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HEALTH IMPLICATIONS OF SOME HEAVY METALS IN SOIL AND EDIBLE VEGETABLES IN OBANLIKU URBAN AREA OF CROSS RIVER STATE, NIGERIA

MICHAEL AKOMAYE AKPE[1], BASSEY ENYI INAH[2], PROVIDENCE BETELWHOBEL ASHISHIE[3]

DEPARTMENT OF PURE AND APPLIED CHEMISTRY, UNIVERSITY OF CALABAR, CALABAR, NIGERIA[1, 2,3.]

Abstract— Edible vegetable and soil samples were collected from Obanliku Urban Area of Cross River State, digested and analyzed for the cobalt (Co), Nickel (Ni), lead (Pb) and zinc (Zn) concentration in them, using Flame Atomic Absorption Spectrometer (AAS) in Chemistry Laboratory, University of Calabar. The eight vegetables considered in the study were Amaranthus spp., Corchorus olitorius, Murraya koenigii, Ocimum grattissimum, Solanum melongena, Talinum triangulare, Telfaira occidentalis and Vernonia amygdalina. The results showed that the average amount of the metals in the soil in mgkg-1 ranged from (0.027-1.075) and (0.029-1.070) in rainy and dry seasons respectively for Co, (0.009-0.018) and (0.010-0.016) in rainy and dry season respectively for Pb, and (0.320-1.077) and (0.319-1.079) in rainy and dry season respectively for Zn. Also, the average amount of the metals accumulated by the vegetables in mgkg-1 ranged from (0.015-0.127) and (0.008-0.072) in rainy and dry season for Co, (0.006-0.013) and (0.005-0.010) in rainy and dry season respectively for Pb, and (0.021-0.209) and (0.019-0.207) in rainy and dry season respectively for Zn. The amount of Ni was not detected in the soil or vegetables. The average concentration accumulated by the vegetables and that present in the soil was in the order: Zn > Co > Pb > Ni. These values revealed that there is no significant difference between the concentration 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 varies directly as the amount present in the soil where they are planted. The Target Hazard Quotients (THQ) was all less than 1. These results suggest that the concentration of Co, Pb, Zn & Ni in the soil and vegetables were still low and within the allowable limits of WHO/FAO. Thus, the consumption of the vegetables in the area at the time of carrying out this study may not pose any health risk.

Keywords— Health implications, Heavy metals, soil, Vegetables, Obanliku.

1. Introduction

Cobalt (Co), nickel (Ni), lead (Pb) and zinc (Zn) are chemical elements often classified as trace or heavy metals. According to Duffus (2002), a heavy metal is a collective term which refers to the group of trace metals and metalloids with an atomic density greater than 4 g/cm3. 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 [17]. 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 atomic density or specific gravity. Examples of these elements are transition metals, some metalloids, lanthanides and actinides. Co, Ni, Pb and Zn belong to this group of elements. Based on their toxic or poisonous effect at high or even low 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, in Makurdi, Benue State of Nigeria, Raphael and Adebayo (2011) assessed the heavy metals level in vegetables irrigated with water from River Benue and reported that the water used for irrigation contain an average level of 0.0013 µg/g for Cu, 0.0022 µg/g for Mn and 0.0024 µg/g for Zn, while Cd, Ni and Pb were not detected. The amounts of metals accumulated by the vegetable and fruit samples were within the allowable limits of WHO/FAO and EU due to the low level of metals in the soil and water. Also, 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) [22]. Similarly, Saha and Zaman (2013) studied the health risk of heavy metals via the consumption of food stuffs and vegetables in the Central market of Rajshahi city, Bangledesh and reported that the metals pose a health risk for consumers especially arsenic that exceeded the acceptable limits. 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 [16]. In the Netherlands, a research has 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 (Ellen et al., 1990). Despite these 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 [1].

