Journal of Scientific Research & Reports

24(6): 1-8, 2019; Article no.JSRR.51460
ISSN: 2320-0227

Concentration of Selected Heavy Metals in Soil and Edible Vegetables in Obanliku Urban Area of Cross River State, Nigeria

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Authors' contributions

This work was carried out in collaboration among all authors. Author MAA designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors JO and JAA managed the analyses of the study. Author JAA managed the literature searches. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/JSRR/2019/v24i630171
Editor(s):
(1) Assoc. Prof. Dr. Suleyman Korkut, Department of Forest Industry Engineering, Duzce University, Division of Wood Mechanic and Technology, 81620 Beciyorukler Campus Duzce, Turkey.
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(3) Jaime Moises Horta Rangel, University of Queretaro, Mexico.
Complete Peer review History: https://sdiarticle4.com/review-history/51460

Original Research Article

Received 11 July 2019
Accepted 19 September 2019
Published 04 October 2019

ABSTRACT

The soil and edible vegetable samples were collected from Obanliku Urban Area of Cross River State and were digested and analyzed for the cadmium (Cd), chromium (Cr), iron (Fe) and mercury (Hg) (heavy metals) concentration using Flame Atomic Absorption Spectrometer (AAS) in Chemistry Laboratory, University of Calabar. The eight vegetables were considered such as *Amaranthus spp., Corchorus olitorius, Murraya koenigii, Ocimum grattissimum, Solanum melongena, Talinum triangulare, Telfaira occidentalis* and *Vernonia amygdalina*. The results revealed that the mean concentration of the metals in the soil in $mgkg^{-1}$ ranged from (0.003-0.017) and (0.003-0.015) for Cd, (0.005-0.040) and (0.004-0.038) for Cr, and (0.052-1.541) and (0.050-1.511) for Fe in rainy and dry seasons respectively. Also, the mean concentration of the metals accumulated by the vegetables in $mgkg^{-1}$ ranged from (0.002-0.010) for Cd, (0.003-0.018) and (0.003-0.016) for Cr, and (0.013-0.175) and (0.013-0.150) for Fe in rainy and dry season respectively. The concentration of Hg was not detected in the soil or vegetables. The mean concentration accumulated by the vegetables and that present in the soil was in the order: Fe > Cr

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> Cd > Hg. These results showed that there is no significant difference between the amount of metals in the soil or that accumulated by the vegetables in rainy and dry seasons of the year. Also the amount of metals accumulated by most of the vegetables was directly proportional to the amount present in the soil where they are planted. The bioaccumulation ratios and Target Hazard Quotients (THQ) were all less than 1. The results indicate that the concentration of Cd, Cr, Fe & Hg in the soil and vegetables were still low and within the permissible limits of WHO/FAO. Thus, the consumption of the vegetables in the area at the time when this study was carried out may not pose any health risk.

Keywords: Concentration; heavy metals; soil, edible; vegetables; Obanliku.

1. INTRODUCTION

Cadmium (Cd), chromium (Cr), iron (Fe) and mercury (Hg) are chemical elements often referred to as trace or heavy metals. Trace elements (metals) have been defined as those elements or metals present in living organisms only in very small levels but necessary for normal metabolism [1]. Trace metals also occur naturally in very small amounts in the earth's crust and are also known as heavy metals in terms of their density or specific gravity. Examples of these elements are transition metals, some metalloids, lanthanides and actinides. According to Hardy [2], heavy metal has a specific gravity of 5.0 or its greater and is usually poisonous. However, the term heavy metal is often widely applied to include other potentially toxic elements even if they do not meet up with the apt chemical definition. Cd, Cr, Fe, and Hg belong to this group of elements. Based on their toxic or poisonous 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. As a result of this, several studies have been carried out on heavy metals in different parts of the world by researchers, some of which the results revealed that the metals concentration were within the acceptable limits in their various localities and a few others were above the acceptable limits; to ascertain their food and environment quality/safety. For instance, Chandorka and Deota [3] studied the heavy metal content of cereals and vegetables in Vadodara, India and reported that As, Cd and Pb content exceeded critical limits. Mercury, chromium and cadmium levels of agricultural soils and vegetables in Pearl River delta, South China have been studied and reported to be below the FAO/WHO limits of 0.01, 0.5 and 0.2 mg/kg respectively [4]. Heavy metals level; namely Pb, Co, Cd and Mn of cassava flour in Kogi State, Nigeria have also been studied and stated to be very low and within the permissible limits of WHO/FAO [5]. In suburbs of Baoding city, China, heavy metals in edible parts of vegetables in sewage-irrigated soil were investigated and their average level in mg/kg recorded to be Cd (0.29), Ni (27.81), Cu (35.06), Pb (38.35) and Zn (157.77) [6]. The health risk of heavy metals via the consumption of food stuffs and vegetables in the Central market of Rajshahi city, Bangledesh were studied and reported to pose a health risk for consumers especially arsenic that exceeded the acceptable limits [7]. Also, human health risk of heavy metals in contaminated edible vegetables from irrigation sources in Lahore, Pakistan were studied and reported to have exceeded the permissible limits of EU and could pose a severe health risk [8]. In the Netherlands, a research have been carried out on the trace metals level of some vegetables and fruits and the results revealed that the median levels of Cd, Cu, Mn, Hg, Pb and Zn were tolerable [9]. Similarly, the heavy metals level of some fruits and vegetables in Saudi Arabia were studied in four major cities and concluded that Fe, Mn , Cd, Hg, Pb and Zn values exceeded maximum recommended limits of WHO/FAO [10]. Despite this numerous researches, there are still other areas where their food and environmental quality with respect to heavy metal pollution is not studied and known yet, like the current study area. Heavy metals are the major contaminating agents of our food and a problem of our environment [11].

