

Assessment of Heavy Metal Bioaccumulation in Spinach, Jute Mallow and Tomato in Farms Within Kaduna Metropolis, Nigeria

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Abstract The heavy metals levels in soil and the edible parts of three popular vegetables, widely consumed in Nigeria; spinach (*Amaranthus hybridus*), jute mallow (*Corchorus olitorius*) and tomato (*Lycopersicon esculentum*) were assessed in farms within the city of Kaduna, Nigeria. The city was divided into 20 zones, for the purpose of this study, and composite samples of soils and vegetables were collected from farms and gardens in each zone and also from two rural villages, about 30 km from the city (as control). Samples were digested using a 3:1 mixture of concentrated HNO₃ and HClO₄ acids. Recovery test on method of digestion gave % recoveries > 95% while in the analysis of reference materials of soil and plant, t-test results (at 95% Confidence Interval) show that statistically, there exists no significant difference between certified and obtained values. Digests were analysed using Flame Atomic Absorption Spectrophotometer. The mean and range of heavy metals concentrations (µg/g dry weight) in digested soil samples were Pb; 134+94 (18.2 – 441), Cd; 3.2+1.6 (1.8 – 9.1), Ni; 36+40 (13.5 – 195) and Cr; 58+39 (31.8 – 212), respectively, while that of vegetable samples were Pb; 19.2+4.9 (1.6 – 67.2), Cd; 3.2+1.0 (1.0 – 12.5), Ni; 9.6+2.5 (1.6 – 23.1) and Cr; 14.1+2.3 (2.8 – 32.4), respectively. Pollution Load Index (PLI) values indicated that the city farm soils were moderately enriched with Cd and Cr, but strongly enriched with Pb and Ni, due to anthropogenic contributions. The Soil-Plant Transfer Factor (TF) shows that the order of uptake of metals by vegetables is Cd > Ni > Cr > Pb. The mean concentrations of metals in soil samples were generally higher than the WHO/FAO maximum permissible limits in agricultural soil for Pb and Cd, but lower for Ni and Cr, while for vegetables the mean concentrations of metals were generally higher than the permissible limits for all the metals, except Ni. This calls for concern especially in the case of Pb and Cd which are highly toxic and of no known biological use.

Keywords Heavy Metals, Soil, Spinach, Jute, Tomato, Kaduna City

1. Introduction

Although trace quantities of certain heavy metals, such as chromium, cobalt, copper, manganese, zinc, etc are essential micronutrients for higher animals and plant growth, they are of considerable environmental concern due to their toxicity and cumulative behavior[1]. Heavy metals are non-biodegradable and persistent environmental contaminants, which may be deposited on the surfaces and then absorbed into the tissues of vegetables. Plants take up heavy metals by absorbing them from deposits on the parts of the plants exposed to the air from polluted environments as well as from contaminated soils[2].

As a result of urbanization and increasing anthropogenic activities, the heavy metal pollution of soil, water, and at

mosphere, represents a growing environmental problem affecting food quality and human health in cities. Sources of heavy metal in city environment include domestic and industrial wastes, traffic emissions, agricultural activities, mining and metal works[3]. Consumption of vegetables is one of the pathways by which heavy metals enter the food chain. Prolong consumption of unsafe concentrations of heavy metals through foodstuffs may lead to the chronic accumulation of heavy metals in the kidney and liver of humans causing disruption of numerous biochemical processes, leading to cardiovascular, nervous, kidney and bone diseases[4].

Urban farming is a common practice in developing countries, including Nigeria. Many residents of these urban areas are engaged in farming activities. Those who are not full-time farmers are also involved in farming to support their income. As a result of the prevailing land tenure system, land spaces for agricultural purposes are usually scarce. Urban farmers usually make use of any available land spaces that are free or the so called 'no man's land'. Such land

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usually include dumpsites, rail and road sides, and others close to market places, polluted water bodies, mechanic workshops, and industrial areas, among others, which are potential sources of heavy metal pollution.

The aim of this study was to determine the concentration of the heavy metals Pb, Cd, Ni and Cr (which are among the most toxic heavy metals) in soil and in the edible parts of commonly consumed vegetables of farms within Kaduna metropolis, and to evaluate the levels of bioaccumulation of the metals by the different vegetables and their risk of pollution and human health effects.

