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Kinetics of zinc transformation in calciorthids soils of western Rajasthan, India

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Abstract: The present study was under taken to investigate the kinetics of transformation process of applied and native Zn as influenced by soil moisture regime, available moisture and organic matter additions in Aridisols of western Rajasthan. The incubation experiment was conducted with exact amount of the soil samples (250 g), put in a number of small containers, made of corning glass. Three levels of moisture regimes i.e. field capacity (W_0), continuous submergence (W_1), alternate submergence and saturation (W_2) and two levels of organic matter as starch at 0 per cent (M_1) and 0.5 per cent (M_2) of the soil weight; and two levels of zinc i.e. native (N) and applied (A) (Zn @ 5 mg kg^{-1} soil as $ZnSO_4.7\ H_2O$). The soils then incubated for 30, 60 and 90 days. Destructive sampling was done after each incubation period, and then different fractions of Zn were sequentially extracted by different extracting solutions and determined with the help of atomic absorption spectrophotometer. Based on the results, it can be concluded that the transformation of Zn is largely controlled by organic matter, moisture regimes and Zn application due to considerable changes in the chemical and electrochemical properties of soil and thereby influence the transformation of zinc. Organic matter application significantly increased Zn fractions due to the retention of Zn on exchange complex owing to producing organic acid by decomposition of organic matter in soil. Further, the results showed that if such condition was maintained in the field, and it increased the availability of Zn for different crops in Aridisols.

Keywords: Amorphous sesquioxide bound, Aridisols, Calciorthids exchangeable, Crystalline sesquioxide bound Zn, Organic complexed

INTRODUCTION

Soils, the medium of plant growth is biologically vibrant and chemically active. Therefore, behavior of native or applied nutrients is continuously modulated by a number of biochemical processes (Reyhanitabar and Gilkes, 2010). The studies that determine how changes in properties bring micronutrients into available forms are of at most importance, especially to determine from which form they become available and what changes are necessary to cause redistribution. Plants take their nutrients mostly from soil. It is well known that the optimum plant growth and crop yield depends not only on the total amount of nutrients present in the soil at a particular time but also on their availability which in turn is controlled by physico-chemical properties like: soil texture, organic carbon and calcium carbonate, cation exchange capacity, pH and electrical conductivity of soil (Bell and Dell, 2008). Thus, not only are the form themselves important, but possibly to even greater significance are the potential changes among forms due to outside influences. Transformation of micronutrient includes (Viets, 1962) precipitation, fixation, or interlattice entrapment (occluded nutrients) by clay minerals, immobilization or conversion of nutrients into organic forms, sorbed on the soil exchange complex, and water soluble fraction.

The soil solution is the central focus of soil chemistry, since it is from this medium that plants absorb nutrients and it is the center of all chemical processes (Lindsay, 1979). Soil water is known to regulate the kinetics of precipitation and dissolution of micronutrients by controlling the chemical as well as microbiological redox potential (Ponnamperuma, 1972). Soil water content is most important, in that, under wet conditions, elements dissolve or move by diffusion. The element concentrations in soil solution are in constant flux, influenced by a host of factors including soil types, moisture regimes, pH, temperature, oxidation/reduction status, organic matter, fertilizer additions and plant uptake (Ponnamperuma, 1972).

Aridisols are mineral soil occurring extensively in the western half of Rajasthan divided by Aravali axis (Joshi *et al.*, 1983). The region (Agro-climatic zone) falls under zone IA of Arid western region includes the districts of Jodhpur and Barmer. Soil types in this zone are desert soils and sand dunes, aeolian soil, coarse sand texture and in some places calcareous. Major portion of Aridisols in Rajasthan is covered by the sub-order orthids, which have one or more pedogenic

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horizons, these horizons form the basis for defining the great group of this sub-order, camborthids, calciorthids, salorthids and paleorthids, which commonly occur in the state. There are sporadic reports of zinc deficiency in these soils (Joshi and Sharma, 1986). Therefore, present study has been under taken to investigate the kinetics of transformation process of applied and native Zn as influenced by soil moisture regime, available moisture and organic matter additions in Aridisols of western Rajasthan.

MATERIALS AND METHODS

Sampling site and climate: Aridisols are mineral soil occurring extensively in the western half of Rajasthan divided by Aravali axis. The region falls under zone IA -Arid western (where average rainfall between 200 to 370 mm) of Agro-Climatic Zones includes the districts of Jodhpur and Barmer. Soil types in this zone are desert soils and sand dunes, aeolian soil, coarse sand texture and in some places calcareous. Major portion of Aridisols in Rajasthan is covered by the sub-order orthids, which have one or more pedogenic horizons, these horizons form the basis for defining the great group of this sub-order, camborthids, calciorthids, salorthids and paleorthids, which commonly occur in the state. The winter season rudiments from second half of October and continue up to February last. The period of summer season was long compared to winter, beginning from March to first half of July. Bulk soil sample (25–30 kg) from surface layer (0-15 cm) were collected from the farmer's field at nearby areas of Jodhpur district, representing major calciorthids great group soil of western Rajasthan and prepare composite sample for the study.

