

Assessment of Toxic Metals in Soil and Vegetable Samples from Irrigated Farmland in Kaduna Metropolis, Nigeria

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Abstract: Levels of Cd, Cr and Pb in (mg/kg) were determined in topsoil and vegetable samples from irrigated farmland using Atomic Absorption Spectrophotometer (AAS). The vegetables available as at the time of sampling and sample collection were spinach and 'yakuwa' leaves. The soil physico-chemical parameters, pH and percentage organic matter (%OM) content were also determined. Levels of Cd, Cr and Pb in all the soils were 0.1-6.5, 2.00-38.00 and 2.90-24.00 mg/kg dry weight, respectively. Concentration ranges of all the plants were 0.01-1.00, 0.80-8.00 and 0.20-11.00 mg/kg dry weight for Cd, Cr and Pb respectively. The soil pH showed slightly acidic to neutral which ranged from 5.05-7.50 while the soil percentage organic matter ranged from 0.29-2.23%. The mean concentrations of soil and plant samples studied were found to follow the decreasing orders; Cr > Pb > Cd and Pb > Cr > Cd respectively. There is correlation between soil physico-chemical parameters and metals such as Cr and Pb in soil samples while for vegetable plants there is correlation between metals such as Cd, Cr and Pb content. The levels of toxic metals are within tolerable levels except for Cd in soil and Pb in vegetable samples that has values which are higher than the FAO/WHO recommended values. The slightly high level of Pb in the vegetables could be ascribed to deposits of the metal from vehicle emissions.

Keywords: Toxic metals, soil, vegetables, irrigated farmland, correlation

1. Introduction

Soil contamination by heavy metals due to anthropogenic activities has remained a great problem all over the world especially in developing countries. Anthropogenic activities as agricultural processes, industrialization and domestic activities have caused the increase of heavy metals in soils and plants grown on such soils. The processes could also affect surface and ground water.

Some trace heavy metals are significant in nutrition, either for their essential nature or their toxicity. Metals such as chromium, cobalt, copper, iron, manganese and zinc are essential with known biochemical functions Underwood, 1971 while lead and cadmium are non-essential with toxic effects.

The main sources of heavy metals to vegetable crops are their growth media (soil, air, nutrient solutions) from which these are taken up by the roots or foliage. Vegetables constitute essential diet components by contributing protein, vitamins, iron, calcium and other nutrients, which are usually in short, supply Thompson and Kelly, 1990. They also act as buffering agents for acidic substances produced during the digestion process. However, they contain both essential and toxic elements over a wide range of concentrations. Metal accumulation in vegetables may pose a direct threat to human health Türkdogan et al., 2003. Vegetables take up metals by absorbing them from contaminated soils, as well as from deposits on different parts of the vegetables exposed to the air from polluted environments Zurera-Cosano et al., 1989.

Fruits and vegetables are of great nutritional value. They are important sources of vitamins and minerals, thus, essential

components of human diet. Consequent upon this, there had been increased trade/commerce activities surrounding these commodities Egharevba, 1995.

Kaduna metropolis (Lat. 10.52_N, Long. 7.44_E) located in Kaduna state occupies central portion of Northern Nigeria (Kaduna, 2005). Founded in 1917 as an administrative headquarters of Northern Nigeria, it is presently one of the most important cities in the country. As at 1991 census it had a population of 993,600 but projected to be about 1.56 million people WG, 2005.

Vegetables mostly grown by irrigation are spinach, tomatoes, onion, pepper pumpkin and 'yakuwa'. The aim of this work is to determine the content of toxic metals in soil and vegetables from a suspected contaminated site of irrigated farmlands around Malali area in Kaduna City.

2. Materials and Methods

2.1 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.

2.2 Sampling Sites

The research was carried out on soil and vegetable samples collected from irrigated farmlands around Kaduna metropolis between the months of May and June, 2010. The samples were collected from farm sites/locations in Malali area.

3. Sample Collection

Soil and vegetable 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. The soil and vegetable samples were collected from Malali area with a source of water close to the farmland. Control samples were also collected from a less suspected contaminated soil and these gave thirty four (34) samples altogether. The vegetables available at the time of sampling were spinach and 'yakuwa' but at the control site only spinach was available. The samples were collected in clean polythene bags and transported to the laboratory for further processing.