2. Materials and Methods

Composite samples of soils were collected from 7 - 10 farms and gardens per zone, in July 2010. Samples were collected with a stainless steel hand-trowel, within 0 - 20 cm depths. The sub-samples were collected along independent zig-zag paths to achieve randomness. The trowel was carefully cleaned after each sampling exercise, to avoid cross-contamination[5]. The soil sampling spots were cleared of debris before sampling. The soil samples were air-dried for seven days to avoid microbial degradations. Prior to analysis, the soil samples were re-dried in the oven at 110°C for about 3 hours and crushed in a porcelain mortar and sieved through a 2 mm plastic sieve to obtain fine soil particles. 1 g of the oven-dried (<2mm) composite soil sample from each of the 22 zones (in triplicates) were first moistened with a few drops of water (to prevent sputtering) followed by the addition of 10 cm³ concentrated nitric acid (HNO₃). The mixture was slowly evaporated over a period of 1 hour, on a hot plate. The solid residue obtained was digested with 20 cm³ of a 3:1 mixture of concentrated HNO₃ and HClO₄ for ten minutes at room temperature before heating was continued. The temperature of the hot plate was slowly raised over a period of 1 hour until the fumes of HClO₄ starts to escape, heating was continued until a clear solution was obtained. The mixture was allowed to cool to room temperature. The cooled mixture was then filtered using Whatman No. 1 filter paper into 100cm³ volumetric flask and made up to mark with distilled water. The digests were stored in polythene bottles till analysis[6].

Vegetable samples were collected with gloved hands to avoid contamination. Samples of spinach (*Amaranthus hybridus*) and jute mallow (*Corchorus olitorius*) were collected by randomly picking up some mature bottom leaves from the matured plants until a sizable bundle was gathered from each farm or garden where soil samples were taken. Ripe fruits of tomato (*Lycopersicon esculentum*) were collected by randomly plucking the fruits from the plants[5]. On reaching the laboratory, for each type of vegetables, collections from each zone were washed with distilled water to remove dirt and other particulate matters. Each collection or bundles were then sub-divided to give triplicate samples weighing approximately 100g fresh weight. Prior to analysis, fresh vegetable samples were dried in the oven at 70°C until a

constant weight was obtained. Samples were then pulverized using a porcelain mortar, sieved through 1 mm mesh sieve, and stored in polythene bags ready for digestion and analysis. 1 g of oven-dried and ground sample of each type of vegetable and from each of the 22 zones were weighed (in triplicates) into a 50 cm³ beaker. This was followed by the addition of 10 cm³ mixtures of analytical grade acids HNO₃ and HClO₄ in the ratio 3:1. The beakers were then covered with watch glasses and left overnight. Digestion was done on a hot plate at a temperature of about 90°C in a fume cupboard until about 4cm³ of the mixture was left in the beaker. A further 10 cm³ of the acid mixture was then added and evaporated to a volume of about 4 cm³ while still on hot plate, giving a clear solution. The mixture was cooled to room temperature and the solution filtered using Whatman No. 1 filter paper, to remove small quantities of waxy solids and made up to a final volume of 50 cm³ with distilled water in a volumetric flask. These were stored in polythene bottles till analysis[1].

In order to confirm the efficiency of the HNO₃ – HClO₄ method of sample digestion a recovery study was carried out by spiking 1 g of five different soil samples each with 1 cm³ of standard solutions of the metals Pb, Cd, Ni and Cr. Furthermore, reference samples of soil and plant were analyzed, under similar conditions. Recovery test gave % recoveries > 95% while in the analysis of reference materials t-test results (at 95% Confidence Interval) show that statistically, there exists no significant difference between certified and obtained values.

Metal concentrations in working standards and digests were determined using Flame Atomic Absorption Spectrophotometer (Perkin Elmer A-ANALYST 200). Air-acetylene flame was used. The instrumental settings and operating conditions were carried out according to the manufacturer's specifications. Blanks were also determined to ascertain the contribution of reagents to metal levels.

3. Results and Discussion

The mean concentrations of the heavy metals (µg/g dry weight) in soil, spinach, jute and tomato are given in Tables 1, 3, 5 & 6 respectively. The concentrations of the metals were generally higher in samples from the study site than the control site. Pollution Load Index values (Table 2) shows that the city farm soils were moderately enriched with Cd and Cr, but strongly enriched with Pb and Ni, due to anthropogenic contributions. The order of accumulation of metals in both soil and vegetables samples was Pb > Cr > Ni > Cd. Plants generally have low uptake of Pb, high concentration of Pb in vegetables in this study could be attributed to its high concentration in soil and possible aerial deposition and absorption.

