Madras Agric. J. 89 (10-12) : 639-645 October-December 2002
https://doi.org/10.29321/MAJ.10.A00278

Distribution of zinc fractions in different taxonomical groups of base unsaturated soils in Karnataka

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Abstract : Distribution of different forms of zinc in seven profiles of base unsaturated soils of Karnataka and their relation to soil characters were studied. The results showed that more than 82.7 per cent of total zinc occurred as residual zinc, whereas exchangeable zinc occurred only 1.1 per cent of total zinc content. Soils contained exchangeable Zn from 0.04 to 2.3 μg g^{-1}, organically bound Zn from 0.07 to 6.44 μg g^{-1}, manganese oxide bound from 0.1 to 4.3 μg g^{-1} amorphous iron oxide bound Zn from 0.5 to 7.7 μg g^{-1}, crystalline iron oxide bound from 0.5 to 8.2 μg g^{-1}, residual zinc from 9 to 109 μg g^{-1}. Although the exchangeable pool was very low in all the soils when compared to other fractions, still it is very important from the plant availability point of view. Amorphous iron oxide bound form of zinc is the seat for zinc adsorption because of its high specific surface area. Crystalline iron oxide bound form of zinc dominated when compared to exchangeable, organically bound, manganese oxide bound and amorphous iron oxide bound zinc fractions.

Key words: Zinc fractions, Exchangeable, Organically bound, Manganese oxide bound, Amorphous and crystalline oxide bound, Residual, Total zinc.

Introduction

Knowledge of different chemical forms of zinc in soil solutions is necessary for evaluating their toxicity, mobility and bioavailability. The desorption of zinc from exchange complex to solution, release of zinc from organic matter, crystalline minerals and other precipitates to the solution phase are the process that control the mobility of zinc in soils. The sequential desorption of zinc to a number of discrete forms which differ in their solubility can be broadly grouped under exchangeable, organically bound, manganese oxide bound, amorphous iron oxide bound, crystalline iron oxide bound and residual fractions.

Sarkar and Deb (1982) opined that complexed zinc was found to be the most important fraction from the point of plant uptake. Residual fraction constituted bulk of the native zinc in soil, followed by crystalline iron oxide bound and least dominant was exchangeable zinc fraction. But exchangeable and organically bound forms are considered to be the most available. Contribution of these forms to the available pool of zinc may vary depending upon the physical and chemic properties of the soils. A proper understandir of which of these fractions control tł distribution of zinc between active soil coı stituents and soil solution is fundamental ı an understanding of the soil chemistry of zir (Viets, 1962).

Nearly forty per cent of the cultivate area in Karnataka are acidic. The belief th: zinc is readily available in acid soils and cro may not respond to zinc application has prove to be wrong in these soils. Rice is the princip: cereal crop, besides plantation crops like coffe tea, rubber and cardamom. Zinc at the rat 8 to 10 kg ha^{-1} is recommended to wet lan rice. All the plantation crops are reported t respond to zinc application at varying degree:

Further, zinc applied to the soil react with the soil constituents forming a numbe of sparingly soluble to insoluble component which together determine the concentration c zinc in the soil solution and availability t plants (Iyengar and Deb, 1977). Such infoı mation is lacking in the base unsaturated soil of Karnataka. Hence this study.

