# Levels of Toxic Metals in Soil from Irrigated Farmland in Kaduna Metropolis, Nigeria

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Abstract: Levels of Cd, Co, Cr and Pb in (mg/kg) were determined in topsoil from an irrigated farmland using Atomic Absorption Spectrophotometer (AAS). The soil physico-chemical parameters, pH and percentage organic matter (%OM) content were also determined. Levels of Cd, Co, Cr and Pb in the soils were 0.17-0.50, 1.50-7.00, 1.00-6.00 and 7.00-69.00 mg/kg dry weight, respectively. The soil pH showed slightly acidic to neutral which ranged from 4.27-7.63 and the mean pH was  $6.05\pm0.84$  while the soil percentage organic matter ranged from 0.17-2.52% and the mean percentage organic matter content was  $1.19\pm0.74$ . The mean concentrations of soil samples studied were found to follow the decreasing orders; Pb > Co > Cr > Cd respectively. There is correlation between soil physico-chemical parameters and metals such as Co, Cr and Pb in soil samples. The toxic elements were examined for dependency upon some soil factors through the use of correlation analysis, pH and organic matter. pH correlated positively with Pb indicating that this factor largely controls the concentration of these element in the soil. The study has found out that the use of river water from these sites for irrigation has increased the contamination of Pb in the soils which can lead to plant uptake causing potential health risk in the long term from this practice.

**Keywords:** Toxic metals, topsoil, irrigated farmland, correlation analysis.

## 1. Introduction

Heavy metal pollution can arise from many sources but most commonly arises from the purification of metals, e.g., the smelting of copper and the preparation of nuclear fuels. Electroplating is the primary source of chromium and cadmium. Through precipitation of their compounds or by ion exchange into soils and muds, heavy metal pollutants can localize and lay dormant. Heavy metals, such as cadmium, copper, lead, chromium and mercury, are important environmental pollutants, particularly in areas with high anthropogenic pressure. Their presence in the atmosphere, soil and water, even in traces, can cause serious problems to all organisms. Heavy metal accumulation in soils is of concern in agricultural production due to the adverse effects on food quality (safety and marketability), crop growth (due to phytotoxicity) Ma et al. 1994; Mskaky and Calvert, 1990; Fergusson, 1990 and environmental health (soil flora/fauna and terrestrial animals). The mobilization of heavy metals into the biosphere by human activity has become an important process in the geochemical cycling of these metals. This is acutely evident in urban areas where various stationary and mobile sources release large quantities of heavy metals into the atmosphere and soil, exceeding the natural emission rates Nriagu, 1989; Bilos et al. 2001. Heavy metal bioaccumulation in the food chain can be especially highly dangerous to human health. These metals enter the human body mainly through two routes namely: inhalation and ingestion, and with ingestion being the main route of exposure to these elements in human population. Heavy metals intake by human populations through the food chain has been reported in many countries with this problem receiving increasing attention from the public as well as governmental agencies, particularly in developing countries.

Soil contamination is caused by the presence of man-made chemicals or other alteration in the natural soil environment. This type of contamination typically arises from the rupture of underground storage tanks, application of pesticides, and percolation of contaminated surface water to subsurface strata, oil and fuel dumping, leaching of wastes from landfills or direct discharge of industrial wastes to the soil. The most common chemicals involved are petroleum hydrocarbons, solvents, pesticides, lead and other heavy metals. The occurrence of this phenomenon is correlated with the degree of industrialization and intensity of chemical usage. The concern over soil contamination stems primarily from health risks, both of direct contact and from secondary contamination of water supplies EPA, 1993.

# 2. Materials and Methods

## Reagents and Glasswares

All the chemicals used for this work were of analytical grades obtained from AG Scientific Kaduna. Deionised water was used throughout the work. All glass wares used were soaked in 20% HNO3 over night and then washed with detergent, thoroughly rinsed with tap water and then with deionised water.

## **Sampling Sites**

The research was carried out on soil collected from irrigated farmlands around Kaduna metropolis between the months of June and July, 2009. The samples were collected from farm sites/locations in Nassarawa area.

# **Sample Collection**

Soil samples were collected from irrigated farmlands within the vicinity of Kaduna State, Nigeria. The sampling process was random; at each sampling point four (4) sub-samples from the top layer were collected at a depth of 0-20cm and 20m apart using a stainless steel auger. The collected sub-samples were then pooled together to form a composite of each individual sample. Control samples were also collected from a less suspected contaminated soil and these gave twenty nine (29) samples altogether. The samples were collected in clean polythene bags and transported to the

laboratory for further processing.

