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Quantification and Risk Assessment of Some Trace Metals in Vegetables Obtained in Sand Mining Environment of Ukat Nsit, Nigeria

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Abstract: Quantification and risks of Cd, Cu, Pb, Zn, Ni, Fe, As and Cr were assayed in two vegetables (*Lasianthera africana* and *Telfairia occidentalis*) obtained from the sand mining environment of Ukat Nsit. Vegetable and soil samples were collected from four farms. Samples were also collected from a farm out of Ukat Nsit where there are no sand mining activities to serve as controls. The results revealed variable levels of the trace metals in the samples. In the soil, the metals levels ranged from 3.67 mg/kg Pb to 19.10 mg/kg Cu. In the vegetables, the trace metals levels ranged from 0.150 mg/kg Ni to 17.3 mg/kg Cu in *L. africana* and from 0.00 mg/kg Ni to 10.16 mg/kg Fe in *T. occidentalis,* respectively. Cd in the soil and vegetables exceeded the safe limits set by USEPA and WHO. The metal levels in the vegetables and soil from the control site were lower than those of the study area. This could be attributed to the negative impact of sand mining activities. Positive correlation at $p < 0.01$ was seen between Cd and Pb, Cd and Fe, Pb and Zn, As and Fe as well as Fe and Zn, indicating that Cr, Pb, Fe, Cu and Zn originated from the same anthropogenic sources. The target hazard quotient (THQ) for all the measured trace metals for the vegetables were lower than 1 (except Cd), indicating that the vegetables are relatively safe for consumption, except that their Cd levels could have adverse health effects.

Keywords: Quantification, Risk Assessment, Trace Metals, Contamination, Vegetables, Sand Mining

1. Introduction

Vegetables form the major part of human diet today in Nigeria. Apart from being a ready source of vitamins and essential nutrients to the body, they are much readily available today from numerous different sources. With the recent emphasis on agriculture and agro-products, vegetables are cultivated at different locations with different soil qualities and other concomitant activities such as mining. Indeed, vegetables are rich sources of essential components for human life and health, including proteins, vitamins, minerals, fibers and other beneficial bio-active ingredients [1]. The results of a global nutrition and health survey indicate that the dietary intake of vegetables is higher than meat [2]. Therefore, consumption of vegetables is regarded as one of the main pathways for the intake of essential nutrients. However, the presence of hazardous chemical factors is also observed in vegetables, including toxic trace metals, pesticide residues, and organic environmental contaminants [3, 4].

Trace metals pollution of agricultural soil and vegetables is one of the most severe ecological problems on a world scale because of their toxicity for plants, animals and humans, and their lack of biodegradability [5, 6]. It poses potential threats to the environment and can damage human health through various absorption pathways such as direct ingestion, dermal contact, and diet through the soil-food chain, inhalation and oral intake [7]. Recently, possible trace metals contamination in plants has motivated great concerns. The increasing contamination of trace metals in vegetables is attributed to multiple pathways, such as industrial emissions, sewage discharge, mining, agro-chemicals and fertilizers abuse, originating with storage and/or at the point of sale, and it has become a serious issue worldwide, especially in developing countries [4]. Once the trace metals such as Cd, Pb, As, Hg, and Cr are dispersed into the environment, they are able to be absorbed and accumulated on edible and non-edible parts of vegetables due to their unique characteristics, including persistence and non-biodegradability in environmental media, high environmental stability, bio-accumulation, and bio-magnification in organism and food chains [6]. Undoubtedly, chronic accumulation of trace metals in the organs of living things caused by high exposures poses different deleterious effects on human health, including cardiovascular, bone and nervous diseases, carcinogenic and developmental effects [8]. It is reasonable to assume that dietary intakes of vegetables containing trace metals may pose potential health risks to consumers [9]. It is also reasonable to assume that vegetables polluted by trace metals are recognized as one of the most significant aspects of food safety in Nigeria [10, 11]. Of the many sources of soil trace metals, little attention has been given to mining (especially sand mining) which is a predominant practice in almost every part of the world as sand is an important component in every brick work, hence it is a major source of soil trace metal with potentials of transfer to edible vegetables and other plants. Trace metals such as lead (Pb), zinc (Zn), cadmium (Cd), mercury (Hg) and chromium (Cr) are generally refer to as heavy metals having densities greater than 5 g/cm^3 [12]. Trace metal pollution is covert, persistent and irreversible [13]. This kind of pollution not only degrades the quality of the atmosphere, water bodies, and food crops, but also threatens the health and well-being of animals and humans by way of the food chain [14]. For example, Pb is a non-essential element to the human body, and excessive intake of the metal can damage the nervous, skeletal, circulatory, enzymatic, endocrine, and immune systems of those exposed to it [15]. Accordingly, chronic exposure to Cd can have adverse effects such as lung cancer, pulmonary adenocarcinomas, prostatic proliferative lesions, bone fractures, kidney dysfunction, and hypertension, while the chronic effects of arsenic (As) consist of dermal lesions, peripheral neuropathy, skin cancer, and peripheral vascular disease [2]. Although trace metals may occur naturally in soil, additional contributions come from anthropogenic activities such as agriculture, urbanization, industrialization, and mining [16].

