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HEALTH RISK ANALYSIS OF HEAVY METALS (Cr, Fe, Hg & Ni) IN EDIBLE VEGETABLES IN YALA URBAN AREA OF CROSS RIVER STATE, NIGERIA.

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7 ABSTRACT

Aim: The aim of the study was to determine concentration of heavy metals in 8 the soil and edible vegetables planted consumed Yala Urban Area of Cross 9 River State, Nigeria, ascertained the level of metals contamination and the 10 possible health risk or implication. **Sampling:** Forty eight (48) soil and edible 11 vegetable samples (6 of each kind of the 8 vegetables) were collected randomly 12 from Yala Urban Area of Cross River State. The eight vegetables considered for 13 the study were Amaranthus spp., Corchorus olitorius, Murraya koenigii, 14 Ocimum grattissimum, Solanum melongena, Talinum triangulare, Telferia 15 occidentalis and Vernonia amygdalina. They were collected between January 16 and March for dry season, and July and September for rainy season of the year. 17 **Methodology:** The samples were digested and analyzed for the Cr, Fe, Hg and 18 Ni (heavy metals) concentration using Flame Atomic Absorption Spectrometer 19 (AAS) in the Chemistry Laboratory, University of Calabar. **Results:** The results 20 showed that the mean concentration of the metals in the soil in mgkg⁻¹ ranged 21 from (0.063 - 0.108) and (0.049 - 0.104) in rainy and dry seasons respectively 22

for Cr, and (0.026 - 0.124) and (0.013 - 0.119) in rainy and dry season respectively for Fe. The mean concentration accumulated by the vegetables ranged from (0.037- 0.063) and (0.029 - 0.066) in rainy and dry season respectively for Cr and (0.012- 0.071) and (0.008- 0.086) in rainy and dry season respectively. Hg and Ni were neither detected in the soil nor in the vegetables. The trend of the metals in both the soil and vegetable was in the order: Cr > Fe> Hg> Ni. The Target Hazard Quotients were all less than 1, indicating no health risk. **Conclusion:** 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. These results indicate that the concentration of Cr, Fe, Hg and Ni 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 pose any risk at the moment.

Keywords: Health risk analysis, Heavy metals, Consumption, Vegetables,Yala.

Introduction

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A heavy metal has a specific gravity of 5.0 or greater and is usually poisonous [1]. The term heavy metal however, is often widely applied to

include other potentially toxic elements even if they do not meet up with the apt chemical definition [1]. It has also 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. Chromium (Cr), Iron (Fe), Mercury (Hg) and Nickel (Ni) 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. Hence, several researchers have been carried out on heavy metals by researchers like Chang [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].

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In addition, Khan [10] opined that the consumption of contaminated vegetables constitutes an important route for animal and human exposure to heavy metals. Halwell [11] earlier stated 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 reduced 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 poisonous substances in high doses [24]. Consequently, the aim of this study is to determine the concentration of some heavy metals (Cr, Fe, Hg and Ni) in the soil and edible vegetables in the study area (Yala) and ascertain the soil and vegetable quality with respect to heavy metal pollution.

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Yala urban area is characterized with low land, plains and hills. The soil is well drain sandy loam in texture, which makes it suitable for agriculture. It has population of over 50 thousand people. Besides, the people are 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 eastern and northern part of the country and most times experience heavy vehicular traffic. In addition, its major urban centre; Okpoma and the adjoining Okuku where Cross River University of Technology mini-campus is located have business centres, State and Local Government institutions among other urban features. 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 manure 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 edible vegetables and soil quality with respect to heavy metals pollution, and also evaluate the possible health risk associated their consumption.