# Sample Pre-Treatment

The different soil samples were air-dried in the laboratory for a week, after which it was pulverized and passed through a 2.0-mm sieve (for pH and total metal ) while for Organic Matter (OM), some portion of the individual sieved soil samples were further pulverized to fine powder and passed through 0.5-mm sieve.

# 3. Experimental

# **Soil Properties**

Some properties of the soil samples investigated were determined using standard methods. Soil pH was determined using deionized water in the ratio 1:1 (soil: water) suspension according to Tan 1996, percentage organic matter was determined by Walkley-Black titration method.

## **Digestion of Samples**

# Soil samples

5g of the air-dried soil samples were placed in 250 cm<sup>3</sup> conical flask and 50cm3 of 2M HNO3 was added and placed in a boiling water bath for 2hrs after which it was filtered with a Whatman (110mm) filter paper into a 50cm3 volumetric flask for metal analysis Onianwa and Fakayode 2000.

# 4. Analysis

Appropriate working standards were prepared for each of the metal solution by serial dilution of the stock solutions. Each of the sets of serial dilutions was then aspirated one after the other into the Atomic Absorption Spectrometry and their absorbance recorded. The sample solutions were also aspirated one after the other and the absorbance recorded. Calibration curves were plotted for each of the trace metals standard using absorbance against concentrations (ppm) and the actual concentration of the metal interpolated from the curves.

### 5. Results and Discussions

## **Soil Properties**

The values of pH obtained from all the sites of the farmlands were weakly acidic to neutral (Table 1).

**Table 1:** Total metal content (mgkg<sup>-1</sup>), pH and %OM Cd Co Pb OM (%) Sites Cr pН  $(H_2O)$ 

Site 1							
1	ND	3.50	1.00	10.00	6.03	0.66	
2	ND	3.00	1.00	12.00	6.53	0.59	
3	ND	3.80	2.00	15.00	6.26	0.41	
4	ND	3.00	4.00	13.00	5.83	0.69	
5	ND	3.90	2.5	19.00	6.31	0.66	
6	ND	2.50	5.00	7.00	6.75	1.00	
7	ND	2.80	ND	8.00	5.91	0.48	
8	ND	2.80	1.00	9.00	6.01	1.52	

Site 2						
1	0.18	4.00	ND	27.00	6.77	1.52
2	0.18	5.50	2.00	16.50	6.47	0.52
3	0.18	7.00	5.00	19.00	6.30	0.88
4	0.19	4.80	3.00	22.0	6.39	0.17
5	0.20	4.70	6.00	69.00	6.92	1.38
6	0.40	4.80	4.00	23.00	7.23	1.59
7	0.18	5.00	1.00	37.00	7.39	2.46
8	0.35	3.00	1.00	17.00	6.46	1.88
9	0.40	3.80	1.00	12.00	5.64	1.07
Site 3						
1	0.40	3.5	2.00	23.00	4.95	1.49
2	0.40	3.5	4.00	25.00	4.89	2.49
3	0.17	3.00	6.00	22.50	6.19	0.17
4	0.30	3.00	4.00	25.00	5.93	2.52
5	0.20	3.50	4.00	18.00	5.05	1.80
6	0.19	2.50	3.00	20.00	6.89	0.59
7	0.50	1.50	ND	22.60	7.63	0.24
8	0.20	2.00	4.00	9.00	5.76	0.35
Control						
Site						
1	ND	2.00	1.00	6.0	4.98	1.42
2	ND	2.80	1.00	7.00	4.79	2.31
3	ND	2.00	ND	6.00	4.86	1.73
4	ND	3.00	1.00	10.50	4.27	1.78
ND- Not I	Detecto	d				

ND= Not Detected

Table 2: Range, median, mean and SD of soil physicochemical parameters of irrigated farmlands in Kaduna

	metroj	metropolis s						
Sites	Range	Median	Mean_+ SD*					
Site 1								
$(n^a = 8)$								
pН	5.83-6.75	6.15	$6.20\pm0.32$					
OM (%)	0.41-1.52	0.66	$0.75\pm0.36$					
C:4- 2								
Site 2 $(n^a = 9)$								
pH	5.64-7.39	6.47	6.62±0.50					
OM ( % )	0.17-2.46	1.38	1.27±0.66					
0111 ( 70 )	0.17 2.10	1.50	1.27_0.00					
Site 3								
$(n^a = 8)$	4.89-7.63	5.85	5.91±0.98					
pН	0.17-2.52	2.01	1.21±-0.99					
OM (%)								
Control Site	4.27-4.98	4.83	4.73±0.31					
$(n^a = 4)$	1.31-2.39		1.81±0.37					
(II – 1)	1.31 2.37	1.70	1.01±0.57					
All Soils								
pН	4.27-7.63	6.19	$6.05\pm0.84$					
OM (%)	0.17-2.52	1.07	$1.19\pm0.74$					
*= Standard Deviation								
Number of Samples								

SD na= Number of Samples

The pH values ranged from 4.27-7.63. An average pH value

for all the soils studied within the vicinity was  $6.05 \pm 0.84$  (Table 2). The value is slightly lower than the mean pH value of 6.40 reported by Iyaka and Kakulu 2009 but higher than the mean pH value of 5.2 reported by Onofiok and Ojobo 1993 in their studies of some agricultural soils.

