CONCENTRATION OF HEAVY METALS (Cd, Co, Cr, & Fe) IN SOIL AND EDIBLE VEGETABLES IN OBUDU URBAN AREA OF CROSS RIVER STATE, NIGERIA.

ABSTRACT

The soil and edible vegetable samples were collected from Obudu Urban Area of Cross River State and were digested and analyzed for the Cd, Co, Cr, and Fe (heavy metals) concentration using Atomic Absorption Spectrometer (AAS) in the University of Calabar Laboratory. The eight vegetables considered for the study were *Amaranthus spp.*, *Corchorus olitorius*, *Murraya koenigii*, *Ocimum grattissimum*, *Solanum melongena*, *Talinum triangulare*, *Telferia occidentalis* and *Vernonia amygdalina*. The results showed that the mean concentration of the metal in the soil in $mgkg^{-1}$ ranged from (0.004-0.0048) and (0.005-0.046) in rainy and dry seasons respectively for Cd, (0.004-0.025) and (0.006-0.016) in rainy and dry season respectively for Cr, and (0.112-0.173) and (0.116-0.151) in rainy and dry season respectively for Fe. The concentration of Co 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> Cd> Cr> Co. These results suggest 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 were all less than 1. These results indicate that the concentration of Cd, Co, Cr, & Fe 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 may not cause any harm for now.

Keywords: Concentration of heavy metals, soil, edible vegetables.

Introduction

A heavy metal has been described as a member of a loosely defined subset of elements that exhibit metallic properties (Wikipedia free encyclopedia). Examples of these elements are transition metals, some metalloids, lanthanides and actinides. According to Duffus [1], it is a general collective term which applies to the group of metals and metalloids with atomic density greater than 4gcm^{-3}. They are widely recognized as widespread contaminants of land and fresh water ecosystems [1]. Cadmium (Cd), Cobalt (Co), Chromium (Cr), and Iron (Fe) among others belong to this group of elements. They are used to produce many household goods like cooking utensils, alloys, electrical wires/appliances, and magnets/electromagnets etc. which are later discarded as waste. 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. Hence, several researches have been carried out on heavy metals by researchers like Kanake [2], [3], [4], [5], [6], [7], [8] etc. most of which were within the acceptable limits in their various localities to ascertain their food and environment quality/safety. Heavy metals are the major contaminating agents of our food and a problem of our environment [9].

Moreover, Khan [10] has opined that the consumption of contaminated vegetables constitutes an important route for animal and human exposure to heavy metals. 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 reduced as pollutants from the soil will be accumulated by the vegetables [11]. Thus, nutritionally and medicinally valuable as vegetables are, they should not be planted on soils contaminated with hazardous waste like heavy metals which can affect the health of human negatively when they consume these vegetables and accumulate these poisonous substances in high doses. Consequently, the aim of this study is to determine the concentration of some heavy metals (Cd, Co, Cr, & Fe) in the soil and edible vegetables in the study area (Obudu) and ascertain the soil and vegetable quality with respect to heavy metal pollution. The metals were chosen based on their toxic nature especially Cd, and Fe because it is a common metal or metal waste in the environment.

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Obudu urban area is characterized with mountainous land forms, hills and rocks which make it a good haven for quarry activities during road construction in the State. 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 major link to the northern part of the country and most times experience heavy vehicular traffic.

Moreover, the inhabitants of the area practice rotational waste dump sites around their premises and later plant vegetables in old waste dump sites with a view to tap the compost for good yield even though wastes were disposed there indiscriminately. All these characteristics/features together with erosion during the rainy season make heavy metal contamination of the area inevitable. Hence, there is need to ascertain the vegetables and soil quality with respect to heavy metals pollution.

Materials and Methods

Sampling and sample pre-treatment: forty soil samples and vegetables (with five of each vegetable) were collected randomly at different locations within Obudu urban area at a distance of about a kilometer apart from each other. The soil samples (about 10g each) were collected at the root level of the vegetables at the depth of about 12 to 15 cm, and at the same time, about 5g each of the edible vegetable leaves were collected and wrapped in plastic separately with identification labels before taking them to the laboratory.

The edible vegetables considered for this study, and were planted in each of the forty soil samples include: *Amaranthus spp* (Green vegetable), *Corchorus olitorius* (Ewedu), *Murraya koeningii* (Curry leaf), *Ocimium grattissimum* (scent leaf), *Solanum melongena* (egg plant 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 the year. The vegetable samples were washed with distilled water and oven-dried at 80-85 ^{0}C for about 2 hours. Each dried sample was ground into powder, sieved with 0.3 mm sieve and stored in a labeled plastic jar with cap. The soil samples were also oven-dried, ground into fine powder and homogenized using pestle and mortar. They were then sieved and stored in labeled plastic jars separately.

