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# Effects of long term fertilizer use on trace metal levels of soils in a farm settlement

S.O. Ajayi<sup>1\*</sup>, B.O. Odesanya<sup>1</sup>, A.O. Avwioroko<sup>2</sup>, G.S. Adebambo<sup>2</sup> B. Okafor<sup>3</sup>

<sup>1</sup>College of Pure and Applied Sciences, Caleb University, Imota. Lagos State;

<sup>2</sup>Chemistry Department, University of Ibadan, Oyo State;

<sup>3</sup>National Institute for Horticultural Research, Ibadan, Nigeria.

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Long term use of fertilizers for agricultural purposes has been an issue of concern to researchers. The presence of metals in some agricultural fertilizers raised fears that continued use could lead to accumulation of these metals to toxic levels in the soil. We investigated the effects of long term fertilizer use on the distribution of selected trace metals in soils at the National Institute for Horticultural research (NIHORT), Ibadan, Oyo state where extensive agricultural practices have taken place for over 33 years. Results indicate that the total metal concentration after prolonged fertilizer use is of the order Mn>Zn>Pb>Cu>Cd. Metal concentrations obtained from the fertilized sites of the plots studied were higher than that of the unfertilized site. However, testing at  $P < 0.05$  indicate that there has not been significant accumulation of these metals due to prolonged fertilizer use. This indicates that the distribution of metals among the various metal fractions between fertilized/unfertilized sites have not changed significantly following the long-term use of fertilizers in the Institute(NIHORT). Recovery studies establish the accuracy of the results at 97% for copper and 84% for zinc in the carbonate fraction of typical fertilized and unfertilized soil samples.

**Keywords:** Trace metal concentration, fertilizers, agricultural practices.

## INTRODUCTION

Increased yields resulting from the use of crop fertilizers have adequately justified its introduction as an adjunct in agriculture. However, the discovery that some phosphorus and trace element fertilizers contained elevated quantities of metals like cadmium (Cd), lead (Pb), arsenic (As) and other metals of environmental concern that are either naturally derived from the geologic source of the fertilizer or very occasionally from recycled industrial by-products has instigated research into fertilizer usage especially over long periods.

Williams and David (1973) have shown that the average cadmium (Cd) content of Australian fertilizers manufactured in New South Wales over a 12-year period was 42ppm. They also showed that this value is highly correlated ( $r = 0.960$ ) with the mean zinc (Zn) content.

This encouraged a flurry of research activities to determine the long term effects of fertilizer use especially with respect to Cd and Zn. Rothbaum et. Al (1986) analyzed soils for Cd accumulation from three long-term experiments in England and one in New Zealand. The results indicated that at neutral pH, the A-horizon (0-22.5cm) of the soil absorbed very little Cd while about 25% of applied Cd was found in the B-horizon (22.5-45.0cm). At acidic pH, 50% of the applied Cd was found in the A-horizon with little in the B-horizon. They were thus able to conclude that differences in accumulation of Cd in soils was related to pH differences and/or organic matter content as well as the interplay of these two factors with adsorption and desorption of Cd and that the interaction of the applied Cd with soil organic matter apparently affected its mobility in soils. Mortvedt (1981) reported that Cd, Nickel (Ni) and Zn were not affected by Farmyard manure (FYM) and/or triple superphosphate (TSP) applications compared to control plots in top soils

\*Corresponding Author's E-mail: skipaodes@yahoo.com

of some plots but showed significant differences in Cd, Ni and Zn content on other plots. This further emphasizes the effects of soil properties on retention of these metals on application. Jones et al (2002) established that fertilized soils in general had significantly ( $P < 0.05$ ) lower levels of available and total metals than those of non-fertilized soils indicating that long-term fertilization does not increase metal concentration in soils. This was further confirmed by Franklin et al (2005) using NPK blends, phosphate and potash fertilizers at high application rates over a long period. These tally with the report of the investigation by McBride and Spiers (2001) who concluded that at the concentrations of Cd, Arsenic(As) and Molybdenum(Mo) in high-phosphorus fertilizers, agronomic rates of application would not significantly increase total soil concentrations above background levels for decades although their availability to plants for root uptake into tissue might increase. The results of these studies indicate that metal contamination of soils is dependent on location of the soil, fertilizer source and organic matter of the soil.

