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The Distribution of Zinc Fractions in Surface Samples of Selected Agricultural Soils of Zambia

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ABSTRACT

Soil parent material, pedo-chemical transformations and anthropogenic interventions play important roles in the distribution of zinc (Zn) into its various forms in the soil and ultimately, its bio-availability for plant uptake. Therefore knowledge of the soil Zn forms is useful for its management. This study defined five mechanistic Zn pools in 11 cultivated agricultural soils of Zambian and their uncultivated pairs. A batch extraction scheme was used to estimate exchangeable (Ex-Zn), carbonate (CO_3-Zn), organic (Org-Zn), sesquioxide (Ox-Zn) and residual (Res-Zn) Zn pools in each soil. Total Zn was calculated as a sum of the pools and it ranged from 13.11 to 108.02 mg kg^{-1} with an average of 52.26 mg kg^{-1}. The distribution of Zn in the soils on the basis of average concentrations was in the order 22.99 mg kg^{-1} Ox-Zn (44%)>14.97 mg kg^{-1} Res-Zn (29%)>7.51 mg kg^{-1} CO_3-Zn (14%)>4.81 mg kg^{-1} Org-Zn (9%)>1.98 mg kg^{-1} Ex-Zn (4%). Cultivation depressed Tot-Zn and Ex-Zn concentrations in several of the soils. Correlation analysis (n = 44) showed that Tot-Zn increased along with soil clay content (r = 0.50, p = 0.03) as well as soil Cation Exchange Capacity (CEC) (r = 0.60; p = 0.007), CO_3-Zn increased with CEC (r = 0.68, p = 0.001) and Res-Zn increased with soil clay content (r = 0.53; p = 0.02). The fact that the chemistry of Zn in this set of soils appears to be dominated by the more stable fractions offers an explanation for the common notion held that majority of Zambian soils have low soil Zn test levels which accounts for low Zn bio-availability.

Key words: Agricultural soils, correlations, soil fractionation, Zambia, zinc pools

INTRODUCTION

Zinc (Zn) is an important essential element which is required only in limited amounts by plants, animals and humans for various physiological and reproductive functions. It influences the quality and yield of crops (Madyiwa *et al.*, 2002; Alloway, 2003; Chidanandappa *et al.*, 2008) and in humans it is a necessary cofactor in more than 300 enzymes and numerous transcription factors (FAO/WHO/IAEA, 1996; Haug *et al.*, 2010). The deficiency of Zn in human diet has been recognized to commonly cause impaired growth (stunting) in children and consequently poor human development (Hambridge *et al.*, 1986). This phenomenon is common in the southern Africa region and requires urgent attention. Previous concern about Zn focused more on the potential for heavy metal toxicities to humans from high levels of pollution emitted by mining operations (Tembo *et al.*, 2006) than in its role in crop production. Clinical symptoms including headaches,

nausea, loss of appetite and diarrhea have been recorded from high amounts of Zn intake by humans (Panel on Micronutrients, 2001).

In a recent review of soil analysis data from the University of Zambia Soil Analysis Laboratory a large number of agricultural soils across the nation were observed to have tested low in bio-available Zn. However, there have not been consistent concurrent visual observations of widespread incidence of Zn deficiency in crops grown on these soils. This is plausibly because of the higher likelihood for deficiencies of nitrogen, phosphorus and potassium to appear on crop grown in low fertility soil with moderate to advanced weathering, while Zn deficiency will more likely manifest as hidden hunger and contribute to low crop productivity (Mapiki and Phiri, 1995). On the other hand, aluminium and manganese toxicities manifested in acid soils also act to negatively affect crops before the influence of Zn is visually observed. This hidden form of Zn deficiency has been reported to contribute as much as 40% reduction in crop yields (Alloway, 2003).