Table 1. Physico-chemical characteristics of soils from different profiles

Profile	Clay(%)	pH (1:2.5 1N KCl)	Org. C (g kg^{-1})	Free Al_2O_3 (%)	Free F_2O_3 (%)	Total Al_2O_3 (%)	Total FeO_3 (%)	Total R_2O_3 (%)	Base saturation (%)	CEC (c mol (p$^+$) kg^{-1})
Harave, Taluk : Hunasur, District : Mysore, Soil Group : Ultic haplustalfs, Land use : Dry land field crops										
	20.00-27.50	5.20-5.60	3.20-7.00	0.20-0.25	2.00-2.30	14.90-17.16	12.76-13.72	27.76-13.72	41.50-49.70	6.30-10
Annamlae, Taluk : Sakaleshpur, District : Hassan, Soil Group : Oxic humitropepts, Land use : Coffee plantation										
	15.40-17.40	5.00-5.40	1.80-1.00	0.10-0.17	1.90-2.00	9.80-10.92	14.31-17.18	24.10-27.94	30.30-55.20	4.90-9
Aggragona Taluk : Anokla, District : Uttar Kannada, Soil Group : Typic ustipsmments, Land use : Cultivated rice										
	7.00-19.60	3.00-4.70	2.90-10.60	0.09-0.15	1.70-1.82	10.30-11.90	9.37-10.11	19.70-22.00	6.10-69.60	3.40-4
RRS, Mudigere, Taluk : Mudigere, District : Chickamagalore, Soil Group : Ustic haplohumults, Land use : Sapota orchard										
	13.00-23.00	4.20-5.50	8.00-20.50	0.17-0.24	2.22-2.29	16.90-18.40	14.50-18.76	31.40-35.80	15.00-32.00	4.10-5
Theralu, Taluk : Virajpet, District : Kodagu, Soil Group : Typic paleustalfs, Land use : Rice fallow										
	15.00-19.00	5.40-5.60	2.38-4.12	0.17-0.21	1.58-1.66	7.80-58.00	5.60-6.90	12.60-15.50	34.70-42.00	6.70-5
Thirthahalli, Taluk : Thirthahalli, District : Shimoga, Soil Group : Fluventic ustropepts Land use : Arecanut garden										
	11.50-19.50	4.50-5.10	16.50-34.30	0.13-0.20	1.46-1.60	13.16-18.93	13.56-15.21	28.30-30.90	9.50-32.10	3.80-6
Admar, Taluk : Udupi, District : Udupi, Soil Group : Ultic paleustalf, Land use : Rice fallow										
	25.00-57.00	4.20-5.30	0.80-36.90	1.57.2.28	4.60-8.67	22.00-25.00	9.30-17.40	33.30-40.40	22.40-46.00	3.17-7

Materials and Methods

Seven soil profiles from base unsaturated conditions were used in this study in 1999. The place of collection, taxonomy of soil, physico-chemical characteristics and land use are given in Table 1. Samples were processed and analysed for important physico chemical parameters following standard procedures. Fractionation of soil zinc was carried out by following the procedure outlined by Singh *et al.* (1988). The fractionation scheme is presented in Table 2. Total zinc was determined by digesting the soil sample with hydrofluoric acid-aqua-regia mixture in closed polypropylene bottles as given by Page *et al.* (1982). Available zinc in the soil was extracted by DTPA extractant (Lindsay and Norvell, 1978). Concentration of zinc in the filtrate was determined by Atomic Absorption Sepctrophotometer (GBC 960 AA).

Results and Discussion

The important physico chemical characters of soils are presented in Table 1. Variations in values are clay (7-57%), pH in 1N KC1 (3.0-5.6), OC (1.8-36.9g kg^{-1}), Free Al_2O_3 (0-09-2.28%), Free Fe_2O_3 (1.46-8.67%), Total Al_2O_3 (7-25%), Total Fe_2O_3 (5.5-18.76%), Total R_2O_3 (12.6-40.4%), Base saturation (6.1-41.5%), CEC (3.17-7.54 c mol (P+) kg^{-1}).

The data on different inorganic zinc fractions are presented in Table 3. Zinc content in exchangeable pool was very low in all the soils. It ranged from 0.04 to 2.35 μg g^{-1} and it constituted 0.04 to 5.26 per cent of the total zinc. There was no specific pattern in its distribution within the profiles. This could be due to variation in physico chemical characteristics, eluviation and illuviation. Similar results were reported by Prasad and Shukla (1996). Exchangeable zinc had a negative correlation with pH, clay, CEC, total R_2O_3 and