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 [12] thus: 1.0 g of each sample was placed in a beaker and 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 allowed to cool for some time and was removed from the fume cupboard.

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 AOAC as reported by Akan

[13] 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 90^0C 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.

Element Analysis: the soil and vegetable samples were analyzed for Cd, Co, Cr and Fe using a VGP 210 (BUCK Scientific) Model of Flame Atomic Absorption Spectrometer (AAS) at the following wavelengths: Cd (228.9nm), Co (240.7nm), Cr (357.0nm) and Fe (248.0nm).

Calculations: the bioaccumulation ratio which is the ratio of the concentration of the heavy metal or pollutant in the vegetable shoot or leaf to its concentration in the soil (where the vegetable is planted) was calculated thus:

$$Bioaccumulation\ ratio = \frac{Cmp}{Cms}$$

Where C_{mp} is the concentration of heavy metal (pollutant) in vegetable or plant and C_{ms} is the concentration of the same metal in the soil.

Statistical Analysis: The data collected were 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: 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.

Table 1: Mean concentration of Cd, Co, Cr, & Fe in $mgkg^{-1}$ (dry weight) in the soil and vegetables during the rainy season in Obudu.

Vegetable	**Cd**	**Co**	**Cr**	**Fe**
Amarathus spp.	0.013± 0.001	ND	0.008±0.002	0.108±0.005
Soil	0.048±0.003	ND	0.013±0.003	0.148±0.035
Corchorus olitorius	0.011±0.002	ND	0.009±0.005	0.094±0.053
Soil	0.031±0.003	ND	0.013±0.007	0.173±0.011
Murraya koenigii	0.010±0.002	ND	0.009±0.003	0.097±0.030
Soil	0.035±0.002	ND	0.012±0.006	0.146±0.010
Ocimum grattissimum	ND	ND	0.002±0.002	0.066±0.048
Soil	0.003±0.001	NsD	0.004±0.003	0.152±0.069
Solanum melongena	0.010±0.002	ND	0.010±0.003	0.089±0.038
Soil	0.025±0.002	ND	0.025±0.002	0.142±0.030
Talinum triangulare	0.004±0.001	ND	0.002±0.002	0.073±0.038
Soil	0.016±0.003	ND	0.004±0.003	0.131±0.051
Telferia occidentalis	0.003±0.001	ND	0.003±0.001	0.091±0.019

Soil	0.005±0.002	ND	0.007±0.001	0.135±0.053
Vernonia amygdalina	0.006±0.002	ND	0.010±0.003	0.101±0.052
Soil	0.014±0.003	ND	0.017±0.002	0.112±0.044

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

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

Vegetable	**Cd**	**Co**	**Cr**	**Fe**
Amarathus spp.	0.017±0.001	ND	0.009±0.002	0.103±0.010
Soil	0.046±0.002	ND	0.013±0.002	0.137±0.027
Corchorus olitorius	0.013±0.001	ND	0.009±0.005	0.091±0.057
Soil	0.032±0.002	ND	0.012±0.006	0.158±0.010
Murraya koenigii	0.010±0.002	ND	0.007±0.006	0.094±0.026
Soil	0.033±0.003	ND	0.012±0.004	0.140±0.007
Ocimum grattissimum	ND	ND	ND	0.063±0.049
Soil	0.002±0.002	ND	ND	0.151±0.072
Solanum melongena	0.011±0.001	ND	0.008±0.003	0.090±0.018
Soil	0.025±0.001	ND	0.011±0.002	0.135±0.014
Talinum triangulare	0.006±0.002	ND	ND	0.062±0.051

Soil	0.015±0.002	ND	ND	0.129±0.048
Telferia occidentalis	ND	ND	0.003±0.001	0.087±0.022
Soil	0.005±0.001	ND	0.006±0.002	0.132±0.053
Vernonia amygdalina	0.009±0.001	ND	0.009±0.002	0.153±0.047
Soil	0.016±0.003	ND	0.016±0.002	0.116±0.038

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

Table3: Bioaccumulation ratios of Cd, Co, Cr, & Fe (heavy metals) in vegetables in Obudu in rainy season

