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Distribution of zinc and its fractions in paddy growing soils of Upper Krishna command area of Karnataka

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Abstract
An investigation was undertaken to characterize the distribution of zinc and zinc fractions in paddy soils of UKP command area. Twenty-six soil samples at two depths (0-15 and 15-30) were collected from paddy growing areas of Surpur (Shorapur) taluk. The results revealed the order of availability of zinc fractions in those soils was, water soluble plus exchangeable zinc < organically bound zinc < crystalline bound zinc < amorphous sesquioxide bound zinc < manganese oxide bound zinc < residual zinc. The correlation studies revealed that, water soluble plus exchangeable zinc and total zinc correlated negatively with pH and $CaCO_3$ and positively with organic carbon and clay content. Organically bound zinc showed positive correlation with organic carbon content of soils. Manganese oxide bound zinc and amorphous sesquioxide bound zinc and crystalline sesquioxide bound zinc correlated positively with clay content. Residual zinc positively correlated with organic carbon and clay content of soils. The different forms of zinc present in Surpur taluk at surface and subsurface paddy soils were positively correlated.

Keywords: zinc, zinc fractions, paddy soils, surface soils and subsurface soils

Introduction
Upper Krishna Project (UKP) is one of the major multipurpose irrigation projects of Karnataka, which is economic lifeline of chronically drought hit districts of Bijapur and Raichur districts of North-Eastren Karnataka. It can irrigate a command area of 1 m ha on full development. Water was first let out for irrigation in September 1982. Since, then the project is progressing in phases and the current area under irrigation is 0.534 m ha. The command area has predominantly deep black soils constituting 59 per cent area, to some extent medium black soils and red soils constitute 29 and 14 per cent, respectively. In rice, zinc deficiency is called as Khaira disease where in plants show white patches on foliage and become stunted in growth. The concentration of zinc in plants is a function of available zinc in soil. Solution concentration and plant available zinc are governed predominantly by solution pH and zinc adsorbed on clay and organic surface in soil. Zinc is known to exist in soil in number of discrete chemical forms namely water soluble, sorbed, easily reducible manganese bound, carbonate bound, organic matter bound and iron and aluminium oxides bound forms which vary in their solubility and mobility. Several workers observed a dynamic equilibrium among these fractions in soil and contribute zinc differently to the available pool of zinc in soils. Available zinc status, distribution of various fractions of zinc and their relationship with properties of soils under rice soils in Surpur (Shorapur) taluks of UKP command area was found insufficient

Material and Methods
The study area (Surpur taluk) lies between 16°31' N to 16°71' N latitude and 76°45' E to 77°10' E longitude covering an area about 900 sq. miles. Geology of Surpur taluk is influenced greatly by the formation of the Deccan trap. The basalts, granite-gneiss and schists are the parent materials of the red and black soils. The Surpur area has a semi aridsub tropical climate with short monsoon. Average maximum and minimum temperature of atmosphere in Surpur taluk were 33.73 ºC to 19.82 ºC, respectively. The mean annual rainfall of Surpur taluk is 7.76 cm per year.
To characterize the soil samples from paddy growing soils the soil samples were collected randomly from the paddy growing soils at depth intervals of 0-15 and 15-30 cm which represents different parent materials from which the soils were derived. Twenty-six samples were collected from Surpur taluk of Yadgiri district having paddy cropping pattern and their sampling location was enmarked by using GPS.

The processed soil samples were analyzed for total zinc extracted with a hundred milligrams of finely ground soil was digested with hydrofluoric acid (5ml) and perchloric acid (0.5ml) mixture in a platinum crucible at 200 ºC to 225 ºC temperature. The digest was dissolved in 6*N* HCl and made upto (50ml) volume. The total content of zinc in the extract was determined using atomic absorption spectrophotometry as outlined by Black (1965) [1]. For statistical analysis of data, Microsoft Excel (Microsoft Corporation, USA) and SPSS window version 10.0 (SPSS Inc.,
Chicago, USA) packages were employed. The level of significance referred in the results is $P<0.05$.

