Copper and Zinc Amounts and Distribution in Soils around Dumpsites as Affected by Dumped Manure in Kudenda and Dirkaniya Dumpsites in Kaduna Metropolis

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Abstract- The increase in use of manure requires a knowledge on the fate and distribution of residual manure Cn and Zn in soils around dumpsites. To address this issue, amounts of soil Cu and Zn in the different organic and inorganic fractions were investigated in soil under long term dumping of industrial and animal wastes, especially swine and cattle manure and in two plots that are under intense vegetation around the dumpsites. The annual rates of manure application were based on the N contents in the various manures, and were approximately equivalent to 0, 50, 10, and 300 1G total N ha^{-1} y^{-1} in the vegetated area and 0, and 50 kg total N ha-1 y^{-1} in the grassland plot. In both the field plot and grassland manure plots there were insignificant increase in total Cu and Zn in soils associated with manure application. Moderate increases in labile Cu and Zn were observed in treatment with large amount of animal manure. The liquid swine manure had less effect than the cattle manure on increasing the labile Cu and Zn fraction. The results indicate that annual addition of animal manures at rates approximately 100kg N ho^{-1} for about 4 years does not constitute an environmental risk from Cu and Zn loading in these soils.

Index Terms- dumpsites, manure, copper, zinc, phytotoxicity,

I. Introduction

The application of animal manures to agricultural lands is to enhance the supply of essential nutrients and organic matter from these soils. However, there is concern over the application in the soil of heavy metals present in the manures of animals and several other organic wastes because of repeated use of manures in agriculture (Smith, 1994). There are documented evidences of DTPA – extractable Cu and Zn after the use of cattle and swine manures (Eneji et al, 2001). The risk associated with the accumulation of trace metals in soils due to the use of organic wastes includes phytotoxicity and the increased entry of toxic metals into the food chain (Heckman et al, 1987). However, the above risk are difficult to assess directly through determining the total contents of metals in the organic wastes from dumpsites because the physic-chemical form of the metal in the manure strongly affect their mobility, reactivity and availability to plants. To provide a clearer picture of the fate of metals in the soil after application of wastes from dumpsites, use of fractionation schemes have been introduced to separate the metal contents in the organic dumps and soil into fractions, using a series of chemical extractants. The information obtained is potentially valuable in predicting the bioavailability and transformation between chemical forms in soils (Jenne and Luoma, 1977). This study investigated the amount and distribution of Cu and Zn from soils subjected to repeated dumping of organic wastes. The two sites used are one cropped farm land and the other grassland both receiving dumped organic liquid and solid waste for a long time.

II. Materials and Methods

Soil and Organic Waste Used

The soils used in this study were from two sites namely Kudenda – cropped land receiving dumped liquid swine manure.

Dirkaniya – grassland receiving dumped solid cattle wastes. The treatments sampled for the metal distribution study included control and the manure applied of various rates low, medium, high, equivalent to 50, 100, 150 kg total N ha^{-1}, and urea application at 50, 100, and 200 kg N ha^{-1} as comparisons. The cropped (Kudenda) and grassland (Dirkaniya) plots were set up in a randomized complete block design with four replicates.

Table 1. Some Characteristics of the Soil used in the Experiment

		Total		Extractable (DTPA)	
Soil	**otal Soil Organic C (%)**	**Cu Mg kg^{-1}**	**Zn**	**Cu Mg kg^{-1}**	**Zn**
Kudenda	1.8	17.6	68.2	0.64	0.84
Dirkaniya	1.5	14.6	61.1	0.71	1.64

Table 2. Cu and Zn Content in the Liquid and Solid Dumped Manure

	Dumped	Manure		
	Cu	Zn	Cu	Zn
	Mg L^{-1}		Mg kg^{-1}	
Liquid dumped manure	4.6	3.8		
Solid dumped manure			43	38

Soils were sampled at 0 – 15cm. Three cores were taken from each plot randomly and mixed thoroughly to provide a composite sample. Soils samples were further air-dried, crushed, passed through 2mm sieve, mixed and stored at room temperature before analysis. Basic soil characteristic were determined. Soil organic carbon by Walkley-black method whole Cu and Zn were determined by mixed acid digestion (Shuman, 1979) and determined by atomic absorption spectrometry (Baker and Amache, 1982). The concentration of Cu and Zn in the manure is reported in table 2.