Trace element and heavy metal concentrations of common commercial fertilizers are low. However, high P-blended fertilizers and pure phosphate fertilizers contain relatively high levels of several elements of potential environmental concern like Cd, V, As, Mo, Cr, Ni, Pb, V, Sb and Be. It is generally agreed, however, that at the concentration levels of these metals in fertilizers, agricultural applications would not significantly increase total soil concentrations above background levels for decades although availability for root uptake into plants may increase. Heavy metals are known to occur in soil in a variety of chemical forms- water soluble, exchangeable but bound to specific sites of the organic and inorganic components and in the structure of primary and secondary minerals like et al (1984), with an equilibrium existing between these forms McLaren and Crawford (1993). Although this equilibrium may change due to changes in physical, chemical and biological properties of the soil Sims and Patrick (1978) and Sims (1986). In another study, Tu et al (2001), examined the influence of N, P and K application on various fractions in a red soil in China using the sequential extraction method and showed a similarity for distribution of heavy metals for treatments with N, P or K fertilizers using pH changes to explain the reduction in the soluble plus exchangeable fractions. They concluded that the application of fertilizers not only provides nutrients to plants but may also change the speciation and bioavailability of heavy metals in the soil.

At the National Horticultural research Institute (NIHORT), cultivated land has been subjected to fertilizer use for over thirty (30) years and the effects on background concentration and distribution of trace metals in the soils are largely unknown. This study sought to investigate these effects as well as its attendant environmental impacts. Since environmental impact depends on the

bioavailability/mobility of these metals, the evaluation is done by the method of chemical speciation using the sequential extraction method of Tessier et al (1979).

## MATERIALS AND METHOD

NIHORT is situated on a 350 hectare expanse of Land located between longitudes  $3^{\circ}5' - 7^{\circ}23'$  and  $7^{\circ}23' - 7^{\circ}25'$  north respectively. It enjoys tropical, humid climate with dry and rain seasons with an annual rainfall between 1220mm – 1280mm with temperature and humidity between  $20^{\circ}\text{C} - 34.7^{\circ}\text{C}$  and 62% - 96% respectively. Crops cultivated include citrus fruits, pineapple and vegetables and soil management practices include cover cropping, tillage, mulching, irrigation and use of fertilizers like NPK, organo-chemicals and poultry manure.

Paired (fertilized/non fertilized) sites were chosen from the citrus and vegetable farms. A pineapple farm close to a compost dump that has been in cultivation for about 3 years was also chosen. A fallow area used as control. The citrus farm had a 4-year history of fertilization with poultry manure while the vegetable plant, in addition to being irrigated during the dry season has a fertilizer (NPK 15-15-15) application history of over 10 years. The Auger soil sampler was used to obtain soil samples from these farms at 0 – 15cm and 15 – 30cm using the stratified sampling approach. The following sample coding and identification legend was adopted:

<u>Sample I.D.</u>	<u>Code</u>
<u>Citrus farm</u>	
Unfertilized plot top soil	CUT
Unfertilized plot sub soil	CUS
Fertilized plot top soil	CFT
Fertilized plot sub soil	CFS
<u>Vegetable farm</u>	
Unfertilized plot top soil	VUT
Unfertilized plot sub soil	VUS
Fertilized plot top soil	VFT
Fertilized plot sub soil	VFS
<u>Pineapple farm</u>	
Composite top soil	PT
Composite sub soil	PS
<u>Fallow land</u>	
Composite top soil	FT
Composite sub soil	FS

The samples were transferred onto clean, smooth wooden slabs and spread out to dry in a dust free environment. Each sample was ground with a mortar and pestle and passed through a 2.00mm sized sieve. The sieved samples were used for physicochemical analysis and chemical speciation studies. Tessier et al's method was used to obtain exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter and residue fractions.

**Table 1:** Selected soil properties of studied samples

Sample	pH	Organic carbon g/kg	Fe mg/kg	ECEC Cmol/kg	Particle size distribution		
					% clay	% silt	% sand
CFT	6.2	18.4	1393.52	22.1	5.40	9.40	85.2
CFS	6.2	29.3	1265.37	22.7	9.40	7.40	83.2
CUT	5.9	8.46	1510.09	18.7	9.40	5.40	85.2
CUS	5.7	13.9	1459.29	17.9	7.40	7.40	85.2
VFT	5.8	30.1	1368.01	19.9	13.4	25.4	61.2
VFS	5.9	14.4	1301.20	19.6	17.4	23.4	59.2
VUT	5.2	31.1	1318.61	18.5	3.40	25.4	71.2
VUS	5.6	16.9	1138.47	16.2	11.4	21.4	67.2
PT	5.6	12.4	1650.00	16.5	9.40	25.4	65.2
PS	5.3	6.30	1577.64	19.7	7.40	3.40	89.2
FT	6.3	20.7	1275.63	20.2	9.40	21.4	69.2
FS	5.9	14.0	1086.16	17.6	3.40	25.4	71.2

