

## Speciation of Metals and Risk Assessment in Selected Food Crop Samples Grown in Ohaji/Egbema LGA, Imo State, Nigeria

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### Abstract

Ohaji Egbema is known for its oil production and exploration activities and so crops grown in this area could be contaminated. Chemical speciation was carried out on four commonly grown food crops in the area so as to determine the level of metal contamination. The samples were analyzed sequentially and the metal species in the extract determined by ASS. Results revealed that mean concentrations of all studied metals to fall within the WHO/FAO permissible limits. Significant bioavailability was observed for Pb in Okoro (0.67) and Orange (0.7). Zn showed the highest concentration and its bioavailability was highest for Okoro (12.6)>Pawpaw (7.9)>Orange (5.5)>Cassava (0.28). The sum of EDI for both adult and children exhibited similar trend with Cassava having the least value in both adult and children. Though metals showed low values of EDI, excessive consumption can have adverse effect in humans due to bioaccumulation in living system. Hazard Quotient (HQ) was highest for Pb (3.524) in Pawpaw for children while Fe (0.705) was highest in Pawpaw for adult. Generally, HQ was found to be highest in children for all the metals indicating great health risk for children. Risk associated with consuming these four fruit crops in terms of summation of RAC revealed the order of decrease to be: Okoro (1620)>Pawpaw (1021)>Orange (861)>Cassava (178). This study has shown that the consumption of these fruit crops could be a great health risk for children.

**Keywords:** Fruit crop; Metal speciation; Bioavailability; Estimated dietary intake; Hazard quotient

### Introduction

Ohaji Egbema is known for its oil production and exploration activities and so crops grown in this area could be contaminated. Crops grown on soil will reflect the soil health in their products and so soil is a vital tool aspect of agricultural activity [1,2].

The top soil on which crops grow is made up of heterogeneous material such as decomposing plants and animals, inorganics, clay and silt particles solutions and mixture of gaseous substances [3]. Soil is exposed to atmospheric depositions from various human activities and natural sources, such as eruption, erosion and runoff from rains. This has earned soil the general name sinks and source of pollutants by some researchers [4].

According to Ure [5], the term chemical speciation is the art of identifying and quantifying the species and or phases of a substance be it an element or compound. Researchers have shown that immense and relevant information that could improve analytical methods, in health sciences, food, agriculture and environmental issues can be generated from speciation studies [6].

More recent researchers have defined speciation as the quantity or descriptions of various forms of substances which finally sum up as the amount of the substance in a matrix.

Barra [7] considered speciation as the surest method of assessing toxicity of a substance because not all forms of a substance in a media are available for absorption or uptake. However, little information

exists on chemical speciation of food substances and food crops sample [8].

Various extraction procedures exist including single and multiple extraction protocol being applied on every segment of the environment. Data from such analysis are used to compute mobility and bioavailability of metals [9-14].

Amongst the various factors that affect availability of mineral, the plants specie or form of metal is paramount and so speciation analysis is important in understanding mineral up and micro nutrients in crops.

Heavy metals in soil exist in several different forms and are associated with range of other components [15]. The accumulation of metals in soil, particularly Pb, Cd, Cu, Ni, Cr and Zn is of concern [16-19]. Heavy metals emanating from anthropogenic sources are more dangerous because of their instability and solubility leading to high bioavailability [20]. The various forms have been known to affect uptake and hence bioavailability to crops [21,22].

Plants absorb mineral elements from soil and accumulate same in tissues of roots, and shoots at various levels of concentrations. Irrigation through contaminated water is one source of metal contamination of crops and fruits around the world. Reports exist on the various severe heavy metals contamination of agricultural products [23-27].

Other sources of contamination of plants by heavy metals include; rain in atmospherically polluted areas, high traffic density, fossil fuels uses, dusts, fertilizers which could be adsorbed through leaf blades.