Materials and Methods

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Sampling and sample pre-treatment: forty eight soil samples and vegetables (with 6 of each vegetable) were collected randomly at different locations within Yala urban area at a distance of about 1km apart. 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 (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 °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 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 put in a beaker and placed in a fume cupboard, 20 mL of concentrated (HCl), 10 mL of concentrated HNO₃ and 5 mL of H₂SO₄ 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 [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 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% 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 Cr, Fe, Hg and Ni using a VGP 210 BUCK Scientific Model of flame Atomic Absorption Spectrometer (AAS) at the following wavelengths: Cr (357.0 nm), Fe (248.0 nm), Hg (253.7 nm) and Ni (232.0 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 138 of pollutant (heavy metal) in the vegetable in mgkg⁻¹, B is the average body 139 weight of humans in kg, while RfD is the oral reference dose of the pollutant 140 permissible and it is fixed by United States Environmental Protection Agency 141 (US-EPA). **Note:** B is assumed by US-EPA to be 70kg for adult males and 60kg 142 for adult females. For this study, 65kg (the average of 70kg and 60kg) was used 143 for all adults, while the DIV was assumed to be 100g (0.1kg/day) per day. In 144 some countries or places, up to 150 or 200g per day has been assumed 145 especially for vegetarians. From the formula, THQ is a dimensionless parameter 146 or ratio. According to US-EPA through Integrated Risk Information System-147 database IRIS [14], if THO is less than 1(THO<1), it shows that there is no 148 potential health risk associated with the pollutant. But if THQ>1, there is a 149 health risk associated with the pollutant (heavy metal) at that moment. The RfD 150 values for Cr, Fe, Hg and Ni from IRIS are 0.0003, 0.007, 0.001 and 0.01 mgkg 151 ¹ respectively [14]. 152

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.

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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 vegetables have been presented in Tables 4 and 5 for the both seasons. WHO/FAO permissible limits for the metals in soil, vegetables and medicinal plants are presented in Table 3.

Table 1: Mean concentration of Cr, Fe, Hg and Ni in mgkg⁻¹ (dry weight) in the soil and vegetables during the rainy season in Yala.

Vegetable	Cr	Fe	Hg	Ni
Amarathus spp	0.042±0.003	0.022±0.005	ND	ND
Soil	0.069±0.011	0.033 ± 0.004	ND	ND
Corchorus olitorius	0.052 ± 0.008	0.038 ± 0.010	ND	ND
Soil	0.069 ± 0.017	0.075 ± 0.019	ND	ND
Murraya koenigii	0.054 ± 0.004	0.017 ± 0.003	ND	ND
Soil	0.063±0.014	0.027 ± 0.004	ND	ND
Ocimumgratissimum	0.040 ± 0.006	0.029 ± 0.011	ND	ND
Soil	0.071±0.012	0.056 ± 0.014	ND	ND
Solanum melongena	0.050 ± 0.009	0.019 ± 0.003	ND	ND
Soil	0.064 ± 0.004	0.026 ± 0.004	ND	ND
Talinum triangulare	0.037 ± 0.007	0.071 ± 0.019	ND	ND
Soil	0.084 ± 0.027	0.124 ± 0.014	ND	ND
Telferia occidentalis	0.063±0.022	0.029 ± 0.011	ND	ND
Soil	0.108 ± 0.004	0.056 ± 0.012	ND	ND
Vernoniaamygdalina	0.072±0.012	0.012 ± 0.002	ND	ND
Soil	0.105±0.036	0.026 ± 0.004	ND	ND

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

Table 2: Mean concentration of Cr, Fe, Hg and Ni in mgkg⁻¹ (dry weight) in the soil and vegetables during the dry season in Yala.

Vegetable	Cr	Fe	Hg	Ni
Amarathus spp	0.035±0.005	0.019±0.001	ND	ND
Soil	0.066±0.013	0.030 ± 0.002	ND	ND
Corchorus olitorius	0.048 ± 0.008	0.036±0.010	ND	ND
Soil	0.070 ± 0.019	0.072±0.019	ND	ND
Murraya koenigii	0.049 ± 0.002	0.015±0.004	ND	ND
Soil	0.058 ± 0.014	0.024 ± 0.005	ND	ND
Ocimum grattissimum	0.037 ± 0.005	0.025±0.009	ND	ND
Soil	0.066±0.011	0.052±0.007	ND	ND
Solanum melongena	0.046 ± 0.008	0.015±0.004	ND	ND
Soil	0.060±0.012	0.027±0.003	ND	ND
Talinum triangulare	0.034 ± 0.006	0.086±0.014	ND	ND
Soil	0.079±0.021	0.119±0.012	ND	ND
Telferia occidentalis	0.029±0.011	0.059±0.020	ND	ND
Soil	0.049 ± 0.003	0.099±0.015	ND	ND
Vernonia amygdalina	0.066±0.011	0.008 ± 0.002	ND	ND
Soil	0.104±0.026	0.013±0.005	ND	ND

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

Table 3: WHO permissible limits of heavy metals in soil, vegetables and medicinal plants in mgkg⁻¹.

