

Cadmium, Cobalt, Lead and Zinc Levels in Soil and Edible Vegetables in Yala Urban Area of Cross River State, Nigeria

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ABSTRACT: The average level of cadmium (Cd), cobalt (Co), lead (Pb) and zinc (Zn) in the soil and edible vegetables samples collected randomly in Yala Urban Area of Cross River State was determined using flame Atomic Absorption Spectrometer. The samples were digested and analyzed for the metals level or concentration in Chemistry Laboratory, University of Calabar. The eight vegetables selected for the study were Amaranthus spp., Corchorus olitorius, Murraya koenigii, Ocimum grattissimum, Solanum melongena, Talinum triangulare, Telferia occidentalis and Vernonia amygdalina. The results indicated that the average level of the metals in the soil in mgkg⁻¹ ranged from (0.005-0.021) and (0.004-0.019) in rainy and dry seasons respectively for Cadmium, (0.162-0.475) and (0.163-0.472) in rainy and dry season respectively for Cobalt, and (0.434-1.030) and (0.432-1.027) in rainy and dry season respectively for Zinc. Also, the average level of the metals accumulated by the vegetables in mgkg-1 ranged from (0.002-0.009) and (0.001-0.007) in rainy and dry season respectively for Cadmium, (0.050-0.198) and (0.048-0.195) in rainy and dry season respectively for Cobalt, and (0.158-0.383) and (0.156-0.380) in rainy and dry season respectively for Zinc. The level of Lead in the soil or vegetables was not detected. The average level of metals accumulated by the vegetables and that present in the soil was in the order: Zinc > Cobalt > Cadmium > Lead. These results revealed that there is no significant difference between the level of metals in the soil or that accumulated by the vegetables in rainy and dry seasons of the year. Also the level of metals accumulated by most of the vegetables was directly proportional to the amount present in the soil where they are planted. The Target Hazard Quotients of these metals was less than 1. These results imply that the concentration of Cadmium, Cobalt, Zinc and Lead in the soil and vegetables were still low and within the permissible limits of World Health Organization. Thus, the consumption of the vegetables in the area may not pose any health risk for now.

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Cadmium, Cobalt, Lead and Zinc belongs to the transition metals. Due to their poisonous or toxic effect at high doses and their contamination of food plants and animals when present in the soil or water environments, they have recently attracted the attention of many researchers worldwide as food safety and quality is a matter of public interest. Also, increasing demands for food and its safety has drawn the attention of researchers to the health risk associated with consumption of contaminants in vegetables (Dmello, 2003). There is an increasing concern about the quality of foods in several parts of the world. The studies of toxicological and environmental hazards have spurred the interest in the determination of toxic elements in food. Food safety and quality determines its value or acceptability to consumers. As a result of this, researchers like Jackson and Alloway (1993) have stated from their study that application of residuals to soil introduces heavy metals into the soil. The cultivation of lands contaminated with heavy metals from industrial effluents, vehicular emissions and other anthropogenic activities have resulted in the growth of contaminated vegetables (Rattan et al., 2005). Obasi et al. (2012) have also studied heavy metals contamination of soil along Enugu-Port Harcourt expressway in Ngeria and reported mean

concentration of Cd, Cr, Cu, Fe, Mn, Ni Pb and Zn ranging from 10.58 to 635 mg/kg, with Cd, Fe and Pb in decreasing order the most mobile and bioavailable to the environment. A study on the heavy metals contamination of soil and vegetables in sub-urban areas of Varanasi in India revealed that Cr, Cu, Mn, Ni Pb and Zn except Cd were below WHO permissible limits for agricultural use (Kumar et al., 2007). Also, the assessment of heavy metals contamination of different vegetables grown in and about Urban areas of in a certain region in Iran have shown that the average level of Pb, Cu, Cr and Cd are a health hazard for human consumption according to Iran National Nutrition and Food Research Institute (Suruchi and Khanna, 2011). In Australia, Rahman et al. (2014) analyzed heavy metals in rice grown in Australia and those imported, and vegetables on sale and revealed that heavy metals levels in Australian grown rice were higher than those imported from Bangladesh and their levels in vegetables were higher than the Australian Standard maximum limits. Several other researchers have carried out studies on heavy metals in different parts of the world to ascertain their food and environment quality/safety. Cadmium is emitted to the air by mines, metal smelters and industries using cadmium compounds for alloys, batteries, pigments

