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Distribution of Zinc Fractions and Its Association with Soil Properties in Some Rice-Wheat Growing Soils of Jammu Region, India

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A B S T R A C T

Distributions of different zinc (Zn) forms in seven blocks of rice-wheat growing soils of Jammu region were studied. Understanding the Zn distribution in soil is important for efficient and effective management of the fertilizers recourses and to achieve a higher productivity rate. Sequential extraction scheme was used to fractionate Zn into Water Soluble + Exchangeable (WSEX), Organic Complexed (OCx), Amorphous sesquioxide (AMOX), Crystalline Sesquioxide (CRYoX) and Residual zinc (Res Zn). Total zinc (T Zn) was calculated as the sum of all the pools and it ranged between 18.31-64.59 with an average of 43.94 mg kg^{-1}. The distribution of Zn in the soils on the basis of average concentrations was in the order 34.32 mg kg^{-1} Res Zn (78%)> 4.82 mg kg^{-1} OCx (11%) > 3.39 mg kg^{-1} AMOX (8%)> 0.89 mg kg^{-1} CRYoX (2%)> 0.52 mg kg^{-1} WSEX (1%). Percentage of potentially available Zn fraction was highest in Bishna block (26.57%) and lowest in Hiranagar block (11.48%). Correlation analysis (n=55) showed all the fractions were significantly negatively correlated with pH except for OCx, while as a positive relation with electrical conductivity (EC), organic carbon (OC) and clay content.

Introduction

For an effective and efficient management of the fertilizer recourses, a deep understanding of the distribution of Zn fractions is important. Factors like parent material, pedo-chemical transformations and anthropogenic interventions contribute in the distribution of Zn and its bio availability for plant uptake (Chirwa and Yorokun, 2012). Zinc being a micronutrient is required in a very low quantity by the crops but never the less it is indispensible from a nutritional point of view and its deficiency can lead to several disorders in plants as it is associated with several enzymes. The soils of Jammu region where the rice-wheat growing pattern is practiced majorly and the rice grown in this area plays an important role in the economy of the state especially the aromatic variety of basmati (B-370) (Anonymous, 2015). The soils of J&K suffer severely due to the intense soil erosion which is more than 20 t ha^{-1} each year (Singh *et al*., 1997). It causes a huge loss to the fertility and nutrient content of soil. The Zn content of Jammu soils range between 0.1-0.61 mg kg^{-1} and these soils have been reported deficient in Zn by various authors (Ali 2011; Mondal *et al*., 2006a; 2006b).

Availability of Zn for plants was reported to be associated with the distribution of this nutrient among soil fractions. Therefore understanding the distribution of Zn among various fractions of soil will help to characterize chemistry of Zn in soils and possibly its availability for plant uptake. However, distribution of Zn among various chemical forms may vary significantly in response to changing soil properties (Adhikari and Rattan, 2007). For a better understanding, total Zn can be broadly described in five mechanistic fractions which can be quantified using sequential or batch fractionation schemes (Saffari *et al*., 2009). Sequential fractionation quantifies the element distribution between fractions of different binding strength, as defined by properties of selected extractants. Viets (1962) defined five distinct pools for micronutrients. These are (i) water soluble (ii) exchangeable, (iii) adsorbed, complex and chelated species, (iv) associated with secondary minerals and insoluble metal oxides, and (v) associated with primary minerals. Zinc deficiency in soils suggests that both native and applied Zn react with the inorganic and organic phases in the soils, which influence plant-availability. Viets (1962) reported that the distribution of Zn among active and non-active soil constituents, and soil solution, was also fundamental to an understanding the chemistry of Zn in soil. These fractions give detailed information about the biological, geological and chemical processes occurring in the soil and give a detailed account of the available Zn for plants. Residual and oxide bound Zn is known to be more stable while as exchangeable and water soluble Zn fractions are more soluble (Rahmani *et al*., 2012). The extent to which each fraction is present and the transformations in equilibrium between fractions is influenced by soil properties such as pH, texture and soil organic matter (Ramzan *et al*., 2014). Information and studies on Zn in these areas were limited only to DTPA extractable Zn. Zinc being an important micronutrient for rice and rice being an important crop in these areas, the present study was therefore aimed at obtaining a more detailed and critical information and understanding the transformations of soil Zn fractions and their Zn supply potential.