<mark>Metal</mark>	Soil	Vegetables	Med. plants
Cr	100	0.1-0.2	1.5
Fe	100	<mark>7.0</mark>	20
Hg	1.0	0.03	<u> </u>
Ni	<mark>35</mark>	0.1	10

Source: [15, 16 & 17]

Table 4: Target Hazard Quotients (THQ) of heavy metals in edible vegetables in Yala Urban area of Northern Cross River State in rainy season.

Vegetables	Cr	Fe	Hg	Ni
Amaranthus spp.	0.215	0.005	ND	ND
Corchorus olitorius	0.267	0.008	ND	ND
Solanum melongen	0.277	0.004	ND	ND
Murraya koenigii	0.205	0.006	ND	ND
Ocimumgrattissimum	0.256	0.004	ND	ND
Talinum triangulare	0.190	0.016	ND	ND
Telfairia occidentalis	0.323	0.006	ND	ND
Vernoniaamygdalina	0.369	0.003	ND	ND

Table 5: Target Hazard Quotients (THQ) of heavy metals in edible vegetables in Yala Urban area of Northern Cross River State in dry season

Vegetable	Cr	Fe	Hg	Ni	
Amaranthus spp.	0.180	0.004	ND	ND	
Corchorus olitorius	0.246	0.008	ND	ND	
Murraya koenigii	0.251	0.003	ND	ND	
Ocimum grattissimum	0.190	0.006	ND	ND	
Solanum melongena	0.236	0.003	ND	ND	
Talinum triangulare	0.174	0.019	ND	ND	
Telfairia occidentalis	0.149	0.013	ND	ND	
Vernonia amygdalina	0.339	0.003	ND	ND	

Discussions: The results in Tables 1 and 2 showed that the mean concentration of the metals in the soil in mgkg⁻¹ ranged from (0.063-0.108) and (0.049-0.104) in rainy and dry seasons respectively for Cr, and (0.026-0.124) and (0.013-0.119) in rainy and dry season respectively for Fe. The mean concentration accumulated by the vegetables ranged from (0.037-0.063) and (0.029-0.066) in rainy and dry season respectively for Cr, and (0.012-0.071) and (0.008-0.086) in

rainy and dry season respectively. Hg and Ni were neither detected in the soil nor in the vegetables in both seasons. 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. The availability of heavy metals in the soil for plants accumulation depends on several factors like P^H, soil texture, the chemical form of the metal etc. It has been proven by several researchers 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 [18, 19, 20, & 21]. Thus, acidic soils favour the accumulation of metals by vegetables than neutral or alkaline soils. The accumulation of Cr and Fe by plants is also higher in acidic soils due to their availability in such soils among other factors [22]. An earlier research in the study area by Free Library [23] has shown that the soil is quite acidic and porous with a pH range of 4 to 6. However, the concentration of Cr and Fe in the soil and that already accumulated by the edible vegetables is still very low and within the permissible limits of WHO/FAO as shown in Table 3. Besides, Hg and Ni were 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.

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Target hazard quotients: The results in Tables 3 and 4 reveals the Target Hazard Quotients (THQ) of the heavy metals in the edible vegetables in the study area (Yala) for the rainy and seasons respectively. These results indicate that the THQ values for Cr and Fe which were detected in the vegetables are far less than 1 for all vegetables in both seasons, especially Fe. 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 [14], 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

The results of this study have shown that there is some level of Cr and Fe in the soil, which have been accumulated by the edible vegetables in the area. The concentrations of Hg and Ni were not detected in the area and seem 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 may not pose any health risk at the moment.

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1. Hardy, D.H., Myers, J. & Strokes, J. Heavy metals in North Carolina soils:
Occurrence and significance. North Carolina, USA, Agronomy Division,
Dept. of Agriculture and Consumer Service, 2008.

252

253 2. Chang, C.Y., Yu, H. Y., Chen, J. J., Li, F. B., Zaary, H. H., & Liu, C. P. Accumulation of heavy metals contamination in leafy vegetables from selected agricultural soils and associated potential health risk in the Pearl River delta, South China. Environmental monitoring and assessment, 2014; 186(3):1547-1560.

258

3. Buteh, D.S., Chindo, I.Y., Ekanem, E.O., & Williams, E.M. Impact
Assessment of Contamination pattern of solid waste dumpsites soil: A
comparative study of Bauchi metropolis. World Journal of Analytical
Chemistry, 2013; 1(4):59-62.