Vegetables	**Cd**	**Co**	**Cr**	**Fe**
Amarathus spp.	0.271	ND	0.615	0.730
Corchorus olitorius	0.355	ND	0.692	0.543
Murraya koenigii	0.286	ND	0.750	0.664
Ocimum grattissimum	ND	ND	0.500	0.434
Solanum melongena	0.400	ND	0.818	0.627
Talinum triangulare	0.250	ND	0.500	0.557
Telferia occidentalis	0.600	ND	0.428	0.674
Vernonia amygdalina	0.428	ND	0.588	0.902

Table 4: Bioaccumulation ratios of Cd, Co, Cr, & Fe (heavy metals) in vegetables in Obudu in dry season

Vegetables	Cd	Co	Cr	Fe
Amarathus spp	0.370	ND	0.692	0.752
Corchorus olitorius	0.406	ND	0.750	0.576
Murraya koenigii	0.303	ND	0.583	0.671
Ocimum grattissimum	ND	ND	ND	0.417
Solanum melongena	0.440	ND	0.727	0.667
Talinum triangulare	0.440	ND	ND	0.481
Telferia occidentalis	ND	ND	0.500	0.659
Vernonia amygdalina	0.563	ND	0.563	0.457

Discussion

The results in Table 1 and 2 showed that there is some level of heavy metals in the study area (Obudu), especially Cd, Cr, and Fe, and the edible vegetables have also accumulated some of these metals present in the soil. Cobalt (Co) 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 can detect concentrations as low as 0.001. From the data, the mean concentration of Cd in the soil in $mgkg^{-1}$ ranged from (0.004 – 0.048) and (0.005-0.046) for rainy and dry seasons respectively. Cr level in the soil in $mgkg^{-1}$ ranged from (0.004 – 0.025) and (0.006 – 0.016) for the rainy and dry season respectively. The mean concentration of Fe in the soil ranged from (0.112 – 0.173) and (0.116 – 0.151) for rainy and dry season respectively. These results showed that the metals availability in the soil was in the order Fe> Cd> Cr> Co. The results also revealed that there is no significant difference between concentration of the metals in the soil and vegetables for both seasons, implying 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, leachate from auto-mechanic workshops etc. or anthropogenic activities like quarrying and road construction among others.

The bioaccumulation ratios of the metals as 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 in both seasons ranged from (0.250-0.600) and (0.303 – 0.563) for rainy and dry seasons respectively. The ratio of Cr ranged from (0.425 – 0.8181) and (0.500 – 0.750) for rainy and dry seasons respectively. For Fe, it ranged from (0.434 – 0.902) and (0.417-0.752) for rainy and dry season respectively.

The bioaccumulation ratios of the metals were in the order shown below: for Cd, *T. occidentalis* > *V. amygdalina* > *S. melongena*> *C. olitorius* > *M. koenigii* >*Amarathus spp.* > *T. triangulare*>. *O. graattissimum*, for *Cr*, *S.*

melongena > *M. koenigii* > *C. olitorius* >*Amarathus spp.*> *V. amygdalina*> *O. grattissimum* >*Amarathusspp.*> *T. occidentalis* > *C. olitorius* > *O. grattissimum* and for Fe, *V. amygdalina* >*Amarathus spp.*> *T. occidentalis* > *M. koenigi* > *S. melongena* > *T. triangulane* > *C. olitorius* > *O. granttisimum.* These results also show that the amount of metals accumulated by most of the vegetables is directly proportional to the amount present in the soil. Bioaccumulation ratio is a dimensionless quantity or parameter which gives the ratio of the concentration of a pollutant (heavy metal) in a vegetable or plant to the concentration in the soil. It indicates the rate or extent of transfer of the pollutant or heavy metals 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. The bioaccumulation 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. Shuman [14] and Kiekens [15] for instance have reported earlier that Zn availability to plants in the soil depends on its chemical form in the soil and the dynamic equilibrium among its different forms or fractions in the soil. Ngole [16] have also stated that the accumulation of Cr and Fe depends on the pH and their availability in acidic soil among other factors. Besides, an earlier research by

Free Library [17] in the area have revealed that soil is quite porous and acidic with a pH range of 4-6, making the availability of the metals for accumulation by the vegetables possible. However, the concentration of Cd, Cr, and Fe in the soil is still low and the amount already accumulated by the edible vegetables is still very low and within the permissible limits of 0.1mgkg^{-1} set by WHO/FAO. 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.

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 Co was not detected in the area and seems negligible at the moment. The level of the metals presents 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 may not pose any health risk at the moment.

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