Moreover, Khan (2008) 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 (1994), phosphate fertilizers are the main source of heavy metals pollution because cadmium is an impurity in phosphate rocks. Some of these metals are released into the environment as waste when house hold goods, gadgets or utensils containing them are disposed indiscriminately after use. Lenntech (1998) have reported that Cobalt is used in alloys and in electromagnets; Nickel is used in making alloys, batteries and dry cells. Lead is used as stabilizers in paints, pigments and in making batteries and accumulators, while Zinc is also used in making alloys and in electroplating of iron objects or tools against corrosion. Most of these alloys are used in making many house hold goods like electronics, cooking utensils, tools etc. that are used and disposed sometimes indiscriminately, thus introducing heavy metals into the environment. 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, toxic levels of lead causes brain, foetus, kidney and nervous system damages, and low IQ (Intelligent Quotient) in children. Toxic levels of Nickel can lead to skin irritation, heart and liver damage, and decreased body weight [15]. Most heavy metals in high doses can possibly cause disruption of or interference in endocrine system [4], phyto/cytotoxicity [21] and dysfunction of the mitochondria [9] among other health problems. Thus, cobalt and zinc are not exempted in high doses. Consequently, the aim of this study is to determine the concentration of some heavy metals (Co, Ni, Pb and Zn) 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 [3]. 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:

40 soil samples and vegetables (with 5 of each vegetable) were collected randomly at different locations within Obanliku urban area. 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* (eggplant 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 ^{0}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:

Soil samples were digested following the procedure 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 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 ^{0}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.

Similarly, the vegetable samples were digested following the procedure reported by Sobukola *et al*. (2010)

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 in a volumetric flask and made up to 100 mL. The solution of the digest was stirred and filtered to obtain the supernatant liquid ready for heavy metals analysis. The digestion procedures used in this study conforms to methods of the Association of Official Analytical Chemists (AOAC).

Element Analysis: the soil and vegetable samples were analyzed for Co, Ni, Pb and Zn using a VGP 210 BUCK Scientific Model of flame AAS at the following wavelengths: Co (240.7 nm), Ni (232.0 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 adult males and 60kg for adult females. 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 Co, Ni, Pb and Zn from IRIS are 0.1, 0.01, 0.0035 and 0.3 $mgkg^{-1}$ respectively [11].

2.3 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.

2.4 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 Target Hazard Quotients of the heavy metals accumulated by the vegetables have been presented in Tables 3 and 4 for the rainy and dry season respectively.

Table 1: Average concentration of some heavy metals in mgkg-1 (dry weight) in the soil and vegetables during the rainy season in Obanliku urban area.

Vegetable	Co	Ni	Pb	Zn
Amarathus spp.	0.033±0.013	ND	0.008±0.002	0.029±0.068
Soil	0.078±0.011	ND	0.012±0.004	1.022±0.039
C. olitorius	0.028±0.004	ND	0.010±0.003	0.021±0.007
Soil	0.049±0.014	ND	0.016±0.004	0.320±0.031
M. koenigii	0.050±0.012	ND	0.012±0.005	0.062±0.030
Soil	0.085±0.026	ND	0.016±0.007	0.392±0.069
O. gratissimium	ND	ND	0.007±0.003	0.038±0.011
Soil	ND	ND	0.015±0.004	0.913±0.039
S. melongena	0.037±0.021	ND	0.006±0.004	0.125±0.041
Soil	0.063±0.031	ND	0.009±0.003	1.077±0.081
T. triangulare	0.015±0.008	ND	0.012±0.004	0.063±0.034
Soil	0.027±0.009	ND	0.018±0.003	0.554±0.058
T. occidentalis	ND	ND	0.006±0.003	0.118±0.029
Soil	ND	ND	0.014±0.003	0.789±0.037
V. amygdalina	0.127±0.045	ND	0.013±0.005	0.209±0.031
Soil	1.075±0.016	ND	0.016±0.004	1.017±0.050

Values reported in mean ± SD format with N=3, ND – Not Detected.

Table 2: Average concentration of some heavy metals in $mgkg^{-1}$ (dry weight) in the soil and vegetables during the dry season in Obanliku.

