

Industrial Impact on Selected Heavy Metals in Economic Crops

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Abstract

Industrial impact on selected heavy metal concentrations in economic food crops samples of Nnewi-North, Anambra State, Nigeria was studied. The levels of seven heavy metals (Pb, Mn, Zn, Ni, Cr, Cu, and Cd) in common food crops (*Manihot esculenta*, *Colocasia esculenta*, *Vernonia amygdalina*, *Corchorus olitorius*) from the area were determined using Flame Atomic Absorption Spectrophotometric technique. The HNO₃-H₂O₂ method was used in the food sample digestion. The mean concentrations (µg/g), of heavy metals in the food crops from the studied area were 2,72 for Pb, 5.10 for Mn, 19.42 for Zn, 0.97 for Ni, 5.79 for Cr, 5.75 for Cu, 0.61 for Cd and were higher than samples from the control sites although they were within the acceptable levels in food crops with the exception of Pb and Cd. The THQ and HI values were evaluated in order to assess the health risk of the inhabitants of Nnewi-north and environs due to heavy metal intake from food crops. The correlation coefficients and their properties were generated, proved and applied to the variable series of heavy metals investigated in the study. The correlations for most of the pairs of heavy metals considered were found to be significant. The values were less than 1 in all the food crops signifying that their consumption does not pose any health risk. In conclusion, the investigated area has been affected by the industrial activities and so control measures should be enforced by regulatory authorities.

Keywords: Heavy metals, Food crops, Target hazard quotient, Hazard index, Health risk, Industrial impact, Correlation coefficient

1. Introduction

Industrialization is essential for economic growth of any nation as it acts as a vehicle for development. Increasing population and industrial growth have impacted negatively on the environment at global scale (Asamudo et al., 2005). The establishment of different industries such as pulp and paper, textile, cement, petrochemical, metal processing, food processing, fertilizer, sugar, pharmaceutical, distilleries among others have helped to fulfil the basic requirements of increased population. The fermentation industry is considered as one of the most polluting industry and has posed serious environmental problems throughout the world while chemical and metallurgical industries are the most important sources of heavy metals in soils (Ene et al., 2009). Heavy metals are in various raw materials, such as fossil fuels and metal ores, as well as in industrial products (Pacyna & Pacyna, 2011). Some trace metals are emitted entirely or partially from raw materials during the high-temperature production of industrial goods, combustion of fuels, and incineration of municipal and industrial wastes, entering the ambient air with exhaust gases (Pacyna & Pacyna, 2011).

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Atmospheric emissions from industrial complexes are considered as the main source of the environmental pollution. These emissions travel along vast areas by the effect of the meteorological factors and be accumulated in soil, plant, animal and may reach the food chain (Mohamed, 2006).

Concentration of heavy metals in the soil cannot be used as best index for the measurement of food crops pollution but rather the actual metal concentration in plant materials. This is because soil condition and characteristic determine the speciation and availability of heavy metals in them (Arshad et al., 2011). The major factor governing metal availability to plants in soils is the solubility of the metal associated with the solid phase, since in order for root uptake to occur, a soluble species must exist adjacent to the root membrane for some finite period. The rate of release and form of this soluble species will have a strong influence on the rate and extent of uptake and, perhaps, mobility and toxicity in the plant and consuming animals (Okereke et al., 2016).

The accumulation of heavy metals in agricultural soils is of increasing concern because of food safety issues, potential health risks, and its detrimental effects on soil ecosystem (Cui et al., 2004). Many heavy metals are environmentally stable and non-biodegradable, toxic to the living things and tend to accumulate in them, thereby causing chronic adverse effects on human health (Vijaya et al., 2010). Hg, Pb, Cd and Cr are of great concern due to their toxicity to human health and other organism, whereas Zn and Cu are essential elements for plants and human (NaZ et al., 2007). Vegetable plants are known to take up Hg, Pb, Cd, Zn, and Cu and accumulate them in their edible and non-edible parts with various concentrations (NaZ et al., 2007). Vegetable is a major part of Nigerian diet and is very susceptible to environmental pollution due to the activities and processes going on or practiced in the area where it is cultivated.

The amount of concentrations of heavy metals that move from soil into plants can be measured by the “transfer factor” which is defined as the ratio that exists between the concentrations of metals in the plant and that of the soil. This transfer factor could be different for different plant species and will change as soil physical and chemical properties are altered (Arshad et al., 2011). Nevertheless, heavy metals in the environment, are of immense concern, because of their persistent nature to bio accumulate, and bio magnify along the food chain, thereby causing eco-toxicity to plants, animals, and human beings (Alloway, 2009). The comparison in the concentrations of heavy metals in soil, crops and water with established safe limits provides a basis for guiding further activities aimed at preventing excessive exposure of toxic substances such as heavy metals to human beings (Rajesh, 2007). Earlier study in potential health risk from heavy metals via consumption of vegetables in the vicinity of Warri Refining and Petrochemical Company showed slight heavy metals toxicity (Patrick-Iwuanyanwu & Nwokeji, 2018). In another study performed in Nnewi-North, the lead content in food and soil samples were found to be high (Orisakwe et al., 2004a). This study, however, would holistically cover the impacts of industrial discharges on food crops grown around the vicinity of rivers in Nnewi-North. Nnewi-North LG is an area with many industries such as lead battery, metal processing, food processing, petrochemical, pharmaceutical, distilleries amongst others which we know to emit heavy metals into the environment. In spite of these activities, the local population depends on agriculture for most of the food requirement. Since the soil is a sink for heavy metal pollution, these metal are invariably transferred to plants and hence food crops which are consumed by man. The aim of this study is to determine the concentration of some heavy metals in selected food crops grown and consumed by the resident local population of Nnewi-North Local Government Area of Anambra State, Nigeria. This would help to assess their suitability for consumption by the measurement of their health index.

2. Materials and Methods

2.1 Study Area

Nnewi is the second largest city in Anambra State, South Eastern Nigeria (Figure 1). Nnewi-North Local Government Area is commonly referred to as Nnewi Central, and comprises four autonomous quarters: Otolo,

Uruagu, Umudim, and Nnewichi (Nigerian Association of Chambers of Commerce, Industry, Mines and Agriculture (NACCIMA, 2015). Its geographical coordinates are 6°1'0" North and 6° 55'0" East. The city is located east of the Niger River, and about 22 kilometers south east of Onitsha in Anambra state, Nigeria (Erosion, 2009).

The main occupation of Nnewi people is trading and farming, therefore they depend mainly on agriculture and commerce for their daily livelihood. Nnewi by virtue of her geographical location and availability of natural water like MmiriEle, MmiriEze, Ulasi, Ukwaka rivers etc was originally an agricultural community. MmiriEle is located at Umudim Nnewi beside Nnewi-North Local Government Headquarters. It flows from Umudim and moves northward where it joins with Rivers Fada into Eze before changing its course westward passing via the back of Okongwu Memorial Grammer School before leaving Nnewi towards Ozubulu as shown in Figure 2.

Nnewi is home to many major indigenous manufacturing industries. Nnewi is part of eastern Nigeria's industrial axis and acts as sophisticated networks expanded to include an international dimension through trading relations with exporters from Asia (NACCIMA, 2015). Infact, Nnewi is usually referred to as the Japan of Nigeria because of its high industrialization and has about thirty giant manufacturing plants and over a hundred cottage industries (Rose et al., 2005). By 1940, Nnewi residents were at the center of an international trading network that dominated the supply of motor parts in Nigeria. The town subsequently became a center for commerce and industry, and is known to have one of the largest automotive parts markets in Africa (Onwutalobi, 2015).