Sand is an important mineral for our society in protecting the environment, buffer against strong tidal waves and storm, habitat for crustacean species and marine organisms, used for making concrete, roads construction, building sites (such as construction of dams, schools, health facilities and houses), brickmaking, making glass, and in our tourism industries in beach attractions. Sand mining is the process of removal of sand and gravel from their natural states. Sand mining has indeed becomes an environmental issue, as the demand for sand increases daily in industries and in construction works. Unscientific mining has caused degradation of land, accompanied by subsidence and consequential mine fires and disturbance of the water table leading to topographic disorder, severe ecological imbalance and damage to land use patterns in and around the mining regions [17]. Sand mining activities are mostly deemed to be unsustainable not only because they exploit resources, but also because they destroy the environment and society and leave impacts that are irreversible [18].

Mining and its associated activities can be responsible for considerable environmental damage in areas where these activities are carried out without proper guidelines and that can lead to clearing of vegetation, soil erosion, and landslides as well as contributing to increasing trace metals pollution in and around the sand mining sites [19]. Studies have shown that plant uptake is one of the main pathways through which pollutants enter the food chain. Sand mining causes soil contamination which affects food qualities. These pollutants can easily be taken up by vegetables in levels high enough to cause health problems to consumers. Serious sand mining activities are carried out on daily basis in Ukat Nsit, Nsit Ibom Local Government Area, Akwa Ibom State, Nigeria. These activities have negative impacts on the environment and agricultural activities in the area. Hence the need for this study to ascertain the health risk associated with the consumption of the vegetables grown in Ukat Nsit and the suitability of the vegetables in terms of trace metals contamination, for human consumption.

2. Materials and Methods

2.1. Samples Collection

Soil samples were collected randomly at 0 - 5 cm depth using hand trowel from four different farmlands designated as 1, 2, 3, and 4 around the sand mining environment of Ukat Nsit. At each of the farmlands, the soil samples were collected from four points and were homogenised to obtain four composite soil samples. Leaves of commonly available vegetables [fluted pumpkin (*Telfairia occidentalis*) and editan (*Lasianthera africana*)] were equally collected from the four farmlands using stainless steel knife. The vegetable samples were equally homogenized to obtain four composite samples for each of the two vegetables. Soil and the two vegetables samples were similarly collected from a farmland but out of Ukat Nsit where there are no sand mining activities, to serve as the controls. Collected soil samples were properly labeled and stored in clean polythene bags and transported to the laboratory. The sampling area is as shown in Figure 1.

2.2. Sample Preparation

Soil samples were dried under the sun for two (2) days to remove moisture. The dried soil samples were sieved to remove extraneous fragments, then ground to obtain fine particle size of < 200 nm fraction. Vegetable samples were washed with deionized water and air dried to remove moisture, after which each sample was milled into fine powdery form using agate pestle and mortar.