Determination of physico-chemical characteristics of the soil: Soil sample was air dried in shadow, gently crushed with a wooden pastle and passed through 2 mm sieve. Processed soil sample used for detail laboratory analysis. The pH and Electrical Conductivity of soil was determined in 1:2 soil water suspension (Richards, 1954), mechanical composition by Hydrometer method (Bouyoucos, 1951), organic carbon by rapid titration method (Walkley, 1947), calcium carbonate by titration method (Piper, 1950) and cation exchange capacity by centrifuge method (Richards, 1954).

Incubation study: The incubation experiment was conducted in Department of Agricultural Chemistry and Soil Science laboratory, Rajasthan College of Agriculture, Udaipur, which is located at latitude of 24.3^{0}N and longitude of 73.4^{0}E and at an altitude of 583 meters above mean sea level. Exact amount of the soil samples (250 g) were put in a number of small containers, made of corning glass. Three levels of moisture regimes i.e. field capacity (W_0), continuous submergence (W_1), alternate submergence and saturation (W_2) and two levels of organic matter as starch at 0 percent (M_1) and 0.5 percent (M_2) of the soil weight; and two levels of zinc i.e. native (N) and applied (A) (Zn @ 5 mg kg^{-1} soil as $ZnSO_4.7\ H_2O$). Starch (A.R. Grade), instead of any conventional manure, was used to avoid any complication that might arise due to the release of mineral elements from the decomposition of such organic matter. The experiment was laid dawn in completely randomized design (CRD) with factorial concept. The treatment combinations were 12 in number (W0M1N, W_0M_1A, W_1M_1N, W_1M_1A, W_2M_1N, W_2M_1A, W_0M_2N, W_0M_2A, W_1M_2N, W_1M_2A, W_2M_2N, W_2M_2A) with three replications of each. The soils then incubated for 30, 60 and 90 days in ambient summer season. In the ambient summer temperature, the incubation experiment was started from the March 5 to June 5, in the laboratory. The ambient temperature during this period ranged from 29.3 to 41.2^o C (maximum) and 9.9 to 26.2^o C (minimum). Destructive sampling was done after each incubation period, and then different fractions of Zn were sequentially extracted by different extracting solution as per details outlined in flow sheet of fig. 1 (Mandal and Mandal, 1986) and determined with the help of atomic absorption spectrophotometer (GBC AAS Modal No. 932).

Statistical analysis: The data on different fractions of zinc were statistically analyzed using analysis of variance techniques (Fisher, 1949). Test of significance (F-test) was used for estimation of the treatment differences (Cochran and Cox, 1959). Critical differences were calculated to assess the significance between different fractions of Zn wherever they were found significant. In all the statistical tests, a significance level of 0.05 was chosen.

RESULTS AND DISCUSSION

The physico-chemical analysis of experimental soil revealed that it had sand 67.10%, silt 18.60%, clay 14.30%, textural class sandy loam, pH (1:2.5) 8.11, EC (1:2.5) 0.52 dSm^{-1}, organic carbon 0.294%, $CaCO_3$ 4.90%, CEC 12.08 c mol (p+) kg^{-1}, moisture at field capacity (At 1/3 bar) 5.52% and WHC 23.64%, available nitrogen 203.4 kg ha^{-1}, available phosphorus 7.81 kg ha^{-1}, available potassium 379.70 kg ha^{-1}. Initially among different fractions of Zn water soluble + exchangeable Zn was minimum 0.41 followed by Organic complexed 0.45, Crystalline Sesquioxide-bound 0.64 and amorphous Sesquioxide-bound 0.95 mg kg^{-1} were recorded.