Agricultural activities are major source of income for the community people of Ohaji/Egbema. Since the dawn of oil exploration in the area, land degradation by oil spills have cause decreasing agricultural products thereby making agricultural activities less attractive. Heavy metals abound in crude oil have been reported to be a source of concern as contaminants to crops. Little information is known about the level of contamination. Equally the risks of consumption of crops grown in this area have not been investigated. Hence the focus of this research was to assess metal contamination of food crops and hazard quotient of selected food crops. Such as information generated could be useful for policy makers in environmentalist and health issues.

Selected fruits belong to the favourite list for both children and adults and therefore attract great concern that toxic levels of heavy metal in these fruits could attained as a result of crude oil pollution which is rampant in the area. This study draws heavily on this fact to investigate concentrations of Pb, Fe, Cu, Zn and Cr in Orange, Cassava, Pawpaw and Okoro fruit at same time assessing the potential risk to consumers of fruit crops grown in the area.

## Materials and Methods

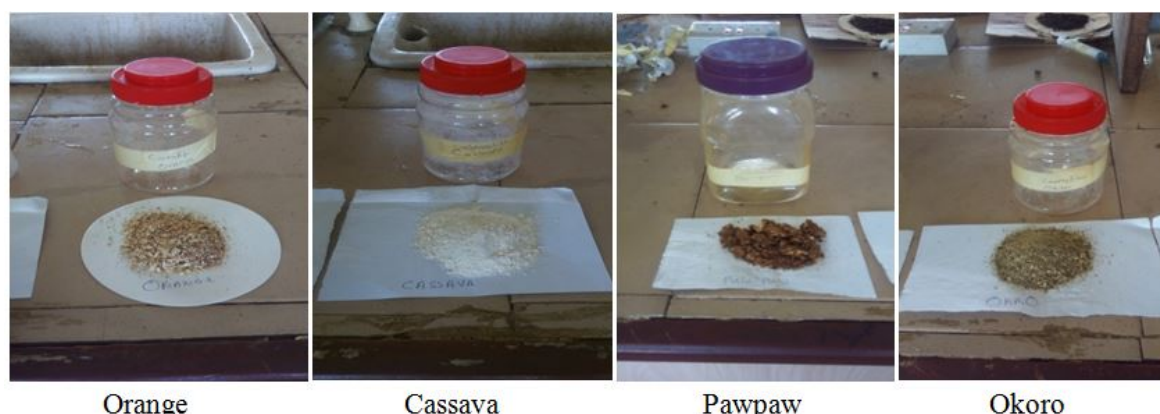
### Study area

This study was carried out at Ohaji/Egbema local government area, Imo State, Nigeria. Geographically, it lies within latitude 5°24'8.53" N

and longitude 6°49'28.24" E. Ohaji/Egbema shares boundary to the east with Owerri, to the North with Oguta, to the South East with Ndori River state. Many companies and organizations are located in Ohaji/Egbema due to out exploration. Shell petroleum, Chevron, Agip and numerous oil servicing compound are found amongst government and non-governmental agencies farming, especially fish farming and fishing are major occupations. The area has an area of 800 km<sup>2</sup> and over 182.538 million inhabitants. The area equally has Ada Palm Ltd, rubber Estate and forest reserves which all contributes to its touristic qualities.

### Sample collection and preparation

Four fruit samples which include Orange (*Citrus sinensis*), Cassava (*Manihot esculenta*), Okoro (*Abelmoschus esculentus*) and Pawpaw (*Carica papaya*) were collected from Ohaji/Egbema local government area with emphasis that they were grown in the area (Figure 1). The choice of fruit species was based on their availability at the study area. Fruit samples were gently washed under running tap water to remove adhered soil particles and then rinsed with distilled water. The samples were air dried to remove the residual moisture and then oven dried for 48 h at 80°C. Each sample was dried and after grinding with mortar and pestle were sieved and the fine texture obtain was stored in an air tight container awaiting analysis.



**Figure 1:** Dried samples of the selected food crops used for this study.

### Metal speciation analysis

Two grams of each powdered fruit sample was weight out and transferred in a 50 ml tube of polypropylene for centrifuge and extraction was done according to the processes:

**Water-soluble fraction (F1):** Two grams of the meshed fruit sample was extracted with 20 ml of deionised water for 2 hours.