The high concentrations of Pb and Cr in soil samples could be attributed to high level of industrial activities, metal works, vehicular emissions, small scale tanning operations, e.t.c. The distribution of metals in farm soils in each zone

was mainly affected by the location of the zone and the prevailing anthropogenic activities. Spinach accumulated more metals, followed by jute mallow and then tomato. This is in agreement with some earlier reports that leafy vegetables have greater potential for accumulating heavy metals in their edible parts than grains and fruit crops, due to their higher transpiration rate[5]. It is essential to note also that spinach has broader leaves than jute mallow, while tomato is a fruit vegetable. There existed strong correlation between concentrations of metals in soil. These correlations were statistically significant ($p < 0.05$), indicating similar sources of pollution[7]. In addition positive correlation indicates mutual existence and enrichment of the metals in soil, whereas negative correlation indicates their competition to occupy the same sites in soil exchange base or lattice. However, other factors for significant correlation of the metals in soil are similar atomic radii for Cd, Cr and similar chemical and physical factors controlling element association in parent material and during soil forming processes[8]. This result is consistent with previously published data[9]. The general weak correlation between concentrations of metals in soil and in vegetables, which had also been reported[10], indicates that other sources, such as foliar absorption, might have contributed to the metal burden in vegetables.

Table 1. Mean Concentration ($\mu\text{g/g}$ dry weight) of Heavy Metals in Soil Samples

Zone	Pb	Cd	Ni	Cr
1	67.8±0.4	3.0±0.4	19.6±4.6	53.2±0.8
2	190±24	2.5±0.1	31.7±0.2	56.9±4.5
3	256±44	2.5±1.6	15.8±0.8	56.5±9.8
4	425±77	6.2±0.4	38.4±6.5	43.9±9.9
5	327±14	7.7±0.4	46.8±0.6	64.7±7.6
6	43.5±0.2	1.8±0.3	22.1±0.1	42.7±7.1
7	32.1±7.4	2.3±0.1	30.6±0.2	51.4±0.2
8	256±8	3.8±0.2	27.4±1.3	42.1±2.5
9	99.4±2.3	2.2±0.1	26.4±2.8	40.4±6.5
10	35.9±6.7	2.3±0.9	20.8±2.8	31.8±1.1
11	18.2±3.1	2.1±0.1	13.5±1.9	34.4±2.8
12	48.6±7.6	3.9±1.1	28.5±3.1	51.5±6.9
13	28.0±1.4	1.9±0.2	22.8±1.7	40.5±0.9
14	25.2±0.2	1.9±0.3	30.2±0.4	54.7±5.3
15	441±42	9.1±0.5	195±8.3	212±11
16	104±10	2.5±0.4	28.1±3.1	58.9±7.4
17	74±16	2.3±0.5	25.2±2.1	54.7±3.6
18	144±29	2.3±0.4	52.9±3.5	70.1±3.9
19	22.3±2.5	1.8±0.1	13.5±0.7	51.9±7.1
20	48.7±2.7	2.8±0.5	25.4±3.1	45.8±4.2
21 ^c	17.9±2.6	1.2±0.1	4.1±1.2	13.7±2.2
22 ^c	11.4±1.1	1.3±0.3	2.5±1.3	17.6±2.5

c = control

The Soil-Plant Transfer Factor (TF) differed between the vegetables species and sampling zones (Table 4). The difference in sampling zones for the same vegetable could be attributed to differences in soil properties[11]. The TF values showed that the order of uptake of metals by vegetables is $\text{Cd} > \text{Ni} > \text{Cr} > \text{Pb}$. Cd had the highest TF in all the vegetables. This is due to its high mobility[7]. The trend is in consistent with the result obtained by Khan, et al[12]; with Cd having the highest TF and Cr and Pb the lowest. Spinach generally had the highest TF for all metals followed by jute

mallow; this could be attributed to their relative transpiration rate[13].