2.2 Sample Collection and Preparation

Fresh samples of four (4) commonly consumed plant samples were obtained in large quantities from farm lands lying along the banks of five different rivers in the community. The samples were collected at the peak of the harvest time. The rivers are captured in (Figure 2). Ele river in Umudim (5°59.140'N/6°55.575' E), Eze river in Umudim (05°58.986'N/06°52.896'E), Fada river in Umudim (05°59.706' N/06°54.536' E), Ubu river in Otolo (5°55.278' N/06°51.847'E) and Ebenato river in Nnewi-south (05°55.976'N/06°56.784'E). The details of the plant species, local names and parts of plant used for analysis are shown in Table 1. The samples were properly tagged according to rivers in polythene bags and taken to the Botany Department laboratory, University of Abuja for identification. The freshly collected plant samples were washed up with tap water thoroughly to remove the attached dust particles, soil, unicellular algae, etc. The samples were washed with distilled water and the leaves were shredded. The root crops were peeled to remove their coats and sliced into smaller sizes using a stainless-steel knife and weighed. They were placed on trays and dried in an electric oven at 55±1°C for four hours. Then, the food crops were crushed into fine powder that was sieved using a porcelain mortar and pestle. The resulting powder was kept in air tight polythene packet at room temperature and taken to the laboratory for digestion and metal analyses (Hart et al., 2005).

Table 1 List of food crops used in this study

Scientific name	Family	Local name	Common name	Parts used
<i>Manihot esculenta</i>	Euphorbiaceae	Akpu	Cassava	Roots
<i>Colocasia esculenta</i>	Araceae	Ede	Cocoyam	Roots
<i>Vernonia amygdalina</i>	Asteraceae	Onugbu	Bitter leaf	Leaves
<i>Corchorus olitorius</i>	Tiliaceae	Ahihiaria	Jute leaf	Leaves

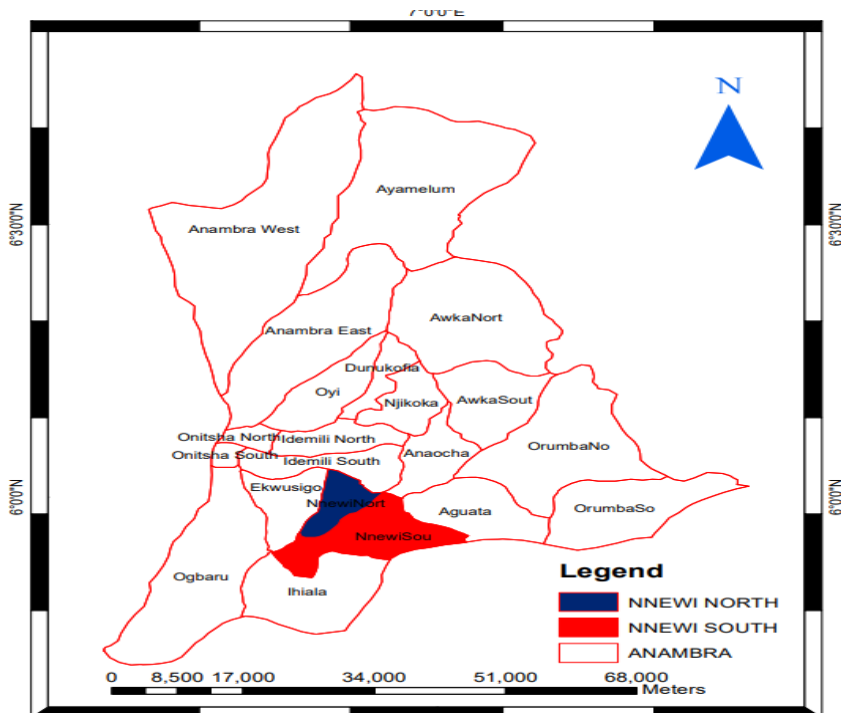


Fig. 1 Map of Anambra State showing Nnewi-North

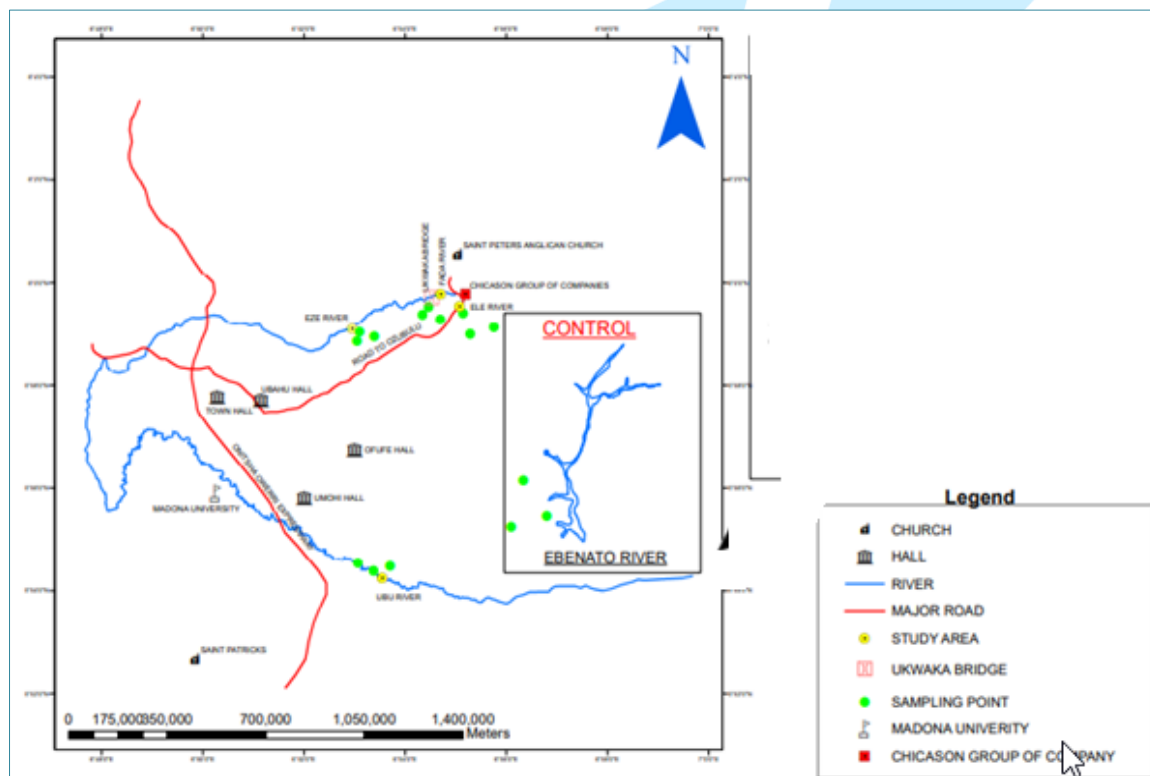


Fig. 2 Map of the Study Area Showing all Rivers and Sample Points

2.3 Digestion and Metal Analysis

The methodology described by (Bortey-Sam et al., 2015) with slight modification was used in the preparation of the samples for heavy metal concentrations. 2.0 g each of the grounded sample was digested with 20 cm³ of a mixture of HNO₃-H₂O₂ in ratio of 5:1 on an electric heating plate placed in a fume hood until a clear solution was obtained. 5 cm³ of the acid mixture was also added to ensure complete digestion. After digestion, the digest was filtered into a 50ml volumetric flask, diluted to volume with distilled water and stored in polyethylene bottles for analysis. The analysis of heavy metals (Pb, Mn, Zn, Ni, Cr, Cu and Cd) was conducted using the Flame Atomic Absorption Spectrometry (AAS) situated in Sheda Science and Technology Complex, Abuja.