The Zn requirement of crops is largely met from soluble portions released through chemical transformations of native soil Zn (Shuman, 1991). In addition Zn may be supplied to plants from soluble forms in synthetic or organic sources, as well as anthropogenic atmospheric inputs (Iyengar *et al.*, 1981; Johnson and Petras, 1998). Typically soil total Zn ranges between 10-300 mg kg^{-1} with a mean value of 55 mg kg^{-1} (Kiekens, 1995), however knowledge of total Zn provides only limited information about its transformations and bio-availability. For a better understanding, total soil Zn can be broadly described in five mechanistic fractions which can be quantified using sequential or batch fractionation schemes (Zerbe *et al.*, 1999; Hseu, 2006; Fedotov and Spivakov, 2008; Saffari *et al.*, 2009). Generally these are: (1) water soluble Zn in the soil solution, (2) easily exchangeable Zn in electrostatic reaction with soil particles, (3) organic Zn complexed, chelated or adsorbed to organic ligands, (4) inorganic Zn associated with secondary minerals such as carbonates or insoluble metal oxides and (5) residual Zn held in primary minerals (Sposito *et al*, 1982; Alloway, 2003; Saffari *et al.*, 2009). These fractions provide broad information on the biological, geological and chemical processes which have occurred in a soil and are useful for predicting the availability of Zn for plant uptake. The extent to which each fraction is present and the transformations in equilibrium between fractions is influenced by soil properties such as pH, cation exchange capacity, presence of metal oxides and soil organic matter. It has been widely reported that the residual Zn and oxide bound Zn are the more stable fractions while the exchangeable Zn and water soluble Zn fractions are rather more soluble (Saffari *et al.*, 2009).

Low levels of bio-available Zn found in soils has been attributed to one or a combination of low native Zn, very slow solubilization of Zn from soil minerals, strong adsorption of Zn on soil surfaces, or co-leaching of Zn with dissolved organic matter (Zimdahl and Skogerboe, 1977; Rieuwerts *et al.*, 2006). These mechanisms appear to be active in many soils such that incidences of widespread soil Zn deficiency have been reported in several regions of the world including Australia (McDonald *et al.*, 2001), Spain (Obrador *et al.*, 2007), India (Karak *et al.*, 2006), the Savannas (Agbenin, 2003), Brazil (Furlani *et al.*, 2005), Turkey (Cakmak *et al.*, 1999) and Iran (Maftoun and Karimian, 1989). Soil Zn has not been well studied in Zambia and there is insufficient information that could be used in predicting Zn bio-availability. Therefore to the extent that our communities have low meat and milk protein intake and Zn requirements are largely met from food crop supply, it is important to have a better understanding of the transformations of soil Zn fractions and their potential to supply plant requirement. The objective of this study was to characterize the distribution of Zn in its various fractions in selected Zambian soils and to determine if cropping affects their distribution.

MATERIALS AND METHODS

Soils: The soils used for this study were collected from eleven locations across Zambia where samples were obtained from both a cultivated and an adjacent uncultivated field (Table 1). The lengths and intensities of cultivation and management of crops at the various locations were not uniform but they were in excess of five years with fertilizer application. Maize production was common to the farms.

Laboratory analyses: Soil samples were collected from the 0-20 cm depth at ten random spots per field and mixed together to obtain one composite sample. All samples were air dried and crushed to pass through a 2 mm sieve. Soil analysis was done using standard procedures (Van-Ranst *et al.*, 1999). Particle size distribution was determined by the hydrometer method. The pH was measured in a 1:2.5 (w/v) ratio of soil to 0.01 M $CaCl_2$ solution. Soil organic matter was determined using the Walkley-Black chromate reduction method. Cation Exchange Capacity (CEC) was determined in neutral 1 N NH_4OAc with steam distillation.