Materials and Methods

Seven blocks were selected from the rice-wheat growing areas of Jammu region namely Kathua, Hiranagar, Samba, Vijaypur, Ghagwal, Bishna and R.S.Pura. Fifty five (55) composite surface soil samples were collected using global positioning system (GPS). The soils were analyzed for the various physico chemical properties following the standard procedures. Soil reaction (pH) of the samples was measured in 1:2.5 soil: water suspension with a digital glass electrode pH meter (Jackson 1973). Electrical Conductivity (EC) was determined by method given by Richards (1954). Walkley and Black's (1934) rapid titration method was used for determination of organic carbon (OC). The mechanical analysis of the soil samples was done by following the international Pipette method as described by Piper (1966). The international society of soil science textural triangle was used for determining the textural class.

Chemical fractionation of zinc

The sequential extraction of soil Zn was carried out as per the procedure Murthy (1982) modified by Mandal and Mandal (1986).

Water soluble + exchangeable Zn (WSEX) was determined by taking 5 gm soil samples in a 100 ml polyethylene centrifuge tubes. 20 ml of 1 M NH_4OAc with pH maintained at 7.0 was shaken for 1 hour.

For Organically Complexed zinc (OCx) the residue of 1st fraction was taken and 20 ml of

0.05 M Cu $(OAc)_2$ was added and it was shaken for 1 hour.

For Amorphous Sesquioxide bound Zn (AMOX), the residue of 2nd fraction was taken and it was acidified with 20 ml of 0.2 M NH_4 $(OX)_2$ with pH maintained at 3.0 and shaken for 1 hour.

For Crystalline Sesquioxide bound Zn (CRYoX), the residue of 3rd fraction was taken and 40 ml 0.3 M sodium citrate + 5ml of 1.0 M $NaHCO_3$ was added and it was stirred and kept in a water bath at temperature 70º to 80º C for 10 min then 1gm $Na_2S_2O_4$ was added and it was kept in a water bath at temperature 70º to 80º C for 15 min with occasional stirring and it was cooled

Residual Zn (Res Zn) was extracted by digesting the residue of 4rd fraction with a mixture of 5ml of concentrated HNO_3, 10 ml of hydrofluoric acid and 10 ml of perchloric acid, the cooled solution was transferred to a 50 ml volumetric flask and subsequently diluted to volume with deionized water and stored for analysis.

Total Zn (T Zn) was calculated as the sum of all the fractions determined.

After each extraction the suspension was centrifuged at 4000 rpm for 20 minutes. The solution was filtered with Whatman no 42 filter paper and the residue were used for the subsequent extractions. All extracts were analyzed for Zn by flame atomic adsorption spectrophotometer model Z.2300 (Hitachi, Japan).

Results and Discussion

Physico- chemical properties of soil under study

The various physico chemical properties of the rice-wheat growing soils of the Jammu region used in the study are given in Table-1. The studies revealed the value of pH for the soils ranged from between 6.10-7.68 with an average value of 6.92. The soils exhibited near neutral to slightly alkaline reaction. The amount of O.C ranged between 3.20-7.80 with an average value of 5.73 g kg^{-1} respectively. Similar ranges of pH values and OC values have been reported by Jatav *et al*., (2007). The EC ranged between 0.14-0.67 with an average value of 5.73 dS m^{-1} with the soils being non saline in nature. The very low EC of soils can be attributed to the loss of soluble salts due to surface runoff during monsoon season because of undulating topography of the region (Jatav *et al*., 2007). The mechanical separate (sand, silt and clay) percentage of these soils revealed that the sand content ranged from 23.20-56.70 with an average value of 39.35 %. The silt content ranged between 14.00-38.40 with an average value of 27.39 %. The clay content ranged between 18.80-48.90 with an average value of 33.07 %. The divergent textural classes of the soils were noted from sandy clay loam (SCL) to clay loam (CL) and the majority of soil samples were clayey loam in texture. These results are in close agreement with Similar results were reported by Singh and Mishra (2012).