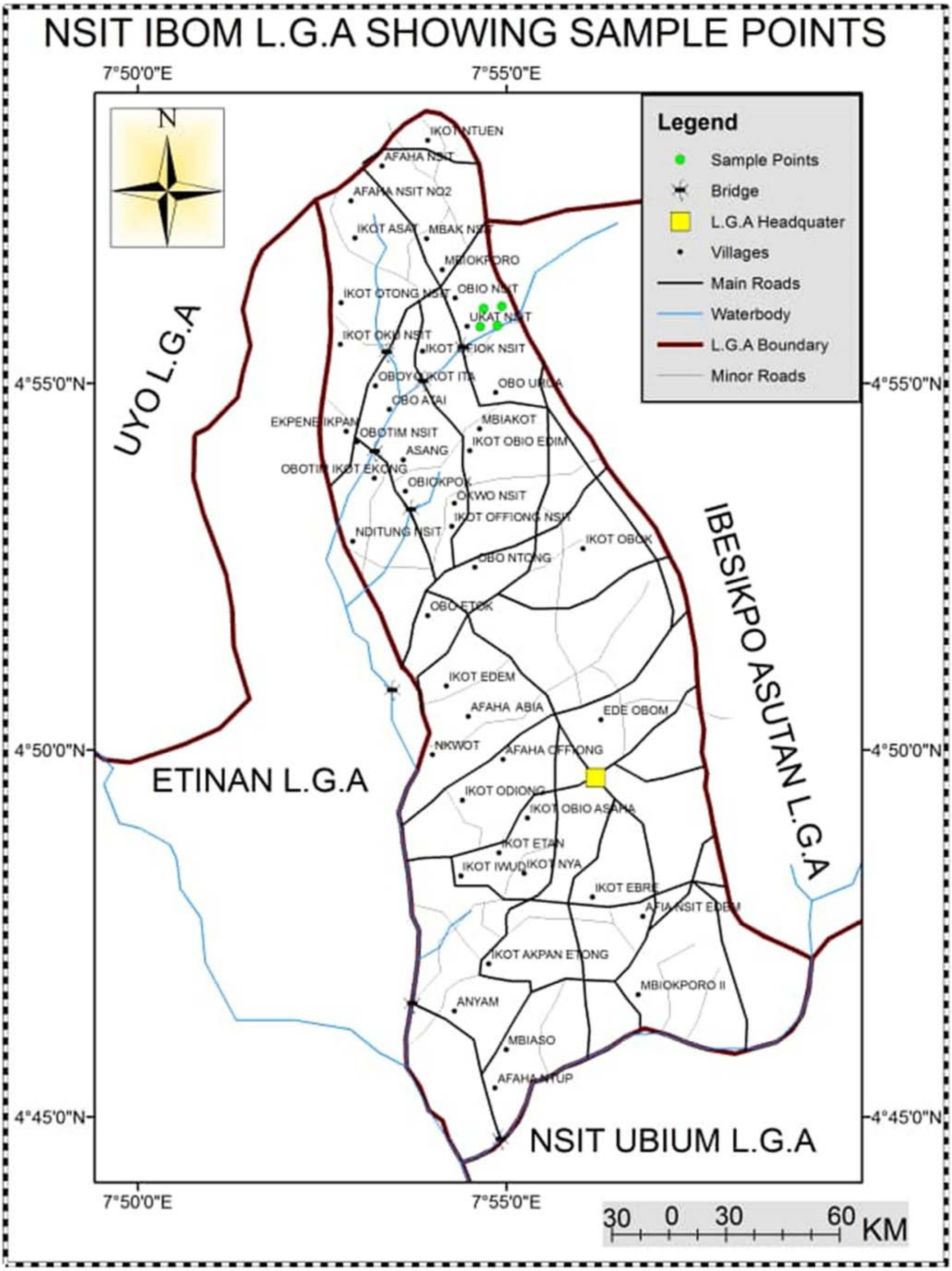


Figure 1. The sampling area.

2.3. Sample Treatment

Exactly 1g of each soil samples was digested using Aqua Regia (3:1 ratio of HCl and HNO_3) while the plant materials were digested using dry ashing method in a muffle furnace at 400°C. The levels of Cr, Cd, Cu, Pb, Ni, Fe, As and Zn in the digested samples were determined using atomic absorption spectrophotometer.

2.4. Bio-concentration Factor (BCF)

Bio-concentration factor is the ratio of the level of toxic metal in a plant sample to the level of the toxic metal in soil sample. This was computed based on Equation 1.

$$\mathrm{BCF} = \frac{C_{\mathrm{plant}}}{C_{\mathrm{soil}}} \quad (1)$$

Where BCF is Bio-concentration factor; C_{plant} is the level of trace metal in the vegetable sample and C_{soil} is the level of trace metal in the soil sample.