Fractionation of Cu and Zn

The scheme used for the fraction is the modified version (Liang et al, 1990), of the one proposed by Miller et al (1986). 2g of air-dried soil were first extracted with 20ml of 0.5m (Ca $(No_3)_2$ (16h), followed by sequential extraction by 20ml of 0.05m Pb $(No_3)_2$ + 0.1m Ca $(NO_3)_2$ (16h), 20ml of 0.01m NH_2OH HCl + 0.1m HNO_3 + 0.1m HNO_3 (0.5), 20ml of 0.1M $_4P_2O7$ (24h) and 10ml 0.112m $(NH_4)_2$ C_2O_4 + 0.0087M $H_2C_2O_4$ (in darkness 4h). After each extraction using a rotation shaker, the suspension was centrifugal for 10 minutes at 10,000 rpm. The supernatant was diluted 10 times with deionized water. After centrifugal, Cu and Zn in the supernatant from each of the above extraction was determined by atomic absorption spectrometry. The first extraction represents water-soluble and exchangeable fractions of Cu and Zn in soil. The fraction extracted by Pb $(NO_3)_2$ represents adsorbed Cu and Zn forms that can be displaced by Pb salt solution. The fraction extracted by CH_3COOH (acid) are mainly metals HCl on soil surfaces by covalent bonding, so-called inner sphere complexes metals (Sposito, 1984). The fractions extracted by NH_2 OH HCl, $K4P_2{}^07$ and $(NH_4)_2$ $C_2{}^04$ are the structural (occluded) forms bound by Mn oxide (MnO^-). Organically (om_) and by Fe and Al oxide (FeO_) respectively. The residual Cu and Zn (Res-) represent the metals strongly held within the silicate mineral structure which could be a substantial portion of the total Cu and Zn in soils.

Statistical Analysis

The difference in metal fractions among the components were examined statistically based on the least significant difference (LSD) and multiple comparison via The Duncan IL-ratio procedure (SAS Institute Inc. 1985).

III. Results and Discussion

The procedure employed divided Cu and Zn into seven fractions to represent four classes. One is the exchangeable form (Ex) that was extracted by Ca reagent and can be considered a labile fraction. The second is the adsorbed component of Cu and Zn that was extracted by Pb reagent (Pb-), representing more loosely sorbed forms along the acidic reagent (acid-) for more strongly adsorbed forms and together may be considered moderately labile. The third class represents structural metal forms that include those occluded (bound) by hydrous oxides of Mn (MnO^-) and organic matter (om) as well as hydrous oxides of Fe (FeO^-) extracted by a weak reducing agent (NH_2OH HCl) oxidant ($K_uP_2O_7$) and oxalate reagent respectively. The last category are the metals that are held within the silicate mineral structure termed residual and extracted by HF-based acid digestion (Mollar et al, 1986). In the study, the Cu in Ex-, Pb- and Aci- forms in all the treatments of all the soils tested lower than the level that could be accurately detected. The percentages of total Cu in the MnO^-, FeO^- and Res- forms are 3.5-6%, 21.2-24.7%, 12.1-18.2% and 42.1-48.6% in cropped land (Kudenda).

Table 3
Distribution of Cu Fractions in Kudenda Cropped Land

Treatment	MnO^-	Om-	FeO^- Mg Kg^{-1}	Res-	Total	DTPA
Swine Manure Dump						
Control	1.11	4.10	3.20	10.7	17.2	0.84
Low	1.20	5.20	2.61	11.5	16.4	0.82
Medium	1.30	5.11	3.32	11.6	17.3	1.01
High	1.76	5.21	3.12	11.50	18.2	0.81
Urea low	1.17	4.40	2.78	10.60	17.1	0.82
Urea medium	1.15	5.10	3.10	10.50	17.2	0.81
Urea high	1.21	5.40	3.20	11.10	17.1	0.91
LSD 0.05	0.30	0.76	0.66	0.88	1.31	0.25
P > 1	0.01	NS	0.05	60.01	C0.05	60.01
Cattle Manure Dump						
Control	1.12	4.26	2.11	10.6	18.1	0.82

Cm low	1.21	4.17	2.12	11.3	19.6	0.81
Cm medium	1.24	4.21	2.21	11.6	18.5	0.83
Cm high	1.16	4.11	3.21	11.5	18.4	1.00
Urea low	1.21	3.96	4.01	10.60	19.2	0.82
Urea medium	1.11	4.11	3.72	10.5	18.1	0.81
Urea high	1.21	3.87	3.21	11.6	13.6	1.01
LSD 0.05	0.22	0.81	1.1	1.8	1.9	0.24
P > F	NS	0.01	<0.05	NS	NS	NS

Total Cu determined by acid digestion
Sm Swine manure
Cm Cattle manure

Soils tested and 4.1 – 5.4%, 26.4 – 29%, 11.1 – 20.1% and 45-51% in the Dirkaniya grassland, respectively. Zinc in the exchangeable fraction was also lower than the level that could accurately be detected. However there was 1.2 – 2.7% of total Zn measured in the Kudenda cropped, soil and 2.5 – 3.8% in Pb – form and 1.7 – 2.0% in Aci – form measured.

Dirkaniya Soils

The percentage of total Zn in the MnO^-, Om-, FeO^- and Res-forms was 3.0 – 6.1%, 2.1 – 2.6%, 2.8 – 3.1% and 81-86% in Kudenda cropped land, and 9.2 – 12.4%, 2.5 – 3.1%, 1.8 – 2.1% and 75.1 – 80.1% in Dirkaniya soils.