Table 1: Sequential extraction procedure for zinc fractions from soil

Fraction	Solution	Soil (g) : Solution (ml)	Conditions	Reference
1. Water soluble + Exchangeable (WSEX)	I M $(NH_4)OAc$ (pH 7.0)	5 : 20	Shake 1 hr	Murthy (1982) [7] modified by Mandal & Mandal (1986) [6]
2. Organically Complexed (OC)	0.05 M $Cu(OAc)_2$	5 : 20	Shake 1 hr	
3. Amorphous Sesquioxide bound form (AMOX)	0.2 $M(NH_4)_2C_2O_4.H_2O$ + 0.2 M $H_2C_2O_4$ (pH 3.0)	5 : 20	Shake 1 hr	
4. Crystalline Sesquioxide bound form (CRYOX)	0.3 M Sodium citrate + 1.0 M $NaHCO_3$ + 1 g $Na_2S_2O_4$ [Citrate-Bicarbonate-Dithionite (CBD)]	5 : 20	Boiling water bath, 10min, stir occasionally, keep on water bath (70 – 80°C), 15 min, stir occasionally	
5. Manganese Oxide bound (MnOX)	0.1 M $NH_2OH.HCl$ 0.2 (pH 2.0)	5 : 20	Shake 30min	Chao (1972) [2]

Result and Discussion

The forms of zinc studied in soils of Surpur taluk were water soluble plus exchangeable (WSEX), organically complexed (OC), Manganese oxide bound (MnOX), Amorphous sesquioxide bound (AMOX), crystalline sesquioxide bound (CRYOX), residual (RES) zinc and total zinc in Surpur taluk (Figure 1 and 2). Water soluble zinc fraction decreased with depth in all the soil samples. The decrease in water soluble + exchangeable zinc upon submergence might be due to the precipitation of soluble Zn as hydroxide and carbonates (Kumar and Basavaraj, 2008) [5]. The stability of the Zn-organic complexes decreases under reducing condition and the zinc released from such complexes subsequently undergoes precipitation and adsorption. Organically bound zinc decrease may partly be due to microbial immobilization of zinc. The declining trend towards latter period might be due to the decrease in stability of Zn-organic complexes at the lower Eh of the soils attained after prolonged submergence (Kumar and Basavaraj, 2008) [5]. The increase in Manganese oxide bound zinc in subsurface this may be attributed to the reduction of some crystalline form of iron oxides upon submergence as reported by Wijebandara (2007) [11] and thus releasing some amount of occluded zinc for its subsequent adsorption on the hydrous oxide form. 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 (Kumar and Basavaraj, 2008) [5]. Under the reduced condition there was an increase in the formation of hydrated oxides of Fe and Mn. This fraction was dominant when compared to water soluble plus exchangeable and organically bound zinc fractions due to predominance of crystalline iron oxide content. Similar results were obtained by Wijebandara (2007) [11]. This fraction is more stable particularly in upland condition of soil. Residual zinc fraction constituted the largest proportion of Zn fraction of soils. Under reduced condition, some of the crystalline sesquioxides might have undergone transformation to amorphous form resulting in the release of a part of the occluded zinc by the former. The residual form of zinc is associated with mineral fraction of soil. The submergence cause marked increase in residual zinc content of soil. The results showed that water logging resulted in marked increase in the residual zinc in soil, which indicates considerable mobilization of zinc to residual fraction. Similar results were also observed by Saha and Mandal (1996) [9]. Total zinc content of soils depends on the parent material. Although total zinc content is considered as a poor indication of zinc supplying capacity of soil for long term management of a cropping system.