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and in plastics, although many nations have stringent controls in place for such emissions (Harrison, 2001). Cobalt is used in many alloys (super alloys for parts in gas turbine aircraft engines, corrosion resistant alloys, high speed steels, cemented carbides), in magnets and magnetic recording media, as catalysts for the petroleum and chemical industries, as drying agents for paints and inks. Human exposure to Co takes place through air, drinking water and food (ATSDR, 2011). Food is one of the major sources of Lead exposure; others are air (mainly its dust emanating from petrol) and drinking water. Plant food may be contaminated with Lead through its uptake from ambient air and soil; animals may then ingest the Lead-contaminated vegetation. In humans, its ingestion may arise from eating Lead-contaminated vegetation or animal foods (Ming-Ho, 2005). Zinc is the most abundant element occurs in the earth's crust and is used mostly in the manufacture of communications equipment and instruments (Emsley, 2001). It is also used in making alloys like Brass. Thus, most metal find their way into the ecosystem or food chain either by natural occurrence, their mining or extraction and their uses or applications. Halwell (2007) have reported that the nutritional value of vegetables depends on the growing method and the quality of the soil because when vegetables are grown in contaminated soils, like those polluted with heavy metals; their nutritional value will be depreciated as pollutants from the soil will be accumulated by the vegetables. Thus, vegetables should not be planted on soils contaminated with hazardous waste like heavy metals because they are nutritionally and medicinally valuable. Besides, the health of humans can be affected negatively when they consume these vegetables and accumulate these toxic substances in high doses. For instance, cadmium in high doses causes adverse effect on kidney, liver, bones, immune system and chronic poisoning (Ndukwu et al., 2008). Children are more sensitive to the effects of lead than adults. Most heavy metals in high doses can possibly cause disruption of or interference in endocrine system (Alvarez-Ayuso et al., 2011), phyto/cytotoxicity (Tan and Xiao, 2012) and dysfunction of the mitochondria (Fujimaki et al., 2004) among other health problems. Thus, cobalt and zinc are not exempted in high doses. Moreover, the heavy metals, viz; cadmium, lead and mercury are considered as strict and toxic contaminants for living beings, even at very lower concentrations (Salama et al., 2005 and Dauguet et al., 2011). The aim of this study is to determine the level of Cd, Co, Pb and Zn in the soil and edible vegetables in Yala (the study area) and ascertain the soil and vegetable quality with respect to their pollution.

MATERIALS AND METHODS

Description of Study Area: Yala urban area is characterized with low land, plains, some swamps and hills. The soil is well drain sandy loam in texture, which makes it suitable for agriculture. It has population of about 115 thousand people. Besides, the people engaged in subsistence and commercial farming, growing rice, cassava, yam in large quantities as well as vegetables for consumption as food and medicine. This often results in the use of insecticides, herbicides and other agrochemicals. By its location, it is a link to the eastern and northern part of the country and sometimes experience heavy vehicular traffic. In addition, its major urban centre; Okpoma and its neighbourhood Okuku where Cross River State University of Technology mini campus is located have business centres, auto-mechanic workshops, and State and Local Government institutions among other urban features. Moreover, 'the inhabitants plant vegetables in old waste dump sites at their backyards with a view to tap the compost manure for good yield even though wastes were indiscriminately disposed in these sites' (Akpe et al., 2019). All these features together with erosion during the rainy season make heavy metal contamination of the area inevitable. Hence, there is need to assess the edible vegetables and soil quality with respect to heavy metals pollution, and also evaluate the possible health risk related to their consumption.

Sampling and sample pre-treatment: 40 soil samples and vegetables (with 5 of each vegetable) were collected randomly at different locations within Yala urban area at a distance of about 1km apart. The vegetables were grown or planted in gardens by the inhabitants of the area at their backyards or premises at old domestic waste dumpsites where wastes were disposed indiscriminately in order to tap the compost manure for good yield. The soil samples were collected at the root level of the vegetables at the depth of about 12 to 15 cm, using a hand trowel. At the same time, a handful of the edible vegetables were collected and wrapped separately with identification labels, and taken to the laboratory for further analysis. The edible vegetables considered for this study include: Amaranthus spp (Green vegetable), Corchorus olitorius (Ewedu), Murraya koeningii (Curry leaf), Ocimium grattissimum (scent leaf), Solanum melongena (eggplant leaf), Telfairia occidentalis (pumpkin), Talinum triangulare (water leaf) and Vernonia amygdalina (Bitter leaf). They are commonly used for food and medicinal purposes in the area. The samples were collected between January and March for the dry season and between July and September for the rainy season of 2019. The vegetable samples were washed with distilled water and ovendried at 90 °C for about 3 hours. Each dried sample was ground into powder, sieved with a 0.3 mm sieve and stored in a labeled plastic jar with cap. The soil sampled was also oven-dried, ground into powder and homogenized using pestle and mortar, sieved and store in labeled plastic jars separately.