2.5. Health Risk Assessment

The potential health risks of trace metal consumption through fluted pumpkin (*Telfairia occidentalis*) leaves and editan (*Lasianthera africana*) leaves were assessed based on daily intake of metal (DIM) using Equation 2.

$$\mathrm{DIM} = \frac{C_{\mathrm{metal\ conc}} \times C_{\mathrm{factor}} \times D_{\mathrm{vegetable\ intake}}}{B_{\mathrm{average\ weight}}} \quad (2)$$

Where, DIM is the daily intake of metals; $C_{\mathrm{Metal\ conc}}$ is the trace metal concentration in vegetables (mg/kg); C_{Factor} is the Conversion factor (0.085); and $D_{\mathrm{Vegetable\ intake}}$ is the daily intake of vegetable (kg person^{-1} day^{-1}). The conversion factor of 0.085 was set to convert fresh vegetable weight to dry weight. The average daily vegetable intakes for adults and children were considered to be 0.345 and 0.232 kg/person/day, respectively, while the average adult and child body weights were considered to be 55.9 and 32.7 kg, respectively [20]. The target hazard quotient (THQ) for the consumption of contaminated vegetables was assessed using Equation 3 which is the ratio of daily intake of metal (DIM) to the oral reference dose (RfD) for each metal. The RfD values for As, Fe, Zn, Cd, Pb, Ni, Cu and Cr are 0.005, 2.50, 0.30, 0.001, 0.004, 0.02, 0.04 and 1.5 mg/kg bw/day, respectively [21]. The consumption of the vegetable would be of no risk if the ratio is less than 1 and if the ratio is equal or greater than 1, then the potential health risk is possible.

$$\mathrm{THQ} = \frac{E_F \times E_D \times F_{IR} \times C \times 10^{-3}}{R_{FD} \times W_{AB} \times T_A} \quad (3)$$

Where E_F is the Exposure frequency, E_D is the Exposure duration, F_{IR} is the Vegetable is the vegetable ingestion rate, C is the concentration of the metal, R_{FD} is the oral reference dose, W_{AB} is the average weight of the body, T_A is the average time of non-carcinogenic effects.

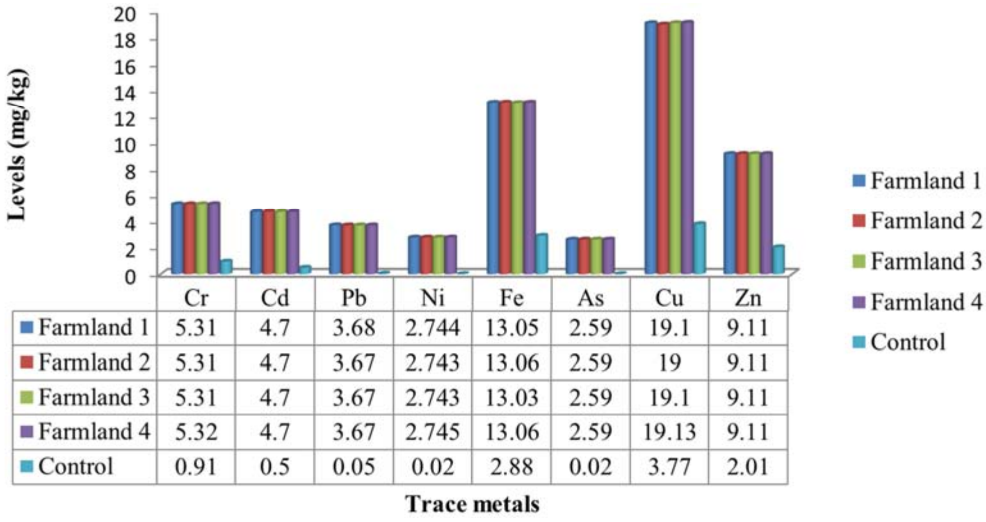
2.6. Statistical Analysis

The statistical analyses were performed using the Statistical Package for Social Sciences (SPSS) version 20.0 (SPSS Inc., Chicago, USA). One-way analysis of variance (ANOVA) followed by Duncan's post hoc test was used to determine the differences between sampling points. $P < 0.05$ was considered the level of statistical significance.

