International Journal of Chemical Studies

P-ISSN: 2349–8528 E-ISSN: 2321–4902 IJCS 2019; 7(4): 180-185 © 2019 IJCS Received: 01-05-2019 Accepted: 03-06-2019

CP Mohammed Nisab

Department of Soil Science and Agricultural Chemistry, Palli Siksha Bhavana, Visva-Bharati, Bolpur, West Bengal, India

GK Ghosh

Department of Soil Science and Agricultural Chemistry, Palli Siksha Bhavana, Visva-Bharati, Bolpur, West Bengal, India

Correspondence

CP Mohammed Nisab Department of Soil Science and Agricultural Chemistry, Palli Siksha Bhavana, Visva-Bharati, Bolpur, West Bengal, India

Different fractions of zinc and their relationship with physico-chemical properties in red and lateritic soils of Birbhum district, West Bengal

CP Mohammed Nisab and GK Ghosh

Abstract

Distribution of different zinc forms and its relationship with physico-chemical properties in three blocks under red and lateritic soils of West Bengal were studied. Sequential extraction scheme was used to fractionate Zn into Water Soluble and Exchangeable (WE), Organic bound (Org), Amorphous sesquioxide (Amor), Crystalline Sesquioxide (Cry), Manganese bound (Mn) and Residual zinc (Res). Results of the study indicated that the most of soils were sandy clay loam in texture with strong to moderately acidic pH (4.35-6.94). The organic carbon content of these soils ranged from 0.25 to 0.76 percent. DTPA-zinc varied from 0.37 to 1.28 mg kg⁻¹. Total zinc was calculated as the sum of all the pools and it varied in between 25.97 and 54.46 with an average of 39.51 mg kg⁻¹. The distribution of Zn in the soils based on average concentrations was in the order of 25.49 mg kg⁻¹. The distribution of Zn in the soils based on average concentrations was in the order of 25.49 mg kg⁻¹ Amor-Zn(66.51%)> 5.05 mg kg⁻¹ Mn-Zn (12.7%) > 4.96 mg kg⁻¹ Cry-Zn (12.5%) > 2.61 mg kg⁻¹ Amor-Zn(6.6%) > 1.04 mg kg⁻¹ Org-Zn(2.6%) >0.48 mg Kg⁻¹ WE-Zn (1.21%). Correlation analysis showed all the fractions were significantly and negatively correlated with soil pH, while as a positive relation with organic carbon (OC), DTPA-Zn and clay content. All the fractions were significantly and positively correlated among themselves, indicating existence of dynamic equilibrium among the different pools of zinc.

Keywords: Zinc fraction, DTPA-Zn, organic carbon, correlation analysis

Introduction

Zinc is known to occur in soil in a number of discrete chemical forms differing in their solubility and thus availability to plants (Sarkar and Deb, 1982) ^[43]. Proper understanding of fractions which control the distribution of Zn between active soil constituents and soil solution is fundamental to understand chemistry of zinc in soil Zinc exists in five distinct pools in soils *viz.*, water soluble, exchangeable, adsorbed, chelated or complexed zinc (Viets, 1962) ^[58].

The equilibrium among the different pools is influenced by pH and concentration of zinc and other cations, particularly iron and manganese. The readily available zinc forms *viz.*, water soluble, exchangeable and chelated zinc forms were in reversible equilibrium with each other (Viets, 1962)^[58]. Several workers observed a dynamic equilibrium among these fractions in soil and contribute zinc differently to the available pool of zinc in soils. Therefore, knowledge about their extent of distribution and their relationship with soil properties would help in assessing the zinc availability in soils. In view of the above facts, the information available in respect of available zinc status, distribution of various fractions of zinc and their relationship with the following objectives includes,to study the different fractions of zinc in red and lateritic soils of Birbhum district and to study the relationship between fractions of zinc and physico-chemical properties in red and lateritic soils of Birbhum district.