Moreover, Khan [12] has opined that the consumption of contaminated vegetables constitutes an important route for animal and human exposure to heavy metals. Sources of these metals vary from area to area depending on human activities in each area. According to Zhou [13], phosphate fertilizers are the main source of heavy metals pollution because cadmium is an impurity in phosphate rocks. It has been reported also that heavy metals are natural constituents of the earth's crust which are accumulated by plants and transferred to the food chain [14]. Halwell [15] 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 might be affected negatively when they consume these vegetables and accumulate these toxic substances in high doses. High doses of chromium for example can cause chronic bronchitis, diarrhea, itching of respiratory tract, liver diseases, lung cancer, etc, in humans; and chlorosis and stunted growth in plants [16]. Mercury causes brain damage, blindness, digestive problems, kidney diseases, mental retardation, etc. [17]. High dose of cadmium causes adverse effect on kidney, liver, bones, immune system and chronic poisoning [18]. Consequently, this study aims to determine the concentration of some heavy metals (Cd, Cr, Fe and Hg) in the soil and edible vegetables in the study area (Obanliku) and ascertain the soil and vegetable quality with respect to heavy metal pollution.

Obanliku urban area is characterized with low land, plains and mountainous landforms like hills and plateaus with rocks of different kinds which also make it a good haven for quarry activities. In facts, it is the home of the famous Obudu Cattle Ranch, a world tourist site. The soil is well drain sandy loam in texture, which makes it suitable for agriculture. It has population of about 100 thousand people. Besides, the people engaged in subsistence and commercial farming, growing rice, cassava, yam, cocoa 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 northern part of the country and sometimes experience heavy vehicular traffic. In addition, its major urban centre; Sankwala 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 discarded there indiscriminately [19]. 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.

2. MATERIALS AND METHODS

2.1 Sampling and Sample Pre-treatment

Forty soil samples and vegetables (with 5 of each vegetable) were collected randomly at different locations within Obanliku urban area at a distance of about 1 km apart. The vegetables were grown or planted in gardens at the backyards or premises of the inhabitants of the area 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), *Ocimum grattissimum* (scent leaf), *Solanum melongena* (egg plant leaf), *Telfaira 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 the year (2018). The vegetable samples were washed with distilled water and oven-dried at 85-90°c for about 2 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.

2.2 Digestion of Samples

Vegetable samples were digested following the procedure of one of the methods of the Association of Official Analytical Chemists (AOAC) as reported by Sobukola [20] thus: 1.0 g of each sample was put in a beaker and placed in a fume cupboard, 20 mL of concentrated (HCl), 10 mL of concentrated HNO_3 and 5 mL of H_2SO_4 were added. After digestion was complete, the beaker was heated in a fume cupboard for about 30 minutes. The digested sample was removed and allowed to cool.

De-ionized 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 supernatant liquid ready for heavy metals analysis. Similarly 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 [21] 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 HNO_3, 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°c for about 2 hours; the beaker was removed, allowed to cool, washed together with the watch glass using de-ionized 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. The pH of the soil samples was also 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 AAS at the following wavelengths: Cd (228.9 nm), Cr (357.0 nm), Fe (248.0 nm) and Hg (253.7 nm).