Vegetable	Co	Ni	Pb	Zn
Amarathus spp.	0.027±0.009	ND	0.006±0.002	0.087±0.033
Soil	0.076±0.013	ND	0.011±0.003	1.079±0.059
C. olitorius	0.022±0.005	ND	0.009±0.003	0.019±0.009
Soil	0.046±0.004	ND	0.015±0.003	0.319±0.027
M. koenigii	0.048±0.010	ND	0.007±0.003	0.061±0.021
Soil	0.074±0.024	ND	0.011±0.003	0.388±0.069
O. grattissimium	ND	ND	0.006±0.003	0.034±0.012
Soil	ND	ND	0.014±0.003	0.905±0.037
S. melongena	0.033±0.012	ND	0.005±0.002	0.099±0.021
Soil	0.061±0.027	ND	0.010±0.003	1.073±0.057
T. triangulare	0.008±0.004	ND	0.010±0.003	0.065±0.015
Soil	0.029±0.005	ND	0.016±0.004	0.551±0.056
T. occidentalis	ND	ND	0.008±0.003	0.109±0.031
Soil	ND	ND	0.013±0.004	0.782±0.032
V. amygdalina	0.072±0.024	ND	0.010±0.003	0.207±0.033
Soil	1.070±0.036	ND	0.014±0.004	1.015±0.059

ND- Not Detected, Values in mean ± SD format with N=3

Table 3: Target Hazard Quotients of some heavy metals in Obanliku Urban area of Cross River State in rainy season.

Vegetables	Co	Ni	Pb	Zn
Amaranthus spp.	0.0005	ND	0.0035	0.0007
C. olitorius	0.0004	ND	0.0044	0.0001
M. koenigii	0.0008	ND	0.0053	0.0003
O. grattissimium	ND	ND	0.0031	0.0002
S. melongena	0.0006	ND	0.0026	0.0006
T. triangulare	0.0002	ND	0.0053	0.0003
T. occidentalis	ND	ND	0.0026	0.0006
V. amygdalina	0.0020	ND	0.0057	0.0011

Note: ND- Not Detected.

Table 4: Target Hazard Quotients of some heavy metals in Obanliku Urban area of Cross River State in dry season

Vegetable	Co	Ni	Pb	Zn
Amaranthus spp.	0.0004	ND	0.0026	0.0004
C. olitorius	0.0003	ND	0.0040	0.0001
M. koenigii	0.0007	ND	0.0031	0.0003
O. grattissimium	ND	ND	0.0026	0.0002
S. melongena	0.0005	ND	0.0022	0.0005
T. triangulare	0.0001	ND	0.0044	0.0003
T. occidentalis	ND	ND	0.0035	0.0006
V. amygdalina	0.0011	ND	0.0044	0.0011

Note: ND- Not Detected.

3. Discussion

The results in Table 1 and 2 showed that there is some level of heavy metals in the study area (Obanliku), especially Co, Pb, and Zn, and the edible vegetables have also accumulated some of these metals present in the soil. Nickel (Ni) was not detected in the soil or the vegetables and is considered in this study as a string variable. Probably, its concentration in the soil is still insignificant to be detected or available for the vegetables to accumulate at the moment because the AAS used in this study can detect concentrations as low as 0.001. From the data, average concentration of Co in mgkg-1 in the soil ranged from 0.027 to 1.075 and 0.029 to 1.070 for rainy and dry seasons respectively. The level of Pb in the soil in mgkg-1 ranged from 0.009 to 0.018 and 0.010 to 0.016 for the rainy and dry season respectively. The average concentration of Zn in the soil ranged from 0.320 to 1.077 and 0.319 to 1.079 for rainy and dry season respectively. These results showed that the metals availability in the soil and the amount accumulated by the vegetables was in the order Zn> Co> Pb> Ni. 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).' Some researchers like Chlopecka et al.,1996; Evans et al., 1995; Kelly and Tate, 1998 etc. have reported that the solubility of the cationic forms of most metals in the soil solution increases as the soil pH decreases, and they become readily available for plants to accumulate. That is, acidic soils tend to favour the availability of most metals for plants or vegetables to accumulate than alkaline or neutral soils. However, these results also revealed that there is no significant difference between the concentration of the metals in the soil and that accumulated by the 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 from industrial sewage, leaching of metal waste from auto-mechanic workshops during the rainy etc. or anthropogenic activities like quarrying and road construction among others.

Target hazard quotients (THQ) of Co, Pb and Zn that were detected in the vegetables were far less than 1 for all vegetables in both seasons as presented in Tables 3 and 4.. This implies that the heavy metals concentration in the edible vegetables is not posing any threat and there is no potential health risk associated with their consumption for now. According to US-EPA through 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.

4. Conclusion

The results of this study have shown that there is some level of Co, Pb and Zn 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 moment may not pose any health risk.

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