# DISTRIBUTION OF ZINC FRACTIONS IN RELATION TO PROPERTIES OF SOME SOILS OF BANGLADESH

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Key words: Distribution, Zinc fractions, Speciation procedure

#### **Abstract**

An investigation was conducted to determine the distribution and concentrations of different forms of Zn in the soils of Gazipur. Gerua, Kalma and Khilgaon soil series were identified in three land types, named as highland, medium high land and medium low land, respectively. Soil samples were collected from each soil series at three different depth such as surface (0 - 15 cm), subsurface (15 - 40 cm) and substratum (40 cm+) to determine soil characteristics and the distribution pattern of Zn fractions. Results indicated that amount of total Zn varied significantly, ranges from 14.99 to 36.11  $\mu$ g/g at different depth of different land types. Moreover, the purpose of the sequential extraction or fractionation was to find out the Zn in the exchangeable (Exch.), organic matter (Org.) bound, Mn oxide (Mn-O), amorphous Fe oxide (Am. Fe-O), crystalline Fe oxide (Crys. Fe-O) and residual (Res.) fractions. In Gerua, Kalma and Khilgaon soils, Zn concentrations predominated in Res. followed by Crys. Fe-O and Am. Fe-O fractions. Results reflected that soil properties influence the distribution of different Zn fractions in soils.

## Introduction

Zinc is a heavy metal of much interest since it is a plant micronutrient as well as a potential contaminant in soils. Zinc in high concentrations can be toxic to flora and fauna, a subject of current environmental research<sup>(1)</sup>. Total Zn in soils indicates the potential capacity of soils to supply Zn for crop production given the capacity of crop to exploit it. However, total Zn in soil does not indicate Zn availability to plants. Availability of Zn for plants is reported to be associated with the distribution of this nutrient into fractions in soils and these fractions can be measured in order to understand how this metal influences the environment, is important to distinguish between the total quantities in the soil and the amounts that can be transferred into more soluble forms, becoming bioavailable.

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20 BEGUM et al.

The bio-available fraction is most crucial for assessing the environmental quality and possible health risk<sup>(2)</sup>. Therefore, understanding of the distribution of Zn fractions in soils will help to characterize the behaviour of Zn in soils and possibly its availability for plant uptake.

The soil is a dynamic system where changes in its properties, management and environmental factors affect the availability of metals<sup>(3)</sup>. However, distribution of Zn varies significantly in response to soil properties<sup>(4)</sup>. The distribution of microelements among fractions in soils is influenced by several properties like pH, organic matter, CEC and soil texture<sup>(5, 6)</sup>.

Zinc is a transition element and is able to form complexes with a variety of organic ligands, interacts with organic matter, and both soluble and insoluble Zn-organic complexes are formed. In soil solution, the speciation of Zn, and thus the free Zn activity determines the availability of Zn for plants as a micronutrient and its characteristics as a heavy metal contaminant. The solubility of Zn in soil solution must be quantified to evaluate bioavailability and transport of Zn in soils<sup>(7)</sup>. Kabata-Pendias and Pendias<sup>(8)</sup> have stated that chemistry of Zn is governed by the pH of the soil. In acidic soil, Zn adsorption is related to cation exchange sites<sup>(8)</sup>. While in alkaline soils the chemistry is dominated by organic ligands. In more alkaline soils Zn can form an organo-zinc complex, which would also increase the metals mobility. Thus, the aim of this research was to determine the total concentration of Zn and its fractions using a speciation procedure in Madhupur Tract soils and to assess the correlation between the zinc content, its fractions and physical, chemical and physico-chemical properties of soils.

#### Materials and Methods

The sampling site is located about 24° 01' and 24° 21' North Latitude and 90° 18' and 90° 33' Longitude of village Bangnahati, post Kewabazar, Upazila: Sreepur, district Gazipur. Composite soil samples at the rate of three per location were collected from three different land types (Gerua-high land, Kalma-medium high land and Khilgaon-medium low land) at a depth of surface (0 - 15 cm), subsurface (15 - 40 cm) and substratum (40° cm).

Soil samples were air-dried, ground by wooden hammer and passed through 2 mm stainless steel sieve. Bulk density, particle size analysis, moisture %, CEC and pH were determined following standard methods<sup>(9)</sup>. The organic matter of the soils was determined by wet oxidation following the method of Walkley and Black<sup>(10)</sup>. Total concentration of Fe, Mn, Zn and Cu in soil was analyzed by digesting soil with aquaregia at a ratio of 1 : 10. Total Fe, Mn, Zn and Cu were estimated by AAS (Atomic Absorption Spectrophotometer)<sup>(9)</sup>. The Zn fractionation procedure was largely based on the method of Shuman <sup>(11)</sup>. The results were statistically analyzed using Stata software.