2.4 Health Risk Assessment

The potential health risks of heavy metal consumption through vegetables/tubers were assessed on the daily intake rate of metal (DIR) (Orisakwe et al., 2012).

$$\text{Estimated Daily Intake Rate} = \frac{C_{\text{metal}} * D_{\text{food intake}}}{B \text{ average weight}}$$

Where C_{metal} is heavy metal concentration in plants ($\mu\text{g/g}$), $D_{\text{food intake}}$ is daily intake of vegetable (g/person) and B average weight is average body weight

The average daily vegetables intakes for adults was considered to be $0.345\text{kg/person/day} = 345\text{g/person/day}$ in this study. The value was adapted based on the report of (Song, et al., 2015) and also considering that vegetable is widely consumed as a major part of the diet in the area. Average body weight was considered to be 70kg.

The daily maximum intake of 0.8kg for cassava and cocoyam meals was assumed for this study (Hayford et al., 2009, Zango, et al., 2013). The daily intake of cassava and cocoyam were converted to g/person/day (Osu et al., 2015).

Target Hazard Quotient (THQ): The target hazard quotient (THQ) is used to quantify the amount of metal taken in through ingestion. The target hazard quotient was calculated based on the formula, $THQ = \frac{EDI}{RFD}$ (Osu et al., 2015).

Hazard Index (HI): The hazard index is the sum of the hazard quotients for all heavy metals, which was calculated following the equation: $HI = \sum HQ$ (United State Environmental Protection Agency [USEPA], 1989). When the HI is more than 1; the food involved is considered a risk to the concerned consumers. When the HI is less than 1, the food involved is considered as acceptable (no concern) to the concerned consumer (USEPA, 2002). The calculated values can be found in Table 8 in the discussion.

2.5 Correlation Coefficient of Variable Series

Correlation Coefficient measures the degree of covariability of two variables, say X and Y. It is a statistical method used for measuring the intensity or magnitude of linear relationship between two variable series (Biyi et al, 2014; Kothari & Garg, 2014).

Karly Pearson's measure otherwise known as Product Moment Correlation Coefficient (PMCC) between two variables (X and Y) denoted by $r(x,y) = r_{xy}$ is used as a numerical measure of linear relationship between pairs of heavy metals considered in this study.

PMCC is defined as the ratio of the covariance between two variables, X and Y, written as $cov(x, y) = \sigma_{xy}$ to the product of the standard deviations of X and Y (σ_x and σ_y). Symbolically,

$$r = \frac{Cov(x,y)}{\sigma_x \sigma_y} \quad (1)$$

If $(x_1, y_1), (x_2, y_2), \dots, (x_n, y_n)$ are n pairs of observations of the variables X and Y in a bivariate distribution, then

$$Cov(x, y) = \frac{1}{n} \sum (x - \bar{x})(y - \bar{y}); \sigma_x = \sqrt{\frac{1}{n} \sum (x - \bar{x})^2}; \sigma_y = \sqrt{\frac{1}{n} \sum (y - \bar{y})^2} \quad (2)$$

Substituting in (1), we have

$$r = \frac{\frac{1}{n} \sum (x - \bar{x})(y - \bar{y})}{\sqrt{\frac{1}{n} \sum (x - \bar{x})^2} \cdot \sqrt{\frac{1}{n} \sum (y - \bar{y})^2}} = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sqrt{\sum (x - \bar{x})^2} \sqrt{\sum (y - \bar{y})^2}} = \frac{\sigma_{xy}}{\sigma_x \sigma_y} \quad (3)$$

Simplifying (2), we have

$$\text{Cov}(x, y) = \frac{1}{n} \sum (x - \bar{x})(y - \bar{y}) = \frac{1}{n} \sum (xy - \bar{x}y - y\bar{x} + \bar{x}\bar{y}) = \frac{1}{n} \sum xy - \bar{x}\bar{y} \quad (4)$$

$$= \frac{1}{n} \sum xy - \bar{x} \cdot \frac{1}{n} \sum y - \bar{y} \cdot \frac{1}{n} \sum x + \frac{1}{n} \cdot n\bar{x}\bar{y} \quad (5)$$

$$= \frac{1}{n} \sum xy - \bar{x}\bar{y} - \bar{y}\bar{x} + \bar{x}\bar{y}$$

$$= \frac{1}{n} \sum xy - \bar{x}\bar{y} = \frac{1}{n} \sum xy - \left(\frac{\sum x}{n} \right) \left(\frac{\sum y}{n} \right) \\ = \frac{1}{n^2} [n \sum xy - (\sum x)(\sum y)] \quad (6)$$

$$\text{Thus, } \sigma_x^2 = \frac{1}{n} \sum (x - \bar{x})^2 = \frac{1}{n^2} [n \sum x^2 - (\sum x)^2] \quad (7)$$

$$\text{Similarly, } \sigma_y^2 = \frac{1}{n} \sum (y - \bar{y})^2 = \frac{1}{n^2} [n \sum y^2 - (\sum y)^2] \quad (8)$$

Substituting (6), (7) and (8) in (1), we have

$$r = \frac{\frac{1}{n^2} [n \sum xy - (\sum x)(\sum y)]}{\sqrt{\frac{1}{n^2} \{n \sum x^2 - (\sum x)^2\}} \sqrt{\frac{1}{n^2} \{n \sum y^2 - (\sum y)^2\}}} \\ = \frac{n \sum xy - (\sum x)(\sum y)}{\sqrt{[n \sum x^2 - (\sum x)^2]} \sqrt{[n \sum y^2 - (\sum y)^2]}} \quad (9)$$

2.5.1 Characteristics of Correlation Coefficient

Some of the properties of Pearson's correlation coefficient are established and proved in this research work:

- (a) The numerical value of correlation coefficient lies between -1 and 1 ($-1 \leq r \leq 1$).

Proof:

$$\sum \left[\frac{x - \bar{x}}{\sigma_x} \pm \frac{y - \bar{y}}{\sigma_y} \right]^2 \geq 0$$

Consider the sum of squares

This implies that

$$\sum \left[\left(\frac{x - \bar{x}}{\sigma_x} \right)^2 + \left(\frac{y - \bar{y}}{\sigma_y} \right)^2 \pm 2 \left(\frac{x - \bar{x}}{\sigma_x} \right) \left(\frac{y - \bar{y}}{\sigma_y} \right) \right] \geq 0 \\ \sum \left[\left(\frac{x - \bar{x}}{\sigma_x} \right)^2 + \left(\frac{y - \bar{y}}{\sigma_y} \right)^2 \pm 2 \left(\frac{x - \bar{x}}{\sigma_x} \right) \left(\frac{y - \bar{y}}{\sigma_y} \right) \right] \geq 0 \\ \frac{\sum (x - \bar{x})^2}{\sigma_x^2} + \frac{\sum (y - \bar{y})^2}{\sigma_y^2} \pm \frac{2 \sum (x - \bar{x})(y - \bar{y})}{\sigma_x \sigma_y} \geq 0 \quad (10)$$

Dividing through by n, we have

$$\frac{1}{\sigma_x^2} \cdot \sigma_x^2 + \frac{1}{\sigma_y^2} \cdot \sigma_y^2 \pm \frac{2}{\sigma_x \sigma_y} \text{Cov}(x, y) \geq 0$$

$$-1 \leq r \text{ or } r \leq 1$$

$$\Rightarrow -1 \leq r \leq 1 \quad (11)$$

(b) Correlation Coefficient is independent of the change of origin and scale

If X and Y are the given variables (i.e., heavy metals) and they are transformed to the new variables U and V by change of origin and scale, then

$$u = \frac{x-A}{h} \quad \text{and} \quad v = \frac{y-B}{k}; \quad h > 0, k > 0, \quad (12)$$

where A, B, h and k are constants, then the correlation coefficient between x and y is the same as that of u and v.