4. 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 (this is for pH and Total Metal) while for Organic Matter, some portion of the individual sieved soil samples were further pulverized to fine powder and passed through 0.5-mm sieve. The spinach and 'yakuwa' samples were cut into nearly uniform sizes. This was done to facilitate drying of the pieces at the same rate. The cut pieces were placed in clean acid-washed porcelain crucibles according to label and oven-dried at 105°C for 24 hours in an oven until they were brittle and crispy. At this stage no micro-organisms can grow on it. All crucibles were labeled according to sample numbers. The dried vegetable samples were grounded into fine particles using washed porcelain mortar and pestle. The powdered samples were placed in labeled Petri dishes and dried to constant weight in desiccators until they were digested.

4.1 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.

5. Digestion of Samples

5.1 Soil samples

One gram (1g) of the air-dried ground soil samples was mixed with 20cm³ (1:1) HCl / HNO₃ acid mixtures and the content was heated on a hot plate until dryness. The residue was dissolved using 2M HCl and filtered into 50cm³ volumetric flask for metal analysis. A Unicam Atomic Absorption Spectrophotometer (AAS) equipped with an air-acetylene burner was used to determine the metal contents. The acid mixture was adopted according to Abulude 2005. Duplicate samples were prepared and a blank was incorporated into a batch of every 5 duplicate samples.

5.2 Vegetable samples

A slightly modified procedure according to Awofolu 2005 was used for digestion of the vegetable samples. 0.5 g of sieved leaf samples were weighed into 100 ml beaker. A mixture of 7ml concentrated trioxonitrate (IV) acid and 4ml of 70% perchloric acid was added and this was digested at low heat using hot plate until near dryness. The digest was allowed to cool, filtered into 50 ml standard flask using Whatman (110) filter paper and made up to the mark with 5M HNO₃. Duplicate digestion of each sample was carried out together with a blank digest which was incorporated in every batch of 5 duplicate samples. The blank was prepared using the same procedure as above with an exception of the samples.

6. 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.

7. Results and Discussions

Table (1) shows the concentrations of Cd, Cr and Pb pH and percentage organic matter content of the soil. The values of soil pH obtained shows slightly acidic to neutral with a range of 5.05- 7.50. The pH range of this study is lower than the pH range of 6.22-8.40 reported by Okunola et al., 2007 in their study. The mean pH of 6.73± 0.73 in this study is similar to the mean value reported by Okoronkwo et al., 2006 in their study.

The percentage organic matter ranged between 0.29-2.23% with a mean percentage organic matter (%OM) of 1.40±0.54. The mean %OM in this study was lower than the mean value (3.47±0.41) reported by Okoronkwo et al., 2006.

Table 1: Total metal contents (mg/kg) and soil properties of Malali irrigated farmlands

Samples	Cd	Cr	Pb	pH	%OM
1.	ND	16.0	4.4	5.64	0.50
2.	0.8	10.0	10.6	6.48	1.14
3.	1.1	2.0	12.0	6.88	2.00
4.	2.0	7.0	13.5	6.78	2.23
5.	3.0	11.0	15.6	5.91	1.19
6.	1.1	17.0	14.0	7.40	1.85
7.	ND	23.0	16.0	7.50	2.00
8.	ND	22.0	18.0	7.44	0.81
9.	5.0	19.0	19.0	6.78	1.87
10.	4.4	20.0	20.0	7.23	1.33
11.	6.5	24.0	22.3	7.39	1.44
12.	3.0	38.0	11.3	7.50	0.29
13.	5.5	23.0	24.0	6.75	1.92
Control	0.1	30.0	3.6	5.05	1.33
Site (n=4)	0.1	22.0	2.9	5.90	1.30
	0.2	19.0	4.0	6.88	1.33
	2.3	11.0	5.0	6.89	1.35

ND = Not Detected

The results of the soil samples showing the range, median and the mean (\pm SD) are shown on Table 2 below. The ranges of Cd (0.8-6.5mg/kg), Cr (2.0-38.0 mg/kg) and Pb (4.4-24.0mg/kg) and the mean concentration of the toxic metals Cd, Cr and Pb for soil are Cd (4.88 ± 2.03 mg/kg), Cr (17.85 ± 9.14 mg/kg) and Pb (15.44 ± 5.33). The concentration level of Cd in the soil is higher than the recommended value of 0.2mg/kg by FAO/WHO 2001.