Fractionation and distribution of zinc in soils under study

The results of the different chemical fractions of Zn are presented in Table 2 and Fig 1. The evaluations of the Zn fractions in these soils revealed that the Zn were present in the following order Res Zn (34.32 mg kg^{-1}) > OCx (4.82 mg kg^{-1}) > AMOX (3.39 mg kg^{-1}) > CRYoX > (0.89 mg kg^{-1}) > WESX (0.52 mg kg^{-1}).

The percentage of Zn fractions studied is given in Fig 2. WSEX was found to be the least fraction of Zn available with a range of 0.11- 0.99 mg kg^{-1}. The percentage of WSEX forms of Zn was 1.0 percent among the entire Zn fractions studied this fraction of Zn was the least dominant fraction of Zn. This might be due to high zinc buffering capacity of soils which resulted in low amount of WSEX Deb (1997). The WSEX was found to be least among Zn fractions as Zn in this form is mobile and readily available for biological uptake in the environment. Similar results were found by Kumar and Babel (2011) and Ramzan *et al*., (2014). The percentage of CRYoX forms of Zn was 2.0 percent among the entire Zn fractions studied. This fraction of Zn was present in a range of 0.06 - 1.86 mg kg^{-1}. This might be due to chemical affinity or specific adsorption and also due to predominance of crystalline iron oxide contents. Similar results obtained by Pal *et al*., (1997). This fraction is more stable particularly in upland condition of soil. The crystalline oxide exhibit defect structures in which Zn^{2+} is incorporated to compensate change in values, thereby Zn^{2+} gets bound or adsorbed Schwertmann *et al*., (1985). The percentage of AMOX forms of Zn was 8.0 percent among the entire Zn fractions studied. This fraction of Zn was present in a range of 1.14-9.74 mg kg^{-1}. This may be attributed to greater ability of amorphous sesquioxide to adsorb Zn because of their high specific surface area, Devis and Leckie (1978). Water logging causes an increase in the AMOX forms of native soil Zn with a constant decrease in other forms, suggesting equilibrium of this form in soil (Mandal and Mandal, 1986). Similar results were observed by Tehrani (2005); Bahera *et al*., (2008) and Safari *et al*., (2009). Among the non residual fractions the OCx bound fraction was found to be the major fraction of Zn present. The percentage of OCx forms of Zn was 11.0 percent among the entire Zn fractions studied. This fraction of Zn was present in a range of 1.20-9.00 mg kg^{-1}.It is known to play a significant role in Zn nutrition of lowland rice and water logging causes an increase in the OCx forms of native soil Zn with a constant decrease in other forms, suggesting equilibrium of this form in soil Mandal and Mandal (1986). Similar values of organically complexed Zn have been reported by Prasad and Shukla (1996). The OCx fraction of Zn varied directly with the organic carbon content of the soils Mandal and Mandal (1986). Similar results were also reported by Tehrani (2005); Bahera *et al*., (2008); Safari *et al*., (2009) and Ramzan *et al*., (2014). The concentration of Zn in residual fraction varied between 15.26-49.12 mg kg^{-1}. Major portion of the total Zn constituted of this fraction and its concentration in greater availability indicated its likely hood to be in non labile form. This being the residual fraction represents metals which are largely embedded in sedimentary matrix and might not be available for remobilization except under very extreme conditions (Mao and Rao, 1997). Similar results of residual Zn consisting of large proportions of total Zn was also reported by Singh, (2011) and Kamali *et al*., (2010).