Zinc fractionation: A modified version of the batch or single extraction scheme (Johnson and Petras, 1998) was used to define the various Zn fractions in the soils. Rather than using the same soil residue in the next extraction step, fresh sample was weighed into the next reagent, as follows:

- **Extractable Zn (Ex-Zn):** Representing the water soluble and exchangeable fraction: Twenty grams of soil was extracted in 40 mL 0.005 M DTPA for 2 h
- **Carbonate bound Zn (CO_3-Zn):** Representing the inorganically bound fraction: One gram soil was extracted in 20 mL 1 M CH_3COONH_4/CH_3COOH mixture at pH 5 for 5 h
- **Organic bound Zn (Org-Zn):** Representing the fraction complexed, chelated or adsorbed to
- **Organic ligands:** One gram soil extracted in 40 mL 0.1 M $K_2P_2O_7$ for 17 h
- **Sesquioxide Zn (Ox-Zn):** Representing the amorphous bound fraction: one gram soil was extracted in 50 mL acid Oxalate at pH 3 (four parts 0.2 M ammonium oxalate and three parts 0.23 M oxalic acid) for 17 h
- **Residual Zn (Res-Zn):** One gram soil sample was digested in 25 mL aqua regia (one part HNO_3 to three parts HCl) for twenty minutes on a hot plate and then allowed to cool
- **Total Zn (Tot-Zn):** Total Zn was calculated as a sum of all the fractions determined

Each soil suspension was filtered after shaking or digestion. The concentration of Zn in the extracts was determined using the atomic absorption spectrophotometer (Analyst 400 Perkin Elmer). All the soils were analyzed in triplicates.

Statistical analysis: The data obtained was analyzed using the SAS Statistical Program (SAS, 6.12) to obtain the means and standard deviations of Zn concentration in the different pools. In addition, correlation analysis was done to obtain the relationship between Zn concentrations in the various pools and soil properties.

RESULTS AND DISCUSSION

Soil properties: The soil samples used in this study varied in classification (Table 1) and their pH ($CaCl_2$) values ranged from 4.1 to 7.5 (Table 2). Half of them were acidic while the other half were alkaline. Although there was no significant difference (t-test, $p = 0.05$) in mean soil reaction

Table 1: Description of soils used in the study

Soil series	Location	Classification
Nakambala	Syrenga farm, Mazabuka	Fine-loamy, mixed, hyperthermic Oxic Paleustalf
Makeni	York farm, Lusaka	Fine, mixed, isohyperthermic Udic Paleustoll
Kashinka	Kashima farm, Lusaka	Fine, mixed, isohyperthermic Ultic Haplustalf
Chilimboyi	University of Zambia field station	Fine loamy, mixed, isohyperthermic Ultic Kandic Haplustalf
Chelstone	Liempe farm, Lusaka	Fine, mixed, isohyperthermic Oxic Paleustalf
Ifisa	SADC gene bank, Lusaka	Coarse loamy, siliceous, isohyperthermic Ultic (Kan) Haplustalf
Chalimbana	Huntley farm, Chisamba	Fine loamy to clayey, mixed, isohyperthermic, Aquic Eutropept
Mushemi	ZARI, Kabwe	Fine, kaolinitic, isohyperthermic, Oxic Paleustalf
Mpongwe	Mpongwe farm, Mpongwe	Clayey, kaolinitic, isohyperthermic Typic Eutrustox
Misamfu Red	Misamfu regional research station, Kasama	Fine-loamy, siliceous, isohyperthermic Oxic Rhodic Paleustult
Mufulira	Misamfu regional research station, Kasama	Clayey, kaolinitic, isohyperthermic Oxic Paleustult