Digestion of samples: vegetable samples were digested as follows: 2 g of homogenised and sieved

powder of each vegetable was transferred into a clean dry round-bottomed flask and digested using a mixture of concentrated acids namely; 15 mL of HCl, 10 mL of HNO₃, 5 mL of H₂SO₄ and 2 mL of H₂O₂, at about 100 °C on a hot plate for about three hours in a fume cupboard. Each digest was allowed to cool and deionized water was added to the digest and made up to 100 mL in a volumetric flask. The solution was stirred and filtered to obtain the filtrate ready for AAS analysis of heavy metals. In a similar way, the soil samples were digested following the procedure of one of the methods of the Association of Official Analytical Chemists (AOAC) as reported by Akan et al. (2010) thus: '2.0 g of each soil sample powder was weighed into an acid washed beaker. 20 mL of aqua regia (mixture of HCl and HNO₃, in the ratio 3:1) was added to the sample in the beaker. The beaker was covered with a clean dry watch glass and heated at 90 ⁰c for about 2 hours; the beaker was removed, allowed to cool, washed together with the watch glass using deionized water into a volumetric flask and made-up to 100 mL solution. The solution was filtered and supernatant liquid solution was used for heavy metal analysis.'

Measurement of pH: 20 g of oven-dried soil samples were weighed into a 50 mL beaker and 20 mL of distilled water was added and the pH of the soil samples was determined using a pH meter and the results were recorded.

Element Analysis: the soil and vegetable samples were analyzed for Cr, Fe, Hg and Ni using a VGP 210 BUCK Scientific Model of flame Atomic Absorption Spectrometer (AAS) at the following wavelengths: Cd (228.9 nm), Co (240.7 nm), Pb (283.3 nm) and Zn (213.1 nm).

Calculations: The Target Hazard Quotient which is the ratio of the body intake dose of a pollutant to the reference dose was calculated thus:

$$THQ = \frac{DIVxCm}{RfDxB}$$

Where DIV is the daily intake of vegetable in kg/day, Cm is the concentration of pollutant (heavy metal) in the vegetable in mgkg⁻¹, B is the average body weight of humans in kg, while RfD is the oral reference dose of the pollutant permissible and it is fixed by United States Environmental Protection Agency (US-EPA). Note: B is assumed by US-EPA to be 70kg for men and 60kg for women. For this study, 65kg (the average of 70kg and 60kg) was used for all adults, while the DIV was assumed to be 100g (0.1kg/day) per day. In some countries or places, up to 150 or 200g per day has been assumed especially for vegetarians. From the formula, THQ is a dimensionless parameter or ratio. According to US-EPA through Integrated Risk Information System-database IRIS (2011), 'if THQ is less than 1(THQ<1), it shows that there is no potential health risk associated with the pollutant. But if THQ>1, there is a health risk associated with the pollutant (heavy metal) at that moment.' The RfD values for Cd, Co, Pb and Zn from IRIS are 0.001, 0.1, 0.0035 and 0.3 mgkg⁻¹ respectively IRIS (2011).

Statistical Analysis: The data collected was analyzed using SPSS version 20. The data were expressed in terms of descriptive statistics and figures were presented with mean values of triplicates. Significance test was also computed using paired t-test at P < 0.05 for dry and rainy season data in order to check whether there was any significant difference.

RESULTS AND DISCUSSION

The mean heavy metal concentration in mgkg⁻¹ (dry weight) in the soil and vegetables during the rainy and dry season have been presented in Tables 1 and 2 respectively, while the Target Hazard Quotients of the metals have been presented in Tables 3 and 4 for the both seasons.