Proof:

Consider $r(x, y) = r(u, v) \Rightarrow r_{xy} = r_{uv}$

$$\text{From (12), } x = A + hu \text{ and } y = B + kv \quad (13)$$

Summing up both sides and dividing by n, we have

$$\bar{x} = A + h\bar{u} \quad \text{and} \quad \bar{y} = B + k\bar{v} \quad (14)$$

Subtracting (13) from (12), we have

$$x - \bar{x} = h(u - \bar{u}) \quad \text{and} \quad y - \bar{y} = k(v - \bar{v})$$

Substituting these values in (3), we have

$$r_{xy} = \frac{\sum [h(u - \bar{u}) \times k(v - \bar{v})]}{\sqrt{[\sum h^2 (u - \bar{u})^2] [\sum k^2 (v - \bar{v})^2]}} = \frac{\sum (u - \bar{u})(v - \bar{v})}{\sqrt{\sum (u - \bar{u})^2 \sum (v - \bar{v})^2}} = r_{uv} \quad (15)$$

(c) Two independent variables are uncorrelated but the converse is not true.

Proof:

It has been shown in (4) that

$$\text{Cov}(x, y) = \frac{1}{n} \sum xy - \bar{x} \cdot \bar{y} = E(xy) - E(x)E(y) \quad (16)$$

If x and y are independent variables, then $E(x \cdot y) = E(x)E(y)$

Substituting in (16), we have

$$\text{Cov}(x, y) = E(x)E(y) - E(x)E(y) = 0$$

Hence, if x and y are independent, then

$$r_{xy} = \frac{\text{Cov}(x, y)}{\sigma_x \sigma_y} = 0 \quad (17)$$

(d) Correlation matrices are symmetrical and the diagonal elements are all denoted by 1 since the correlation between a variable and itself is unity (Gupta, 2013).

(e) Correlation coefficient measures only linear correlation between two variables. If the variables are connected by $ax + by + c = 0$, then

$$r = r(x, y) = \begin{cases} +1, & \text{if } a \text{ and } b \text{ are of opposite signs} \\ -1, & \text{if } a \text{ and } b \text{ are of same sign} \end{cases}$$

Proof:

Take n observations on each of the variables x and y

As given, the linear equation is

$$ax + by + c = 0 \quad (18)$$

Summing both sides of the given linear equation by n, we have

$$a\bar{x} + b\bar{y} + c = 0 \quad (19)$$

Subtracting (19) from (18), we have

$$y - \bar{y} = -\frac{a}{b}(x - \bar{x}) \quad (20)$$

From (20),

$$\begin{aligned} \sigma_y^2 &= \frac{1}{n} \sum \left[-\frac{a}{b}(x - \bar{x}) \right]^2 = \frac{a^2}{b^2} \sigma_x^2 \\ \Rightarrow \sigma_y &= \frac{a}{b} \sigma_x \end{aligned} \quad (21)$$

Also, from (20),

$$\text{Cov}(x, y) = \frac{a}{b} \sigma_x^2 \quad (22)$$

$$\text{Thus, } r(x, y) = \frac{\text{Cov}(x, y)}{\sigma_x \sigma_y} = \frac{-\frac{a}{b} \sigma_x^2}{\sigma_x \left| \frac{a}{b} \right| \sigma_x} = \frac{-\frac{a}{b}}{\left| \frac{a}{b} \right|} \quad (23)$$

2.5.2 Test of Significance for Correlation Coefficient

Correlation coefficient test is carried out to establish whether or not a sample correlation comes from a population with a correlation coefficient of zero i.e., null hypothesis $H_0: \rho = 0$. The standard error of

correlation coefficient is denoted by $SE(r) = \sqrt{\left[\frac{(1-r^2)}{n-2} \right]}$, where n is the sample size. For small sample size, t

test is utilized with test criterion specified as:

$$t = \frac{|r-0|}{SE(r)} = \frac{r}{\sqrt{\left[\frac{(1-r^2)}{(n-2)} \right]}} = r \left(\frac{n-2}{1-r^2} \right)^{\frac{1}{2}}$$

with n-2 degrees of freedom at α level of significance.

For large sample size, Normal distribution test is utilized with correlation coefficients r_1 and r_2 and sample sizes n_1 and n_2 based on the transformation:

$$Z_1 = \frac{1}{2} \log \frac{1+r_1}{1-r_1} \quad \text{and} \quad Z_2 = \frac{1}{2} \log \frac{1+r_2}{1-r_2} \quad (24)$$

The test criterion is specified as:

$$Z = \frac{|Z_1 - Z_2|}{\sqrt{\frac{1}{n_1-3} + \frac{1}{n_2-3}}} \sim N(0,1)$$

at α level of significance (Rao, 2007).

3. Results and Discussion

All the plant samples collected around the banks of the four rivers contained the seven metals analyzed and the mean values were higher in concentration of the study area than the control samples. The heavy metals concentrations ($\mu\text{g/g}$) in the commonly consumed vegetables/tubers and at various locations are shown in Tables in 2 and 3 respectively while the summary of heavy metals in tubers/leafy vegetables from all sites are summarized in Table 4.

3.1 Lead

Lead concentrations in the analyzed plant samples within the vicinity of various rivers ranged from (0.010-6.05g/g) dry weight (Table 2). The highest level of Pb was recorded in *M.esculenta* (6.05 $\mu\text{g/g}$) dry weight obtained in Ubu and while the least value were both recorded in *V. amygdalina* (Eze) and *C.acutangulus* (0.01 $\mu\text{g/g}$) dry weight in Ebenato (Table 2).The level of lead was greater in tubers (2.88 $\mu\text{g/g}$) dry weight than recorded in leafy vegetables(2.57 $\mu\text{g/g}$)dry weight (Table 4).

3.2 Manganese

Manganese concentrations in the analyzed plant samples within the vicinity of various rivers ranged from 0.50-12.50 $\mu\text{g/g}$ dry weight (Table 2). The highest level of Mn was recorded in both *V.amygdalina* and *C.acutangulus* (12.50 $\mu\text{g/g}$) dry weight obtained in Eze as well as in Ubu and the least was also recorded in *C.acutangulus* (0.5 $\mu\text{g/g}$) dry weight from Ebenato. For mean concentrations of manganese, leafy vegetables had significantly higher concentrations than the tubers (Table 4).

3.3 Cadmium

Cadmium concentrations ranged from 0.05-1.25 $\mu\text{g/g}$ dry weight (Table 2). The highest level of Cd was recorded in *V.amygdalina* (1.25 $\mu\text{g/g}$) dry weight obtained in Eze and the least was recorded also in *V.amygdalina* (0.05 $\mu\text{g/g}$) dry weight from Ebenato. For mean concentrations of cadmium, leafy vegetables had significantly higher concentrations than the tubers (Table 4).