The concentration range of Pb in soil of this study is higher than the reported value of 0.14mg/kg by Adeyeye and Ayejuyo 2002 but has Pb values lower than 8-235mg/kg recorded by Savoskull and Drechsel 2003. Furthermore, the value of Pb in the soil is lower than that reported by Hooda et al., 1997 in a similar study. However, the values of Cr and Pb in soil of this study are higher than the values reported by Rasheed and Awadallah (1998) in their study of Agricultural soil.

Table 2: Summary of Total Metal Contents in Soils (mg/kg), pH and Percentage Organic Matter of Irrigated Farmland in Kaduna

Samples	Metal	Range	Median	Mean \pm SD*
Soil (n=13)	Cd	0.8-6.50	3.00	4.88 ± 2.03
	Cr	2.0-38.00	19.00	17.85 ± 9.14
	Pb	4.4-24.00	15.60	15.44 ± 5.33
Control (n= 4)	Cd	0.1-2.30	0.15	0.68 ± 1.08
	Cr	1.0-12.00	0.24	0.68 ± 1.04
	Pb	2.9-5.00	3.80	8 ± 0.88
All soil (n=17)	Cd	0.1-6.50	2.15	2.51 ± 2.14
	Cr	2.0-38.0	16.00	15.88 ± 8.82
	Pb	2.9-24.00	13.50	12.72 ± 6.86
pH		5.6-7.50	6.88	6.90 ± 0.61
%OM		0.29-2.23	1.40	1.43 ± 0.62

SD* = Standard Deviation

n = Number of Samples

%OM = Percentage Organic Matter

The concentration of toxic metals can be seen on (Table 3) while the ranges of vegetable samples is shown on (Table 4) with a range of Cd (0.1- 0.5mg/kg), Cr (1.0 -8.0mg/kg) and Pb (2.7 -11.0mg/kg) and the mean concentration values are Cd (0.64 ± 0.34 mg/kg), Cr (2.67 ± 2.31 mg/kg) and Pb (4.41 ± 2.09 mg/kg). The concentration ranges of Cd, Cr and Pb in vegetables of this study are lower than the concentration ranges of Cd, Cr and Pb reported by Abdullahi et al., 2007 in their study of some vegetables samples. However, the mean concentration values of 2.5 ± 2.07 mg/kg Cr and 5.43 ± 2.75 mg/kg Pb respectively in spinach of this study were higher than that reported by Audu and Lawal in all the varieties of spinach studied. These values are also higher than all the values of vegetables recorded by the above mentioned authors. Furthermore, the values of Pb in spinach of this study are higher than the values of 3.24 and 1.20 reported by Erwin and Ivo 1992; John and Stephen 1982 respectively in a similar study. The value of Cr is also higher than that reported by John and Stephen 1982.

Flaming and Parle 1977 reported normal plant metal levels for Pb to range between 1-12mg/kg dry weight. However, the value of Pb in this study is higher than the 1-12mg/kg reported as normal by Flaming and Parle 1977. Furthermore, the concentration values of spinach were higher than the reported value of 0.95mg/kg reported by Hooda et al., 1997. Also, the concentration ranges for Cr and Pb mg/kg of vegetables is higher than the concentration ranges reported by Abulude 2005 in a similar study. Furthermore, the mean value of Pb is lower than that reported in soil and plant samples analyzed by Onianwa and Fakayode 2000 in their study around battery factory in Nigeria.

The toxic doses of Cr and Pb to plants are 0.5-10mg/kg and 3-20mg/kg respectively while the toxic levels to man are Cr 200 and Pb 1.00mg/day FAO/WHO, 2001.