Mobility factor of zinc in soils under study

The most mobile and bio-available factors of Zn are extracted early by any sequential extraction procedure. The mobility factor value determines the Zn present in mobile form or those which are biologically available to the plants. On this basis high mobility factor (MF) values have been reported or interpreted as evidence of relatively high reactivity, high liability and high biological availability of heavy metals in soil (Kabala and Singh, 2001; Ramzan *et al*., 2014). The mobility of the metals in the soil may be evaluated on the basis of absolute and relative contents of fractions weakly bound to soil components. The relative index of metal mobility has been calculated as a mobility factor using sequential extraction scheme (Narwal *et al*., 1999; Ramzan *et al*., 2014). Mobility factor was calculated as the sum of all the mobile fractions of Zn which were WSEX, OCx, AMOX and CRYoX fractions of Zn (Tessier *et al*., 1979; Kabala and Singh, 2001). The mobility factor percentage was observed to be maximum in Bishna (26.57) >R.S.Pura (22.72)> Ghagwal (22.60) Kathua (20.47) > Vijaypur (17.97) >Samba (16.11) and Hiranagar (11.48) Fig 3, low levels of labile or bio available Zn has been attributed to the low levels of native Zn, slow solubilization Zn in soil, strong adsorption of Zn and leaching of Zn dissolved with OM (Rieuwerts *et al*., 2006).

Table.1 Physico-chemical characteristics of rice-wheat growing soils of Jammu region

Block		pH (1:2.5)	EC (dSm^{-1})	OC (g kg^{-1})	Sand %	Silt %	Clay %	Textural Class
Kathua	**Range** **Mean**	6.25-7.16 6.76	0.22-0.35 0.31	4.60-7.80 6.71	35.60- 47.10 39.27	22.00- 32.00 28.10	29.00- 39.30 32.55	Clay loam
Hiranagar	**Range** **Mean**	7.29-7.50 7,40	0.27-0.36 0.31	3.70-4.60 4.22	25.10- 49.20 37.90	26.00- 32.00 29.36	18.80- 48.90 32.74	Clay loam
Samba	**Range** **Mean**	7.40-7.44 7.41	0.14-0.41 0.34	3.20-4.70 4.00	33.80- 49.00 39.40	18.20- 32.50 28.30	18.80- 48.00 32.26	Clay loam
Vijaypur	**Range** **Mean**	6.33-7.68 6.88	0.21-0.38 0.30	3.40-7.30 5.90	27.10- 46.50 40.72	22.10- 30.60 28.10	26.10- 42.30 31.18	Clay loam
Ghagwal	**Range** **Mean**	6.10-6.58 6.31	0.25-0.38 0.33	6.00-7.60 6.76	26.50- 44.80 35.26	24.00- 30.10 28.40	24.10- 43.70 36.34	Clay loam
Bishna	**Range** **Mean**	6.33-7.34 6.71	0.22-0.47 0.35	3.90-7.40 6.20	23.20- 56.30 35.38	14.00- 38.40 27.35	29.70- 48.80 36.28	Clay loam
R.S.Pura	**Range** **Mean**	6.22-7.55 6.89	0.28-0.67 0.39	3.50-7.70 6.14	26.30- 56.70 42.49	14.00- 34.20 24.96	27.70- 39.80 32.28	Clay loam

Table.2 Chemical speciation of zinc (mg kg^{-1}) in rice-wheat growing soils of Jammu region