3.4 Chromium

Chromium concentrations in the analyzed plant samples within the vicinity of various rivers ranged from 0.21-12.25 $\mu\text{g/g}$ dry weight (Table 2). The highest level of Cr was recorded in *M.esculenta* (12.25 $\mu\text{g/g}$) dry weight obtained in Ubu and the least was recorded in *C.xanthosama* (0.21 $\mu\text{g/g}$) dry weight from Ebenato. The level of chromium was greater in tubers (7.84 $\mu\text{g/g}$) dry weight than recorded in leafy vegetables (3.74 $\mu\text{g/g}$) dry weight (Table 4).

3.5 Zinc

The highest concentration of Zn recorded in sampled food crops was 30.00 $\mu\text{g/g}$ dry weight (Table 2) in *V.amygdalina* obtained from Fada and the least was 4.50 $\mu\text{g/g}$ dry weight in *C.acutangulus* from Ebenato. The mean concentration of zinc was highest in vegetables than in tubers (Table 4).

3.6 Nickel

Nickel recorded the least mean concentration amongst other metals examined (Table 2). Eze recorded the highest Ni content in *V.amygdalina* (3.12 $\mu\text{g/g}$) dry weight but not detected in Ebenato.

3.7 Copper

Copper level of vegetables from vicinity of these rivers ranged between 1.09 and 12.00 $\mu\text{g/g}$ dry weight (Table 2). Copper was found to occur in highest concentrations in leafy vegetables (6.82 $\mu\text{g/g}$)dry weight than in tubers (4.68 $\mu\text{g/g}$) dry weight (Table 4).

Table 2 Mean Heavy Metals concentrations ($\mu\text{g/g}$) in the Commonly Consumed Vegetables/Tubers

Location	Sample type	Pb	Mn	Cd	Cr	Zn	Ni	Cu
Eze river	<i>C. xanthosama</i>	0.04 \pm 0.01	0.85 \pm 0.05	0.65 \pm 0.00	6.82 \pm 0.03	9.50 \pm 0.50	2.25 \pm 0.61	1.75 \pm 0.05
	<i>M. esculenta</i>	1.25 \pm 0.15	3.37 \pm 0.25	0.37 \pm 0.03	9.50 \pm 0.50	5.25 \pm 0.09	0.10 \pm 0.01	4.75 \pm 0.28
	<i>C. acutangulus</i>	2.37 \pm 0.03	6.25 \pm 0.02	0.95 \pm 0.13	5.82 \pm 0.42	25.83 \pm 1.32	0.25 \pm 0.22	4.65 \pm 0.05
	<i>V. amygdalina</i>	0.01 \pm 0.00	12.50 \pm .50	1.25 \pm 0.05	5.32 \pm 0.02	27.50 \pm 2.20	3.12 \pm 0.03	5.50 \pm 0.79
Ele river	<i>C. xanthosama</i>	1.75 \pm 0.01	2.37 \pm 0.02	0.38 \pm 0.025	6.00 \pm 0.87	14.25 \pm 0.13	1.25 \pm 0.05	3.00 \pm 0.50
	<i>M. esculenta</i>	3.87 \pm 0.11	1.13 \pm 0.03	0.25 \pm 0.05	5.75 \pm 0.79	7.75 \pm 0.23	0.20 \pm 0.01	1.62 \pm 0.06
	<i>C. acutangulus</i>	2.00 \pm 0.50	6.25 \pm 0.66	0.78 \pm 0.03	1.62 \pm 0.06	24.20 \pm 0.17	2.12 \pm 0.02	6.25 \pm 0.25
	<i>V. amygdalina</i>	3.75 \pm 0.05	4.37 \pm 0.02	0.73 \pm 0.03	4.38 \pm 0.10	24.50 \pm 0.48	1.37 \pm 0.02	5.00 \pm 0.50
Fada river	<i>C. xanthosama</i>	3.85 \pm 0.10	3.06 \pm 0.00	0.93 \pm 0.07	6.50 \pm 1.30	12.75 \pm 0.05	1.62 \pm 0.02	3.12 \pm 0.01
	<i>M. esculenta</i>	1.25 \pm 0.15	4.25 \pm 0.05	0.40 \pm 0.03	5.12 \pm 0.07	29.50 \pm 0.13	0.10 \pm 0.01	5.12 \pm 0.06
	<i>C. acutangulus</i>	4.25 \pm 0.05	5.50 \pm 0.50	0.30 \pm 0.01	2.60 \pm 0.08	25.00 \pm 1.70	0.15 \pm 0.00	12.00 \pm 0.61
	<i>V. amygdalina</i>	2.00 \pm 0.50	7.12 \pm 0.02	0.72 \pm 0.01	1.84 \pm 0.04	30.00 \pm 2.60	0.32 \pm 0.03	10.00 \pm 0.42
Ubu river	<i>C. xanthosama</i>	5.00 \pm 0.91	2.87 \pm 0.17	0.30 \pm 0.01	10.85 \pm 0.04	19.50 \pm 0.38	0.12 \pm 0.02	11.12 \pm 0.04
	<i>M. esculenta</i>	6.05 \pm 0.04	2.37 \pm 0.01	0.50 \pm 0.12	12.25 \pm 0.40	7.75 \pm 0.04	0.75 \pm 0.09	7.00 \pm 0.88
	<i>C. acutangulus</i>	3.75 \pm 0.06	12.50 \pm 0.50	0.83 \pm 0.03	3.37 \pm 0.02	21.25 \pm 0.04	1.25 \pm 0.16	7.50 \pm 0.67
	<i>V. amygdalina</i>	2.50 \pm 0.50	6.87 \pm 0.44	0.60 \pm 0.01	5.00 \pm 0.17	26.25 \pm 0.04	0.62 \pm 0.08	3.75 \pm 0.14
Ebenato river	<i>C. xanthosama</i>	0.32 \pm 0.02	2.05 \pm 0.92	0.21 \pm 0.02	0.21 \pm 0.02	10.70 \pm 0.24	0.00 \pm 0.00	2.00 \pm 0.86
	<i>M. esculenta</i>	0.21 \pm 0.02	2.50 \pm 0.43	0.38 \pm 0.11	1.35 \pm 0.04	9.32 \pm 0.27	0.00 \pm 0.00	3.20 \pm 0.25
	<i>C. acutangulus</i>	0.01 \pm 0.00	0.50 \pm 0.10	0.09 \pm 0.01	0.24 \pm 0.02	4.50 \pm 0.43	0.00 \pm 0.00	1.09 \pm 0.11
	<i>V. amygdalina</i>	0.16 \pm 0.00	2.00 \pm 0.10	0.05 \pm 0.01	1.20 \pm 0.17	10.75 \pm 0.21	0.08 \pm 0.01	1.60 \pm 0.36

Table 3 Summary of Mean Concentration of Heavy Metals ($\mu\text{g/g}$) in all Food Crop at various Location of the Studied Area

No	River	Heavy metals							Mean
		Pb	Mn	Cd	Cr	Zn	Ni	Cu	
1	Eze	0.91 \pm 1.12	5.74 \pm 5.01	0.80 \pm 0.37	6.86 \pm 1.84	17.02 \pm 11.29	1.43 \pm 1.49	4.16 \pm 1.62	5.27 \pm 3.83
2	Ele	2.84 \pm 1.12	3.53 \pm 2.25	0.53 \pm 0.26	4.43 \pm 2.00	17.67 \pm 8.15	1.23 \pm 0.79	3.96 \pm 2.05	4.88 \pm 2.65
3	Fada	2.83 \pm 1.44	4.98 \pm 1.78	0.58 \pm 0.29	4.01 \pm 2.17	24.31 \pm 8.02	0.54 \pm 0.72	7.56 \pm 4.13	6.40 \pm 2.66
4	Ubu	4.32 \pm 1.53	6.15 \pm 4.68	0.55 \pm 0.22	7.86 \pm 4.34	18.68 \pm 7.83	0.68 \pm 0.46	7.34 \pm 3.01	6.51 \pm 2.71
5	Ebenato	0.17 \pm 0.12	1.76 \pm 0.87	0.18 \pm 0.14	0.75 \pm 0.60	8.81 \pm 2.95	0.02 \pm 0.04	1.97 \pm 0.89	1.95 \pm 1.01