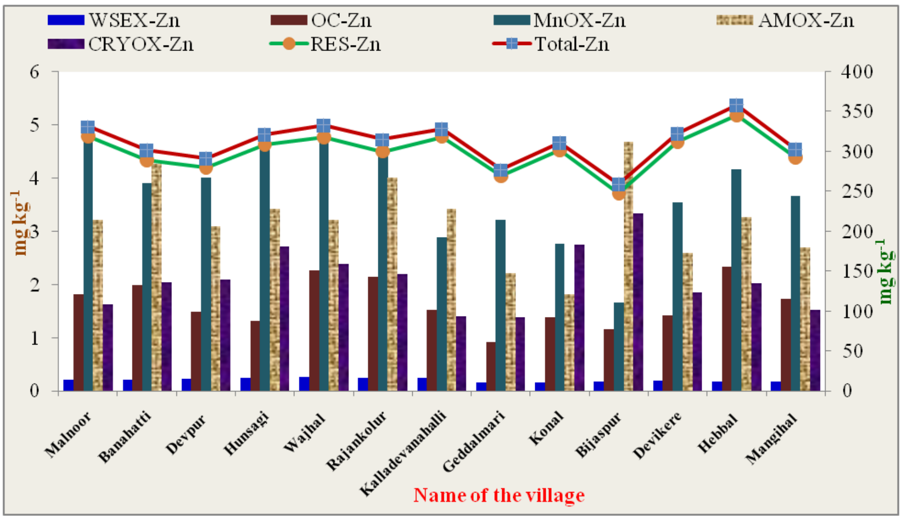

Fig 1: Distribution of zinc fractions in surface soils (0 -15 cm) of Surpur taluk

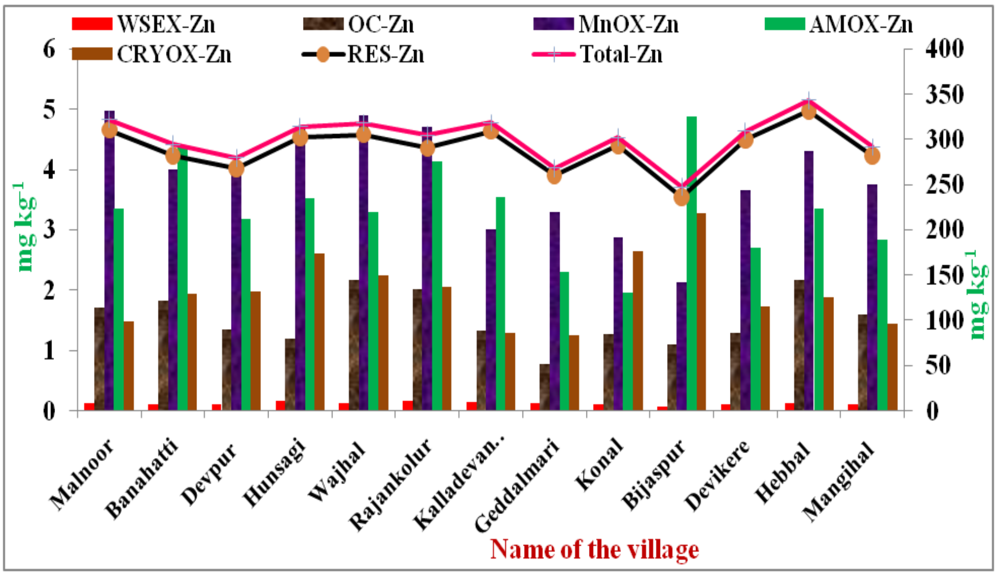

Fig 2: Distribution of zinc fractions in subsurface soils (15-30 cm) of Surpur taluk