Table 3: Total Metal Contents (mg/kg) in Vegetables of Irrigated Farmland in Kaduna

Samples	Cd	Cr	Pb
Spinach (n = 7)	ND	1.0	3.8
	ND	1.0	4.3
	0.4	4.0	4.7
	0.1	6.0	1.1
	0.2	2.0	4.0
	0.1	1.0	4.8
	0.4	1.0	2.7
Yakuwa (n = 6)	ND	1.0	4.0
	1.0	3.0	4.4
	1.0	1.0	4.1
	0.5	3.0	3.0
	0.4	8.0	2.9
	0.3	ND	3.6
Control (n = 4)	ND	0.9	1.1
	0.03	2.0	0.2
	0.01	0.8	0.2
	0.02	1.0	0.3

ND = Not Detected

Table 4: Summary of Total Metal Content in Vegetables (mg/kg) of Irrigated Farmland in Kaduna

Vegetables	Ranges	Median	Mean± SD*
Cd sp	0.1-0.4	0.15	0.2± 0.14
Cr sp	1.0-6.0	1.50	2.5± 2.07
Pb sp	3.8-11.0	4.50	5.43± 2.75
Cd yk	0.3-1.0	0.45	0.60± 0.32
Cr yk	1.0-8.0	2.00	2.83± 2.72
Pb yk	2.7-4.4	3.60	3.53± 0.67
Both plants			
Cd	0.1-0.5	0.50	0.64± 0.34
Cr	1.0-8.0	1.50	2.67± 2.31
Pb	2.7-11.00	4.00	4.41± 2.09
Control plant			
Cd sp	0.01-0.03	0.02	0.02± 0.02
Cr sp	0.8-2.00	0.95	1.18± 0.56
Pb sp	0.2-1.10	0.25	0.45± 0.44
All plants			
Cd	0.01-1.00	0.35	0.37± 0.34
Cr	0.8-8.00	1.00	2.29± 2.10
Pb	0.2-11.00	3.80	3.48± 2.51

sp = spinach
yk = 'yakuwa'

Table 5 shows the correlation results between physico-chemical parameters with metals and between metals in soil.

Table 5: Correlation between some soil parameters and Toxic Metals in Soil

Factor	pH	%OM	Cd	Cr	Pb
pH	1.0000				
%OM	0.180021	1.0000			
Cd	0.186679	-0.03873	1.0000		
Cr	0.504607	-0.47739	0.541358	1.0000	
Pb	0.46423	0.405696	0.904564	0.281331	1.0000

Table 6: Correlation between some soil parameters and Toxic Metals in Plants

Factor	pH	%OM	Cd	Cr	Pb
Cd	0.158135	-0.14211	1.0000		
Cr	0.193563	-0.04849	-0.21308	1.0000	
Pb	-0.14196	0.449283	-0.33051	0.339802	1.0000

pH of the soil correlated positively and significantly with Cr and Pb. Also, there was positive correlation between %OM and Pb this is an indication that pH and %OM is the major factor controlling the mobility and availability of these metals in the soil. Among metals, Cd correlated positively and significantly with Cr and Pb which means these metals has the same source (sources) in the soil. There was also positive correlation of %OM with Pb in vegetables. Furthermore, Cd and Cr correlated positively with Pb in the vegetables.

8. Conclusion

The results indicate that the soil had slightly high levels of Cd while the levels of soil Cr and Pb are still within tolerable levels. However, the obtained mean values of toxic metals in the site studied are higher than that found in the control site. For vegetables (exposed) however relatively high levels of the trace metals were also observed than the control have. Though, the trace metal levels were close to the toxic levels for Cr and Pb in plants recommended by the Food and Agricultural Organization (FAO) and the WHO/EU joint limits but has not reached the toxicity level of Cd 1-30 mg/kg, Pb 30-300 mg/kg but is within the normal range of Cd (0.1-2.4mg/kg) and Pb (5-10mg/kg) Awofolu et al., 2007. The slightly high levels of these toxic metals in vegetables could be ascribed to deposits from vehicle emission and probably from the water use for irrigation where waste of all kinds is dumped. This put the consumers of these and other vegetable crop grown within this farmland at health risk with time and as such continues monitoring of this farmland and the water used for irrigation is needed.

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