Table 4 Summary of Mean Heavy Metals ($\mu\text{g/g}$) in tubers and leafy vegetables from all sites in the Studied Area

Metals	Tubers	Leafy vegetable
Pb	2.88 \pm 0.46	2.57 \pm 0.15
Mn	2.53 \pm 0.062	7.66 \pm 0.18
Cd	0.47 \pm 0.026	0.78 \pm 0.026
Cr	7.84 \pm 0.34	3.74 \pm 0.12
Zn	13.27 \pm 0.16	25.56 \pm 0.31
Ni	0.79 \pm 0.19	1.14 \pm 0.058
Cu	4.68 \pm 0.24	6.82 \pm 0.18

3.8 Comparison of the Levels in Food Crops to Acceptable Levels in Foods

The present study showed that Pb and Cd were above the limits for food crops by various international standards and guidelines such as (National Environmental Protection Agency of China, Beijing, China [NEPAC], 2005, State Environmental Protection Administration, China [SEPA], 2005) whereas manganese, zinc, nickel and copper were lower than the above standards and guidelines (Table 5). The recommended limits for various heavy metals vary depending on the food being considered and the country sometimes as well as the organization (Adedokun et al., 2016).

Table 5 Comparison of Mean Concentrations ($\mu\text{g/g}$) in Food Crops of the Studied Area with some Reference Standard

Heavy Metal	Region	[32]	[48]	[49]
	Nnewi-North (This study)			
Pb	2.72 \pm 1.39 0.01-6.05	0.30	0.20	9
Mn	5.10 \pm 1.15 0.50-12.50	500	-	-
Zn	19.42 \pm 3.33 5.25-30.00	100	50	100
Ni	0.97 \pm 0.42 0.10-3.12	66.9	-	10
Cr	5.79 \pm 1.86 1.62-12.25	-	0.50	0.50
Cu	5.75 \pm 1.96 1.62-12.00	73.3	10	20
Cd	0.61 \pm 0.12 0.25-1.25	0.21	0.20	0.20

3.9 Pearson Correlation for Food Crops from all the Rivers

Correlation was significant in food crops for the pairs of Cu/Zn, Cu/Pb, Ni/Cd, Cr/Mn in the positive direction (Table 6). This served as an indication of pollution from the same source, for instance, from agricultural chemicals or materials such as impurities in fertilizers, pesticides, air deposition and industrial effluents from chemical industries (Orisakwe et al., 2004a; Andreu & Gimeno, 2008). Correlation was also significant for the pairs of Cu/Ni, Ni/Zn, Ni/Pb, Zn/Cr and Cd/Pb in negative direction and this indicated that the pollution could be from a common source.

3.10 Health Risk Assessment

To assess the health risk of the inhabitants of Nnewi-north and environs due to heavy metal intake from food crops, target hazard quotient (THQ), and hazard index (HI) were calculated and the results are presented in Tables 8.

Table 6 Pearson Correlation, Lower Triangle for Food crops from all the rivers

	Pb	Mn	Cd	Cr	Zn	Ni	Cu
Cu							1
Ni						1	-0.968
Zn					1	-0.807	0.746
Cr				1	-0.559	0.126	0.073
Cd			1	0.344	-0.334	0.604	-0.419
Mn		1	0.434	0.806	-0.013	-0.247	0.478
Pb	1	0.066	-0.863	0.129	0.249	-0.732	0.657

Based on average values, the result showed that the estimated daily intake of heavy metals through food consumption within the vicinity of the studied area appeared in descending order Zn>Cr>Cu>Mn>Pb>Ni>Cd. In the control site (Ebenato), the estimated daily intake of heavy metals based on average value was also in descending order Zn>Cu>Mn>Cr>Cd>Pb>Ni. The EDI results were compared with the recommended daily intake (DI) of heavy metals and the upper tolerable daily intake level (UL) established by the Institute of Medicine for people between the ages of 19 to 70 years (Food and Drug Agency [FDA] 2001, Garcia-Rico et al., 2007). The average EDI in food crops species for Pb (ND-0.0690 µg/g) dry weight and Cd (0.0014-0.0074 µg/g) dry weight exceeded the recommended daily intake(DI) but falls between the upper tolerable daily intake (UL). However, Mn, Zn, Ni, and Cu with (0.0097-0.0616, 0.0600-0.3370, ND-0.0257 and 0.0180-0.1270 µg/g) dry weight respectively were all significantly lower than the recommended daily intake of metals (DI) and the upper tolerable daily intake level (UL).

A tolerable upper intake level for Cr has not been established. Target hazard quotient and hazardous indexes of heavy metals (Table 8) in selected food crops were calculated in order to give an estimate of the non-carcinogenic health risk due to oral exposure of heavy metals. The THQ values range showed that Pb was 0.0001-0.0490, Mn was 0.0004-0.0025, Cd was 0.0028-0.0200, Cr was 0.0026-0.0460, Zn was 0.0002-0.0011, Ni was ND-0.0012 and Cu was 0.0005-0.009. In the control (Ebenato), the THQ values range showed that Pb was ND-0.0017, Mn was 0.0001-0.0011, Cd was 0.0008-0.0086, Cr was 0.0004-0.0050, Zn was ND-0.0004, Ni was ND and Cu was 0.0001-0.0006.

In this study, the THQ values in all the metals were far less than 1 in all the food crops indicating that their consumption does not pose any health risk concern. Similarly, HI values for the study ranged from 0.0208-0.1100 while in the control, the HI ranged from 0.0018-0.0179. Though the HI values for the study area were a little higher than the control sites the results were less than 1 indicating that their consumption does not pose any health risk to the population.

Table 7 EDI of Heavy Metals (mg/kg/day/Bw) via Consumption of Leafy Vegetables/Tubers

Location Limit	Samples	Pb	Mn	Cd	Cr	Zn	Ni	Cu	TOTAL
Eze river	<i>C. xanthosama</i>	0.0004	0.0097	0.0074	0.0779	0.1085	0.0257	0.0200	0.6576
	<i>M. esculenta</i>	0.0143	0.0385	0.0042	0.1085	0.0600	0.0011	0.0540	0.5377
	<i>C. acutangulus</i>	0.0117	0.0300	0.0046	0.0286	0.1200	0.0012	0.0220	0.5982
	<i>V. amygdalina</i>	0.0000	0.0616	0.0061	0.0262	0.1355	0.0150	0.0270	0.4070
Ele river	<i>C. xanthosama</i>	0.0200	0.0270	0.0043	0.0680	0.1620	0.0140	0.0340	0.9573
	<i>M. esculenta</i>	0.0440	0.0129	0.0028	0.0657	0.0880	0.0022	0.0190	0.9766
	<i>C. acutangulus</i>	0.0098	0.0308	0.0038	0.0079	0.1100	0.0100	0.0300	0.6923
	<i>V. amygdalina</i>	0.0180	0.0200	0.0035	0.0210	0.1200	0.0067	0.0240	0.7232
Fada river	<i>C. xanthosama</i>	0.0440	0.0340	0.0100	0.0740	0.1457	0.0180	0.0360	0.7617
	<i>M. esculenta</i>	0.0140	0.0480	0.0045	0.0580	0.3370	0.0014	0.0585	0.8864

