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

6

7 **ABSTRACT**

8 **Aim:** The aim of the study is to determine concentration of heavy metals in the
9 soil and edible vegetables planted consumed Yala Urban Area of Cross River
10 State, Nigeria, ascertain the level of metals contamination and the possible
11 health risk or implication. **Sampling:** Forty eight (48) soil samples and edible
12 vegetable samples (6 of each kind of the 8 vegetables) were collected randomly
13 from Yala Urban Area of Cross River State. The eight vegetables considered for
14 the study were *Amaranthus spp.*, *Corchorus olitorius*, *Murraya koenigii*,
15 *Ocimum grattissimum*, *Solanum melongena*, *Talinum triangulare*, *Telferia*
16 *occidentalis* and *Vernonia amygdalina*. They were collected between January
17 and March for dry season, and July and September for rainy season of the year.

18 **Methodology:** The samples were digested and analyzed for the Cr, Fe, Hg and
19 Ni (heavy metals) concentration using Flame Atomic Absorption Spectrometer
20 (AAS) in the Chemistry Laboratory, University of Calabar. **Results:** The results
21 showed that the mean concentration of the metals in the soil in mgkg^{-1} ranged
22 from (0.063 - 0.108) and (0.049 - 0.104) in rainy and dry seasons respectively

23 for Cr, and (0.026 - 0.124) and (0.013 - 0.119) in rainy and dry season
24 respectively for Fe. The mean concentration accumulated by the vegetables
25 ranged from (0.037- 0.063) and (0.029 - 0.066) in rainy and dry season
26 respectively for Cr and (0.012- 0.071) and (0.008- 0.086) in rainy and dry
27 season respectively. Hg and Ni were neither detected in the soil nor in the
28 vegetables. The trend of the metals in both the soil and vegetable was in the
29 order: Cr > Fe> Hg> Ni. The Target Hazard Quotients were all less than 1,
30 indicating no health risk. **Conclusion:** These results suggest that there is no
31 significant difference between the amount of metals in the soil or that
32 accumulated by the vegetables in rainy and dry seasons of the year. Also the
33 amount of metals accumulated by most of the vegetables was directly
34 proportional to the amount present in the soil where they are planted. These
35 results indicate that the concentration of Cr, Fe, Hg and Ni in the soil and
36 vegetables were still low and within the permissible limits of WHO/FAO. Thus,
37 the consumption of the vegetables in the area may not pose any risk at the
38 moment.

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

41 **Introduction**

42 A heavy metal has been described as a member of a loosely defined
43 subset of elements that exhibit metallic properties (Wikipedia free

44 encyclopedia). Examples of these elements are transition metals, some
45 metalloids, lanthanides and actinides. According to Hardy [1], a heavy metal
46 has a specific gravity of 5.0 or greater and is usually poisonous. The term heavy
47 metal however, is often widely applied to include other potentially toxic
48 elements even if they do not meet up with the apt chemical definition [1].
49 Chromium (Cr), Iron (Fe), Mercury (Hg) and Nickel (Ni) belong to this group
50 of elements. Based on their toxic or poisonous effect at high doses and their
51 contamination of food plants and animals when present in the soil or water
52 environments, they have recently attracted the attention of many researchers
53 worldwide as food safety and quality is a matter of public interest. Hence,
54 several researchers have been carried out on heavy metals by researchers like
55 Kanake [2], [3], [4], [5], [6], [7], [8] etc. most of which were within the
56 acceptable limits in their various localities to ascertain their food and
57 environment quality/safety. Heavy metals are the major contaminating agents of
58 our food and a problem of our environment [9].

59 Moreover, Khan [10] has opined that the consumption of contaminated
60 vegetables constitutes an important route for animal and human exposure to
61 heavy metals. Halwell [11] have earlier stated that the nutritional value of
62 vegetables depends on the growing method and the quality of the soil because
63 when vegetables are grown in contaminated soils, like those polluted with heavy
64 metals; their nutritional value will be reduced as pollutants from the soil will be

65 accumulated by the vegetables. Thus, vegetables should not be planted on soils
66 contaminated with hazardous waste like heavy metals because they are
67 nutritionally and medicinally valuable. Besides, the health of humans can be
68 affected negatively when they consume these vegetables and accumulate these
69 poisonous substances in high doses. Consequently, the aim of this study is to
70 determine the concentration of some heavy metals (Cr, Fe, Hg and Ni) in the
71 soil and edible vegetables in the study area (Yala) and ascertain the soil and
72 vegetable quality with respect to heavy metal pollution.