## **Results and Discussion**

The pH of the investigated soils was moderately acidic, indicating that the soil was acidic in reaction, pH gradually increases from the upper to the lower layers (Table 1), because when rain falls on the surface layers of high land or medium highland, the positive H<sup>+</sup> ions of rain water replaces the other cations in the soil profile, which accumulates in the lower layers by leaching and thus pH increases in the lower layers, as a result mobilization of micro elements take place. Higher is the bulk density lower is the organic matter content. The increasing trend of bulk density from top to bottom indicated organic matter content gradually decreased from high land to medium low land. Among the soils the organic matter concentrations were higher in surface soils for each land type than the subsurface or substratum may be due to the accumulation of plant residues and household wastes.

Table 1. Some physico-chemical characteristics of Gerua, Kalma and Khilgaon soils.

Soils	Layer	pН	BD	CEC	OM	Clay	Texture
			(g cm)	(meq /100g)	(%)	(%)	
Gerua	Surface	4.75	1.13	5.96	1.84	25	Silt loam
	Subsurface	5.29	1.32	7.48	0.73	36	Silty clay loam
	Substratum	4.79	1.54	9.29	0.355	36	"
Kalma	Surface	5.54	1.28	3.97	2.39	20	Silt loam
	Subsurface	5.28	1.71	3.975	0.605	27	Silty clay loam
	Substratum	5.34	1.19	6.31	0.355	35	"
Khilgaon	Surface	5.16	1.39	6.31	1.81	30	"
	Subsurface	5.14	1.35	5.025	0.85	33	"
	Substratum	5.88	1.53	11.105	0.48	47	Silty clay

Fine textured soils increases from surface to substratum for each soil profile, from highland to medium high land, medium highland to medium low land due to clay accumulation by leaching in the bottom layers heavier textures were observed in the lower layers. The total and available Zn gradually decreased in the lower layers, as soil pH increased, the solubility and availability of Zn decreased<sup>(12)</sup>. However, CEC gradually increases from upper layers to the lower layers, also affected the availability, because greater CEC means lower availability as cations were adsorbed by the clay particles.

The mean concentrations of Zn fractions in the soils are presented in the Table 2.

The exchangeable form of Zn represents the most readily available source ranged from 0.21 to 1.05  $\mu$ g/g of the total concentration. The surface of Gerua soil contained the higher exchangeable Zn compared to other soils which reflects the situation of increases solubility of Zn at low pH<sup>(13,14)</sup>. The pH value of surface soils of Gerua was 4.75, while the

22 BEGUM et al.

pH value of substratum soils of Khilgaon was 5.88. As the pH increased down to the profile, Zn concentration decreased.

Table 2. Distribution of different Zn fractions and total Zn in Gerua, Kalma and Khilgaon soils.

		Zn Concentration (μg g <sup>-1</sup> )							
Soils	Layer	Exch.	Org.	Mn-O	Am.Fe-O	Crys.	Res.	Total	
			bound			Fe-O		Zn	
Gerua	Surface	1.05	1.02	0.99	6.09	5.76	20.99	33.04	
	Subsurface	0.26	0.44	0.45	1.99	5.69	20.52	29.04	
	Substratum	0.27	0.96	0.26	3.01	7.27	27.3	36.11	
Kalma	Surface	0.53	1.41	0.68	4.23	3.47	11.58	20.48	
	Subsurface	0.21	0.65	1.47	1.29	1.14	10.41	14.99	
	Substratum	0.26	0.44	0.69	5.14	3.36	13.83	24.12	
Khilgaon	Surface	0.72	0.59	0.67	3.11	5.54	13.24	22.44	
	Subsurface	0.24	1.32	0.65	8.19	2.47	9.26	20.6	
	Substratum	0.45	0.45	0.17	3.24	1.91	19.94	25.96	

The correlations between Zn and soil properties are presented in Table 3. pH shows negative but not significant relationship with Exch. Zn fraction. Similar result was found by others<sup>(15)</sup>. Bulk density shows negative significant relationship at p < 0.01% levels with Exch. Zn fraction it might be due to high bulk density reduces the exchange sites of the soils and organic matter shows positively significant relationship with Exch. fraction at P<0.01% levels indicated complex formation generated by organic matter, promote Zn availability in soils (Table 3) and findings are very similar to the several works<sup>(5,16,17)</sup>. Availability of Zn increased with increasing organic matter. pH, clay and CEC show negative but very poor relationship with Exch. fraction, the results are in disagreement with others<sup>(5)</sup>.