pH: It ranged from 4.2- 6.8 and 4.3- 6.7 in rainy and dry seasons respectively for all soil samples. The results in Tables 1 and 2 above indicated that the average level of the metals in the soil in mgkg-1 ranged from (0.005-0.021) and (0.004-0.019) in rainy and dry seasons respectively for Cd, (0.162-0.475) and (0.163-0.472) in rainy and dry season respectively for Co, and (0.434-1.030) and (0.432-1.027) in rainy and dry season respectively for Zn. Also, the average level of the metals accumulated by the vegetables in mgkg⁻¹ ranged from (0.002-0.009) and (0.001- 0.007) in rainy and dry season respectively for Cd, (0.050-0.198) and (0.048-0.195) in rainy and dry season respectively for Co, and (0.158-0.383) and (0.156-0.380) in rainy and dry season respectively for Zn. The level of Lead (Pb) in the soil or vegetables was not detected. The average level of metals accumulated by the vegetables and that present in the soil was in the order: Zn > Co > Cd >Pd. The results also revealed that there is no significant difference between the level of the metals in the soil and vegetables for both seasons, suggesting that the source of these metals may not be from air pollution sources such as vehicular emissions or irrigation water sources used in dry season. Therefore, the source may be from indiscriminate disposal of waste containing these metals, leaching from auto-mechanic workshops etc.

The accumulation of these metals by vegetables depends on the amount of metal in the soil, its chemical form, the pH of the soil, its porosity which could determine their availability for the vegetables or plants. 'The chemical nature of Zinc and its interaction with other elements or substances in the soil for instance determines its availability in the soil for vegetables or plants to accumulate (Shuman, 1991 and Kiekens, 1990).

836

Table 1: Average level of Cd, Co, Pb and Zn in mgkg⁻¹ (dry weight) in the soil and vegetables during the rainy season in Yala urban area.

Vegetable	Cd	Со	Pb	Zn
Amarathus spp.	0.004 ± 0.002	0.175±0.054	ND	0.206±0.094
Soil	0.010 ± 0.003	0.424 ± 0.067	ND	0.434 ± 0.106
C. olitorius	0.009 ± 0.002	0.198 ± 0.075	ND	0.220±0.091
Soil	0.021 ± 0.004	0.457 ± 0.047	ND	0.909 ± 0.102
M. koenigii	0.007 ± 0.003	0.050 ± 0.015	ND	0.237±0.063
Soil	0.016 ± 0.003	0.162 ± 0.013	ND	0.737±0.073
O. gratissimum	0.002 ± 0.001	0.170 ± 0.036	ND	$0.184{\pm}0.081$
Soil	0.007 ± 0.002	0.405 ± 0.027	ND	0.551±0.115
S. melongena	0.007 ± 0.003	0.148 ± 0.048	ND	0.172 ± 0.036
Soil	0.015 ± 0.005	0.373 ± 0.018	ND	0.509 ± 0.081
T. triangulare	0.002 ± 0.001	0.108 ± 0.024	ND	0.195 ± 0.048
Soil	0.005 ± 0.003	0.434 ± 0.046	ND	0.523 ± 0.074
T. occidentalis	0.004 ± 0.002	0.125±0.024	ND	0.158 ± 0.057
Soil	0.009 ± 0.003	0.340 ± 0.027	ND	0.606 ± 0.084
V. amygdalina	0.004 ± 0.002	0.188 ± 0.023	ND	0.383 ± 0.118
Soil	$0.008 {\pm} 0.003$	0.475 ± 0.005	ND	1.030 ± 0.120

Values reported in mean \pm *SD format, ND* – *Not Detected.*

Table 2: Average level of Cd, Co, Pb and Zn in mgkg⁻¹ (dry weight) in the soil and vegetables during the dry season in Yala urban area.

Vegetable	Cd	Со	Pb	Zn
Amarathus spp.	0.003 ± 0.002	0.170 ± 0.050	ND	0.203±0.089
Soil	0.008 ± 0.003	0.421±0.063	ND	0.432 ± 0.103
C. olitorius	0.007 ± 0.003	0.195 ± 0.080	ND	0.217±0.094
Soil	0.019 ± 0.005	0.454 ± 0.050	ND	0.905±0.100
M. koenigii	0.006 ± 0.003	0.048 ± 0.020	ND	0.232 ± 0.064
Soil	0.015 ± 0.004	0.163 ± 0.018	ND	0.730 ± 0.079
O. grattissimum	0.002 ± 0.001	0.168 ± 0.039	ND	0.179 ± 0.080
Soil	0.005 ± 0.003	0.403 ± 0.029	ND	0.550±0.117
S. melongena	0.006 ± 0.003	0.145 ± 0.050	ND	0.169 ± 0.039
Soil	0.014 ± 0.005	0.370 ± 0.020	ND	0.507 ± 0.082
T. triangulare	0.001 ± 0.001	0.105 ± 0.038	ND	0.189 ± 0.053
Soil	0.004 ± 0.002	0.430 ± 0.040	ND	0.519 ± 0.079
T. occidentalis	0.003 ± 0.001	0.122 ± 0.028	ND	0.156 ± 0.059
Soil	0.008 ± 0.002	0.338 ± 0.029	ND	0.602 ± 0.081
V. amygdalina	0.003 ± 0.001	0.183 ± 0.027	ND	0.380±0.119
Soil	0.007 ± 0.003	0.472 ± 0.026	ND	1.027±0.021