73 Yala urban area is characterized with low land, plains and hills. The soil
74 is well drain sandy loam in texture, which makes it suitable for agriculture. It
75 has population of over 15 thousand people. Besides, the people engaged in
76 subsistence and commercial farming, growing rice, cassava, yam, cocoa in large
77 quantities as well as vegetables for consumption as food and medicine. This
78 often results in the use of insecticides, herbicides and other agrochemicals. By
79 its location, it is a major link to the eastern and northern part of the country and
80 most times experience heavy vehicular traffic. In addition, its major urban
81 centre; Okpoma and the adjoining Okuku where Cross River University of
82 Technology mini-campus is located have business centres, State and Local
83 Government institutions among other urban features. Moreover, the inhabitants
84 of the area practice rotational waste dump sites around their premises and later
85 plant vegetables in old waste dump sites with a view to tap the compost manure

86 for good yield even though wastes were disposed there indiscriminately. All
87 these characteristics/features together with erosion during the rainy season make
88 heavy metal contamination of the area inevitable. Hence, there is need to
89 ascertain the edible vegetables and soil quality with respect to heavy metals
90 pollution, and also evaluate the possible health risk associated their
91 consumption.

92 **Materials and Methods**

93 **Sampling and sample pre-treatment:** forty eight soil samples and
94 vegetables (with 6 of each vegetable) were collected randomly at
95 different locations within Yala urban area at a distance of about 1km
96 apart. The soil samples were collected at the root level of the vegetables
97 at the depth of about 12 to 15 cm, using a hand trowel. At the same time,
98 a handful of the edible vegetables were collected and wrapped separately
99 with identification labels, and taken to the laboratory for further analysis.
100 The edible vegetables considered for this study include: *Amaranthus spp*
101 (Green vegetable), *Corchorus olitorius* (Ewedu), *Murraya koeningii*
102 (Curry leaf), *Ocimum grattissimum* (scent leaf), *Solanum melongena*
103 (egg plant leaf), *Telfairia occidentalis* (pumpkin), *Talinum triangulare*
104 (water leaf) and *Vernonia amygdalina* (Bitter leaf). They are commonly
105 used for food and medicinal purposes in the area. The samples were
106 collected between January and March for the dry season and between
107 July and September for the rainy season of the year. The vegetable
108 samples were washed with distilled water and oven-dried at 80-85 °c for
109 about 2 hours. Each dried sample was ground into powder, sieved with a
110 0.3 mm sieve and stored in a labeled plastic jar with cap. The soil

111 sampled was also oven-dried, ground into powder and homogenized
112 using pestle and mortar, sieved and store in labeled plastic jars separately.

113 **Digestion of samples:** vegetable samples were digested following the
114 procedure of one of the methods of the Association of Official Analytical
115 Chemists (AOAC) as reported by Sobukola [12] thus: 1.0 g of each sample was
116 put in a beaker and placed in a fume cupboard, 20 mL of concentrated (HCl), 10
117 mL of concentrated HNO₃ and 5 mL of H₂SO₄ were added. After digestion was
118 complete, the beaker was heated in a fume cupboard for about 30 minutes. The
119 digested sample was removed and allowed to cool.

120 De-ionized water was added to the digest and made up to 100 mL in a
121 volumetric flask. The solution was stirred and filtered to obtain the supernatant
122 liquid ready for heavy metals analysis. Similarly the soil samples were digested
123 following the procedure of one of the methods of the Association of Official
124 Analytical Chemists (AOAC) as reported by Akan [13] thus: 2.0 g of each soil
125 sample powder was weighed into an acid washed beaker. 20 mL of aqua regia
126 (mixture of HCl and HNO₃, in the ratio 3:1) was added to the sample in the
127 beaker. The beaker was covered with a clean dry watch glass and heated at 90%
128 for about 2 hours; the beaker was removed, allowed to cool, washed together
129 with the watch glass using de-ionized water into a volumetric flask and made-up
130 to 100 mL solution. The solution was filtered and supernatant liquid solution
131 was used for heavy metal analysis.

132 **Element Analysis:** the soil and vegetable samples were analyzed for Cr,
133 Fe, Hg and Ni using a VGP 210 BUCK Scientific Model of flame Atomic
134 Absorption Spectrometer (AAS) at the following wavelengths: Cr (357.0 nm),
135 Fe (248.0 nm), Hg (253.7 nm) and Ni (232.0 nm).