Correlations of Zn fractions with soil physico-chemical properties of the surface and subsurface samples in Surpur taluk are represented in Table 2 and 3. The water soluble zinc was negatively correlated with sand, pH, EC, $CaCO_3$, Ex. Na^+ and ESP content for surface and subsurface soils of Surpur taluk. This is obviously due to the increased solubility of zinc at low pH and its subsequent adsorption on clay complex. Similar observations were made by Wijebandara (2007) [11]. The organically bound zinc correlated positively with organic carbon in soils of Surpur taluk for surface and subsurface soils. Organically bound zinc was negatively related to pH of soil and higher the, pH zinc gets precipitated as hydroxides. Hence, its availability increases (Pal *et al.* 1997) [8]. Mn oxide bound zinc had a positive relationship with clay (r=0.503**), silt (r=0.141), pH (r=0.169), EC (r=0.175), organic carbon (r=0.487**), Ex.Ca^{++} (r=0.210), Ex. Mg (r=0.073), Ex. Na^+ (r=0.049), CEC (r=0.373*) and ESP (r=0.037), in the Surpur taluk at surface soils. Similarly, Mn oxide bound zinc had a positive relationship with pH (r= 0.157), EC (r= 0.143), organic carbon (r= 0.481**), Ex.Ca^{++} (r= 0.036), Ex. Mg (r= 0.067), Ex. Na^+ (r= 0.107), CEC (r= 0.362) and ESP (r= 0.072), but the values were not significant in the Surpur taluk at subsurface soils. Statistical analysis indicated that clay positively correlated with amorphous and crystalline sesquioxide bound zinc fractions in both Surpur taluk at surface and subsurface soils. However, the nature of relationship of pH, clay and organic carbon with amorphous and crystalline sesquioxide bound zinc fractions was in agreement with the findings of Dhane and Shukla (1995) [3]. Positive correlation of residual zinc with organic carbon and clay at surface and subsurface soils indicated that zinc in this fraction is associated with the oxides of iron bearing minerals. This is in conformity with the findings of Tiwari *et al.* (1995) [10]. This indicates that most of the zinc present in residual form is in the clay sized minerals. The positive correlation with organic matter and clay indicates that residual zinc contains some portion which is derived from resistant organic matter and clay (Wijebandara, 2007) [11]. Correlation studies indicated that in Surpur at surface and subsurface soils total zinc was positively correlated with organic carbon (r=0.135 and 0.112), Ex.Ca^{++} (r=0.142 and 0.245), Ex. Mg^{++} (r=0.354 and 0.223) and CEC (r=0.484** and 0.472**). Total zinc in Surpur soils correlated positively with organic carbon and CEC contents of soil. These results suggested that the influence of former fractions on the distribution of total zinc (Katyal and Sharma, 1991) [4].

Table 2: Correlation coefficients (r) between zinc fractions and soilphysico-chemical properties of the surface samples in Surpur taluk

Soil physico- chemical properties	WSEX-Zn	OC-Zn	MnOX-Zn	AMOX-Zn	CRYOX-Zn	RES-Zn	Total-Zn
Sand (%)	-0.329	-0.151	0.138	-0.110	-0.104	-0.170	-0.171
Silt (%)	0.226	0.190	0.141	0.475**	0.328	-0.201	0.176
Clay (%)	0.487**	0.272	0.503**	0.483**	0.446**	0.522**	-0.093
pH (1:2.5)	-0.509**	-0.251	0.169	0.125	0.359	0.005	-0.605**
EC(dS/m)	-0.014	0.209	0.175	0.128	0.318	0.051	-0.155
OC(g kg^{-1})	0.442**	0.519**	0.487**	0.110	0.137	0.424**	0.135
$CaCO_3$ (%)	-0.496**	-0.136	-0.192	0.127	0.277	-0.192	-0.485**
Ex.Ca^{++}	0.147	-0.277	0.210	-0.088	-0.041	0.131	0.142
Ex. Mg^{++}	0.341	-0.097	0.073	-0.213	-0.064	0.339	0.354
Ex. Na^+	-0.179	-0.173	0.049	0.001	0.010	0.017	-0.022
CEC	0.458**	0.154	0.373*	-0.115	-0.293	0.150	0.484**
ESP	-0.078	-0.239	0.037	0.037	0.362	0.195	-0.192

Table 3: Correlation coefficients (r) between zinc fractions and soil physico-chemical properties of the subsurface samples in Surpur taluk