3. Results and Discussion

3.1. Levels and Distribution of Trace Metals in Soil and Vegetable Samples

The levels (mg/kg) of trace metals in soil and vegetable samples obtained in this study are as present in Figures 2 to 4. Figure 2 shows the levels of the metals in the soil. The levels of trace metals in *Lasianthera africana* and *Telfairia occidentalis* are presented in Figures 3 and 4. The metal levels in the soil samples ranged from 2.74 mg/kg Ni in three of the four farmlands to 19.13 mg/kg Cu in one of the four farmlands. In the control sample, the metal levels ranged from 0.02 mg/kg Ni, As to 3.77 mg/kg Cu. In the *L. Africana,* the metal levels ranged from 1.15 mg/kg Ni in all of the farmlands to 17.93 mg/kg Cu in of the four farmlands. In the control *L. Africana* sample, the metal levels ranged from 0.01 mg/kg Pb, Ni to 4.69 mg/kg Cu. In the *T. occidentalis* samples, the metal levels ranged from 0.97 mg/kg Ni in the crop from two of the four farmlands to 17.75 mg/kg Cu in the crop from one of the four farmlands. In the control *T. occidentalis* sample, the metal levels ranged 0.03 mg/kg Pb to 4. 41 mg/kg Cu. Ni and As levels were below the detection limits in the control *T. occidentalis* sample. The low levels of all the investigated metals in the control soil and vegetable samples compared to their levels in samples from the study area could be attributed to the sand mining activities in the area. The Cd levels in soil reported in this study were lower than the values of 115.27 mg/kg and 9.11mg/kg reported respectively in soil by [21 and 22]. The source of Cd in soil could be through wearing of automobile tyres, lubricants and metallurgical activities [22]. However, these reported Cd levels in soil across all the farmlands in this study were all above the maximum permissible levels of 3.0 and 0.14 mg/kg Cd set by WHO and USEPA, respectively. The range of Cd levels obtained in the studied vegetables in this study is higher than 1.15 mg/kg Cd reported in vegetables by [23]. Meaning that, there might have been anthropogenic addition of Cd to the studied soil through sand mining activities.



	Cr	Cd	Pb	Ni	Fe	As	Cu	Zn
Farmland 1	5.31	4.7	3.68	2.744	13.05	2.59	19.1	9.11
Farmland 2	5.31	4.7	3.67	2.743	13.06	2.59	19	9.11
Farmland 3	5.31	4.7	3.67	2.743	13.03	2.59	19.1	9.11
Farmland 4	5.32	4.7	3.67	2.745	13.06	2.59	19.13	9.11
Control	0.91	0.5	0.05	0.02	2.88	0.02	3.77	2.01

Figure 2. *Levels of trace metals (mg/kg) in soil.*

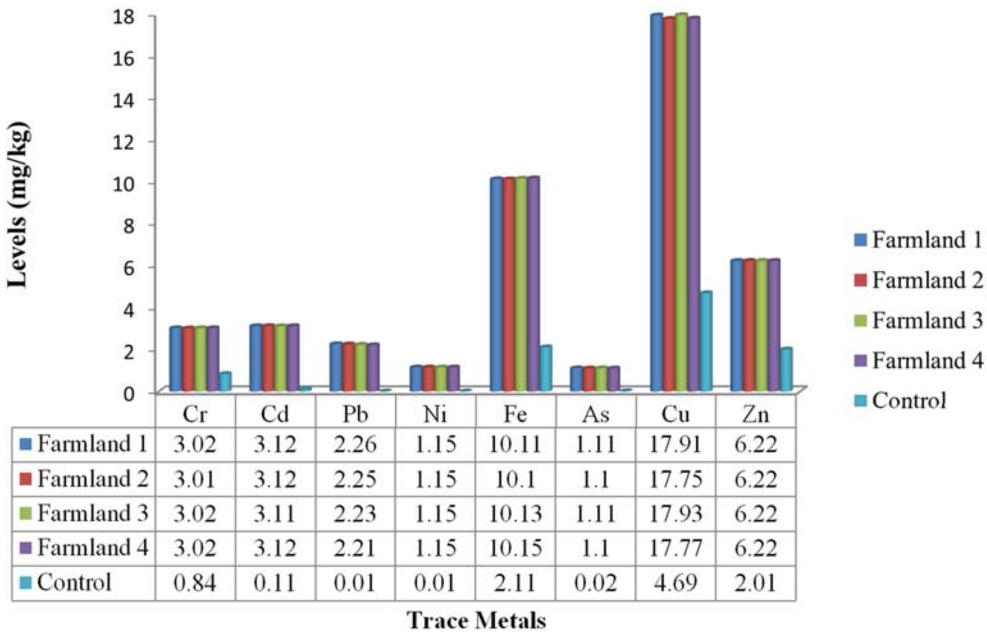
3.2. Bio-concentration Factors (BCF) for Trace Metals from Soil to the Vegetables

The BCF from soil to plants is a key module of human exposure to trace metals via food chain. BCF of metals is essential to investigate the human health risk index [2]. Results of the BCF for trace metals in *L. africana* and *T. occidentalis* are as shown in Table 1. The highest BCF of *L. africana* was recorded by Cu while the lowest was observed by As.