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

$$THQ = \frac{DIV \times Cm}{RfD \times B}$$

138 Where DIV is the daily intake of vegetable in kg/day, Cm is the concentration
139 of pollutant (heavy metal) in the vegetable in mgkg^{-1} , B is the average body
140 weight of humans in kg, while RfD is the oral reference dose of the pollutant
141 permissible and it is fixed by United States Environmental Protection Agency
142 (US-EPA). **Note:** B is assumed by US-EPA to be 70kg for adult males and 60kg
143 for adult females. For this study, 65kg (the average of 70kg and 60kg) was used
144 for all adults, while the DIV was assumed to be 100g (0.1kg/day) per day. In
145 some countries or places, up to 150 or 200g per day has been assumed
146 especially for vegetarians. From the formula, THQ is a dimensionless parameter
147 or ratio. According to US-EPA through Integrated Risk Information System-
148 database IRIS [14], if THQ is less than 1 ($THQ < 1$), it shows that there is no
149 potential health risk associated with the pollutant. But if $THQ > 1$, there is a
150 health risk associated with the pollutant (heavy metal) at that moment. The RfD
151 values for Cr, Fe, Hg and Ni from IRIS are 0.0003, 0.007, 0.001 and 0.01 mgkg^{-1}
152 respectively [14].

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

158 **Results:** The mean heavy metal concentration in mgkg^{-1} (dry weight) in the soil
159 and vegetables during the rainy and dry season have been presented in Tables 1
160 and 2 respectively, while the Target Hazard Quotients of the vegetables have
161 been presented in Tables 3 and 4 for the both seasons.

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163 **Table 1:** Mean concentration of Cd, Co, Cr, & Fe in mgkg⁻¹ (dry weight) in the
 164 soil and vegetables during the rainy season in Obudu.

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

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

166 **Table 2:** Mean concentration of Cd, Co, Cr, & Fe in mgkg⁻¹ (dry weight) in the
 167 soil and vegetables during the dry season in Obudu.

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

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

170 **Table 3:** Target Hazard Quotients (THQ) of heavy metals in edible vegetables
171 in Yala Urban area of Northern Cross River State in rainy season.

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

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179 **Table 4:** Target Hazard Quotients (THQ) of heavy metals in edible vegetables
 180 in Yala Urban area of Northern Cross River State in dry season

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

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182 **Discussions:** The results in Tables 1 and 2 showed that the mean concentration
 183 of the metals in the soil in mgkg^{-1} ranged from (0.063-0.108) and (0.049-0.104)
 184 in rainy and dry seasons respectively for Cr, and (0.026-0.124) and (0.013-
 185 0.119) in rainy and dry season respectively for Fe. The mean concentration
 186 accumulated by the vegetables ranged from (0.037-0.063) and (0.029-0.066) in
 187 rainy and dry season respectively for Cr, and (0.012-0.071) and (0.008-0.086) in
 188 rainy and dry season respectively. Hg and Ni were neither detected in the soil
 189 nor in the vegetables in both seasons. The results also indicate that there is no
 190 significant difference between the concentration of metals in the soil and that

191 accumulated by the vegetables in the rainy and dry season of the year. The
192 availability of heavy metals in the soil for plants accumulation depends on
193 several factors like P^H , soil texture, the chemical form of the metal etc. It has
194 been proven by several researchers that the solubility of the cationic forms of
195 the metals in the soil solution increases as the soil P^H decreases, and they
196 become readily available for plants to accumulate [15], [16], [17], [18]. Thus,
197 acidic soils favour the accumulation of metals by vegetables than neutral or
198 alkaline soils. An earlier research in the study area by Free Library [19] has
199 shown that the soil is quite acidic and porous with a pH range of 4 to 6.
200 However, the concentration of Cr and Fe in the soil and that already
201 accumulated by the edible vegetables is still very low and within the permissible
202 limits of WHO/FAO. Besides, Hg and Ni were not detected in the soil or the
203 vegetables. Therefore efforts has to be made by relevant government agencies to
204 maintain this low concentration of the metals in the study area through public
205 awareness of the effects of pollution and a periodic environmental monitoring
206 and assessment of the metals concentration in the area.

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

212 heavy metals concentration in the edible vegetables is not posing any risk and
213 there is no potential health risk associated with their consumption for now.
214 According to US-EPA/IRIS [14], it is only THQ values greater than 1 that
215 shows there is potential health risk associated with the consumption of food or
216 vegetables contaminated with a certain pollutant or heavy metal. Thus, the THQ
217 values also agreed with the fact that the mean concentrations of these metals in
218 the vegetables are still low and within the permissible limits of WHO/FAO.

219 **CONCLUSION**

220 The results of this study have shown that there is some level of Cr and Fe
221 in the soil, which have been accumulated by the edible vegetables in the area.
222 The concentrations of Hg and Ni were not detected in the area and seem
223 negligible at the moment. The level of the metals present in the soil and
224 vegetable are still very low and within the permissible limits of WHO/FAO.
225 Thus, the concentration of these metals in the edible vegetables may not pose
226 any health risk at the moment.

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