2.3 Calculations

Bioaccumulation ratio which is the ratio of the concentration of a pollutant (metal) in the plant or vegetable to its concentration in the soil was calculated using the formula:

$$Bioaccumulation\ ratio = \frac{Cm\ in\ plant}{Cm\ in\ Soil}$$

Where,

Cm is the concentration of the metal or pollutant. 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 adult males and 60 kg for adult females. For this study, 65 kg (the average of 70 kg and 60 kg) was used for all adults, while the DIV was assumed to be 100 g (0.1 kg/day) per day. In some countries or places, up to 150 or 200 g 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 [22], 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, Cr, Fe and Hg from IRIS are 0.001, 0.003, 0.7 and 0.01 $mgkg^{-1}$ respectively [22].

2.4 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.

3. RESULTS

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 Bioaccumulation ratios of the vegetables have been presented in Tables 3 and 4 for the both seasons. Target Hazard Quotients of only the highest and lowest values the metals accumulated by the vegetables were calculated and their range reported.

3.1 Target Hazard Quotients

These ranged from (0.0061- 0.0154) and (0.0046- 0.0154) in rainy and dry season respectively for Cd, (0.0015- 0.0092) and (0.0015- 0.0087) in rainy and dry season respectively for Cr, and (0.00001- 0.0004) and (0.00001- 0.0003) in rainy and dry season respectively for Fe in all the vegetables.

3.2 pH

It ranged from 4.0- 6.6 and 4.1- 6.4 in rainy and dry seasons respectively for all soil samples.

4. DISCUSSION

The results in Tables 1 and 2 revealed that the mean concentration of the metals in the soil in $mgkg^{-1}$ ranged from (0.003-0.017) and (0.003-0.015) in rainy and dry seasons respectively for Cd, (0.005-0.040) and (0.004-0.038) in rainy and dry season respectively for Cr, and (0.052-1.541) and (0.050- 1.511) in rainy and dry season respectively for Fe. Mercury (Hg) was neither detected in the soil nor in the vegetables in both seasons. These results indicated that the metals availability in the soil was in the order Cd > Cr > Fe > Hg. The results also revealed that there is no significant difference between concentration of the metals in the soil and vegetables for both seasons, suggested that the source of these metals might 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. or anthropogenic activities like quarrying and road construction among others. Although the difference in the concentration of the metals accumulated by the vegetables in the rainy and dry season was not significant, the values of rainy season were slightly higher than those of the dry season because there is more availability of metal ions in the soil solution during the rainy season from erosion and leaching from nearby areas; and plant roots grow deeper, faster and take up more nutrients from the soil.

The bioaccumulation ratios of the metals shown in Tables 3 and 4 revealed the ratios of the concentration of metals in the vegetable to that present in the soil for the rainy and dry season respectively. The bioaccumulation ratio of Cd for the vegetables ranged from (0.583-0.750) and (0.600 – 0.667) for rainy and dry seasons respectively, that of Cr ranged from (0.091 – 0.600) and (0.250 – 0.615) for rainy and dry seasons respectively, while that of Fe ranged from (0.017 – 0.750) and (0.009-0.660) for rainy and dry season respectively.

The bioaccumulation ratios of the metals were in the order: Cd > Cr > Fe > Hg. These results also showed that Cd was accumulated more by the vegetables generally even though its concentration was the lowest in the soil, while Fe was accumulated less by the vegetables even though its concentration was the highest in the soil. 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. 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 instance, Cd is more available at low soil pH (acidic soils) than neutral or alkaline soils [23,24,25]. Cr and Fe are also reported to be more available in low pH soils [26,27]. Mercury bioavailability is also favourable in acidic or low pH soils [28]. That is, acidic soils enhance the availability of these metals for vegetables to accumulate than neutral or alkaline soils. From the results, the soil pH ranged 4.0-6.6 indicating that the soil is quite acidic and should support the accumulation of these metals depending on their amount present in the soil. Bioaccumulation ratio is a dimensionless quantity that gives the ratio of the concentration of a pollutant (metal) in a vegetable or plant to the concentration in the soil. The results also indicate the rate or extent of transfer of the pollutant or metal from the soil to plant or vegetables. Plants or organisms with bioaccumulation ratios highly greater than 1 could be used for bioremediation of that pollutant from a highly contaminated area. This is achieved by growing such plants in a contaminated area till maturity when they are harvested and properly disposed repeatedly until the pollutant level in the soil is reduced [29]. 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 Cd, Cr and Fe in the soil and that accumulated by the edible vegetables is still very low and within the permissible limits of WHO/FAO. Besides, mercury (Hg) 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. Target hazard quotients (THQ) of Cd, Cr and Fe 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 [22], 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.