Table 2. Pollution Load Index (PLI*) of Study Site

	Pb	Cd	Ni	Cr
Soil	9.14	2.46	10.82	3.69
Spinach	2.00	2.29	1.71	1.94
Jute Mallow	3.45	2.19	5.13	4.40
Tomato	4.24	1.53	5.70	4.94

* PLI = [Concentration of metal in study site/Concentration in control site]

Table 3. Mean Concentration ($\mu\text{g/g}$ dry weight) of Heavy Metals in Spinach Samples

Zone	Pb	Cd	Ni	Cr
1	11.7±3.8	4.5±2.1	17.2±1.5	20.4±2.9
2	27.2±4.5	5.1±1.3	12.7±4.1	18.8±1.1
3	14.5±4.1	3.4±0.3	16.3±1.6	10.4±1.7
4	3.4±2.4	3.9±1.8	19.8±2.3	12.5±1.3
5	26.2±4.5	2.9±0.4	11.6±2.9	12.4±2.6
6	18.1±3.9	5.1±1.7	14.4±1.3	7.6±1.3
7	1.9±0.7	4.5±2.8	16.7±2.7	8.4±0.2
8	11.6±1.8	3.9±1.3	13.4±2.2	27.9±2.4
9	4.3±1.7	1.0±0.1	8.7±1.5	12.6±0.7
10	22.1±2.8	4.3±1.3	12.5±1.1	9.9±2.1
11	8.5±2.2	3.6±1.9	12.7±3.3	11.9±1.4
12	11.0±1.9	6.6±0.9	23.1±5.1	28.9±5.7
13	12.5±3.9	2.6±1.4	14.4±2.8	18.9±2.1
14	1.6±1.1	4.2±1.9	18.9±1.2	11.2±2.5
15	12.7±2.6	3.5±1.7	14.2±5.2	15.1±1.5
16	12.4±3.2	3.1±1.3	16.8±4.2	24.7±0.9
17	11.9±1.6	3.2±1.2	15.7±3.7	17.5±1.3
18	28.3±5.6	1.7±1.1	8.7±2.3	25.2±0.8
19	4.7±2.6	3.9±1.4	12.9±2.3	9.7±1.7
20	14.7±1.1	6.6±1.7	17.6±3.4	26.1±1.1
21 ^c	5.8±1.9	1.5±0.7	7.7±1.3	7.7±3.1
22 ^c	7.1±3.1	1.8±0.3	9.6±2.1	9.2±2.8

c = control

Table 4. Mean Soil-Plant Transfer Factor (TF) of Vegetables

	TF _{Pb}	TF _{Cd}	TF _{Ni}	TF _{Cr}
Spinach	0.19±0.14a	1.47±0.54	0.59±0.21	0.33±0.13
Jute Mallow	0.40±0.53	1.4±1.1	0.32±0.16	0.34±0.20
Tomato	0.14±0.11	0.87±0.24	0.22±0.12	0.19±0.06
Mean	0.24	1.25	0.38	0.29

Table 5. Mean Concentration ($\mu\text{g/g}$ dry weight) of Heavy Metals in Jute Mallow Samples

Zone	Pb	Cd	Ni	Cr
1	8.7±3.8	4.6±1.7	7.8±3.1	22.6±3.8
2	7.8±1.1	4.5±2.1	11.8±5.9	32.4±2.7
3	5.8±2.3	2.9±0.6	7.9±3.2	9.8±3.4
4	5.1±3.3	2.6±0.5	7.2±3.9	9.7±2.4
5	42.9±3.5	1.9±0.6	13.5±3.6	26.9±1.8
6	17.3±1.6	2.8±1.1	6.7±1.6	10.9±3.8
7	19.2±3.3	2.5±1.4	12.3±1.4	23.7±2.5
8	16.6±2.1	3.3±1.1	5.7±1.4	17.8±2.9
9	5.1±1.48	1.2±0.2	1.9±0.6	9.2±1.4
10	10.8±1.8	2.2±0.9	6.2±3.5	30.8±4.7
11	26.4±3.6	3.7±1.1	9.9±0.6	8.4±1.6
12	12.9±3.4	2.5±0.1	16.5±1.7	11.5±2.4
13	67.2±1.4	4.7±1.2	14.1±4.8	14.4±3.5
14	18.2±4.9	3.1±0.4	7.1±1.4	16.9±2.6
15	4.2±1.7	2.8±0.1	4.4±1.4	10.7±2.9
16	16.8±1.8	12.5±2.1	12.8±1.3	29.8±4.9
17	10.4±1.7	2.3±0.1	1.6±0.2	12.8±4.2
18	8.3±1.4	2.8±0.2	4.2±1.6	16.6±2.8
19	16.2±2.7	3.7±0.7	6.1±1.4	13.3±1.7
20	17.2±3.2	3.6±1.2	5.4±1.9	15.5±1.5
21 ^c	3.3±0.6	1.4±0.4	1.9±0.4	2.1±0.7
22 ^c	6.6±2.8	1.7±0.7	1.2±0.3	5.6±1.4

c = control

Table 6. Mean Concentration ($\mu\text{g/g}$ dry weight) of Heavy Metals in Tomato Samples