Thirty soil samples (0-15cm) were collected from each three blocks namely Md. Bazar, Nalhati and Bolpur of Birbhum district and these soils were analysed for the various physicochemical properties following the standard procedures. Particle size analysis was carried out by Hydrometer method using sodium hexa metaphosphate as a dispersing agent as described by Bouyoucos (1927) ^[6]. Soil texture was identified using textural diagram given by International Society of Soil Science. Soil reaction (pH) of the samples was measured in 1:2.5 soil: water suspension with a digital glass electrode pH meter (Jackson 1973) ^[23]. Electrical conductivity was measured using conductivity bridge as outlined by Jackson (1973) ^[23] under suitable measuring conditions. Walkley and Black's (1934) ^[59] wet oxidation method was used for determination of organic carbon (OC). Available nitrogen was estimated by alkaline KMnO₄ (Subbaiah and Asija, 1956) ^[54]. Available phosphorus was extracted with Bray No-1 solution as extractant (Bray, 1945) ^[7] and using spectrophotometer at wave length of 660 nm. Available K was extracted with neutral normal ammonium acetate and determined using flame photometer (Jackson, 1973) ^[23]. Plant available (DTPA–extractable) zinc in soils was extracted using DTPA extractant (pH 7.3) at 1:2 soil to extractant ratio as described by Lindsay and Norwell (1978) ^[29].

Zn fractions were determined using a modified sequential extraction procedure of Murthy (1982) ^[33] proposed by Mandal *et al.*, (1986) ^[30]. The Zn pools in soils were divided into seven fractions including residual and total Zn forms in soils, except residual and total, were extracted from soils using 50 mL plastic centrifuge tubes with individual

extracting solutions (see Table 1.2) and shaken in a rotary shaker at room temperature (25 ± 2 °C). The supernatant solutions obtained from each successive stage of extraction were centrifuged at 3,500 rpm for 15 min, decanted and filtered with Whatman No. 42 filter paper. It was absolutely crucial to prevent any delay between adding the extraction solutions and starting shaking them. Three replicates all sequential extractions and analyses were performed for each soil sample. The concentration of zinc in the extractant was determined by Atomic Absorption Spectrophotometer (Page *et al.*, 1982) ^[34]. The total Zinc in soil was determined by using Atomic Absorption Spectrophotometer after HF and HClO₄ digestion method (Page *et al.*, 1982) ^[34]. Residual fraction is obtained by subtracting total zinc fractions from all other fractions.

Table 1: Zinc sequential fractionation procedures.

Fractions	Reagents	Soil(g): Solution(ml)	Conditions	References	
1. Water soluble + exchangeable (WE)	1 M (NH4)OAc (pH7.0)	5:20	Shake 1 h	Murthy (1982) ^[33] modified by Mandal & Mandal (1986) ^[30]	
2. Organically complexed(Org)	0.05 M Cu(OAc) ₂	5:20	Shake 1 h		
3. Amorphous Sesquioxide (Amor)	0.2 M (NH4)2C2O4·H2O + 0.2 M H2C2O4 (pH3.0)	5:20	Shake 1 h	""	
4. Crystalline sesquioxide (Cry)	0.3 M sodium citrate + 1.0 M NaHCO ₃ + 1 g Na ₂ S ₂ O ₄ ,(CBD)	5:20	Boiling water bath,10 min, stir occasionally, keep on water bath, (70–80 °C), 15 min, stir occasionally		
5. Manganese oxide (Mn)	0.1M NH ₂ OH·HCl (pH 2.0)	5:50	Shake 30 min	Chao (1972) ^[9]	

The results obtained in respect of soil properties were subjected for simple correlation analysis and the observed 'r' values were tested at 1% and 5% level of significance (Sundarraj *et al.*, 1972)^[55].

Results and discussion

Physico-chemical properties of soil (Table 2)

The mechanical composition of samples collected from three different blocks of Birbhum district indicated that the texture varied from sandy loam to sandy clay loam texture. Sand was the dominant fraction in these soils, which might be due to high rainfall and the parent material from which the soil was derived. The results of the study was in conformity with the findings of Sathyanarayana and Biswas (1970) ^[44] who reported that soils developed from granite type of parent material had a coarse texture. Similar observation was made Kumar (2017) ^[27] in Soils of Chamarajanagar district, Karnataka.

The pH of the surface soils under present investigation showed that most of the soils are strong to moderately acidic in nature. Acidic pH of the soils might be attributed to the type of parent material from which these soils have been derived and leaching of basic cations. This is in agreement with the findings of Chakravarti *et al.*, (1957) ^[8], who stated that soils of Birbhum districts are acidic in nature.

Electrical conductivity in the soils under study and was found to be normal with respect to plant growth. The electrical conductivity values were low and soils are non-saline in nature. Same trend observed in soils of all three blocks, which may be due to low in salt concentration as observed by Chakravarti *et al.*, (1957)^[8] and Ray *et al.*, (2012)^[40].