Block		OCx	CRYoX	AMOX	WSEX	Res Zn	T Zn
Kathua	**Range**	1.20-3.90	0.52-0.92	1.73-4.64	0.13-0.39	24.75-31.80	28.41-40.71
	Mean	2.98	0.79	3.37	0.32	28.94	36.39
Hiranagar	**Range**	1.30-1.70	0.46-0.66	1.14-1.88	0.11-0.17	24.88-34.03	28.51-37.85
	Mean	1.56	0.55	1.50	0.13	28.81	32.55
Samba	**Range**	1.30-2.10	0.22-0.66	1.14-1.71	0.17-0.36	19.33-21.71	22.88-25.75
	Mean	1.74	0.46	1.50	0.23	20.42	24.34
Vijaypur	**Range**	1.20-2.80	0.42-0.96	1.25-2.88	0.18-0.86	15.26-33.75	18.31-40.99
	Mean	2.26	0.79	2.31	0.67	27.56	33.60
Ghagwal	**Range**	2.50-3.50	0.77-0.93	2.41-4.25	0.71-0.91	26.07-28.53	34.49-37.22
	Mean	2.98	0.89	3.39	0.82	27.69	35.77
Bishna	**Range**	1.80-9.00	0.25-1.86	1.49-9.74	0.16-0.98	41.62-46.07	54.14-64.21
	Mean	6.10	1.24	5.06	0.69	43.35	59.04
R.S.Pura	**Range**	2.40-8.40	0.06-1.86	1.19-4.65	0.19-0.99	33.44-49.12	43.97-64.59
	Mean	5.43	1.02	3.10	0.63	42.81	55.40

OCx: - Organically Complex, AMOX:-Amorphous Sesquioxide Bound Form, CRYoX:-Crystalline Sesquioxide, WSEX:-Water Soluble Oxide, Res Zn- Residual Zinc, T Zn- Total Zinc

Table.3 Correlation coefficients between different chemical fractions of Zn and soil Physico-chemical properties

	OCx	CRYoX	AMOX	WSEX	Res Zn	T Zn
pH	-0.185	-0.617**	-0.481**	-0.724**	-0.343*	-0.385**
EC	0.345**	0.138	0.056	0.120	0.264	0.270*
OC	0.230	0.329*	0.164	0.422**	0.200	0.232
Sand	0.023	-0.239	-0.152	-0.164	-0.061	-0.072
Silt	-0.237	0.047	-0.084	-0.126	-0.184	-0.191
Clay	0.134	0.239	0.222	0.268*	0.188	0.205

***= significant at 0.05 level, **= significant at 0.01 level**

OCx: - Organically Complex, AMOX:-Amorphous Sesquioxide Bound Form, CRYoX:-Crystalline Sesquioxide, WSEX:-Water Soluble Oxide, Res Zn- Residual Zinc, T Zn- Total Zinc

Table.4 Linear regression equation showing the combined influence of soil properties on different forms of soil Zn fractions

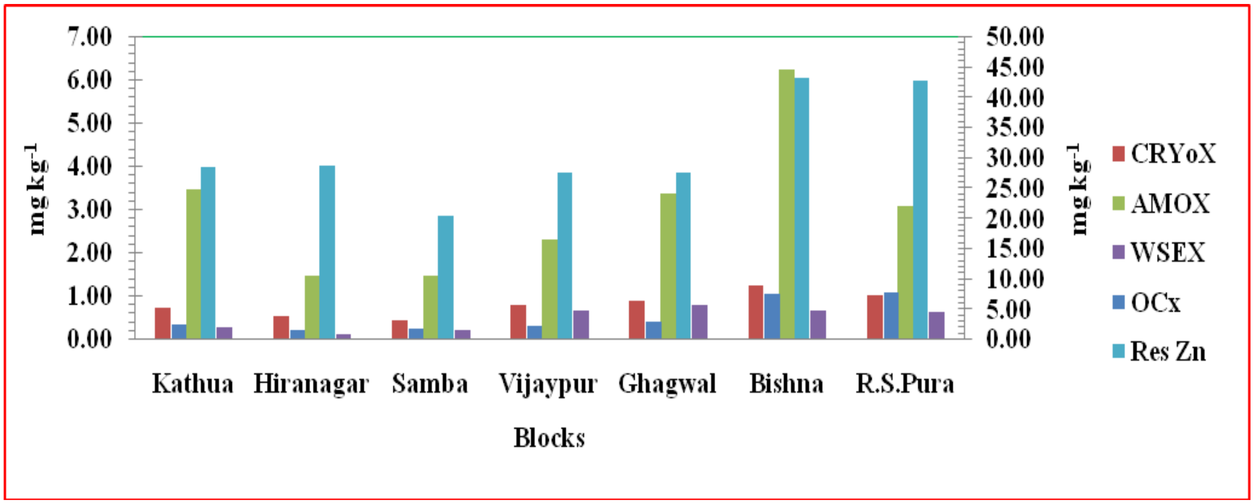
	Equation	R^2
1	**OCx**	
	$Y=46.53+0.190\ (X_1) + 7.939\ (X_2) + 0.488\ (X_3)-0.476(X_4)-0.545(X_5)-0.446(X_6)$	0.205*
2	**CRYoX**	
	$Y=3.307-0.464\ (X_1) + 0.496\ (X_2) + 0.021\ (X_3)-0.001(X_4)-0.012(X_5)-0.008(X_6)$	0.414**
3	**AMOX**	
	$Y=46.38-1.857\ (X_1)- 1.180\ (X_2)-0.044\ (X_3)-0.305(X_4)-0.324(X_5)-0.291(X_6)$	0.270*
4	**WSEX**	
	$Y=7.353-0.359\ (X_1)- 0.147\ (X_2) +0.040\ (X_3)-0.049(X_4)-0.049(X_5)-0.044(X_6)$	0.570**
5	**Res Zn**	
	$Y=208.9-3.530\ (X_1) + 17.631\ (X_2) + 0.715\ (X_3)-1.629(X_4)-1.735(X_5)-1.535(X_6)$	0.203*