The trend of BCF for the trace metals in the vegetable sample was in order of Cu > Fe > Zn > Cd > Pb > Cr > Ni > As. In *T. occidentalis,* the highest BCF was recorded by Fe while the lowest was observed by Ni. The order of trace metal accumulation in the vegetable sample was Cu > Fe > Zn > Cr > Pb > Cd > As > Ni.

3.3. Daily Intake of Metals (DIM) for Children and Adults Through the Vegetables

The estimated DIM through the consumption of *Lasianthera africana* and *Telfairia occidentalis* for adults and children are as presented in Tables 2 and 3. DIM was calculated to estimate the daily metal loading into the body system of a specified body weight of a consumer [24]. DIM could be the realistic estimate for the average intake of metals from the vegetables. For *L. africana*, the trend of the metal intake was Cd > Cr > Cu > Zn > Fe > Pb > Ni >As. For *T. occidentalis*, the trend of the metal intake was Cd > Cr > Cu > Zn > Fe > Pb > Ni > As. The DIM values suggested that the consumption of vegetables grown in agricultural soils around the sand mining environment is nearly free of risks (except for Cd), as the oral reference dose for Fe, As, Cu, Ni, Cd, Cr, Pb and Zn are 0.05, 2.50, 0.04, 0.02, 0.001, 1.5, 0.004 and 0.30 mg/kg bw/day, respectively [2, 25].



	Cr	Cd	Pb	Ni	Fe	As	Cu	Zn
Farmland 1	3.02	3.12	2.26	1.15	10.11	1.11	17.91	6.22
Farmland 2	3.01	3.12	2.25	1.15	10.1	1.1	17.75	6.22
Farmland 3	3.02	3.11	2.23	1.15	10.13	1.11	17.93	6.22
Farmland 4	3.02	3.12	2.21	1.15	10.15	1.1	17.77	6.22
Control	0.84	0.11	0.01	0.01	2.11	0.02	4.69	2.01

Figure 3. *Levels of trace metals (mg/kg) in Lasianthera Africana.*

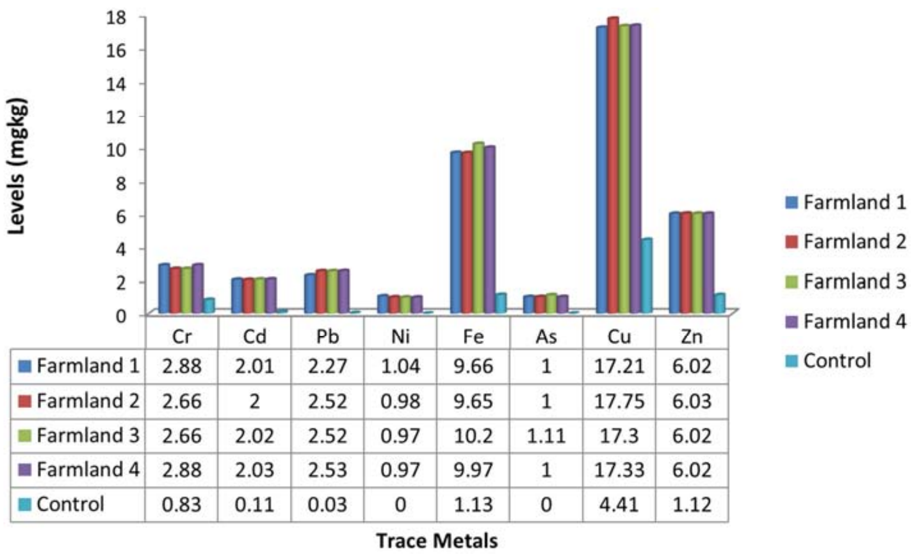


Figure 4. *Levels of trace metals (mg/kg) in Telfairia occidentalis.*

Table 1. *Bio-concentration factors (BCF) of trace metals from soil to vegetables.*