The amount of Zn in organically bound form was highest in the surface soils of Kalma soil. The share of Zn bound with organic matter in the analyzed soil samples was higher in the surface soils of Kalma soils than the surface soils of Gerua and Khilgaon soils because organic matter was highest (2.39%) so organically bound zinc was highest (1.41  $\mu$ g/g) in the surface soils. The relationship between soil organic matter and Org. bound Zn was indicated by the significant positive correlation at p < 0.01% level (Table 3).

Values of Mn-O bound Zn ranged from 0.17 to 1.47  $\mu$ g/g soil, while the highest value is recorded in subsurface layer of Kalma soils (Table 2). Zinc was higher in the crystalline Fe-oxide fraction than in the Mn-oxide fraction, indicating that Zn is more associated with Fe-oxide than Mn-oxides which might be the simple predominance of the Fe oxide

fraction<sup>(11)</sup>. Correlation coefficient between the Zn associated with Mn-O fraction and both the clay and CEC showed that Mn-O bound Zn and clay or Zn and CEC were significantly correlated with each other at p < 0.01% levels. The relationship in each case is negative. Mn-O also shows negative significant relationship with total Zn concentration at p < 0.01% level (Table 3).

Table 3. Relationship between individual Zn fractions and soil properties.

Zinc	Soil Properties							
fractions	рН	Bulk density	Clay	CEC	OM	Total Zn		
(μg/g)		$(g/cm^3)$	(%)	(meq/100g)	(%)	$(\mu g/g)$		
Exch.	-0.2888	-0.5020**	-0.3737	-0.0496	0.7221**	0.3152		
Org.	-0.0359	-0.0941	-0.3498	-0.2248	0.4398**	-0.0334		
Mn-O	-0.2250	0.0864	-0.6439**	-0.7344**	0.2078	-0.5211**		
Am. Fe-O	-0.2386	-0.6097**	-0.1452	-0.2192	0.1997	0.0463		
Cryst. Fe-O	-0.6694**	-0.3386	-0.0717	0.2517	0.1730	0.8227**		
Res.	-0.3308	0.0063	0.4249*	0.7225**	-0.2718	0.9227**		

<sup>\*</sup>Indicates at 0.05% and \*\* 0.01% level of significance.

Crystalline Fe-O bound Zn was much higher than Am. Fe-O bound Zn except the surface and subsurface soils of Kalma soil series (Table 2). Nair and Cottenie  $^{(18)}$  reported that the amorphous Fe<sub>2</sub>O<sub>3</sub> possibly retain a large proportion of the trace elements by surface coating finer particles. The relationship between soil pH and Crys. Fe-O content showed a significantly negative correlation at p < 0.01% levels and between Crys. Fe-O and total Zn concentration the relationship indicated a positively significant relationship at 0.01% level (Table 3).

In all the studied soils, Zn was mostly concentrated in the residual fraction. A considerable amount of Zn was found in residual fraction where possibly most of the total Zn was held within the silicate minerals<sup>(19)</sup>. Among these soils the residual fraction of Zn was found highest in the substratum layer of Khilgaon soil that means the lowest layer of the studied soil. The Zn was highest in the residual fraction than the other fractions of all soils. Residual fraction showed positive and significant relationships with clay at p < 0.05%, CEC at p < 0.01% and with total Zn concentration at p < 0.01% (Table 3). Another study of the Zn fractions reported up to 70% of Zn in agricultural soils in the residual fraction and nearly all the remainder associated with Fe oxides<sup>(20)</sup>.

A sequential extraction technique used to characterize bonding of metals to the soils showed close association between fractions of studied elements and soil properties. It also indicated the preferential reduction of total Zn concentration towards the lower depths of soils, due to comparatively high pH. In case of total Zn the concentration

24 BEGUM et al.

decreased towards the lower depths, the Exch. and Org. bound Zn were also decreased. In all soils, Zn concentration dominated in Crys. and Am. Fe-O fractions.

Distributions of micro elements among chemical fractions are generally dependent on the total concentration of micro elements and soil properties. The values of soil properties were different in three land types, which clearly reflected that soil properties influenced the distribution of different Zn fractions in soils.

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(Manuscript received on 20 August, 2015; revised on 3 January, 2016)