	<i>C. acutangulus</i>	0.0209	0.0270	0.0014	0.0128	0.1230	0.0000	0.0590	0.7611
	<i>V. amygdalina</i>	0.0098	0.0350	0.0035	0.0090	0.1470	0.0015	0.0490	0.6648
Ubu River	<i>C. xanthosama</i>	0.0570	0.0320	0.0034	0.1240	0.2220	0.0013	0.1270	1.0467
	<i>M. esculenta</i>	0.0690	0.0270	0.0050	0.1400	0.0880	0.0085	0.0800	0.8745
	<i>C. acutangulus</i>	0.0180	0.0610	0.0040	0.0166	0.1040	0.0016	0.0360	0.5312
	<i>V. amygdalina</i>	0.0123	0.0338	0.0029	0.0240	0.1200	0.0031	0.0180	0.6241
Average		.0227	0.0330	0.0045	0.0719	0.1370	0.0070	0.0635	-----
Ebenator River	<i>C. xanthosama</i>	0.0036	0.0230	0.0024	0.0024	0.1220	0.0000	0.0228	0.4042
	<i>M. esculenta</i>	0.0024	0.0280	0.0043	0.0150	0.1060	0.0000	0.0360	0.3633
	<i>C. acutangulus</i>	0.0000	0.0025	0.0004	0.0011	0.0221	0.0000	0.0054	0.1605
	<i>V. amygdalina</i>	0.0008	0.0098	0.0002	0.0059	0.0520	0.0004	0.0078	0.3469
Average		0.0017	0.0158	0.0018	0.0061	0.0755	0.0001	0.0180	
Recommended daily intake DL(mg/day/person)		0.0000	0.014	0.000	-	8.00	0.50	0.90	
Upper Tolerable daily intake UL(mg/day/person)		0.2400	11.00	0.064	-	40.00	1.00	10.00	

*Recommended daily intake (DI) and Upper tolerable daily intake(UL) levels of heavy metals in foodstuffs (FDA, 2001, Garcia-Rico et al., 2007)

Table 8 THQ and HI of Leafy Vegetables/Tubers in Exposed Population

Location Limit	Samples	THQ							HI
		Pb	Mn	Cd	Cr	Zn	Ni	Cu	
Eze river	<i>C. xanthosama</i>	0.0003	0.0004	0.0148	0.0250	0.0003	0.0012	0.0005	0.0430
	<i>M. esculenta</i>	0.0100	0.0016	0.0084	0.0360	0.0002	0.0000	0.0014	0.0580
	<i>C. acutangulus</i>	0.0083	0.0012	0.0092	0.0090	0.0004	0.0000	0.0006	0.0292
	<i>V. amygdalina</i>	0.0001	0.0025	0.0120	0.0086	0.0004	0.0008	0.0007	0.0253
Ele river	<i>C. xanthosama</i>	0.0140	0.0011	0.0086	0.0220	0.0005	0.0007	0.0009	0.0487
	<i>M. esculenta</i>	0.0310	0.0005	0.0056	0.0210	0.0003	0.0011	0.0005	0.0610
	<i>C. acutangulus</i>	0.0070	0.0012	0.0076	0.0026	0.0004	0.0005	0.0008	0.0208
	<i>V. amygdalina</i>	0.0120	0.0008	0.0070	0.0070	0.0004	0.0003	0.0006	0.0281
Fada river	<i>C. xanthosama</i>	0.0310	0.0014	0.0200	0.0240	0.0005	0.0009	0.0009	0.0793
	<i>M. esculenta</i>	0.0100	0.0020	0.0090	0.0190	0.0011	0.0001	0.0015	0.0422
	<i>C. acutangulus</i>	0.0149	0.0011	0.0028	0.0043	0.0004	0.0000	0.0014	0.0256
	<i>V. amygdalina</i>	0.0070	0.0014	0.0070	0.0030	0.0005	0.0001	0.0013	0.0209
Ubu river	<i>C. xanthosama</i>	0.0407	0.0013	0.0068	0.0410	0.0007	0.0001	0.0031	0.0944
	<i>M. esculenta</i>	0.0490	0.0011	0.0100	0.0460	0.0003	0.0004	0.0020	0.1100
	<i>C. acutangulus</i>	0.0120	0.0025	0.0080	0.0053	0.0003	0.0001	0.0090	0.0376
	<i>V. amygdalina</i>	0.0087	0.0016	0.0040	0.0080	0.0004	0.0002	0.0005	0.0240
Average		0.0160	0.0014	0.0088	0.0158	0.0007	0.0004	0.0017	0.0064
Ebenato river	<i>C. xanthosama</i>	0.0000	0.0001	0.0040	0.0008	0.0000	0.0000	0.0006	0.0058
	<i>M. esculenta</i>	0.0017	0.0011	0.0086	0.0050	0.0004	0.0000	0.0009	0.0179
	<i>C. acutangulus</i>	0.0003	0.0003	0.0008	0.0004	0.0001	0.0000	0.0001	0.0018
	<i>V. amygdalina</i>	0.0006	0.0004	0.0005	0.0019	0.0002	0.0000	0.0002	0.0042
Average		0.0007	0.0005	0.0035	0.0020	0.0002	0.0000	0.0005	0.0010

With respect to locations, the trend for the mean concentrations of all heavy metals under study followed in this trend Ubu>Fada>Eze>Ele>Ebenato(Table 3). The uptake of metals by crops showed varying result whereby Pb and Cr accumulated more in tubers whereas, Mn, Cd, Zn, Ni, and Cu accumulated more in leaves (Table 4).

Lead concentration was similar in all the crops with high variations in different food crops sampled across different locations. Cadmium was highest in *V.amygdalina* (Table 2). The concentrations of Cu were

higher in *C.acutangulus*, as well as *V.amygdalina*, than in all the other tubers. Zinc and Manganese concentration were highest in *V.amygdalina*, as well as *C.acutangulus*, than recorded in tubers. Chromium accumulated more metals in *M.esculenta* and *C.xanthosamawhile* nickel concentration was similar in all the crops (Table 2).

A large number of industries located in the area include battery plants such as lead-acid battery leading to the release of Pb as well as from the area close to a clustered mechanical and automobile fitting workshop, where automobile repair and related activities (disposal of used batteries and Pb based agricultural insecticides) are carried out.

Various authors have identified sources of lead to industrial effluents (Orisakwe et al., 2004a), paint flakes (Nduka et al., 2008), refuse dumps (Nduka et al., 2006) and electronic wastes (Schmidt, 2006). Most of these wastes are washed into the rivers whereby the plants become contaminated and be consumed by man. This is similar to the results obtained by (Hart et al., 2005), where the lead accumulation in crops harvested in some oil prospecting locations in Rivers state was found to be 1.1-9.1µg/g. However, it has been reported that in industrial areas, up to 0.2-0.4mg lead may be ingested in the food daily, with 90% of this excreted in the feces (Davidson et al., 1979). Thus the higher trends for lead obtained in crops from the highly industrialized locations could be potentially harmful since these common vegetables are frequently consumed in large quantities by the local people (Hart et al., 2005).