Table 2: Some chemical and physical characteristics of soils used in the study

Soil series	Land use/Designation	pH	OM (g kg^{-1})	CEC (cmol kg^{-1})	Sand	Silt (g kg^{-1})	Clay	Texture
Nakambala	Cropped	4.8	3.7	28.8	372	256	372	l
	Fallow	5.6	5.1	34.8	392	216	392	l
Makeni	Cropped–11North	7.0	3.9	35.5	332	286	382	l
	Fallow	6.6	8.9	44.8	472	146	382	l
Kashinka	Cropped	7.2	2.6	15.1	532	176	292	sl
Chilimboyi	Field A	7.2	1.3	14.6	552	136	312	sl
	Field B	7.1	1.3	13.8	512	136	352	sl
	Field C	7.5	1.7	10.7	612	96	292	sl
Chelstone	Field H	4.7	6.7	6.0	632	36	332	sl
	Fallow	5.3	6.6	4.9	672	36	292	sl
	Orchard	7.0	6.6	12.6	562	96	342	sl
Ifisa	Cultivated	7.1	0.5	7.9	612	76	312	sl
	Fallow	5.4	1.4	7.6	572	56	372	sl
Chalimbana	Cultivated	6.7	2.6	15.9	652	86	262	sl
Mushemi	Cultivated	5.7	1.3	6.1	752	36	212	ls
	Fallow	5.7	1.4	7.1	732	36	232	ls
Mpongwe	Cultivated	6.5	4.6	34.0	472	196	332	l
	Fallow	4.4	3.2	21.4	552	156	292	sl
Misamfu Red	Cultivated	4.2	1.6	6.0	756	128	116	sl
	Fallow	4.7	2.6	7.3	816	68	116	ls
Mufulira	Cultivated	4.1	1.3	5.3	836	88	76	ls
	Fallow	4.2	1.6	4.9	736	88	176	sl

l: Loam, ls: Loamy sand, sl: Sandy loam

between cultivated and uncultivated soil samples, cultivation generally had the tendency to reduce soil pH (Table 2). It is known that the nature of soil reaction is influenced by parent material, extent of weathering, erosion and leaching and soil management. In this case, the strongly acidic soils, comprising Mpongwe, Misamfu red, Mufulira, Nakambala and Liempe are alfisols or ultisols belonging to the oxic sub-group (Table 1) and located in moderate to high rainfall agro-ecological regions. The UNZA, York and Kashima soils are formed on relatively less weathered parent material and have high pH values probably owing to continuous irrigation with alkaline water

Table 3: Soil Zn fractions of the 11 Zambian soils collected from different locations

Soil series	Land use/designation	Zn fractions					
		Ex	Carbo	Org	Sesq	Resi	Total
		--(mg kg^{-1})--					
Nakambala	Cropped	1.43	6.80	6.33	74.50	18.96	108.02
	Fallow	0.52	2.68	2.66	44.23	23.30	73.39
Makeni	Cropped	2.28	20.13	5.71	17.55	22.00	67.67
	Fallow	9.08	16.60	Nd	57.27	13.08	96.03
Kashinka	Cropped	2.77	4.73	4.38	7.45	14.95	34.28
Chilimboyi	Field A	0.52	28.00	1.84	4.32	9.55	44.23
	Field B	2.15	7.75	6.16	11.95	72.40	100.41
	Field C	3.16	9.40	7.61	11.55	17.90	49.62
Chelstone	Field H	T	3.03	1.43	11.15	6.55	22.16
	Fallow	T	2.95	Nd	30.45	5.35	38.75
	Former orchad	T	8.95	Nd	31.34	13.25	53.54
Ifisa	Cultivated	0.09	1.95	2.38	22.65	5.85	32.92
	Fallow	T	2.28	1.97	49.65	7.60	61.50
Chalimbana	Cultivated	1.00	4.13	5.29	1.55	10.85	22.82
Mushemi	Cultivated	0.44	0.78	0.74	0.55	10.60	13.11
	Fallow	0.73	15.78	10.86	Nd	7.77	35.14
Mpongwe	Cultivated	7.45	12.18	16.06	25.75	28.27	89.71
	Fallow	T	3.00	2.14	4.80	10.59	20.53
Misamfu Red	Cultivated	0.48	8.53	0.72	34.54	7.25	51.52
	Fallow	0.42	1.95	4.73	15.50	11.60	34.20
Mufulira	Cultivated	0.86	2.13	7.72	27.36	5.30	43.37
	Fallow	0.39	1.40	2.68	9.80	6.35	20.62
Mean		1.98	7.51	4.81	22.99	14.97	52.26
SD		5.68	5.83	4.16	20.02	17.20	32.09