**Exchangeable fraction (F2):** Into the residue of F1, 20 ml of 1 mol L<sup>-1</sup> MgCl<sub>2</sub> was added and pH adjusted to 7 ad mixture allowed for an hour.

**Carbonate-bound fraction (F3):** 20 ml 1 mol L<sup>-1</sup> NH<sub>4</sub>OAc at pH 5 was added into F2 residue and was extracted for five hours.

**Fe-Mn oxide-bound fraction (F4):** Residue from F3 was extracted with 20 ml 0.04 mol L<sup>-1</sup> NH<sub>2</sub>OH.HCl in 25% (v/v) HOAc at 90°C and agitated intermittently.

**Organic-bound fraction (F5):** 15 ml 30% H<sub>2</sub>O<sub>2</sub> was added to F4 residue and at pH adjusted to 2 using nitric acid and allowed for five and half hours at 85°C water bath. After cooling, 5 ml of 3.2 mol L<sup>-1</sup> NH<sub>4</sub>OAc in 20% HNO<sub>3</sub> was added and shaken for 30 minutes before final dilution to 20 ml with deionised water.

**Residual fraction (F6):** Residue from F5 was digested using a HF-HCl/HNO<sub>3</sub> (hydrofluoric/aqua regia) digestion procedure and allowed to stand for 30 minutes.

All the solid phases from F1 to F6 were washed with 10 ml of deionised water before further extraction. The washes were collected with supernatant from the previous fraction. After each extraction, the

supernatant was separated by centrifugation at 10,000 rpm for 30 minutes.

### Data analysis

Using SPSS version 18.0 the means, standard deviations and level of significance were analyzed and results were reported as means  $\pm$  standard deviation of triplicate analysis. P- Values were calculated using paired T-Test and at  $P < 0.05$  were regarded as being significant. Coefficient of variability (CV) was calculated as in equation (1). Values were ranked according to [28] where little variation ( $CV \% < 20$ ), moderate variation ( $CV \% 20-50$ ) and high variation ( $CV \% > 50$ ) were categories used in the present research.

$$CV = \frac{SDV}{\bar{X}_i} \times 100 \quad (1)$$

Sum of fractions for each metal was  $\sum F(x)$  were obtained and used as metal concentration in chemometric methods. Chemometric methods used were estimated daily intake (EDI) and Hazard quotient (HQ) for all samples.

**Estimated Daily Intake (EDI):** This is calculated using the expression 2 in which metal contamination and amount consumed on a daily basis are involved. Body weight can influence on the tolerance of contaminant. EDI is a concept that takes account of these many factors in estimating daily consumption of food [29].

$$EDI = (C \times \text{Cons}) / BW \quad (2)$$

Where, C- concentration of heavy metals; Cons- mean amount of food item consumed daily; BW- body weight.

Experts have recommended a daily intake of at least 400 g of fruit and vegetables [30]. Adult BW was set to 60 kg in this study [31]. In the case of children, the mass was taken as 12 kg.

**Hazard Quotient (HQ):** Hazard Quotient estimates the extent to which an adverse effect is observed or expected as a result of the presence of a contaminant. It is calculated as in equation 3,

$$HQ = (Dif \times C_{\text{metal}}) / (RfD \times BW) \quad (3)$$

Where, Dif- daily intake of fruit ( $\text{kg day}^{-1}$ );  $C_{\text{metal}}$ - metal concentration in each sample ( $\text{mg kg}^{-1}$ ); RfD- metal reference dose considering oral intake only ( $\text{mg kg}^{-1} / \text{BW day}^{-1}$ ); BW- human body mass (kg).

RfD is used in EPA's non-cancer health assessments. RfD for Cr ( $1.5 \text{ mg kg}^{-1} \text{ day}^{-1}$ ) [32], for Pb ( $0.0035 \text{ mg kg}^{-1} \text{ day}^{-1}$ ) [33]. RfD for (Cu=0.04, Zn=0.3  $\mu\text{g g}^{-1} \text{ day}^{-1}$ ) [34], Fe is taken as  $0.17 \text{ mg kg}^{-1} \text{ day}^{-1}$ .