Zone	Pb	Cd	Ni	Cr
1	7.9 \pm 0.4	2.5 \pm 0.2	4.6 \pm 1.3	3.8 \pm 0.7
2	9.4 \pm 1.4	2.1 \pm 0.1	4.6 \pm 1.7	4.2 \pm 0.1
3	9.6 \pm 4.2	3.2 \pm 1.1	4.4 \pm 0.4	9.7 \pm 2.3
4	13.3 \pm 1.7	2.4 \pm 0.7	2.4 \pm 0.9	10.9 \pm 1.1
5	9.7 \pm 1.1	1.8 \pm 0.2	4.8 \pm 0.2	10.1 \pm 1.6
6	10.2 \pm 2.8	1.9 \pm 0.5	5.5 \pm 0.4	9.9 \pm 1.1
7	5.3 \pm 1.9	2.1 \pm 0.4	3.4 \pm 0.4	9.3 \pm 1.8
8	5.1 \pm 1.4	2.2 \pm 0.7	4.6 \pm 1.5	9.7 \pm 0.9
9	29.6 \pm 3.3	2.1 \pm 0.3	5.7 \pm 2.1	13.6 \pm 5.2
10	4.7 \pm 1.4	1.8 \pm 0.2	12.2 \pm 0.9	3.4 \pm 0.7
11	3.9 \pm 0.2	2.5 \pm 0.6	2.5 \pm 0.3	17.1 \pm 1.3
12	23.6 \pm 2.7	2.4 \pm 0.7	9.7 \pm 0.3	11.9 \pm 4.8
13	7.2 \pm 2.3	2.5 \pm 0.8	11.5 \pm 2.1	6.6 \pm 3.1
14	5.4 \pm 2.7	2.3 \pm 0.4	3.4 \pm 0.7	5.6 \pm 0.6
15	5.1 \pm 0.7	2.1 \pm 0.3	5.6 \pm 1.6	7.7 \pm 1.7
16	4.2 \pm 1.3	2.1 \pm 0.6	4.2 \pm 1.7	2.8 \pm 0.1
17	5.9 \pm 2.1	2.3 \pm 0.4	4.2 \pm 1.4	5.7 \pm 0.1
18	8.3 \pm 1.3	2.1 \pm 1.1	12.1 \pm 1.4	16.8 \pm 0.1
19	6.1 \pm 1.7	2.2 \pm 0.6	4.2 \pm 1.5	4.8 \pm 0.4
20	4.4 \pm 0.9	2.6 \pm 0.7	4.1 \pm 0.3	5.3 \pm 0.6
21 ^c	2.9 \pm 0.2	1.7 \pm 0.2	0.5 \pm 0.1	1.6 \pm 0.1
22 ^c	1.2 \pm 0.6	1.2 \pm 0.3	1.4 \pm 0.3	1.8 \pm 0.1

c = control

4. Conclusions

The concentrations of Pb and Cd in the soil samples were generally higher than the WHO/FAO maximum permissible limits while the concentrations of Ni, Cr, in soil samples were generally lower than the maximum permissible limits (Pb 100; Cd 3; Ni 75; Cr 400 $\mu\text{g/g}$) [14], except for few zones. On the other hand, in vegetables, the concentrations of Pb, Cd and Cr (in all zones) were higher than the WHO/FAO maximum permissible limits (Pb 0.3; Cd 0.2; Ni 10; Cr 2.3 $\mu\text{g/g}$) [14], while Ni concentration was higher than the maximum permissible limit in spinach samples only. Furthermore, the study revealed that some areas of the city were more polluted by a particular metal than the other due to the prevailing anthropogenic activities in the area, and that all areas of the city run the risk of pollution by Pb, Cd and Cr in vegetables. There was generally no critical Ni contamination of the vegetables.

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