ECEC= Effective Cation Exchange Capacity

## Soil properties

Selected soil properties determined on the samples were total metal concentration by digestion using a 3:1 nitric acid, hydrochloric acid (aqua regis) mixture, soil pH using a calibrated pH meter on a 1:1 soil water mixture, soil organic matter by the modified Walkley-Black method, particle size distribution by the hydrometer method, effective cation exchange capacity (ECEC) by summation method and free Fe<sub>2</sub>O<sub>3</sub> using atomic absorption spectrophotometry after H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (pH 3.2) extraction. The results are presented in Table 1. Trace metal analyses were done using atomic absorption spectrophotometry (AAS) with the Buck 210 VGP. The method involved direct aspiration of the aqueous extract into the air-acetylene flame. Calibration curves were obtained for the metals from standards from 1000ppm solutions. The accuracy of the results were evaluated by recovery studies on a randomly chosen sample (VUS) for Cu. 4µg from a standard solution (10ppm) of copper was spiked into a sample of concentration 19.4 mg/kg and determined for copper. A recovery of 97% was obtained. Similar studies for zinc in the carbonate fraction of VUS and FS gave recoveries of 85% and 83% respectively.

## RESULTS

The results indicate a tendency towards higher pH (lower acidity) whenever fertilizer applications are made. This is accompanied by increase in organic carbon content and ECEC which indicate availability to the plants as

nutrients. However, there is a general reduction in Fe content on fertilizer application. Most of these increases are more profound in the sub soils.

Table 2 shows the results for total metal concentrations in the soil samples investigated: The results show slight increases in metal concentrations for fertilized sites which were found to be insignificant at  $P < 0.5$ . The concentrations of the metals are of the order Mn > Zn > Pb > Cu > Cd. The results indicate that there is no significant accumulation of these metals despite the use of fertilizers on the sites. Tables 3 to 7 show the distribution of the various trace metals in the different soil fractions.

## DISCUSSION

### Fractionation

For all the soils, including soils from the control plot, concentrations of Pb, Cd and Cu in exchangeable fraction were generally below their respective detection limits. Cd is a soft acceptor. Copper and lead are soft also, though less so than cadmium. Soft acceptors are poorly bound to hard donor (exchange) sites. In contrast, the concentration of Mn and zinc, which are typical hard acceptors, were relatively high in the exchangeable fraction. Carbonate in soil presents a hard donor environment. Consequently, carbonate-bound fraction for the metals is in the order: Cd << Cu ~ Pb < Zn < Mn, which is the order of increasing 'hardness' of the acids (acceptors). The hard metals (Mn and Zn) were found in

**Table 2:** Total metal concentrations in soil samples

Sample	Depth (cm)	Mn (mg/Kg)	Zn (mg/Kg)	Cu (mg/Kg)	Cd (mg/Kg)	Pb (mg/Kg)
CUT	0 – 15cm	348	51.6	4.59	0.82	8.69
CUS	15 – 30cm	317	56.4	2.52	0.82	<4.34
CFT	0 – 15cm	498	78.1	9.00	<0.23	11.9
CFS	15 – 30cm	522	91.1	13.0	1.05	6.52
VUT	0 – 15cm	1597	166	11.0	1.14	63.0
VUS	15 – 30cm	1518	130	19.4	0.87	48.3
VFT	0 – 15cm	1897	165	17.2	1.87	64.6
VFS	15 – 30cm	1678	131	17.8	1.10	46.7
PT	0 – 15cm	306	44.2	5.91	0.54	27.1
PS	15 – 30cm	231	21.6	6.77	<0.23	9.78
FT	0 – 15cm	869	107	12.9	0.46	50.0
FS	15 – 30cm	652	64.8	9.98	0.78	15.7