Soil physico- chemical properties	WSEX-Zn	OC-Zn	MnOX-Zn	AMOX-Zn	CRYOX-Zn	RES-Zn	Total-Zn
pH (1:2.5)	-0.491**	-0.345	0.157	0.154	0.354	0.030	-0.534**
EC(dS m^{-1})	-0.092	0.209	0.143	0.117	0.291	0.008	-0.147
OC(g kg^{-1})	0.428**	0.506**	0.481**	0.153	0.187	0.415**	0.112
$CaCO_3$ (%)	-0.495**	-0.166	-0.217	0.119	0.306	-0.139	-0.468**
Ex.Ca^{++}	0.193	-0.243	0.036	-0.128	-0.018	0.240	0.245
Ex. Mg^{++}	0.363	-0.008	0.067	-0.254	-0.127	0.205	0.223
Ex. Na^{+}	-0.147	-0.143	0.107	0.104	0.079	0.099	-0.099
CEC	0.445**	0.152	0.362*	-0.018	-0.265	0.119	0.472**
ESP	-0.106	-0.154	0.072	0.117	0.369	0.021	-0.013

*.Correlation is significant at the 0.05 level, **.Correlation is significant at the 0.01 level

Correlation coefficients among different forms of zinc in Surpur taluk are represented in Table 4 & 5. The different forms of zinc present in Surpur taluk at surface and subsurface paddy soils are positively correlated among themselves, indicating existence of dynamic equilibrium among the different pools of zinc in soils. This indicates that the depletion of zinc concentration in one pool is replenished from other pools of soil zinc. A positive relation of water soluble plus exchangeable with organically bound zinc, amorphous sesquioxide zinc and crystalline sesquioxide zinc indicates the influence of these fractions on availability of zinc in soils. The maximum correlation was observed between residual and total zinc in Surpur taluk soils suggesting that the dependence of residual zinc on total zinc. The dynamic equilibrium among different pools of soil zinc also indicated the depletion of concentration of readily available zinc by other fractions. The findings are also in conformity with those of Wijebandara (2007) [11].

Table 4: Correlation coefficient (r) among total zinc and different zinc fractions of the surface soils in Surpur taluk

	WSEX-Zn	OC-Zn	MnOX-Zn	AMOX-Zn	CRYOX-Zn	RES-Zn	TOTAL-Zn
WSEX-Zn	-						
OC-Zn	0.529**	-					
MnOX-Zn	0.425*	0.542**	-				
AMOX-Zn	0.510**	0.547**	0.521**	-			
CRYOX-Zn	0.513**	0.493**	0.494**	0.466**	-		
RES-Zn	0.788**	0.495**	0.120	0.196	0.777**	-	
TOTAL-Zn	0.784**	0.481**	0.135	0.538**	0.549**	0.997**	-

Table 5: Correlation coefficient (r) among total zinc and different zinc fractions of the subsurface soils in Surpur taluk

	WSEX-Zn	OC-Zn	MnOX-Zn	AMOX-Zn	CRYOX-Zn	RES-Zn	TOTAL-Zn
WSEX-Zn	-						
OC-Zn	0.543**	-					
MnOX-Zn	0.416*	0.500**	-				
AMOX-Zn	0.534**	0.549**	0.536**	-			
CRYOX-Zn	0.511**	0.482**	0.419**	0.463**	-		
RES-Zn	0.784**	0.490**	0.107	0.190	0.760**	-	
TOTAL-Zn	0.800**	0.477**	0.159	0.529**	0.532**	0.990**	-

WSEX - Water soluble plus exchangeable, OC - Organically complexed, MnOX - Manganese oxide bound, AMOX-Amorphous sesquioxide bound, CRYOX - Crystalline sesquioxide bound, RES-Residual.

Conclusion

For the present study it can be concluded that the order of availability of zinc fractions in those soils was, water soluble plus exchangeable zinc < organically bound zinc < crystalline bound zinc < amorphous sesquioxide bound zinc < manganese oxide bound zinc < residual zinc. The correlation studies revealed that, water soluble plus exchangeable zinc and total zinc correlated negatively with pH and $CaCO_3$ and positively with organic carbon and clay content. Organically bound zinc showed positive correlation with organic carbon content of soils. Manganese oxide bound zinc and amorphous sesquioxide bound zinc and crystalline sesquioxide bound zinc correlated positively with clay content. Residual zinc positively correlated with organic carbon and clay content of soils.

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