Soil organic carbon status in soils of three different blocks ranged from 0.24 to 0.73%, 0.28 to 0.76% and 0.25 to 0.81% respectively. Soils from Nalhati blocks showed high amount of organic carbon content. Organic carbon content in most of the soil showed low to medium in range. This might be due to continuous cultivation and scarce application of FYM. High temperature and good aeration in the soil increased the rate of oxidation of organic matter resulting reduction of organic carbon content as observed by Deshmukh (2012)^[5], Pandit *et al.*, (2016)^[36] and Das *et al.*, (2010)^[14].

The overall available P of the study area was noted from 12.04 to 42.4 kg ha⁻¹ with a mean value of 27.09 kg ha⁻¹, majority of the soils under study showed low available P status. The low available P status in these soils might be due to acidic nature of soil. This result agrees with observations of Deshmukh (2012) ^[5], Pandit *et al.*, (2016) ^[36] and Das *et al.*, (2010) ^[14].

The DTPA-extractable zinc content in the surface soils under study, varied from 0.37 to 1.28 mg Kg⁻¹ with an average value 0.856 mg kg⁻¹. Considering the soil test rating for DTPAextractable Zn (<0.6 mg kg⁻¹ as deficient, 0.6-1.2 mg kg⁻¹ as sufficient and >1.2 mg kg⁻¹ high level) as critical limit for Zn deficiency (Lindsay and Norvell, 1978) ^[29]. The overall samples were found to be 18% in deficient, 67% in sufficient and only 13% samples were found to be high level in available Zn content in soil.

Soils of Nalhati block were found to contain higher amount of DTPA-extractable zinc compared to Md. Bazar and Boplur block soils due to the high organic carbon content as noticed in the present study. A similar trend was observed by Singh *et al.*, (1988) ^[49] and Sharma and Lal (1992) ^[46]. The similar results were observed by Tiwari and Mishra (1990) ^[59], Krishnamurthy and Srinivasamurthy (2001) ^[26] and Chidanandappa *et al.*, (2008) ^[12], and Kumar (2017) ^[27].

Distribution of different forms of Zinc

The results given in the table 3 revealed that the water soluble and exchangeable zinc content was found to be least (1.0 percent) among the zinc fractions; it ranged from 0.28 to 0.83, 0.25 to 0.76 and 0.21 to 0.70 mg kg⁻¹ in the surface soils of Md. Bazar, Nalhati and Bolpur respectively. This might be due to high zinc buffering capacity of soils which resulted in low amount of WE zinc fraction, Deb (1997) [15]. Similar results were found by Kumar and Babel (2011) [28] and Ramzan et al., (2014)^[39]. The contribution of organic bound fraction of Zn (0.48 to 2.17 mg kg⁻¹) was next to amorphous sesquioxide (Amor) bound fraction amongst the non-residual fractions, The mean value of organically bound zinc was found high in the soils of block Nalhati, and was lowest in soils of Bolpur block (1.04 mg Kg⁻¹), it may due to high and low values of OC content in Nalhati block and Bolpur respectively, These results in agreement with the findings of Mandal and Mandal (1986) [30]. Similar results were also reported by Tehrani (2005)^[56]; Bahera et al., (2008); Safari et al., (2009) and Ramzan et al., (2014)^[39].

The percentage of amorphous sesquioxide bound (Amor) forms of Zn was 6.6 among the entire Zn fractions studied. This fraction of Zn was varied in 1.85 to 4.01, 1.59 to 4.03 and 1.14 to 4.02 mg kg⁻¹ in respective blocks. Md. Bazar block showed highest Amor fraction among three blocks. 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 may cause an increase in the Amor forms of native soil (Mandal and Mandal, 1986)^[30]. Similar results were observed by Tehrani (2005)^[56]; Bahera *et al.*, (2008) and Safari *et al.*, (2009).

Amongst the non-residual fractions, the crystalline sesquioxide bound (Cry) fraction was found to be the major fraction of Zn, it varied from (2.99 to 9.28 mg kg⁻¹) in overall study area, among three blocks Nalhati block showed high value of Cry fraction (10.89 mg Kg⁻¹), Higher Zn concentrations of these stable fractions denote their importance as the storage fractions for soil Zn, although their solubilities will determine how available they are for plant uptake. The results are quite near to the results of by Singh *et al.*, (1999)^[48] who reported that oxides bound Zn ranged from 2.05 to 3.40 mg kg⁻¹ in some rice growing red soils of India. The above results are also in conformity with the reports of Alvarez *et al.*, (2001)^[11], Bashir *et al.*, (2007)^[3] and Chen *et al.*, (2009)^[10].