The soil organic matter had concentrations which ranges from 0.17 -2.52% for the farmland with an average concentration values of  $1.19 \pm 0.74\%$  of the soils studied in that vicinity (Table 2). The presence of organic matter has a significant effect on the mobility and bioavailability of heavy metals Bergkvist et al. 1989; de la Rosa et al. 2003; Weng et al. 2004. Furthermore, it has also been reported that about 50% of the total heavy metals in organic rich soils are retained with organic substances Smagunova et al. 2004.

#### **Total metal content**

#### **Cadmium**

The concentrations of Cd, Co, Cr, and Pb are shown in Table 1. Cd was not detected in samples obtained from site 1 and the control site Table 2. However, samples from sites 2 and 3 had detectable Cd with concentrations ranging from 0.18-0.4 mg/kg and 0.17-0.5 mg/kg for sites 2 and 3 Table 3. The average concentrations value of Cd from all the soils is 0.27±0.11 mg/kg (Table 4). The concentration range was higher than the concentration range of 0.07-0.3 mg/kg reported by Agbenin et al. 2009, likewise is higher than 0.2 mg/kg recommended by FAO/WHO, 2001 but was at lower concentrations than the maximum tolerable levels proposed for agricultural soil, 90 - 300 mg/kg Kabata- Pendias and Dudka, 1991. The highest concentration of Cd was found in site 3 (Table 4.4). The values of Cd obtained in the two sites were below the recommended 1-3mg/kg limit by EU. Although, the sources of Cd in the urban cities could be due to metal plating and tyre rubber Hewitt and Rashed, 1988, In the 2 sites where Cd was detected, the levels of Cd could be ascribed to industrial run-off of site 2 and lubricating oils as well as the burning of old tyres that are frequently dumped close to site 3.

## Cobalt

Co had a concentration range of 2.5-3.90 mg/kg, 3.0-7.0 mg/kg and 1.5-3.5 mg/kg for the 3 sites studied (Table 3). The average concentrations of all the soils studied is 3.62±1.19mg/kg (Table 4). The values obtained were lower than the concentration range of 7-65 mg/kg reported by Agbenin et al. 2009 in their study but slightly higher than those obtained by Aller and Deban, 1989 but similar to those reported by Andreu and Gimeno-Garcia 1996 in their study.

### Chromium

The concentration of Cr of all soils studied ranged from 1.0-6.0 mg/kg. The average concentration in all the soils of the irrigated farmland is  $3.02\pm1.68$  mg/kg (Table 4). The concentration range of Cr in this study were however lower than the range reported value of 7-65 mg/kg reported by Savoskull and Drechsel, 2003.

Lead

Pb contents in the soil samples of this study ranged from 7.0-69.0 mg/kg. The average mgPbkg-1 in all the soils is 20.02±12.43 mg/kg (Table 4). The results showed that samples from site 2 gave considerable amount of Pb (Table 3). On the other hand, Pb was lower than EU upper limit of 300 mg/kg EC, 1986 also lower than the values of 2.02-2125.83 mgkg-1 reported by Uda-Umar and Iyaka, 2004 in their study of levels of copper and Pb in soils of Bida Brass industrial sites. The values of Pb in this study were insignificantly higher than the 90 - 300 mg/kg maximum tolerable levels proposed for agricultural soil Kabata -Pendias and Dudka, 1991. The concentrations of Pb in the soils analyzed varied but were similar to those reported by Okunola et al. 2007. The highest concentration level of Pb obtained in the present study was above the reported background values of 25 mg/kg Pb in soil Canadian Environmental Quality, 1992 and also close to the maximum allowable limit of background values of 70mg/kg Pb in agricultural soils Canadian Environmental Quality, 1999. The highest Pb concentration values found in site 2 could be ascribed to accumulation of Pb, possibly due to industrial run-off into the river which is used for irrigation. Furthermore, one of the sources of Pb obtained in the soil samples from site 3 in the present study may be due the deposition of Pb from vehicles emission.