### Results and Discussion

Crop	Metal	F1	F2	F3	F4	F5	F6	$\sum F(x)$	Mean	SDV	CV
Cassava	Cu	0.11	0.32	0.21	0.2	0.23	0.22	1.29	0.22	0.07	31.8
	Cr	ND	ND	ND	ND	ND	ND	ND	ND	ND	0
	Zn	ND	0.13	0.15	0.2	0.15	ND	0.63	0.16	0.03	18.75
	Fe	0.05	0.2	0.34	ND	0.03	0.5	1.12	0.22	0.2	8.6
	Pb	0.05	0.2	0.03	0.15	0.42	0.26	1.11	0.19	0.15	78.9
Orange	Cu	0.35	0.28	0.15	0.18	0.23	0.47	1.66	0.23	0.12	52
	Cr	0.7	ND	ND	1	0.5	0.23	2.43	0.61	0.33	54
	Zn	5.5	ND	ND	4.3	2.5	1.5	6.8	3.4	1.27	37
	Fe	0.05	0.23	0.68	0.15	0.25	0.45	1.66	0.33	0.24	72.7
	Pb	0.15	0.29	0.23	0.3	0.25	0.2	1.42	0.24	0.06	25
Okoro	Cu	0.05	0.23	0.35	0.17	0.9	1	2.7	0.45	0.4	88.9
	Cr	0.65	0.72	0.89	0.95	0.15	1.02	2.77	0.69	0.4	57.9
	Zn	11.5	12.6	13.40	5.9	7.5	11.2	37.2	6.7	1.13	16.8
	Fe	0.65	0.52	0.45	0.35	0.15	0.24	2.01	0.4	0.21	52.5
	Pb	0.15	0.5	0.05	0.02	0.01	0.02	0.75	0.13	0.19	146.2
Pawpaw	Cu	ND	0.3	0.45	0.68	ND	0.79	2.22	0.56	0.22	39.3
	Cr	0.8	0.15	0.06	0.18	0.78	0.63	2.54	0.6	0.29	48.3
	Zn	ND	1.4	6.5	ND	7.8	9.7	15.7	2.6	4.5	173.1
	Fe	0.05	0.01	0.34	0.56	0.78	0.65	2.39	0.37	0.35	94.6

	Pb	ND	0.01	0.2	0.05	0.03	0.06	0.35	0.07	0.08	114.2
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**Table 1:** Heavy metal fractions (mg/kg) in the food crops.

Table 1 shows the concentration of Cu, Cr, Zn, Fe and Pb in Cassava, Orange, Okoro and Pawpaw for their fruits in mg/kg. Lead levels in all samples were below the FAO permissible limits of 0.3 mg/kg but the bioavailable lead for each fruit was above this limit only for Okoro (0.7 mg/kg) and Orange (0.67 mg/kg). Divrikli attributed serious body poisoning by Pb due to consumption of unwashed fruits, water and inhalation of air [35]. Pb has been known to be toxic to red blood cell, damages kidney, distort normal functioning nerves and respiration in humans when compared with WHO/FAO results obtained for all fruits compared well [36]. The mean concentrations (mg/kg) of metal species are shown in Table 1. Results of speciation analysis revealed highest value of mean concentration of metal species to be Zn (6.70 mg/kg) in Okoro while same Zn (0.03 mg/kg) metal had lowest value of mean concentration species overall in Cassava from Ohaji Egbema in Imo State. Cassava showed not detected for all species of Cr. It was believed that Cr species were below detection limit rather than total absence of the metal since researchers [2,37] had earlier detected Cr in the study area. The order of decreasing species concentrations in the studied fruit crops were as follows:

Cassava: Cu>Fe>Pb>Zn, Orange: Zn>Cr>Fe>Pb>Cu, Orange: Zn>Cr>Cu>Fe>Pb and Pawpaw: Zn>Cr>Cu>Fe>Pb.