**Table 3:** Distribution of Cu among the various soil fractions

Sample	Depth (cm)	Soil fractions (mg/kg)				
		1	2	3	4	5
CUT	0 - 15	<0.01	0.87	0.53	1.03	1.08
CUS	15 - 30	<0.01	1.09	0.76	0.85	1.22
CFT	0 - 15	<0.01	0.51	1.91	2.16	2.89
CFS	15 - 30	<0.01	4.50	1.68	3.31	3.82
VUT	0 - 15	0.02	0.76	0.94	1.45	5.27
VUS	15 - 30	<0.01	0.51	1.40	0.60	5.63
VFT	0 - 15	0.13	0.93	2.02	2.39	6.41
VFS	15 - 30	0.28	0.28	2.20	1.56	6.84
PT	0 - 15	<0.01	1.07	1.77	1.01	0.19
PS	15 - 30	0.17	0.64	1.56	0.60	1.19
FT	0 - 15	0.32	0.35	0.80	2.30	5.22
FS	15 - 30	<0.01	0.70	0.92	0.87	4.29

1 Exchangeable, 2 bound to carbonates, 3 bound to iron and manganese oxides, 4 bound to organic matter, 5 residual

their highest concentrations in the Fe-Mn bound fraction. The sequence in this case is Cd << Cu < Pb < Mn. This indicates that the Fe-Mn phase of the soil behaves as a hard base. The order of bonding in the Organic Matter

fraction is Pb < Zn < Cd < Cu < Mn. Cadmium is best bound to this phase, probably because it is the softest phase of all. The sequence seems distorted by the natural abundance of the metals. Fe-Mn Phase is the

**Table 4:** Distribution of Zn among the various soil fractions

Sample	Depth (cm)	Soil fractions (mg/kg)				
		1	2	3	4	5
CUT	0 - 15	4.24	3.56	9.39	<0.17	1.28
CUS	15 - 30	3.85	1.91	11.4	<0.17	<0.01
CFT	0 - 15	3.52	11.3	30.7	<0.17	4.00
CFS	15 - 30	5.53	12.7	24.0	<0.17	5.85
VUT	0 - 15	11.6	9.34	54.4	4.99	26.0
VUS	15 - 30	3.01	4.34	45.6	3.23	24.6
VFT	0 - 15	5.85	7.70	53.1	5.09	20.4
VFS	15 - 30	3.83	3.90	41.9	0.92	22.1
PT	0 - 15	6.23	1.48	8.22	<0.17	0.02
PS	15 - 30	4.24	2.93	0.40	<0.17	0.98
FT	0 - 15	3.91	5.48	42.6	<0.17	13.8
FS	15 - 30	2.37	3.15	19.1	0.34	8.58

1 Exchangeable, 2 bound to carbonates, 3 bound to iron and manganese oxides, 4 bound to organic matter, 5 residual

**Table 5:** Distribution of Cd among the various soil fractions

Sample	Depth (cm)	Soil fractions(mg/kg)				
		1	2	3	4	5
CUT	0 - 15	<0.03	<0.01	0.15	0.77	<0.01
CUS	15 - 30	<0.03	<0.01	0.57	0.71	<0.01
CFT	0 - 15	<0.03	0.02	<0.08	0.37	<0.01
CFS	15 - 30	0.06	<0.01	0.22	0.13	<0.01
VUT	0 - 15	0.15	<0.01	0.20	0.27	<0.01
VUS	15 - 30	<0.03	<0.01	0.24	0.33	<0.01
VFT	0 - 15	<0.03	<0.01	0.27	0.29	<0.01
VFS	15 - 30	0.09	<0.01	0.18	0.44	<0.01
PT	0 - 15	<0.03	0.24	<0.08	<0.06	<0.01
PS	15 - 30	<0.03	0.32	<0.08	0.40	<0.01
FT	0 - 15	0.10	<0.01	<0.08	1.03	<0.01
FS	15 - 30	<0.03	0.04	<0.08	0.16	<0.01

1 Exchangeable, 2 bound to carbonates, 3 bound to iron and manganese oxides, 4 bound to organic matter, 5 residual

**Table 6:** Distribution of Pb among the various soil fractions

Sample	Depth (cm)	Soil fractions (mg/kg)				
		1	2	3	4	5
CUT	0 - 15	<0.96	2.35	7.39	0.43	<8.15
CUS	15 - 30	<0.96	<0.18	6.52	1.30	<8.15
CFT	0 - 15	<0.96	<0.18	7.17	<0.22	<8.15
CFS	15 - 30	<0.96	2.78	17.0	0.43	<8.15
VUT	0 - 15	<0.96	1.04	24.1	<0.22	16.3
VUS	15 - 30	<0.96	0.43	24.8	<0.22	16.6
VFT	0 - 15	<0.96	5.04	23.7	<0.22	21.2
VFS	15 - 30	<0.96	<0.18	20.4	<0.22	86.4
PT	0 - 15	<0.96	0.35	6.30	<0.22	<8.15
PS	15 - 30	<0.96	4.96	3.91	<0.22	<8.15
FT	0 - 15	1.91	0.43	23.7	19.8	11.3
FS	15 - 30	<0.96	0.96	16.9	<0.22	10.4

1 Exchangeable, 2 bound to carbonates, 3 bound to iron and manganese oxides, 4 bound to organic matter, 5 residual

most efficient phase for the binding of metals in the soil. The phase has been described as a scavenger for trace metals Joan et al (1992).