Table 2. Sequential extraction procedure used in this study

Sl No.	Zinc fraction*	Solution	g soil : mL solution	Conditions
1	Exchangeable Zn	1M $Mg(NO_3)_2$	4:16	Shake for 2 hrs
2	Organically bound Zn	0.7 M NaOCl (pH 8.5)	4:8	30 min boiling on water bath. Stir occasionally, Repeat extraction
3	Managanese oxide bound Zn	0.1 M $NH_2OH.HCl$ (pH 2, HNO_3)	4:40	Shake for 30 min
4	Amorphous Fe oxide bound Zn	0.25 M $NH_2OH.HCl$ + 0.25 M HCl	4:40	Shake for 30 min at 50°C in water bath
5	Crystlline Fe oxide bound Zn	0.2 M $(NH_4)_2C_2O_4$ + 0.2 M $H_2C_2O_4$ (pH3) + 0.1M Ascorbic Acid	4:40	for 30 min Stir occasionally
6	Residual Zn	Total zinc-Sum of all the other fractions		
7	Total Zn	100 mg soil + 2 ml aqua-regia + 10 ml hydrofluoric acid		Shake for 16 hrs. Residue is dissolved in boric acid

* a 8 mL water wash was given after extraction of each fraction

Fe_2O_3 (Table 4). At low pH, solubility of zinc increases which is adsorbed by soil exchange complex. Clay and oxides of Fe and Al provide sorption sites for exchangeable zinc (Sposito, 1984).

Organically bound zinc content ranged from 0.1 to 2.03 μg g^{-1} and constituted 0.15 to 4.62 per cent of the total zinc. This fraction was lower than oxide bound and residual forms, but higher than the exchangeable zinc in the soil. This fraction is known to play a significant role in zinc nutrition of low land rice (Mandal and Mandal, 1986). Organically bound zinc showed negative correlation with clay indicating that would be the major form in coarse textured soils as organic matter would release more zinc in coarse textured soil (Gowrishankar and Murugappan, 1998). The association of organically bound zinc with OC, total Fe_2O_3 and total R_2O_3 can be due to high affinity of ligand for the metal to form soluble complex which have high affinity for the adsorbent (Sposito, 1984). Since iron is strongly complexed by organic matter it is also possible that iron blocked sites on organic colloid and there by decreased organically bound zinc.

Manganese oxide bound constituted 0.08 to 9.8 per cent of total zinc. Its content varied from 0.2 to 3.2 μg g^{-1}. It is positively correlated with pH, free Al_2O_3 free Fe_2O_3 and CEC (Table 4). This indicates the association of this fraction with iron and aluminum oxides.

Amorphous iron oxide bound zinc ranged from 0.7 to 10.2 μg g^{-1}. It constituted 1.2 to 21.6 per cent of total zinc. This fraction had a greater ability to adsorb zinc because of their high specific surface area. This fraction was positively correlated with free Al_2O_3, free Fe_2O_3 and total Al_2O_3 (Table 4). The results suggest that soils rich in oxides of iron and aluminum contain much of their zinc in the amorphous iron oxide bound forms.

Crystalline iron oxide bound ranged from 0.8 to 8.2 μg g^{-1} constituting 1.7 to 44.3 percent of total zinc. This fraction dominated when compared to exchangeable, organically bound, manganese oxide bound and amorphous iron oxide bound zinc fractions. This may be due to predominance of crystalline iron oxides in these soils. This fraction is more stable particularly under upland conditions of the soil. The crystalline iron oxide exhibit defective structures (Schwertmann *et al.* 1985), in which Zn^{2+} can be incorporated to compensate change in valances, there by zinc gets occluded. This fraction was positively correlated with OC, CEC,

Table 3. Zinc fraction and total zinc in soil profiles (μg g^{-1})