# **6.** Correlation Analysis

Some of the heavy metals are significantly correlated with each other. Pb correlated positively with pH. There was positive correlation of Co and Cr with Pb. This is an indication that pH is responsible for the bioavailability of Pb in that soil and Co, Cr and Pb have the same source in that soil. Furthermore, there was negative correlation of Co, Cr and Pb with Cd indicating different source(s) of Cd contamination.

**Table 3:** Summary of the total metal contents (mgkg-1) of irrigated farmlands in Kaduna based on sites

Sites	Metal	Range	Median	Mean ± SD
Site 1 $(n^a = 8)$	Cd	ND	ND	ND
	Co	2.5-3.90	3.00	$3.16\pm0.51$
	Cr	1.0-5.00	2.00	$2.36\pm1.60$
	Pb	7.0- 19.00	110	11.63±4.0
Site 2 $(n^a = 9)$	Cd	0.18- 0.40	0.19	0.25±0.10
	Co	3.0-7.00	4.80	4.74±1.13
	Cr	1.0-6.00	1.50	$2.87\pm1.96$
	Pb	12.0- 69.00	22.00	26.94±17.34
Site 3 $(n^a = 8)$	Cd	0.17- 0.50	0.25	0.30±0.15
	Co	1.5-3.5	3.00	2.81±0.75
	Cr	BDL- 1.00	4.00	3.86±1.21
	Pb	9.0-25.0	22.55	20.64±5.26

Control $(n^a = 4)$	Site	Cd	ND	ND	ND
()		Co	2.0-3.0	2.40	$2.45 \pm 0.53$
		Cr	1.00	1.00	$1.00\pm0.00$
		Pb	6.0-10.5	6.50	$7.38 \pm 2.14$

**Table 4:** Summary of range, median and mean ±SD concentrations of all soils of irrigated farmlands in Kaduna

Metal Range		Median	Mean ± SD
Cd	0.17-0.50	0.20	0.27±0.11
Co	1.5-7.00	3.00	3.62±1.19
Cr	1.0-6.00	2.00	3.02±1.68
Pb	7.0-69.00	18.00	20.02±12.43

**Table 5:** Correlation of pH and OM (%) with Metals

FACTOR	Cd	Co	Cr	Pb
Cd	1.000			
Co	-0.38924	1.000		
Cr	-0.33882	0.191587	1.000	
Pb	-0.16705	0.434696	0.45262	1.000
pН	-0.08978	0.276411	0.244838	0.439831
%OM	0.203266	0.024821	-0.18202	0.176649

# 7. Conclusion

The total metal contents of the soils studied are in the ranges considered normal in soils; only Pb showed levels slightly higher than the reported normal ranges. This could be ascribed to the dumping of Pb materials in the water used for irrigation. Mobility of these metals in the soils studied are in the decreasing order, Pb > Co > Cr > Cd. However, the obtained mean values of heavy metals in all the sites studied are higher than that found in the control site. The findings of this study indicates need for constant monitoring of the levels of the heavy metals in the agricultural farmlands or soils in order to assess further increase in the accumulation of these metal especially for Pb due to their potential risks at high concentrations to life and the environment.

# References

[1] J.O., Agbenin, M. Danko, and G., Welp, G., Soil and Vegetable Compositional Relationships of Eight Potentially Toxic Metals in Urban Garden Fields from Northern Nigeria, Journal of the Science of Food and Agriculture, 89(1), pp. 49-54, 2009