***= significant at 0.05 level, **= significant at 0.01 level**

X_1-pH, X_2-EC,X_3-OC,X_4-Sand,X_5-Silt,X_6-Clay

OCx: - Organically Complex, AMOX:-Amorphous Sesquioxide Bound Form, CRYoX:-Crystalline Sesquioxide, WSEX:-Water Soluble Oxide, Res Zn- Residual Zinc, T Zn- Total Zinc

Fig.1 Distribution of Zn fractions in study area



Primary axis: WSEX, CRYoX. Secondary axis: AMOX, OCx, Res Zn

Fig.2 Pie chart of percentage of Zn fractions present in soil sample studied

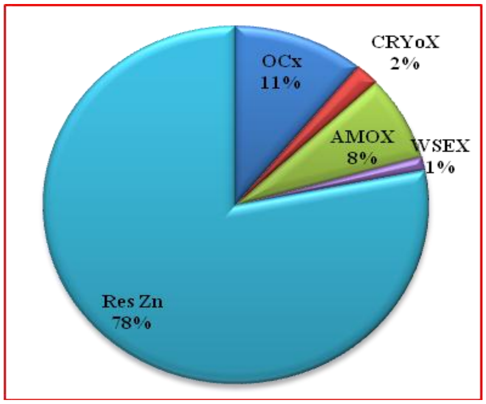
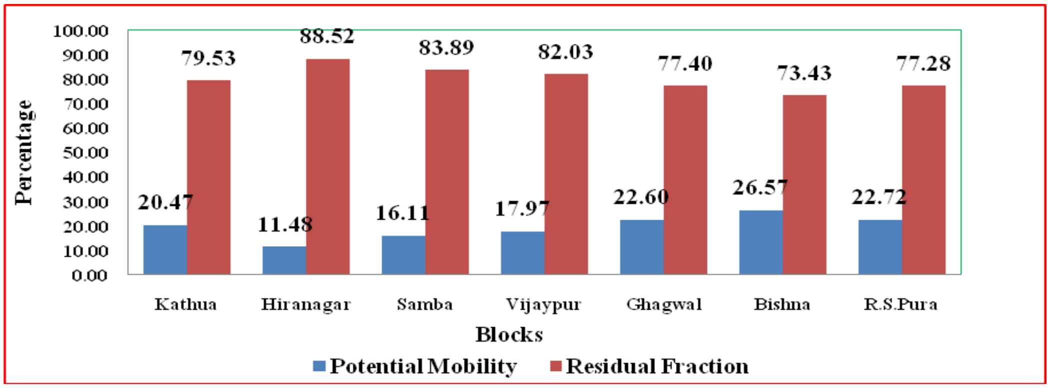