S.No.	Depth (cm)	DTPA Exchangeable Zn	Exchangeable Zn	Organically bound Zn	Manganese oxide bound Zn	Amorphous Fe oxide bound Zn	Crystaline Fe oxide bound Zn	Residual Zn	Total Zn
1. Harave, Taluk : Hunasur, District : Mysore, Soil Group : Ultic Haplustalfs, Land use : Dry land field crops									
	0-19	2.26	0.24	2.032	1.00	1.90	3.20	64.628	73.0
			(0.33)*	(2.78)	(1.36)	(2.60)	4.38)	(88.53)	
	19-44	1.36	0.16	0.344	0.8	1.10	4.70	44.393	51.0
			(0.31)	(0.67)	(1.55)	(2.14)	9.13)	86.21)	
	44-85	1.46	0.16	0.152	0.70	2.20	3.80	38.988	46.0
			(0.35)	(0.33)	(1.52)	(4.78)	(8.26)	(84.76)	
	85-125	1.82	0.12	0.248	1.00	2.00	3.00	46.637	53.0
			(0.23)	(0.47)	(1.88)	(3.77)	(5.66)	(88.00)	
	125-185	2.7	0.32	0.284	0.50	3.40	2.80	48.196	55.5
			(0.58)	(0.51)	0.90)	6.13)	(5.05)	(86.84)	
2. Annamlae, Taluk : Sakaleshpur, Districe : Hassan, Soil Group : Oxic Humitropepts, Land use : Coffee plantation									
	0-17	1.84	1.440	0.708	1.30	2.60	7.50	32.452	46.0
			(3.13)	(1.54)	(2.83)	(5.56)	(16.30)	-70.550	
	17-49	0.34	0.16	0.32	0.80	1.80	1.50	50.520	55.0
			(0.30)	(0.58)	(1.45)	(3.10)	(2.73)	(91.85)	
	49-106	0.44	0.240	0.304	0.50	0.70	1.00	55.756	58.5
			(0.41)	(0.52)	(1.20)	(1.71)	(95.31)		
	106-190	0.32	0.680	0.592	4.30	2.70	1.60	59.628	69.5
			(0.98)	(0.85)	(6.19)	(3.88)	(2.30)	(85.80)	
3. Aggragona Taluk : Anokla, District : Uttar Kannada, Soil Group : Typic Ustipsmments, Land use : Cultivated rice									
	0-15	0.95	0.224	0.588	2.50	2.00	1.30	18.888	25.5
			(0.88)	(2.31)	(9.80)	(7.84)	(5.10)	(74.07)	
	15-30	0.18	0.252	0.240	0.40	0.90	0.90	13.308	16.0
			(1.57)	(1.50)	(2.50)	(5.63)	(5.63)	(83.14)	
	30-45	0.32	0.344	0.216	0.60	1.10	0.80	13.940	17.0
			(2.02)	(1.27)	(3.53)	(6.47)	(4.71)	(82.00)	
	45-60	0.36	0.436	0.264	2.20	1.30	2.40	30.900	37.5
			(1.16)	(0.70)	(5.86)	(3.46)	(6.40)	(82.40)	
	60-75	0.30	0.560	0.312	0.50	0.70	1.20	15.728	19.0
			(2.95)	(1.64)	(2.63)	(3.68)	(6.32)	(82.78)	
	75-105	0.26	0.816	0.716	0.70	0.70	1.30	7.996	15.5
			(5.26)	(4.62)	(4.52)	(4.52)	(8.38)	(51.58)	
	105+	0.56	0.512	0.488	0.50	1.00	1.10	21.400	25.0
			(0.05)	(1.95)	(2.00)	(4.00)	(4.40)	(85.60)	

Table 3. (Contd..)