The kinetics of Zn transformation in calciorthids great group soil at periodic intervals revealed that the application of organic matter @ 0.5 percent significantly increased the Organic Complexed, AMOX and CRYOX fractions of Zn, whereas, WSEX-Zn decreased at all the three stages of incubation (Table 1). Data further indicated that irrespective of the organic matter levels, significant reduction in WSEX, Organic complexed and CRYOX fractions of Zn were observed after 30 days of incubation. However, the AMOX-Zn increased up to 90 days at both the levels of organic matter (i.e., 1.02, 1.17 and 1.22 mg kg-1 for M1; and 1.13, 1.38 and 1.44 mg kg-1 for M2). The organic matter application caused considerable decrease in these three fractions may be due to the complexation of Zn by organic ligands (Sims and Patrick, 1978) and microbial immobilization of Zinc (De Remer and Smith, 1964). Among the different fractions, the AMOX-Zn showed maximum increment due to application of organic matter at 60 and 90 days of incubation (i.e., 15.2 and 15.3%, respectively). The increase might be due to the fact that under the reduced condition in soils there is an increase in the formation of hydrated oxides of Fe and Mn which are the freshly formed compound possess larger surface area and hence have strong adsorption capacity (Kumar and Basavaraj, 2008).

The transformation of Zn during 90 days of incubation at various levels of moisture showed that the maximum content of Zn was recorded under alternate submergence and saturation (W2), having the values as 0.63, 0.53 and 0.45 mg kg-1 for WSEX-Zn; 0.95, 0.86 and 0.75 mgkg^{-1} for Organic Complexed-Zn; 1.13, 1.40 and 1.49 mg kg^{-1} for AMOX-Zn and 1.17, 1.07 and 0.98 mg kg^{-1} for CRYOX-Zn, at 30, 60 and 90 days of incubation, respectively. The minimum content of all these fractions of Zn were observed at field capacity (W0) moisture level, at all stages of incubation. Among the different moisture levels, W1 and W2 for WSEX and CRYOX fractions of Zn at 90 days were increased. On the other hand, irrespective of the moisture levels, the values of AMOX-Zn at 60 and 90 days of incubation were at par, whereas, other three fractions viz., WSEX, Organic complexed and CRYOX fractions of Zn decreased significantly after 30 days of incubation.

The fractions of Zn under study, i.e., WSEX, Organic Complexed, AMOX and CRYOX were increases with the application of zinc to incubated soil and the increased were to the tune of 13.1, 16.0 and 14.6 per cent for WSEX-Zn; 17.2, 22.1 and 17.4 per cent for Organic Complexed-Zn; 11.4, 10.3 and 10.8 per cent for AMOX-Zn and 12.1, 11.2 and 9.3 per cent for CRYOX-Zn at 30, 60 and 90 days of incubation, respectively. Among the different fractions, the CRYOX-Zn was maximum at 30 days, whereas, AMOX fraction of Zn was highest at 60 and 90 days of incubation, irrespective of the zinc levels.

Interactive effect of various treatments: The kinetics of Zn transformation was significantly affected by the interactive effects of organic matter, moisture and zinc application (Table 2, Fig. 2). The results showed that immediately after incubation, the extractable Zn content in WSEX, Organic complexed and CRYOX fractions recorded a marked decrease under 60 and 90 days of incubation; whereas, AMOX-Zn was increased significantly up to 90 days of incubation, without consideration of the various treatment combinations and temperature. The WSEX-Zn was maximum at alternate submergence and saturation, 0% organic matter, applied condition (W_2M_1A) treatment and the decrease was more pronounced when the soils were treated with organic matter content. The minimum content was recorded at field capacity moisture level, 0.5 % organic matter and native condition (W_0M_2N) treatment, irrespective of the incubation period. Contrary to above findings, the organic complexed, AMOX and CRYOX fractions of Zn were increased with organic matter. treatment and zinc levels irrespective of the moisture levels and incubation periods. The maximum content of organic complexed, AMOX and CRYOX-Zn were observed at W_2M_2A treatment (Alternate submergence and saturation, 0.5 % organic matter, Applied condition), whereas, minimum content of these fractions were recorded at treatment of field capacity moisture level combined with no organic matter application and native soil condition (W_0M_1N), irrespective of the incubation periods. Application of organic matter caused a significant increase especially with alternate submergence and saturation, in the content of organic complexed, amorphous and crystalline sesquioxide bound fractions of Zn. This may be attributed to the enhanced release of Zn present in mineral fractions as a result of action of decomposition products of added organic matter and enhanced microbial activity under these conditions (Dutta *et al.*, 1989). The combined application of FYM along with ZnSO4 increased the content of Organic complexed-Zn which 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 (Kumar and Basavaraj, 2008). Significant decrease in Zn fraction under field capacity was also reported by Phogat *et al.* (1994) and could be an account of weak stability of organically complexed Zn as suggested by Sims and Patrik (1978) and also to the subsequent transformations to amorphous sesquioxide form (Singh and Abrol, 1985; Mandal and Mandal, 1986). The data further showed that the WS+EX, Organic complexed and crystalline sesquioxide bound fractions of Zn decreased significantly after 30 days of incubation, irrespective of the various treatment combinations whereas, amorphous sesquioxide bound Zn increased significantly up to 90 days of incubation. Barring few treatment combinations the maximum content of Zn was observed in crystalline sesquioxide bound fraction at 30 days, while at 60 and 90 days amorphous sesquioxide bound Zn was maximum. These results are in conformity to earlier findings that the organic matter application caused considerable decrease in WS+EX-Zn fraction after 30 days of incubation and may be attributed to the complexation of Zn by organic ligands (Sims and Patrick, 1978). A number of investigators (Brar and Sekhan, 1976; Chatterjee *et al.*, 1992) reported that the availablity of Zn in soil decreased with time may be due