Among the soils studied the content of crystalline sesquioxide bound zinc was more in soils compared to Amor forms in Birbhum district. This suggested that more of the free iron oxide may be in crystalline form also observed by Pal *et al.*, (1997) ^[35]. The easily reducible manganese bound zinc fraction varied from 3.14 to 7.36, 3.38 to 7.55 and 3.19 to 7.31mg Kg⁻¹ respectively. Both the content and percent contribution of this fraction to total zinc was next to residual zinc, highest amounts of easily reducible manganese oxide bound form of zinc was observed when compared with Cry zinc fraction indicating that easily reducible manganese oxide might be of greater importance than Fe and Al in these soils. Singh *et al.*, (1988)^[49] also observed similar results.

Residual zinc was the dominant fraction among all the zinc fractions studied and agrees with the findings of Edward Raja and Iyengar (1986)^[20] and Iyengar and Deb (1977)^[22]. The greater percentage of Zn in the residual fraction likely indicated its greater tendency to become unavailable in the soil. Similar results of residual Zn consisting of large proportions of total Zn was also reported by Singh, (2011)^[50]

and Kamali *et al.*, (2010) ^[24]. The total zinc content in the soils of three blocks under study ranged from 25.73 to 51.80, mg kg⁻¹. Higher concentration of total zinc may be due to the increase in clay content as reported by Singh and Abrol (1986) ^[47] and Sharma *et al.*, (2002) ^[45].

Relationship between zinc fractions and physico-chemical properties

Correlation analysis in between Zn fractions and physicochemical properties was carried out and r values mentioned in Table 4. Water soluble zinc was correlated significantly and negatively with EC (r= -0.345^{**}), pH and positively with OC (r= 0.167^{**}), Clay (r= 0.217^{**}) and DTPA-Zn (r= 0.249^{**}) in soils of Birbhum district. The negative correlation with pH indicating that at higher pH, insoluble calcium zincate or higher oxides of zinc will be formed, and zinc bound in these forms does not come into the solution easily. Similar observations were recorded by Hazra *et al.*, (1987)^[21], Pal *et al.*, (1997)^[35] and Prasad and Sakal (1988)^[37]. Positive correlation of this fraction with OC also reported by Dhane and Sukla (1995)^[19] and Edward Raja and Iyengar, (1986)^[20].

Organic matter bound zinc was correlated significantly and positively with organic carbon content in soils under study(r=0.425**). Organic matterprovides exchange sites for the adsorption of zinc. Similar relationship was reported by Bharath Singh *et al.*, (1987) ^[5] and Prasad and Sakal (1988) ^[37] and (Pal *et al.*, 1997) ^[35]. Organic matter bound zinc was correlated significantly and positively with clay content in soils under study, similar relationship was reported by Soltani *et al.*, (2015) ^[52] and Spalbar *et al.*, (2017) ^[53], whereas Org fraction showed significant negative correlation with soil pH (r= -0.217**), Ramzan *et al.*, (2014) ^[39] reported similar results in his studies.

Amorphous sesquioxide bound zinc was correlated significantly and negatively with pH (r= -0.285^{**}) and significantly and positively with clay content (r = 0.312^{**}), whereas a non-significant positive correlation showed between Amor fraction and soil EC and OC. This observation agrees with findings of Spalbar *et al.*, (2017) ^[53], and Wijebandara (2007) ^[60].

Crystalline sesquioxide bound (Cry) zinc was correlated significantly and negatively with soil pH and positively with clay content in soils of Birbhum district. This is in agreement with the research conducted by Wijebandara *et al.*, $(2011)^{[61]}$, Ashraf *et al.*, $(2012)^{[2]}$, Spalbar *et al.*, $(2017)^{[53]}$. Whereas Cry fraction showed significant and positive correlation with soil OC (r=0.283**) in soils of Birbhum district, this is agreement with observation made by Prashantha (2011)^[38]. Manganese oxide bound (Mn) zinc was correlated significantly and positively with clay content in soils of all three blocks, whereas it is positively correlated soil OC (r=0.189**), it is similar to the observation was made by Soltani *et al.*, (2015)^[52] and Wijebandara (2007)^[60].

