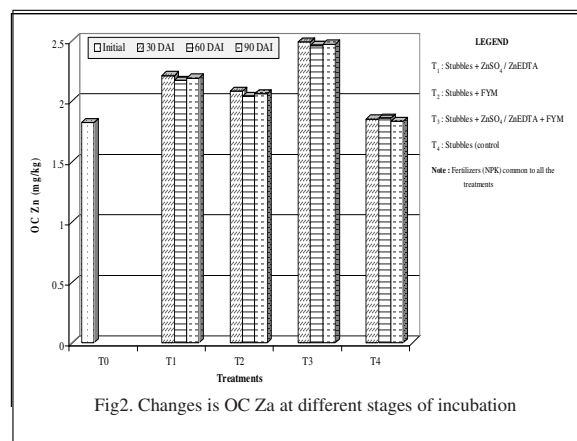
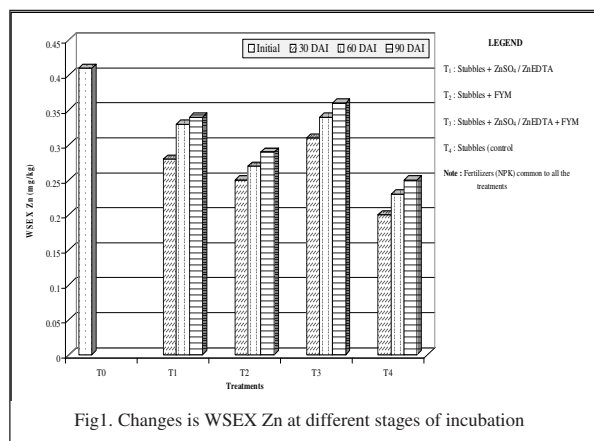


Table 1. Changes in different forms of zinc (mg/kg) at 30, 60 and 90 days after incubation

Treatments*	Forms of Zinc														
	WSEX			OC			MnOX			AMOX			CRYOX		
	30	60	90	30	60	90	30	60	90	30	60	90	30	60	90
T ₁ -Stubbles + ZnSO ₄ / ZnEDTA	0.28	0.33	0.34	2.21	2.17	2.19	3.15	3.08	3.10	3.67	3.59	3.60	3.58	3.52	3.50
T ₂ -Stubbles + FYM	0.25	0.27	0.29	2.08	2.04	2.06	3.0	2.91	2.92	3.36	3.29	3.29	3.31	3.25	3.22
T ₃ -Stubbles + ZnSO ₄ / Zn EDTA	0.31	0.34	0.36	2.49	2.46	2.47	3.47	3.38	3.40	4.19	4.13	4.16	4.15	4.08	4.06
T ₄ - stubbles (control)	0.20	0.23	0.25	1.85	1.86	1.83	2.88	2.74	2.75	3.04	2.92	2.94	3.01	2.95	2.94
Mean	0.26	0.29	0.31	2.16	2.13	2.13	3.12	3.02	3.04	3.56	3.48	3.50	3.51	3.45	3.43
SEm±	0.014	0.0140	0.014	0.081	0.083	0.084	0.076	0.076	0.076	0.094	0.091	0.091	0.033	0.077	0.077
CD at 5%	0.042	0.0420	0.042	0.243	0.250	0.254	0.228	0.228	0.228	0.284	0.274	0.278	0.243	0.232	0.232
* Fertilizers (NPK) common to all the treatments.	Initial values														
WSEX – Water soluble + Exchangeable Zn				OC – Organically complexed zinc									WSEX – 0.41 mg/kg		
MnOX – Manganese sesquioxide bound Zn				AMOX – Amorphous sesquioxide bound Zn									OC – 1.82 mg/kg		
CRYOX – Crystalline bound Zn				Res – Residual Zn									MnOX – 2.92 mg/kg		
													Total- 285 mg/kg		
													AMOX – 3.25 mg/kg		
													CRYOX – 3.60 mg/kg		
													Res – 273 mg/kg		

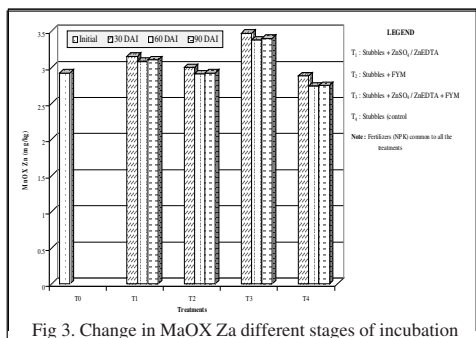


Fig 3. Change in MaOX Zn different stages of incubation

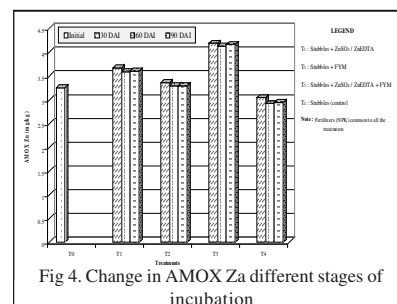


Fig 4. Change in AMOX Zn different stages of incubation

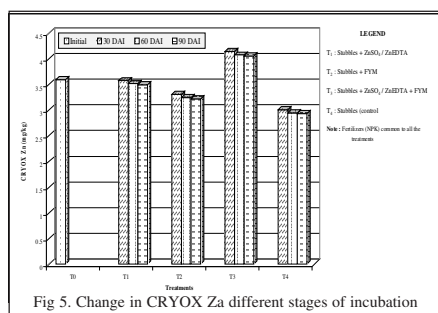


Fig 5. Change in CRYOX Zn different stages of incubation

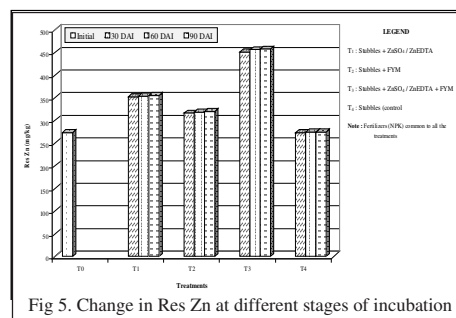


Fig 5. Change in Res Zn at different stages of incubation

Residual zinc: The residual Zn ranged from 273 to 451, 274 to 456 and 274 to 457 mg kg⁻¹ in T₄ and T₃ treatments respectively at 30, 60 and 90 days of incubation (Table 1 and Fig. 6). The submergence caused marked increase in residual zinc content of soil, which indicates considerable transformation of zinc to residual fraction. Similar results were also observed by Saha and Mandal (1996). There was increase in residual zinc throughout incubation period. This might be due to application of ZnSO₄ along with FYM.

Total zinc: The total zinc varied from 284 to 468, 285 to 470 and 285 to 471 mg kg⁻¹ in T₄ and T₃ treatments respectively at 30, 60 and 90 days of incubation (Table 1). The submergence caused marked increase in total zinc content of the soil throughout incubation period. This might be due to application of ZnSO₄ along with FYM. Transformation of water soluble + exchangeable Zn to other unavailable forms of Zn was higher in these soils because of alkaline pH, low organic matter status and presence of free CaCO₃.

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