Table 1. Effect of organic matter, moisture and micronutrient levels on Zn fractions in Aridisols at different incubation periods.

	Zn Fractions (mg kg^{-1})											
	WSEX			Organic complexed			AMOX			CRYOX		
Treat- ments	30 days	60 days	90 days	30 days	60 days	90 days	30 days	60 days	90 days	30 days	60 days	90 days
(A) Organic matter												
M1	0.62	0.53	0.48	0.84	0.75	0.61	1.02	1.17	1.22	1.01	0.96	0.86
M2	0.53	0.50	0.42	0.87	0.77	0.66	1.13	1.38	1.44	1.17	1.06	0.98
SEm±		0.0056			0.0056			0.0049			0.0052	
CD at 5%		0.0157			0.0158			0.0138			0.0146	
(B) Moisture level												
W0	0.50	0.48	0.43	0.78	0.69	0.55	1.02	1.21	1.22	0.99	0.93	0.82
W1	0.59	0.51	0.45	0.84	0.74	0.60	1.07	1.30	1.29	1.11	1.04	0.97
W2	0.63	0.53	0.45	0.95	0.86	0.75	1.13	1.40	1.49	1.17	1.07	0.98
SEm±		0.0068			0.0069			0.0060			0.0064	
CD at 5%		0.0193			0.0194			0.0170			0.0179	
(C) Zinc level												
N	0.53	0.47	0.41	0.77	0.67	0.57	1.01	1.22	1.24	1.02	0.95	0.88
A	0.61	0.56	0.48	0.93	0.86	0.69	1.14	1.36	1.39	1.16	1.07	0.97
SEm±		0.0056			0.0056			0.0049			0.0052	
CD at 5%		0.0157			0.0158			0.0138			0.0146	
(D) Incubation periods												
Days mean	0.57	0.51	0.44	0.86	0.76	0.63	1.08	1.30	1.31	1.09	1.01	0.92
SEm±		0.0039			0.0040			0.0035			0.0037	
CD at 5%		0.0111			0.0112			0.0098			0.0103	

Table 2. Dynamics of Zn fractions in Aridisols at various treatment combinations.

	Zn Fractions (mg kg^{-1})											
	WSEX			Organic complexed			AMOX			CRYOX		
Treatments	30 days	60 days	90 days	30 days	60 days	90 days	30 days	60 days	90 days	30 days	60 days	90 days
W0M1N	0.51	0.44	0.42	0.66	0.61	0.46	0.92	1.03	1.12	0.84	0.79	0.68
W0M1A	0.58	0.50	0.48	0.87	0.76	0.65	1.03	1.16	1.19	0.93	0.90	0.81
W1M1N	0.57	0.51	0.45	0.72	0.66	0.52	0.98	1.08	1.15	0.92	0.91	0.87
W1M1A	0.64	0.54	0.51	0.94	0.83	0.63	1.06	1.22	1.27	1.13	1.05	0.92
W2M1N	0.66	0.52	0.44	0.86	0.78	0.67	1.05	1.19	1.25	1.04	1.02	0.86
W2M1A	0.72	0.66	0.58	1.01	0.98	0.72	1.11	1.32	1.35	1.20	1.12	1.01
W0M2N	0.39	0.46	0.42	0.73	0.61	0.55	0.96	1.26	1.22	1.02	0.94	0.83
W0M2A	0.51	0.56	0.43	0.85	0.75	0.73	1.19	1.39	1.33	1.14	1.11	0.94
W1M2N	0.50	0.44	0.37	0.74	0.62	0.52	1.05	1.32	1.31	1.10	1.02	1.00
W1M2A	0.62	0.58	0.43	0.95	0.84	0.60	1.23	1.57	1.44	1.28	1.17	1.08
W2M2N	0.53	0.43	0.36	0.89	0.72	0.68	1.10	1.42	1.37	1.17	1.04	0.97
W2M2A	0.63	0.52	0.43	1.04	0.98	0.87	1.28	1.67	1.58	1.27	1.10	1.04
SEm±		0.0137			0.0138			0.0120			0.0127	
CD at 5%		0.0385			0.0388			0.0339			0.0359	