Fig.3 Available and non available concentrations of Zn fractions present in the study areas



Relation between soil physico-chemical properties and zinc fractions

Bioavailability of nutrients contribute to the optimum growth of plants which in turn effect the crop productivity and the bioavailability of nutrients are greatly influenced by various soil physico-chemical properties like pH, EC, OM, adsorptive surfaces and various other physical and biological conditions in the rhizosphere (Bell and Dell, 2008; Wijebandara *et al.*, 2011). Change in soil properties contribute in the distribution and availability of Zn in various chemical forms in the soil (Adhikari and Rattan, 2007). Soils which are generally heavy textured, lower pH and higher OM content can generally provide a greater reserve of these elements whereas, coarse textured soils such as sand have fewer reserves and tend to get depleted rather quickly (Yadav and Meena, 2009).

OCx bound Zn had a negative but no significant with pH (-0.185), a positive and significant with EC (0.345**), with OC (0.230), sand (0.023) and Clay (0.134) it showed a positive and with Silt (-0.237) a negative but no significant relationship. Organic acids and other functional groups in organic matter provides exchange sites for the adsorption of Zn. Regression equation (1) (Table 4) showed that 20% variation in OCx bound Zn was due to soil properties studied and significant effects were in relation to EC (Shiowatana *et al.*, 2005; Chirwa and Yerokun, 2012 and Ramzan *et al.*, 2014) reported similar results in their studies.

CRYoX bound Zn showed a negative and significant relationship with pH (-0.617**), with EC (0.138) a positive but no significant and with OC (0.329*) a positive and significant was observed. A negative and non significant with Sand (-0.239) and a positive but no significant relationship with Silt (0.047) and Clay (0.239) was observed. Regression equation (2) (Table 4) showed that 41% variation in CRYoX bound Zn was due to soil properties studied and significant effects were in relation to pH and OC (Shiowatana *et al*., 2005; Chirwa and Yerokun, 2012; Ramzan *et al*., 2014 and Meki *et al*., 2012) reported similar results in their studies.

AMOX bound Zn showed a negative and significant relationship with pH (-0.481**) was observed a reduction in AMOX fraction Zn with increase in pH can be explained by the natural reduction in oxide solubility and concentration as pH increases (Shiowatana *et al*., 2005 and Ramzan *et al*., 2014). While as a positive but no significant relationship between EC (0.056) and OC (0.16) was observed. A negative but no significant relationship was observed with Sand (-0.152) and Silt (-0.084) and a positive but no significant relationship was observed with Clay (0.222). Regression equation (3) (Table 4) showed that 27% variation in AMOX bound Zn was due to soil properties studied and significant effects were in relation to pH (Shiowatana *et al*., 2005; Chirwa and Yerokun, 2012; Ramzan *et al*., 2014 and Ashraf *et al*., 2012) reported similar results in their studies.

WSEX bound Zn showed a negative and significant relationship with soil pH (-0.724**) was observed. While as a positive but no significant was observed with EC (0.120) and positive and significant relationship was observed with OC (0.422**), while as a negative but no significant relationship was observed with Sand (-0.164) and Silt (-0.126) and a positive and significant relationship was observed with Clay (0.268*). Regression equation (4) (Table 4) showed that 57% variation in WSEX bound Zn was due to soil properties studied and significant effects were in relation to pH, OC and Clay (Chirwa and Yerokun, 2012; Ramzan *et al*., 2014 and Ibrahim *et al*., 2011) reported similar results in their studies.

Res Zn had a negative and significant relationship with soil pH (-0.343*) while as a positive but no significant relationship was observed with EC (0.264) and OC (0.200) and Clay (0.188) while as a negative but no significant was observed with Sand (-0.061) and Silt (-0.184). Regression equation (5) (Table 4) showed that 20% variation in Res Zn bound Zn was due to soil properties studied and significant effects were in relation to pH (Chirwa and Yerokun, 2012 and Ramzan *et al*.,2014).

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