T: Trace value, Nd: Not determine, Ex: Extractable, Carbo: Carbonate, Org: Organic, Sesq: Sesquioxide, Resi: Residual

from aquifer sitting in limestone bedrock. The soil samples were dominated by coarse textured soils ranging between loamy sand to loam (Table 2). Soil organic matter was highly variable, being very low or very high (<2.5%>) and uncultivated fields were more likely to have higher values than their cultivated analogs (Table 2). The soil cation exchange capacities were between 4.9 and 44.8 cmol kg^{-1} (Table 2) with most observed to be low (<15 cmol kg^{-1}), probably due to relatively high sand and low organic matter contents of many of these soils.

Zinc distribution in soils: Total Zn in the soils ranged between 13.11-108.02 mg kg^{-1} (Table 3) and many of the soils can be characterized as having low Tot-Zn, evidenced by concentrations below the group average of 52.26 mg kg^{-1}. These values generally reflect the influence of soil parent material, age, weathering and texture wherein the more weathered and coarser soils have lower Tot-Zn concentrations. Nevertheless the average concentration compares well to several reported in literature such as 34 mg kg^{-1} in Australia 56.5 mg kg^{-1} in the USA (Holmgren *et al.*, 1993), 68 mg kg^{-1} in Europe (Angelone and Bini, 1992) and 45-59 mg kg^{-1} in Asia (Katyal and Vlek, 1985). The Australian soils are older and more weathered hence have lower average Tot-Zn concentrations. Tagwira *et al.* (1993) in Zimbabwe and Chahal *et al.* (2005) in India demonstrated that finer textured soils contain higher concentrations of Zn in all the fractions when compared to

coarser textured soils. The lower concentrations can be explained by the presence of fewer exchange sites for Zn adsorption or its loss from mineralization in the older and coarser soils.

In the current study, evaluation of the fractional distribution of soil Zn (Table 3) showed that Ox-Zn (44%)>Res-Zn (29%)>CO$_3$-Zn (14%)>Org-Zn (9%)>Ex-Zn (4%). The more stable Ox-Zn and Res-Zn fractions accounted for more than 70% of soil Zn. This is similar to observations reported by Tagwira *et al.* (1993), Dvorak *et al.* (2003), Tehrani (2005), Milivojevic *et al.* (2005), Behera *et al.* (2008), Chidanandappa *et al.* (2008) and Saffari *et al.* (2009), who found residual Zn to be predominant in soils. However in their studies they reported higher residual Zn than oxide Zn fraction due to more alkaline soil pH and low sesquioxide concentrations. In other studies, Zerbe *et al.* (1999), Ramos *et al.* (1999), Hseu (2006) and Margui *et al.* (2007) reported that the sesquioxide Zn fraction was dominant in the soils studied. According to Chileshe and Wen (1985) and Magai (1985) soil formation in Zambia has been characterized by a mixing of old and new deposits whereby Precambrian Basement Complex has been mixed in with or covered by the more recent deposits of the Kalahari sands and Karoo deposits of various sedimentary rocks including sandstones and calcareous mudstones. This has caused the soils to have variable amounts of sesquioxide and weatherable minerals that can retain significant amounts of Zn. Therefore, whereas the fractional average Ox-Zn in the soils used in this study was higher than Res-Zn, eight of the samples contained more Res-Zn than Ox-Zn. Higher Zn concentrations of these stable fractions denotes their importance as the storage fractions for soil Zn, although their solubilities will determine how available they are for plant uptake. There was no consistent effect of cultivation on Tot-Zn or its fractional distribution in the soils.