In this study, the mean concentration of Pb was quite generally higher than the permissible level of 0.3µg/g by (FAO/WHO, 1989) in food crops. Lead is causing concern in particular due to the possible impacts on children. Lead influences the nervous system, slowing down nervous response. This influences abilities and behavior (Adesuyi, 2015).

Discharge of industrial waste from various industries such as petro-chemicals and metal fabrication [34] release elements such as, Zn, Mn, Cd and Cr as well as from agricultural chemicals for food production. These elements are released into water bodies through runoff or leaching facilitated by agricultural activities (Ngozi & Onyekachi, 2017; Avila et al., 2014).

Hart et al., (2005) also recorded least mean concentration level in *C. xanthosama* in their analysis of food crops within oil prospecting locations in Rivers State. The concentration of zinc was highest in vegetables. This is suggestive of the view that vegetables can serve as rich source of Zn in the diet of the populace (Hart et al., 2005). Hart et al., 2005; Uchechi et al., 2018 recorded the highest concentration of zinc in pumpkin leaves and water leaves respectively in their analysis of food crops within oil prospecting locations in Rivers State and quarry sites in Isiagwu, Ebonyi State. These results are not consistent with literature report by (Boon & Soltanpour, 1992), that leafy tissue concentrations of lead, cadmium and zinc sampled from garden vegetables grown in an old silver mine dump were highest. Zinc was quite abundant in all the sampled vegetable species but the mean value did not exceed the Chinese Department of Protective Medicines safe limit in vegetable of 20µg/g (Asdeo & Loonker, 2011). Zinc is an essential element in human diet and it is required to maintain the functioning of the immune system. It is also a natural constituent of soils in terrestrial ecosystem and it is taken up actively by roots (Adesuyi, 2015).

The values of manganese concentrations recorded in this study were lower than the value of 40.62µg/g in cassava tuber from crude oil impacted soil in Ikot Abasi LGA, Akwa Ibom State (Osu et al., 2015). The mean value of manganese was highest in *V.amygdalina* (7.71µg/g) and this could be attributed to waste water irrigation, air deposition, spillage as a major pathway to heavy metals bioaccumulation in vegetables and plants (Adesuyi, 2015; Oluwole et al., 2013). Typically, manganese toxicity may impair central nervous system and cause progressive disorder of the extra pyramidal system (Moremi et al., 2016).

The most common sources of cadmium in plants and vegetables are sewage sludge application, deposition from fossil fuel combustion, phosphate fertilizers and so on (Adesuyi, 2015). Over a long period of continuous intake, cadmium may accumulate in the kidney and liver and because of long half-life may lead to

kidney damage (Rose et al., 2005). The cadmium levels in all the tubers sampled across the four rivers were higher than the safe limits for food consumption. In this study, the mean concentration of cadmium was quite generally higher than the permissible level of $0.61\mu\text{g/g}$ by (FAO/WHO 1989). in food crops. Okereke et al., 2016 recorded varying ranges of $0.00\text{-}0.46\mu\text{g/g}$ in some selected tubers grown in farmlands in Rivers State.

The highest cadmium concentration of $1.25\mu\text{g/g}$ seen in *V. amygdalina* and the mean cadmium level ($0.610\mu\text{g/g}$) in the plant samples across all rivers (Table 3) were not within safe limits of consumption according to FAO/WHO (1989) with the exception of plants from the control site Ebenato. Moreover, the cadmium levels obtained from this study are much higher than the range of $0.010\text{-}0.23\mu\text{g/g}$ reported by (Patrick-Iwuanyanwu & Nwokeji, 2018) in vegetables grown within the vicinity of Warri Refining and Petrochemical Company, Delta State.

The most common sources of cadmium in plants and vegetables are sewage application, deposition from fossil fuel combustion, phosphate fertilization (Adesuyi, 2015). Cadmium toxicity induces tissue injury through creating oxidative stress, epigenetic changes in DNA expression, inhibition or up regulation of transport pathways particularly in the proximal segment of the kidney tubule (Dufresne & Farnsworth, 2001). Okereke et al., 2016 also recorded the highest level of chromium ($1.26\pm 0.05\mu\text{g/g}$) in *D. rotundata* collected from the Alkahia site. The range values of $10.16\text{-}177.41\mu\text{g/g}$ recorded by (Uchechi et al., 2018) in commonly consumed food crops from quarry sites located at Isiagwu, Ebonyi State was much higher than the range values from this study.

The lowest lead concentration of $1.62\mu\text{g/g}$ was obtained in *C. acutangulus* (Table 2). (Patrick-Iwuanyanwu & Nwokeji, 2018) recorded chromium concentrations which ranged from $0.383\text{-}2.331\text{mg/kg}$ in the analyzed leafy vegetables in the vicinity of Warri Refining and Petrochemical Company, Delta State. Chromium toxicity has been attributed to its highly oxidative properties while cadmium toxicity induces tissue injury through creating oxidative stress, epigenetic changes in DNA expression, inhibition or up regulation of transport pathways particularly in the proximal segment of the kidney tubule (Dufresne & Farnsworth, 2001). Nickel is essential for growth and reproduction in livestock and man, but could be carcinogenic in high amount in the body. In this study, Ni content in vegetables was found to be lower than the estimated maximum guideline set by USFDA of $70\text{-}80\mu\text{g/g}$ (Iwegbue, 2010).

The values of copper concentrations recorded in this study were higher than the range value of $0.03\text{-}0.93\text{mg/kg}$ in root tuber grown in farmlands, River State [6]. The mean value of copper was highest in *C. acutangulus* and this could be as a result of burnt vehicles along the major roads where these food crops were harvested as copper is commonly found in electrical wirings, engine wear, brake linings disposed on the soils (Manno et al., 2006). (Adedokun et al., 2016) recorded copper levels in vegetables from markets ranged between 2.338mg/kg in *T. occidentalis* from Mile 12 and 14.075mg/kg in *T. triangulare* from Ijesha market. Copper is essential to human life as metalloproteins and functions as enzymes. However, critical doses lead to health risks such as anaemia, diabetes, inflammation, kidney and liver dysfunction and vitamin C deficiency (Lokeshappa et al., 2012). (FAO/WHO, 2005) suggested safe limits of 40mg/kg in adults which was significantly higher than the maximum copper levels of vegetables in this study. Although toxicity of copper is rare, its metabolism is enhanced by molybdenum and zinc constituents in the body (Oladele & Fadare, 2015).

4. Conclusion

The present study carried out on food crops from Nnewi-north showed that the plant samples collected from the vicinity of the four rivers contained the seven heavy metals analyzed and the mean values were higher in concentration of the study area than the control samples. This indicates that the cumulative effects in plant tissue over time could be hazardous to human and animal health. The food crops harvested from the industrial city were susceptible to environmental pollution due to activities and processes going on or practiced in the area. The occurrence of heavy metals (Pb and Cr) was higher in roots whereas Mn, Cd, Zn, Ni,

and Cu accumulated more in leaves. These vegetables and food crops are important sources of energy and vital nutrients in human diet. As the area grows industrially, there is need to constantly monitor the activities in the area by the regulatory agencies to prevent an outbreak of diseases in the nearest future.

The values for THQ and HI were less than 1 in all the food crops signifying that their consumption does not pose any health risk. However, the use of chemical fertilizers and pesticides should be greatly monitored and organic agriculture with little use of agrochemicals could be an alternative way of reducing the accumulation of toxic heavy metals especially Pb and Cd which was found to be higher in values according to world standards.

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Declaration of Conflict

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