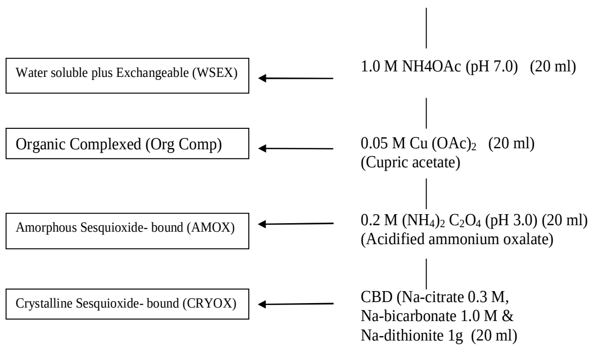

Fig. 1. *Flow sheet for extraction of different fractions of zinc in soil.*

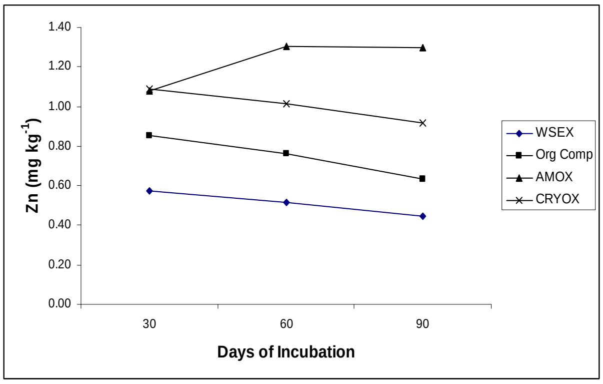

Fig. 2. *Kinetics of Zn transformation at different incubation periods.*

to sorption; whereas, Haldar and Mandal (1979) attributed this to the inactivation of soil Zn by the decomposing organic matter. Takkar and Sindhu (1979) reported that Zn concentration in the soil solution was regulated by both $Zn(OH)^2$-Zn^{2+}(aq) and $ZnCO_3$-Zn^{2+} (aq) systems during the initial periods and thereafter by $ZnCO_3$-Zn^{2+} (aq) system alone because of the buffering effect of the soil carbonate equilibria. Similar findings were also observed by Mandal *et al.* (1993) and concluded that precipitation of Zn as hydroxide, carbonate and sulphide and it's adsorption on the surface of hydrated oxides of iron were at least partly responsible for the decrease.

The significant decrease in the WS+EX-Zn, particularly at 30 to 60 days of incubation were observed under the field capacity moisture regime and application of organic matter, than that of continuous submergence and alternate submergence and saturation and no organic matter application, and the effect was less prominent at later stage i.e. at 90 days of incubation. The decrease may be an account of favourable situation for microbial immobilization and precipitation of zinc as $ZnCO_3$ and $Zn\ (CO_3)_2OH_2$ (Brar and Sekhon, 1976; Joshi and sharma, 1986) and its adsorption on the surface of organic complexes under low Eh values (Sims and Patrick, 1978). Whereas, there was increase in the WS+EX-Zn with application of organic matter under similar condition of incubation, which may be attributed to the retention of zinc on exchange complex and it is in conformity to the earlier reports (Mandal *et al.,* 1988; Kumar and Basavaraj, 2008).

On the other hand, amorphous sesquioxide fraction of Zn increased continuously up to 90 days and the increase might be due to the transformation of WS+EX and Organic complexed fractions of Zn to amorphous sesquioxide fraction (Hazra *et al.,* 1994) and also the transformation of stable native forms of Zn. This could be attributed to the fact that the redox potential of the soils decreased to values where Fe was reduced and consequently, more amorphous oxides formed and sorbed the Zn released from other fractions (Ghanem and Mikkelsen, 1987). The higher content of amorphous sesquioxide bound zinc than crystalline sesquioxide bound zinc could be attributed to greater ability of amorphous sesquioxide to adsorb zinc because of their high specific surface area (Wani *et al*., 2013).

Conclusion

Based on the results, it can be concluded that the kinetics of Zn is largely controlled by organic matter, moisture regimes and Zn application due to considerable changes in the chemical and electrochemical properties of soil and thereby influence the transformation of zinc. Organic matter application significantly increased Zn fractions due to the retention of Zn on exchange complex owing to producing organic acid by decomposition of organic matter in soil. Further, the results showed that if such conditions were maintained in field, there would be an increase in the availability of Zn for different crops in Aridisols.

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