- [2] A.J. Aller, and L., Deban, Total and Extractable Contents of Trace Metals in Agricultural Soils of the Valderas Area, Spain. Science of Total Environment, 79(3), pp. 253-270 1989
- [3] V. Andreu, and E. Gimeno-Garcia, Total Content and Extractable Fraction of Cd, Co, Cu, Ni Pb and Zn in Calcareous Orchard Soils. Community of Soil Science, Plant Analysis, 27(23 and 14), pp. 2633-2648 1996
- [4] B., Bergkvist, L., Folkenson, and D., Berggren, Fluxes of Cu, Zn, Pb, Cd, Cr and Ni in Temperate Forest Ecosystems. A literature review, Water, air and soil pollution, 47, pp. 217-286 1989
- [5] C., Bilos, J.C., Colombo, C.N. Skorupka, and M.J. Rodriguez Presa, Sources, Distribution and Variability of Airborne Trace Metals in La Plata City Area, Argentina, Environmental Pollution, 111(1), pp. 149-158, 2001
- [6] Canada Council of Ministers of the Environment, 'Canadian Soils Environmental Quality for Contaminated Sites', Report CCME EPCC, Winnipeg, Manitoba 1992
- [7] Canadian Council of Ministers of the Environment, 'Canadian Quality Guidelines for the Protection of Environmental and Human Health: Summary tables. In Canadian Soil Quality Guidelines, Canadian Council of Ministers of the Environment, Winnipeg 1999
- [8] G., De la Rosa, J.R. peralta-Videa, and J.L. Gardea-Torresdey, Utilization of ICP/OES for the Determination of Trace Metals Binding to Different Humic Fractions. Journal of Hazardous Materia, 97, pp. 207-218 2003
- [9] European Commission (EC), European Commission, Office for Official Publications of the European Communities, Luxembourg, Council Directive 66/278/EEC on the Protection of Environment, and in Particular of Soil, when Sewage Sludge is used in agriculture 1986
- [10] EPA, Risk Assessment Guidance for Superfund, Human Health Manual, Office of Emergency and Remedial Response, U.S. Washington D.C. 20450 1993
- [11]FAO/WHO, Food Additives and Contaminants, Joint FAO/WHO Food Standards Programme, 2001. ALINORM 01/12A, pp. 1-289, 2001
- [12] J.E. Fergusson, 1990. The Heavy Element, Chemistry, Environmental Impact and Health Effects, Pergamon Press, Oxford, pp. 18-19, 27-40, 55-79
- [13] C.N. Hewitt and M., Rashed "Proc. Int. Conf. Chemicals in the Environment, pp. 5-10 1988
- [14] Y.A Iyaka and S. E Kakulu, Copper and Zinc Content in Urban Agricultural Soils of Niger State, Nigeria, 3 (3), pp. 23-33, 2009
- [15] A. Kabata-Pendias and S. Dudka, Trace Metal Contents of Taraxacum Officinale Dandelion as a Convenient Environmental Indicator. Environmental Geochemistry of Health, 13(2), pp. 108-113, 1991
- [16] Q.Y. Ma, S.J. Traina, and T.J. Logan, Effects of Aqueous Al, Cd, Fe (11), Ni and Zn on Pb Immobilization by Hydroxyapatite. Environmental Science and Technology, 28(7), 1219-12281994
- [17] J.J. Mskaky, and R. Calvert, AdsorptionBehaviour of Copper and Zinc in Soils: Influence of pH on Adsorption Characteristics. Soil Science, pp. 150, 513-522, 1990
- [18] U. I. Nda-Umar, and Y.A. Iyaka, Levels of Copper and Lead in Soils of Bida Industrial Sites. Journal School of

- Environmental Studies, Federal, Polytechnic Bida, Niger State, 23, 29, 2004
- [19] J.O. Nriagu, A Global Assessment of Natural Sources of atmospheric Trace Metals, Nature, 338(6210), pp. 47-49, 1989
- [20] P.C. Onianwa, and S.O. Fakayode, Lead Contamination of Topsoil and Vegetation in the Vicinity of a Battery Factory in Nigeria. Environmental Geochemistry and Health, 22, pp. 211-218 2000
- [21] O.E. Onofiok, and G.O. Ojobo, Inventory of Some Physico-chemical Characteristics of Some Nigerian Soils and their Relationship with Moisture Retention, Plasticity and Sealing Propensity. Samaru Journal of Agricultural Research, 10, pp. 15-27, 1993
- [22] O.S Savoskul, and P. Drechsel , Heavy Metal Concentrations in Urban and Peri-urban Gardens of Dzerzhinsk and Nizhny Novgorod, Russia, City Farmer, Canada's Office of Urban Agriculture, pp. 4-48 2003
- [23] A. N., Smagunova, U.V., Ondar, E. I., Molchanova, H.V., Vashukevich, V. A. Kozlov, and N.G. Aprelkov, X-ray Florescence Determination of Heavy Metals in Humic Acids .Journal of Analytical Chemistry, 59, pp. 1066-1072, 2004
- [24] K.M. Tan, Soil Sampling Preparation and Analysis, (Mercel Dekkes. Inc: New York. Basel. Hong Kong) 1996
- [25] A. Walkley, and I. A. Black, An Examination of the Detjare Method for Determining Soil Organic Matter and a Proposed Modification of the Chromic Acid Titration. Soil Science, 37, pp. 29-36 1934
- [26] L.P., Weng, A., Wolthoom, T.M. Lexmond, E.J.M. Temminghoff, and W.H.O. Van Riemsdijk, Understanding the effects of soil characteristics on phytotoxicity and bioavailability of Ni using speciation models, Environmental Science and Technology, 38, pp. 156-162, 2004

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