ND- Not Detected, Values in mean \pm SD format

Several researchers have reported that the solubility of the cationic forms of the metals in the soil solution increases as the soil pH decreases, and they become readily available for plants to accumulate. For example, cadmium is more available at low soil pH (acidic soils) than neutral or alkaline soils (Filius et al., 1998, Mann and Ritche (1995) and Oliver et al., 1998). Mercury also is more bioavailable in acidic or low pH soils than alkaline soils (Melgar et al., 2009). Thus, acidic soils enhance the accumulation of metals by vegetables than neutral or alkaline soils. From the results, the soil pH ranged 4.2-6.8 indicating that the soil is quite acidic and should support the accumulation of these metals. This pH results agreed with an earlier study on the soil properties it was reported that 'the soil is porous, leached and its pH ranged from 4 to 6 (Free Library, 2014).' The results also indicate that there is no significant difference between the concentration of metals in the soil and that accumulated by the vegetables in the rainy and dry season of the year. However, the concentration of Cadmium, Cobalt and Zinc in the soil and that accumulated by the edible vegetables is still very low and within the permissible limits of WHO/FAO. Besides, Lead was not detected in the soil or the vegetables. Therefore efforts has to be made by relevant government agencies to maintain this low concentration of the metals in the study area through public awareness of the effects of pollution and a periodic environmental monitoring and assessment of the metals concentration in the area.

 Table 3: Target Hazard Quotients of Cd, Co, Pb and Zn in Yala

 Urban area in rainy season

Vegetable	Cd	Čo	Pb	Zn
Amaranthus spp.	0.0061	0.0027	Nil	0.0011
C. olitorius	0.0139	0.0031	Nil	0.0011
M. koenigii	0.0108	0.0008	Nil	0.0012
O. grattissimum	0.0031	0.0026	Nil	0.0009
S. melongena	0.0108	0.0023	Nil	0.0009
T. triangulare	0.0031	0.0017	Nil	0.0010
T. occidentalis	0.0061	0.0019	Nil	0.0008
V. amygdalina	0.0061	0.0029	Nil	0.0020

Note: Pb was not detected and has no THQ values.

 Table 4: Target Hazard Quotients of Cd, Co, Pb and Zn in Yala

 Urban area in dry season

Urban area in dry season					
Vegetable	Cd	Со	Pb	Zn	
Amaranthus spp.	0.0046	0.0026	Nil	0.0010	
C. olitorius	0.0108	0.0030	Nil	0.0011	
M. koenigii	0.0092	0.0007	Nil	0.0012	
O. grattissimum	0.0031	0.0026	Nil	0.0009	
S. melongena	0.0092	0.0022	Nil	0.0009	
T. triangulare	0.0015	0.0016	Nil	0.0009	
T. occidentalis	0.0046	0.0019	Nil	0.0008	
V. amygdalina	0.0046	0.0028	Nil	0.0020	

Note: Pb was not detected and has no THQ values.

Target hazard quotients (THQ) of the metals as shown in Tables 3 and 4 for Cd, Co and Zn that were detected in the vegetables were far less than 1 for all vegetables in both seasons. This implies that the heavy metals concentration in the edible vegetables is not posing any risk and there is no potential health risk associated with their consumption for now. According to US-EPA/IRIS (IRIS, 2011), 'it is only THQ values greater than 1 that shows there is potential health risk associated with the consumption of food or vegetables contaminated with a certain pollutant or heavy metal.' Thus, the THQ values also agreed with the fact that the mean concentrations of these metals in the vegetables are still low and within the permissible limits of WHO/FAO.

Conclusion: This study revealed that there is some amount of Cadmium, Cobalt and Zinc in the soil, which has been accumulated by the edible vegetables in the area. Lead was not detected in the area and seems negligible at the moment. The amount of the metals present in the soil and vegetable are still very low and within the permissible limits of WHO/FAO. Thus, the amount of these metals in the edible vegetables within the period of this study may not pose any health risk.

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