Table 1. Mean concentration of Cd, Cr, Fe and Hg in mgkg^{-1} (dry weight) in the soil and vegetables during the rainy season in Obanliku urban area

Vegetable	Cd	Cr	Fe	Hg
Amarathus spp.	0.010±0.003	0.010±0.003	0.175±0.054	ND
Soil	0.017±0.004	0.017±0.004	0.507±0.062	ND
C. olitorius	0.009±0.003	0.018±0.005	0.013±0.003	ND
Soil	0.015±0.003	0.040±0.012	0.550±0.013	ND
M. koenigii	0.003±0.001	0.017±0.003	0.015±0.005	ND
Soil	0.005±0.002	0.034±0.009	1.541±0.015	ND
O. gratissimum	ND	0.013±0.004	0.039±0.005	ND
Soil	ND	0.022±0.007	0.052±0.007	ND
S. melongena	0.002±0.001	0.004±0.003	0.179±0.041	ND
Soil	0.004±0.001	0.009±0.004	0.537±0.015	ND
T. triangulare	ND	0.007±0.003	0.125±0.027	ND
Soil	ND	0.011±0.003	1.542±0.032	ND
T. occidentalis	ND	0.003±0.001	0.048±0.005	ND
Soil	ND	0.005±0.002	0.209±0.023	ND
V. amygdalina	0.007±0.002	0.009±0.003	0.014±0.005	ND
Soil	0.012±0.003	0.015±0.005	0.832±0.179	ND

Values reported in mean ± SD format, ND – Not Detected

Table 2. Mean concentration of Cd, Cr, Fe and Hg in mgkg^{-1} (dry weight) in the soil and vegetables during the dry season in Obanliku

Vegetable	Cd	Cr	Fe	Hg
Amarathus spp.	0.010±0.003	0.009±0.003	0.150±0.051	ND
Soil	0.015±0.004	0.017±0.003	0.505±0.067	ND
C. olitorius	0.009±0.002	0.016±0.003	0.013±0.002	ND
Soil	0.013±0.003	0.038±0.010	0.536±0.023	ND
M. koenigii	0.003±0.001	0.015±0.003	0.015±0.003	ND
Soil	0.005±0.002	0.033±0.009	1.511±0.039	ND
O. grattissimum	ND	0.009±0.003	0.033±0.005	ND
Soil	ND	0.021±0.007	0.050±0.006	ND
S. melongena	0.002±0.001	0.003±0.002	0.135±0.023	ND
Soil	0.003±0.002	0.010±0.003	0.522±0.032	ND
T. triangulare	ND	0.006±0.003	0.100±0.039	ND
Soil	ND	0.010±0.012	1.529±0.021	ND
T. occidentalis	ND	ND	0.053±0.007	ND
Soil	ND	0.004±0.001	0.203±0.021	ND
V. amygdalina	0.007±0.003	0.008±0.003	0.012±0.007	ND
Soil	0.011±0.003	0.013±0.005	0.820±0.138	ND

ND- Not Detected, Values in mean ± SD format

Table 3. Bioaccumulation ratios of Cd, Cr, Fe and Hg in Obanliku urban area of Cross River State in rainy season

Vegetables	Cd	Cr	Fe	Hg
Amaranthus spp.	0.588	0.588	0.345	Nil
C. olitorius	0.563	0.450	0.024	Nil
M. koenigii	0.600	0.529	0.009	Nil
O. grattissimum	Nil	0.591	0.750	Nil
S. melongena	0.750	0.444	0.333	Nil
T. triangulare	Nil	0.091	0.081	Nil
T. occidentalis	Nil	0.600	0.230	Nil
V. amygdalina	0.583	0.563	0.017	Nil

Table 4. Bioaccumulation ratios of Cd, Cr, and Fe & Hg in Obanliku urban area of Cross River State in dry season

Vegetable	Cd	Cr	Fe	Hg
Amaranthus spp.	0.667	0.529	0,297	Nil
C. olitorius	0.692	0.421	0.024	Nil
M. koenigii	0.600	0.455	0.009	Nil
O. grattissimum	Nil	0.429	0.660	Nil
S. melongena	0.667	0.250	0.259	Nil
T. triangulare	Nil	0.333	0.065	Nil
T. occidentalis	Nil	Nil	0.261	Nil
V. amygdalina	0.636	0.615	0.015	Nil

5. CONCLUSION

The results of this study have shown that there is some level of Cd, Cr and Fe in the soil, which have been accumulated by the edible vegetables in the area. The concentration of Hg was not detected in the area and seems negligible at the moment. The level of the metals present in the soil and vegetable are still very low and within the permissible limits of WHO/FAO. Thus, the concentration of these metals in the edible vegetables at the time when this study was carried out may not pose any health risk.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Peer-review history:
The peer review history for this paper can be accessed here:
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