4. RRS, Mudigere, Taluk : Mudigere, District : Chickamagalore, Soil Group : Ustic Haplohumults, Land use : Sapota orchard								
0-6	1.77	0.420	0.524	1.30	0.90	4.90	38.456	46.5
		(0.90)	(1.13)	(2.80)	(1.94)	(10.54)	(82.70)	
6-42	0.34	0.380	0.212	0.40	1.10	3.60	26.808	32.5
		(1.17)	(0.65)	(1.23)	(3.38)	(11.08)	(82.48)	
42-96	0.26	0.288	0.228	0.30	1.30	3.30	28.584	34.0
		(0.85)	(0.67)	(0.88)	(3.82)	(9.70)	(84.07)	
96-121	0.22	0.384	0.196	0.40	0.80	3.00	36.220	41.0
		(0.94)	(0.48)	(0.98)	(1.95)	(7.32)	(88.34)	
121+	0.26	0.244	0.172	0.30	2.00	3.90	34.884	41.5
		(0.59)	(0.41)	(0.72)	(4.82)	(9.40)	(84.06)	
5. Theralu, Taluk : Virajpet, District : Kodagu, Soil Group : Typic Paleustalfs, Land use : Rice fallow								
0-15	122	0.244	0.132	1.00	4.00	8.204.924	18.5	
		(1.32)	(0.71)	(5.40)	(21.62)	(44.32)	(26.62)	
15-30	0.6	0.184	0.360	0.10	3.30	8.00	109,456	121.0
		(0.15)	(0.30)	(0.08)	(2.73)	(6.61)	(90.46)	
30-45	0.4	0.148	0.220	0.40	2.70	5.90	99,632	109.0
		(0.14)	(0.20)	(0.37)	(2.48)	(5.41)	(91.41)	
45-60	0.80	0.044	0.672	0.20	2.30	3.40	101.880	108.5
		(0.04)	(0.62)	(0.18)	(2.12)	(3.13)	(93.90)	
60-90	0.96	0.668	0.884	0.30	1.60	4.40	38.648	46.5
		(1.44)	(1.90)	(0.65)	(3.44)	(9.46)	(83.11)	
90+	0.72	0.700	0.472	0.20	1.30	8.20	42	52.5
		(1.33)	(0.90)	(0.38)	(2.48)	(15.62)	(79.30)	
6. Thirthahalli, Taluk : Thirthahalli, District : Shimoga, Soil Group : Fluventic Ustropepts, Land use : Arecanut garden								
0-18	2.63	2,352	0.704	3.20	4.30	5.60	36.844	53.0
		(4.44)	(1.33)	(6.04)	(8.11)	(10.57)	(69.52)	
18-44	3.4	1.584	0.556	2.50	3.50	4.70	47.160	60.0
		(2.64)	(0.93)	(4.16)	(5.83)	(7.83)	(78.60)	
44+	2.08	0.736	0.340	1.50	2.70	4.80	41.924	52.0
		(1.42)	(0.65)	(2.88)	(5.20)	(9.23)	(80.62)	
7. Admar, Taluk : Udupi, District : Udupi, Soil Group : Ultic Paleustalf, Land use : Rice fallow								
0-13	2.08	1.216	0.592	2.40	10.20	6.40	57.692	78.5
		(1.55)	(0.75)	(3.06)	(13.00)	(8.15)	(73.50)	
13-16	1.26	0.080	0.248	1.40	4.20	3.70	61.372	71.0
		(0.11)	(0.35)	(2.00)	(5.91)	(5.21)	(86.44)	
16-25	0.60	0.124	0.116	1.20	2.40	520	68.46	77.5
		(0.16)	(0.15)	(1.55)	(3.10)	(6.71)	(88.34)	
25-50	0.58	0.304	0.212	0.90	1.70	2.10	73.784	79.0
		(0.38)	(0.27)	(1.14)	(2.15)	(2.65)	(93.40)	

* Value in parenthesis indicates per cent of total zinc

free Al_2O_3, total Al_2O_3 and R_2O_3 (Table 4). The results suggest that soils rich in oxides of iron and aluminum contain much of their zinc in crystalline iron oxide bound form.

The residual zinc fraction constituted the largest of total zinc content of the soil. It ranged from 4.29 to 109.45 μg g^{-1} constituting 26.6 to 95.97 per cent of total zinc content. It is considered as the primary form of the

Table 4. Correlation coefficient (r) between zinc fractions and some soil properties