Table 4
Distribution of Cu Fractions in Dirkaniya Soils

Treatment	MnO^-	Om-	FeO^- Mg Kg^{-1}	Res-	Total	DTPA
Control	0.81	4.20	1.56	6.61	11.5	0.74
Manure	0.71	4.1	1.60	7.1	10.6	0.71

Total Cu determined by acid digestion

Effect of Dumped Manure on Total Cu and Zn in Soil

The total Cu and Zn were not significantly increased by the addition of both swine and cattle manure (tables 3 and 4) but they were significant different among the soils (table 4).
Similar findings were documented by Canet et al (1977).

Table
Distribution of Zn in Kudenda Cropped Land

Treatment	Pb-	Aci-	MnO^-	Om	FeO^-	Res-	Total	DTPA
				Mg Zn Kg $Soil^{-1}$				
Swine Manure								
Control	0.75	0.61	3.18	1.71	2.44	60.90	68.1	0.66
CM low	1.24	0.47	3.01	1.83	2.41	59.50	74.2	1.07
Cm medium	1.21	0.61	3.20	1.87	2.52	61.2	72.4	1.21
Cm high	1.11	0.86	2.71	2.14	2.59	62.4	72.1	2.04
Urea low	1.21	0.46	3.10	1.86	2.66	65.6	71.6	0.68
Cm medium	1.61	0.50	3.36	1.81	6.42	12.4	70.4	0.80
Cm high	1.05	0.51	0.68	2.05	2.61	6.4	8.2	0.83
LSD	0.52	0.17	0.56	0.32	0.42	5.4	NS	0.32
P > P	60.01	60.01	NS	NS	NS	NS		< 0.01
Cattle Manure								
Control	1.10	0.49	3.65	2.01	2.21	61.6	73.4	1.10
Cm low	1.48	0.61	3.61	2.21	2.30	6.5	70.5	1.21
Cm medium	2.01	0.84	4.14	2.18	2.40	59.5	71.6	1.65
Cm high	2.10	0.60	4.15	2.04	2.61	61.4	72.6	1.80
Urea low	1.20	0.79	4.52	2.15	2.09	59.5	71.4	1.25
Urea medium	1.24	0.60	4.62	2.01	2.41	61.2	65.6	1.10
Urea high	1.31	0.70	3.49	1.98	0.30	62.4	62.4	1.28
LSD	0.68	0.20	4.01	0.46	0.20	7.9	11.6	0.66
P > R	0.01	< 0.05	1.12	NS	0.1	NS	NS	NS

Table 6
Distribution of Zn in Fractions in Dirkaniya Soil

Treatment	Pb-	Aci-	MnO^-	Om	FeO^-	Res-	Total	DTPA
				Mg Zn Kg $Soil^{-1}$				
Control	2.40	1.21	7.74	1.60	1.65	51.2	61.2	1.68
Manure	2.72	1.64	7.40	2.00	1.62	50.4	64.5	2.60

Total Zn determined by acid digestion

IV. Effect of Manure on Cu and Zn Fractions in Soil

Copper and Zn fractions responded differently to the addition of manure and urea in the Kudenda cropped land (tables 3 and 4).

The inability to distinguish the exchangeable (Ex) Cu and Zn in all the treatments both Kudenda and Dirkaniya soils tested reflects the limited importance of this fraction in these soils. The structural fractions also showed little change after series of addition of both cattle and swine manures compared to urea application. There is observed trend of increased Mn-oxide associated Cu in swine manure treatments, and the highest rate of swine manure had significantly higher MnO**-** bitractable Cu than the other treatments. A similar trend was observed in DTPA – extractable Cu in which the highest level of swine manure addition led to a small but significant increase in DTPA – extractable Cu in the Kudenda soil. Moderately labile Zn were detected and the results showed significant increase in this fraction in swine and cattle manure treatments in the Kudenda soil, especially in the medium and high rates applied. In Dirkaniya soils, an increase of moderately labile Zn was less than in the Kudenda soil probably due to low application rate. A small but significant increase of DTPA – Zn was also observed in both the Kudenda and Dirkaniya soils. Long term application of manure had led to increased Cu and Zn forms in the labile and moderately labile fractions (Han et al, 1999). This could be because of an important cumulative effect of manure additions and a decrease in the soil metal adsorption as fixation sites become saturated.

V. Conclusion

Repeated addition of liquid swine manure and solid cattle manure for a long period did not contribute significantly to total Cu and Zn in Kudenda and Dirkaniya soils. Some moderately labile Cu and Zn fractions, especially Zn increased only when large amounts of swine manure and cattle manure were applied. In general, liquid swine manure had less effect on increasing labile Cu and Zn fractions than cattle manure.

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