The concentrations of the CO$_3$-Zn and Org-Zn fractions were intermediate (Table 3). This is probably indicative of their role as transitional fractions in the bioavailability of soil Zn. Behera *et al.* (2008) showed that these fractions declined with years of cropping. Hence, associated soil parameters of such fractions, in this case carbonates and organic matter are important in their soil buffering capacity for Zn (Dvorak *et al.*, 2003). The influence of organic matter can be attributed to formation of organo-Zn complexes producing buffer zones for Zn (Udom *et al.*, 2004). In soils of Iran with high carbonates content, Saffari *et al.* (2009) reported CO$_3$-Zn values similar to these Zambian soils.

The Ex-Zn fraction in the Zambian soils studied always contained the lowest concentrations of Zn (Table 3). As it has been proposed that plant Zn uptake is largely from this fraction (Shuman, 1991) it will therefore be expected that it relies on the other fractions, especially those with intermediate concentrations (CO$_3$-Zn and Org-Zn) to replenish it. However there was no correlation between and among any of the fractions obtained. Elsokkary (1979), Dvorak *et al.* (2003), Milivojevic *et al.* (2005) and Margui *et al.* (2007) also made similar observations that the exchangeable pool had the lowest concentration of the fractions that they defined. Going by the critical index of 0.8 mg kg^{-1} used by the soil analysis laboratories in Zambia at least 60% of the samples test low in EX-Zn.

Correlation between soil Zn and soil characteristics: The Tot-Zn concentration of the soils increased with soil pH, organic matter content, soil clay content and CEC (Table 4). It would appear that even with the dominance of coarse texture in this set of soils with wide ranging pH, the clay type and organic matter and increasing amounts of them provided sufficient charge points for incremental Zn retention. Similarly, Elsokkary (1979) in Egypt showed that Zn adsorption by soil was highly associated with CEC, Fe$_2$O$_3$ and clay. Mclaren *et al.* (1997) also concluded that CEC and

Table 4: Correlation coefficients between soil zinc fractions and the properties of selected Zambian soils

	pH	OC	CEC	Clay
Exch-Zn	0.42	0.14	0.29	0.31
CO$_3$-Zn	0.43	0.19	0.68*	0.35
Org-Zn	0.27	0.23	0.41	0.39
Ses-Zn	-0.03	0.20	0.40	0.23
Res-Zn	0.32	0.11	0.19	0.53*
Tot-Zn	0.30	0.20	0.60*	0.50*

*Significant at 0.05

organic matter influenced the adsorption and desorption of Zn. The Ox-Zn concentration decreased as soil pH increased. This can be explained by the natural reduction in oxide solubility and concentrations as pH increases. Shiowatana *et al.* (2005) made similar observation when they analyzed soils in Thailand. They concluded that soil pH significantly determined the adsorption and sorption of metals and that its reduction increased the concentration of metal ions in the soil solution. Correlation analysis showed that CO$_3$-Zn increased with soil pH and CEC (Table 4) Calcium carbonate tends to adsorb Zn or form complexes such as CaCO$_3$: ZnCO$_3$, a double salt, under favorably high pH values (Ramos *et al.*, 1999). The correlation coefficient between pH and the exchangeable soil Zn was 0.42 (p = 0.12), suggesting that Zn bioavailability is probably more from those soils with higher pH values among the set studied.

CONCLUSION

The fractional distribution of Zn in Zambian soils was in the order Ox-Zn>Res-Zn>CO$_3$-Zn>Org-Zn>Ex-Zn and they can be clustered into stable (Ox-Zn and Res-Zn), intermediate (CO$_3$-Zn and Org-Zn) and available (Ex-Zn) forms. Extractable Zn concentrations of these soils are generally low because the stable fraction is the dominant form in soils. Given low levels of bio-available Zn in many Zambian soils, the implication is that in the transformation of soil Zn, the stable form is only very slowly released into the available fraction and the intermediate forms offer a strong buffering to replenishing the soluble form albeit at a slow equilibrium. Soil Zn concentrations were influenced by the colloidal properties of the soils such that soils with high pH and those with finer texture were more likely to have higher Zn concentration in the various fractions. Land cultivation will probably result into lower soil Zn concentration compared to fallow land.

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