	Clay	pH	OC	Free Al_2O_3	Free Fe_2O_3	Total Al_2O_3	Total Fe_2O_3	Total R_2O_3	Percent base saturation	CEC
Available Zn	0.006	0.27	0.16	-0.001	-0.10	-0.16	-6.38*	-0.31	0.14	0.31
Exchangeable Zn	-0.25	-0.14	0.20	-0.08	-0.24	-0.38	-0.49	-0.53*	-0.04	0.00
Organically bound Zn	-0.22	-0.14	0.16	-0.15	-0.22	0.24	-0.16	-0.27	0.14	0.02
Managanese oxide bound Zn	-0.18	-0.10	0.08	-0.03	-0.05	-0.31	-0.26	-0.37	0.11	0.06
Amorphous Fe oxide bound Zn	0.23	0.10	0.60*	0.53	0.28	0.25	-0.22	0.08	-0.07	-0.04
Crystalline Fe oxide bound Zn	-0.05	0.20	0.28	0.04	-0.03	0.05	0.01	0.04	-0.18	0.03
Residual Zn	0.8*	0.57*	-0.05	0.65*	0.63*	0.58*	0.17	0.52*	0.04	0.29
Total Zn	0.76*	0.56*	0.05	0.66*	0.61*	0.55*	0.11	0.47	0.01	0.27

* Significant at 5% ; ** Significant at 1%

Table 5. Correlation coefficient among various zinc fractions

	DTPA exchange-able Zn	Exchange-able Zn	Organi-cally bound Zn	Manganese oxide bound Zn	Amorphous Fe oxide bound Zn	Crystalline Fe oxide bound Zn	Residua Zn
Exchangeable Zn	0.566*						
Organically bound Zn	0.441*	0.338					
Manganese oxide bound Zn	0.381	0.553*	0.314				
Amorphous Fe oxide bound Zn	0.543*	0.472*	0.175	0.499*			
Crystalline Fe oxide bound Zn	0.484*	0.420*	0.090	0.117	0.387*		
Residual Zn	0.160	-0.206	-0.006	0.083	0.287	0.094	
Total Zn	0.290	-0.048	0.064	0.201	0.439	0.248	0.978*

* Significant at 5%

native zinc and associated with soil mineral fractions.

A positive correlation with clay, OC, iron and aluminum oxides were observed (Table 4). A positive correlation with OC indicates that some portion of residual zinc comes from resistant to degrade pool of organic matter (Singh *et al.* 1988).

Although total zinc content is considered as poor indicator of the zinc supplying capacity of the soil, it may help for long term nutrient budgeting of a cropping system. Total content of the soil zinc depends on the parent material Its content in soils studied varied from 15.5 to 109 μg g^{-1}. This can be attributed to their clay content and surface reactive materials (Gowrishankar and Murugappan, 1998). This was evident from the positive correlation of this fraction with clay (Table 4).

DTPA exchangeable zinc content decreased with depth in majority of the profiles. Its content ranged from 0.18 to 3.4 μg g^{-1}. Although all forms of zinc in soil are known to supply the nutrient to soil solution, their relative contribution to the labile pool from which plants absorb the nutrient depends mainly on the solubility of the several zinc compounds as influenced by the relative characteristics of the soil. The decreased availability of zinc with depth may be attributed to pH, clay and oxides of Fe and Al. The increase in pH with depth leads to less solubility and high content of clay and Fe and Al oxides in lower depths make zinc get adsorbed strongly (Chao, 1972). Addition of plant residues and suitable moisture regime were responsible for more available zinc in surface soils.

In another study (Vasudeva and Ananthanarayana, 2001), path co-efficient analysis for DTPA extractable zinc showed that exchangeable organically bound, manganese oxide bound, crystalline iron oxide bound and total zinc directly contributed zinc pool. But all other forms indirectly contributed to extractable zinc through exchangeable zinc.

Relationship among zinc fractions were evaluated by simple correlation analysis (Table 5). The direct relationship between exchangeable zinc and manganese oxide bound, amorphous iron oxide bound and crystalline iron oxide bound zinc indicate that these forms are interdependent. Manganese oxide bound and crystaline iron oxide zinc are associated with amorphous iron oxide bound zinc. Residual zinc is the function of total zinc.

Correlation studies confirmed the existence of dynamic equilibrium among different fractions of zinc. This indicates that the depletion in the concentration of available form of zinc can be replenished by other fractions of soil zinc.

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(Received : September 2001; Revised : September 2002)