Metals	Cr	Cd	Pb	Ni	Fe	As	Cu	Zn
Metal levels in soil	5.31	4.68	3.68	2.74	13.05	2.59	19.08	9.11
Metal levels in *L. Africana*	3.02	3.12	2.24	1.15	10.12	1.10	17.84	6.22
BCF	0.57	0.67	0.61	0.42	0.78	0.43	0.94	0.68
Metal levels in *T. occidentalis*	2.77	2.01	2.64	0.99	9.86	1.03	17.27	6.02
BCF	0.52	0.43	0.69	0.36	0.76	0.40	0.91	0.66

Table 2. *DIM for children and adults through consumption of Lasianthera africana.*

Metals	Cr	Cd	Pb	Ni	Fe	As	Cu	Zn
Metal levels	3.016	3.116	2.243	1.150	10.123	1.104	17.840	6.221
DIM (Children)	0.018	0.019	0.0014	0.0007	0.0063	0.0006	0.0112	0.0036
DIM (Adults)	0.0016	0.0016	0.0012	0.0006	0.0053	0.0006	0.0093	0.0032

Table 3. *DIM for children and adult through consumption of Telfairia occidentalis.*

Metals	Cr	Cd	Pb	Ni	Fe	As	Cu	Zn
Metal level	2.768	2.014	2.640	0.990	9.860	1.025	17.273	6.024
DIM (Children)	0.002	0.0013	0.0014	0.0006	0.006	0.0006	0.0103	0.004
DIM (Adults)	0.0014	0.0010	0.0013	0.0005	0.0051	0.0005	0.0090	0.0031

3.4. THQ for Children and Adults Through Consumption of the Vegetables

The Target hazard quotients (THQ) for children and adult through consumption of *L. Africana* and *T. occidentalis* are as presented in Tables 4 and 5, respectively. For *L. africana*, the THQ values for all trace metals were less than one (except for Cd with THQ (1.900) for children and (1.600) for adults). The trend of health risk of the trace metals for the consumption of the vegetable is in the order: Cd Pb > Cu > As > Fe> Ni > Zn > Cr. For *T. occidentalis,* the THQ values for all trace metals were equally less than one (except for Cd with THQ (1.300) for children and (1.000) for adults). The trend of health risk of the trace metals for the consumption of the vegetable is equally in the order: Cd> Pb > Cu > As > Fe > Ni > Zn > Cr.

Table 4. *THQ for children and adults through consumption of Lasianthera Africana.*

Metals	Cr	Cd	Pb	Ni	Fe	As	Cu	Zn
Metal levels	3.016	3.116	2.243	1.150	10.123	1.104	17.840	6.221
THQ (Children)	0.001	1.900	0.350	0.035	0.003	0.120	0.280	0.012
THQ (Adults)	0.001	1.600	0.300	0.030	0.002	0.120	0.233	0.011

Table 5. *THQ for children and adults through consumption of Telfairia occidentalis.*

Metals	Cr	Cd	Pb	Ni	Fe	As	Cu	Zn
Metal levels	2.768	2.014	2.640	0.990	9.860	1.025	17.27	6.024
THQ (Children)	0.001	1.300	0.350	0.030	0.002	0.120	0.258	0.013
THQ (Adults)	0.001	1.000	0.325	0.025	0.002	0.100	0.225	0.010

4. Conclusion

Based on the analyses and results, it was concluded that the soil samples contain variable levels of the investigated trace metals. The levels of these metals were lower in the control samples than samples from the study area. These could be attributed to the adverse effect of the sand mining activities in the area. The levels of all the investigated trace metals (except Cd) in the soil samples of the study area were lower than the WHO and USEPA maximum permissible limits of the metals in soil. It is obvious that high Cd level in soil could negate the activities of soil organisms and affect plant growth negatively. Variable levels of the investigated trace metals were observed in the two vegetables, with the control samples having the lowest levels. The levels of all the investigated trace metals (except Cd) in the two vegetables were lower than the WHO and USEPA maximum permissible limits. The target hazard quotient (THQ) for all the measured trace metals in all the studied vegetables were lower than 1 (except for Cd), indicating that the vegetables are relatively safe for human consumption, except that the Cd levels could have adverse health effects to the consumers. Further research should be carried out on remediation of trace metals in the soil around the sand mining environment to reduce it bioaccumulation in plants and possible health risk of consumption.

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