The Coefficient of Variability (CV) of mean concentration metal species of each fruit crop was and Cassava showed a range of 00% for Cr to 78.9% in Pb, Okoro showed highest variability range of 16.8% in Zn to 146.2% for Pb. Over all highest variability was observed in Pawpaw (Cr: 39.3% to Zn: 173.1%). These trends revealed a striking resemblance in metal species of Okoro and Pawpaw despite the fact that Pawpaw had lower of species concentrations than Okoro.

### Bioavailability of metals

0.64 mg/kg of Cu was found to be bioavailable for human consumption. Mean species concentration of copper for all fruits crops

ranged from 0.215-0.555 mg/kg. The available copper for human consumption in the Cassava sample was found to be slightly above the WHO/FAO permissible limit for food. Besides other important functions, Cu fine use as co-factor of many enzymes, maintenance of healthy nervous system, protect against anemia and influence the proper functioning of Zn and Fe in metabolism [38]. However, research has shown deleterious effects due to high amounts of Cu in the body to the extent that kidney and liver damages are traceable to elevated copper concentrations.

The mean concentration of Zn in the tested sample ranges from 0.158-6.7 mg/kg, with Okoro having the highest concentration of Zn. Bioavailable Zn in the tested sample ranges from 0.28-12.6 mg/kg with Okoro having the highest bioavailable fraction of Zn in the four fruit samples tested. However, it is observed that the level of bioavailable Zn in all the samples was below the permissible limit of 99.4 mg/kg [39] of Zn for food by the WHO/FAO and this is not acceptable as this is an indication of Zn deficiency. Zn is an important element for both plants and animals. It plays an important role in several metabolic processes, it activates enzymes and it is involved in protein synthesis and in carbohydrates, nucleic acid and lipid metabolism [25]. Its deficiency may be due to inadequate dietary intake, impaired absorption, excessive excretion or inherited defects in zinc metabolism [40]. However, high concentration of Zn can result to damage of the pancreas, disruption of protein metabolism and arteriosclerosis [24].

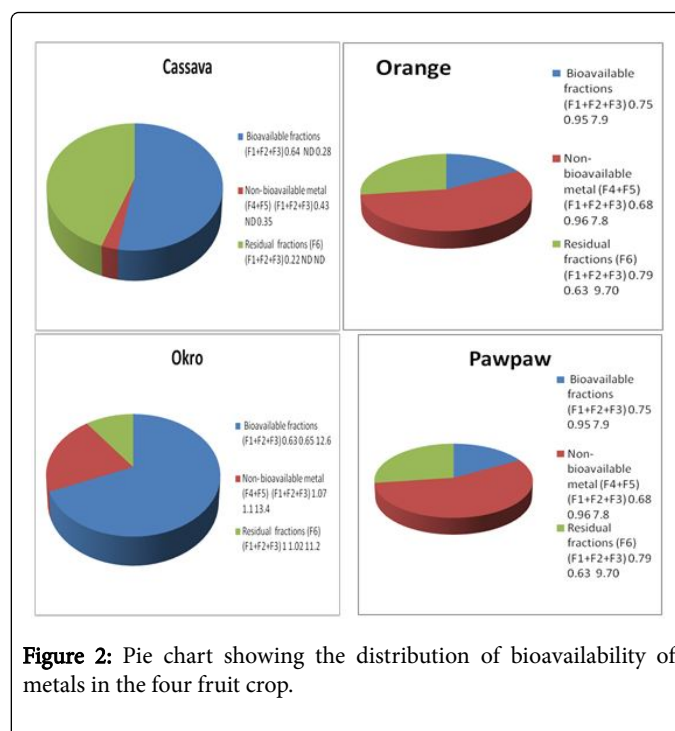
From the result, the levels of Fe were found to be the lowest in all tested samples ranging from 0.2 mg/kg to 0.4 mg/kg. The levels of Fe in fruits samples were found to be within the WHO permissible limits. The lowest concentration of Fe was observed in Cassava. Fe is an important mineral found in animals and humans. Most of the Fe found in the body is located in red blood cells as part of the hemoglobin. Fe in excessive doses can lead to iron poisoning or toxicity.