263

4. Harmanescu, M., Alda, L.M., Bordean, D.M., Gogosa, I. & Gergen, I. Heavy metals health risk assessment for population via consumption of vegetables grown in old mining area; a case study of Banat County, Romania. Chemistry Central Journal, 2011; 5:64; doi: 18:1186/1752-153x-5-64.

269

5. Suruchi, S. & Khanna, P. Assessment of heavy metals contamination in different vegetables grown in and around urban areas. Research Journal of Environment and Toxicology, 2011; 5:162-179.

273

6. Zhuang, P., Mcbride, M.B., Xia, H., Li, N. & Li, Z. Health risk from heavy metals via consumption of food crops in the vicinity of Daboashan mine, South China. Science of the Total Environment, 2009; 407(5):1551-1561.

- 7. Sanayei, U., Ismail, N. & Talebi, S.M. Determination of heavy metals in Zayandeh Road River, Isfahan-Iran. World Applied Science Journal, 2009; 6(9):1209-1214.
- 8. Yakubu, A., Tanko, U.M. & Dangoggo, S.M. The impact of man's activities on the heavy metals level in soils in Wuse District, Abuja, Nigeria. De Chemica Sinica, 2011; 2(6):181-184.
- 9. Abdollatiff, G., Aralan, A. M. Ahmad, M. T., Hoseni, A. M. &Karimaian, N. Solubility test in some phosphate rocks and their potential for direct application in soil. World Applied Science Journal, 2009; 6(2):182-192.
- 10. Khan, S. Cao, Q. Y. Z., Huang, Y. Z. & Zhu, Y. G. Health risk of heavy metals in contaminated soil and food crops, irrigated with waste water in Beijing, China. Environmental pollution, 2009; 124(3): 686-693.
- 11. Halwell, B. *Critical Issue Report: still no free lunch*. The organic center, 2007; Accessed July, 2014. Available at: www.organi-center.org
- 12. Sobukola, O. P., Adeniran, O. P., Odedara, A. A. & Kajihausa, O. E. Heavy metals level of some fruit and leafy vegetables form selected markets in Lagos, Nigeria. African Journal of Food Science, 2010; 4(2):389-393.
- 13. Akan, J.C., Abdulrahaman, F. I., Sodipo, O. A. & Lange, A. G.
 Physicochemical parameter in soil and vegetable samples from Gongalon agricultural site, Maiduguri, Borno State, Nigeria. Journal of American Science, 2010; 12:78-88.
- 14. IRIS. Integrated Risk Information System –database. US Environmental Protection Agency (USEPA), 2011.
- 15. World Health Organization. Permissible limits of heavy metals in soil and plants. Geneva, Switzerland, 1996.
- 16. World Health Organization. Quality control methods for medicinal plants.
 Geneva, Switzerland, 1998.
- World Health Organization. Permissible limits of heavy metals in vegetables. Geneva, Switzerland, 2005.
- 18. Gray, C.W., Mclaren, R.G., Roberts, A.H. & Condron, L.M. Sorption and desorption of cadmium from some New Zealand soils; Effect of pH and contact time. Australian Journal of Soil Research, 1998; 36: 199-216.
- 19. Salam, A.K. & Helmke, P.A. The pH dependence of free ionic activities and total dissolved concentrations of copper and cadmium in soil solution.

 Geoderma, 1998; 83: 281-291.

- 20. Chlopecka, A., Bacon, J.R., Wilson, M.J. & Kay, J. Forms of cadmium, lead and zinc in contaminated soils in South west Poland. Journal of Environmental Quality, 1996; 25:69-79.
- 21. Singh, B.R., Narwai, R.P., Jeng, A.S. & Ahmas, A. Crop uptake and extractability of cadmium in soils naturally high in metals at different pH levels. Communications of Soil Science and Plant Analysis, 1995; 26: 2133-2142.
- 22. Ngole, V.M. Using soil heavy metal enrichment and mobility to determine potential uptake vegetables. Plant soil environment, 2011; 57:75-80.
- 23. Free Library. *Mineralogy and geochemical properties of some upland soils*from different sedimentary formations in south-eastern Nigeria, 2014;
 Accessed July, 2015. Available at: www.thefreelibrary.com
- 24. Ape, Michael Anomie "Health Risk Evaluation of Heavy Metals via Consumption of Contaminated Vegetable in Bekwara, Cross River State, Nigeria, Cross River State, Nigeria"." IOSR Journal of Nursing and Health Science (IOSR-JNHS), vol. 7, no.2, 2018, pp. 28-32.