Significant negative correlation of residual zinc with pH showed in all three blocks, similar observation was made by Mukesh (2013)^[32] and Spalbar *et al.*, (2017)^[53], Residual zinc showed significant and positive correlation with organic carbon (r=0.134**) and clay content (r=0.341**), the positive correlation with organic carbon pointed out that zinc availability in soils would increase with increase in organic matter content, this is in conformity with the findings of Pal *et al.*, (1997)^[35] and Wijebandara *et al.*, (2011)^[61]. A non-significant positive correlation observed residual zinc and soil

EC in all three blocks, this result showed agreement with observation of Spalbar *et al.*, (2017)^[53].

Total zinc showed significant negative correlation with pH in soils from all three blocks of Birbhum district. These observations are in line with those reported by Sankar and Murugapan (1995)^[42]. A highly Significant and positive correlation between total zinc and organic carbon was observed in the soils of study area. Similar finding was also reported by Sankar and Murugapan (1995)^[42]. A significant positive correlation observed between total zinc fraction soil clay content observed in soils under study, similar observation

showed in the studies of Mukesh (2013) $^{[32]}$ and Wijebandara (2007) $^{[60]}$.

A positive correlation was seen between DTPA-extractable zinc and water soluble, easily reducible manganese bound zinc, organic matter bound zinc, amorphous sesquioxide zinc and crystalline sesquioxide zinc indicates the influence of these fractions on availability of zinc in soils, this is evident from the positive relationship of available zinc with these fractions. This kind of relationship was reported by Chidanandappa (2003), Dhane and Shukla (1995)^[19], Edward Raja and Iyengar (1986)^[20] and Singhal and Rattan (1995)^[51].

BLOCK		рН	EC (dSm ⁻¹)	Organic C (%)	Available N (Kg/ha)	Available P (Kg/ha)	Available K (Kg/ha)	DTPA-Zn (mg/Kg)	Textural Class
	Range	4.35-5.84	0.01-0.08	0.24-0.73	117.8-376.32	9.08-43.31	122.3-300.2	0.33-1.30	SCL
Md. Bazar	Mean	4.90	0.04	0.47	285.17	26.38	220.31	0.84	SCL
Nalhati	Range	5.91-6.94	0.01-0.07	0.28-0.76	175.62-401.41	18.02-42.89	193.13-357.26	0.35-1.26	SCL
	Mean	6.47	0.03	0.56	298.55	29.72	271.67	0.88	SCL
Bolpur	Range	4.66-5.75	0.01-0.07	0.25-0.81	234.15-409.77	9.21-41.0	138.92-380.73	0.45-1.28	SCL
	Mean	4.92	0.03	0.49	347.05	25.8	286.28	0.85	SCL

Table 2: Chemical characteristics in the soils of Birbhum district.

Table 3: Different forms	of zinc in	soils of Birbhum	district
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Block		WE-Zn (mg/Kg)	Org-Zn (mg/Kg)	Amor-Zn (mg/Kg)	Cry-Zn (mg/Kg)	Mn-Zn (mg/Kg)	Residual Zn (mg/Kg)	Total Zn (mg/Kg)
Md. Bazar	Range	0.28-0.83	0.43-2.28	1.85-4.01	3.01-9.74	3.14-7.36	11.25-36.92	23.3-51.8
	Mean	0.49	1.02	2.81	5.17	4.89	24.90	39.37
Nalhati	Range	0.25-0.76	0.49-2.03	1.59-4.03	3.01-10.89	3.38-7.55	16.10-36.86	28.90-53.27
	Mean	0.49	1.07	2.54	5.21	5.21	25.26	39.73
Bolpur	Range	0.21-0.70	0.42-2.12	1.14-4.02	2.95-7.23	3.19-7.31	13.99-41.11	25.73-58.27
	Mean	0.46	1.04	2.50	4.50	4.50	25.98	39.43

Table 4: Inter-relationship (correlation coefficient) between physico-chemical properties and different forms of zinc in soils of Birbhum district.

Parameters	WE-Zn (mg/Kg)	Org-Zn (mg/Kg)	Amor-Zn (mg/Kg)	Cry-Zn (mg/Kg)	Mn-Zn (mg/Kg)	Residual Zn (mg/Kg)	Total Zn (mg/Kg)
pH	-0.171**	-0.202**	-0.285**	-0.245**	-0.312	-0.225**	-0.246
EC	-0.345**	0.138	0.056	0.264	0.120	0.187	0.270
OC	0.167**	0.425**	0.143	0.283**	0.189**	0.134**	0.476**
Clay	0.217**	0.346	0.312**	0.395**	0.435**	0.341**	0.441**
DTPA-Zn	0.249**	0.171**	0.213**	0.241**	0.273**	0.199**	0.421**

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

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