### Accumulation

There is no clear-cut accumulation trend for cadmium both in the total form and in the organic matter bound form. The highest fraction of Cd found in the different sites studied was 1.03 ppm for the organic matter fraction in the fallow soil sample. The highest level of cadmium recorded was the total level of 1.87mg/kg in topsoil of the fertilized vegetable farm. All these reflect background concentration.

Concentrations of Mn, Zn and Cu in the carbonate-bound fraction were higher for the fertilized sites of the citrus plot but the differences were insignificant at  $P < 0.05$  when compared with those of the unfertilized site. Cd, Cu, Zn, Mn and Pb were all found in all the plots in detectable quantities. However, no statistically significant

difference was obtained between the concentrations found in the plots in comparison with that of the fallow site.

### Fe-Mn bound

The fertilized site of the citrus plot had higher concentrations of Zn and Cu than the unfertilized site. This may probably be due to the use of poultry manure in the fertilized site as it has been reported to contain elevated levels of Zn and Cu McBride and Spiers (2001).

For the vegetable plots, the concentrations of Cd, Pb and Zn were similar for both fertilized and unfertilized sites. Concentrations of Mn and Cu were however higher for the fertilized plot than the unfertilized plot probably as a result of the organic fertilizer applied in the fertilized site. However, the differences (though insignificant) in metal concentration obtained between the pineapple and fallow sites for Pb, Cu, Zn and Mn may be due to removal of

**Table 7:** Distribution of Mn among the various soil fractions

Sample	Depth (cm)	Soil fractions (mg/kg)				
		1	2	3	4	5
CUT	0 - 15	22.8	11.5	119	0.64	1.05
CUS	15 - 30	23.3	8.45	121	0.84	11.3
CFT	0 - 15	30.2	22.2	113	1.63	12.1
CFS	15 - 30	29.3	20.1	153	1.86	16.7
VUT	0 - 15	66.3	40.5	788	34.0	50.5
VUS	15 - 30	33.0	28.1	797	24.5	40.6
VFT	0 - 15	40.3	39.0	849	41.6	52.7
VFS	15 - 30	8.96	23.7	864	45.8	48.9
PT	0 - 15	29.7	6.85	88.2	0.61	5.34
PS	15 - 30	32.2	8.19	79.6	0.97	6.16
FT	0 - 15	30.1	23.9	552	37.1	21.8
FS	15 - 30	26.8	21.2	158	7.93	17.3

1 Exchangeable, 2 bound to carbonates, 3 bound to iron and manganese oxides, 4 bound to organic matter, 5 residual

plant material at harvest combined with enhanced oxidation of organic matter from tillage practices on the pineapple plot.

### Exchangeable fractions

Manganese accumulated ( $p < 0.5$ ) in both the top and sub-soils of the fertilized citrus experimental plots. An average increase of 29% was recorded. However, manganese accumulated in the top and sub-soils of the unfertilized vegetable experimental farm, at levels of 64.5 and 268% respectively compared to the fertilized soils. Statistical evaluation of the differences between the concentrations of metals found in the plot with those in the fallow site was insignificant at  $p < 0.05$  indicating the non-influence by the compost dump on the pineapple plot on the concentrations of metals.

The results of metal concentrations obtained from the fertilized sites of all the plots studied were generally insignificantly higher than that of the unfertilized site. Similarly, no significant accumulation of the metals was found for metals bound to carbonates and metals bound to organic matter.

### CONCLUSION

From the studies carried out on the respective plots, there were no significant increases over time in the background concentrations of trace metals in the soils of NIHORT due to long-term fertilizer use.

Chemical speciation of the trace metals carried out also showed no significant changes in the distribution of the metals among the different fractions. Generally, low

values were obtained for all metals except Mn in the exchangeable fraction which is readily available for plant uptake. However, the minor differences found between the fertilized/unfertilized sites could be attributed to differences in soil properties (texture, pH, organic matter) and probably fertilizer type but these differences however were not enough to cause significant changes in the distribution/enrichment of metals in soils.

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