Crop	Metal	Bioavailable fractions $\sum (F1+F2+F3)$	Non- bioavailable metal $\sum (F4+F5)$	Residual fractions (F6)	RAC (%)	Significance
Cassava	Cu	0.64	0.43	0.22	64	Very high risk
	Cr	ND	ND	ND	0	No risk
	Zn	0.28	0.35	ND	28	Medium risk
	Fe	0.59	0.03	0.5	59	Very high risk
	Pb	0.28	0.57	0.26	28	Medium risk
Orange	Cu	0.78	0.41	0.47	78	Very high risk
	Cr	0.7	1.5	0.23	70	Very high risk
	Zn	5.5	6.8	1.50	550	Very high risk
	Fe	0.96	0.4	0.45	96	Very high risk
	Pb	0.67	0.55	0.2	67	Very high risk

Okoro	Cu	0.63	1.07	1	63	Very high risk
	Cr	0.65	1.1	1.02	65	Very high risk
	Zn	12.6	13.4	11.2	1260	Very high risk
	Fe	1.62	0.5	0.24	162	Very high risk
	Pb	0.7	0.03	0.02	70	Very high risk
Pawpaw	Cu	0.75	0.68	0.79	75	Very high risk
	Cr	0.95	0.96	0.63	95	Very high risk
	Zn	7.9	7.8	9.70	790	Very high risk
	Fe	0.4	1.34	0.65	40	High risk
	Pb	0.21	0.08	0.06	21	Medium risk

**Table 2:** Distribution of bioavailability and RAC of metals in the four fruit crop.

Table 2 shows concentrations of bioavailable Pb in the fruits. The mean concentration of Pb in the fruit samples ranges from 0.07 mg/kg to 0.24 mg/kg. It was observed that the level of Pb recorded in the sample were below the permissible limit of 0.3 mg/kg. Bioavailable Pb in the fruit samples ranges from 0.21 mg/kg to 0.7 mg/kg. This level of Pb available for plant and human consumption was found to be highest in Okoro (0.7 mg/kg) and Orange (0.67 mg/kg). This high level of Pb could also be attributed to air-borne contamination from leaded fuels of vehicles and other anthropogenic activities. Pb being a serious cumulative body poison enters into the body system through air, water and food and cannot be removed by washing the fruits [35]. It has also been found to be toxic to the red blood cell, kidney, nervous and respiratory system [36]. Adequate chromium concentration in diets is known to maintain sensitivity against insulin while Cr deficiency could lead to diabetes and other metabolic syndromes. Mild deficiencies have been reported to initiate blood sugar metabolic dysfunctions, contributing to fatigue and anxiety. Chromium is equally toxic at high concentrations, however the consumption of all four fruits are normal quantities cannot produce high Cr in the body.



**Figure 2:** Pie chart showing the distribution of bioavailability of metals in the four fruit crop.

Figure 2 above shows the bioavailability of metals in the four fruit crop samples studied. Zn is the most bioavailable in Okoro, followed by Pawpaw>Orange>Cassava). Zinc is highly regarded as an essential mineral element due to its involvement in over 300 metabolic reactions, in the synthesis of DNA, and its role in cell division, co-factors in metabolism of protein, fats and carbohydrates and normal maintenance of serum testosterone. When in high concentration Zn can spring up strong negative affects due to the fact that ability to suppress absorption of Cu and Fe. On the other hand, Zn deficiency could lead to loss of weight, appetite, hair, retarded bones and low blood pressure [41].



Estimated dietary intake of metals from Crop sample								
Metal	Cassava		Orange		Okoro		Pawpaw	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children
<b>Cu</b>	0.0015	0.0073	0.0015	0.0077	0.003	0.015	0.0037	0.0187
<b>Cr</b>	ND	ND	0.0041	0.02	0.0046	0.023	0.004	0.02
<b>Zn</b>	0.0017	0.0053	0.0227	0.1133	0.0447	0.223	0.0173	0.087
<b>Fe</b>	0.0015	0.0073	0.0022	0.011	0.0027	0.0133	0.0025	0.0123
<b>Pb</b>	0.0013	0.0063	0.0016	0.008	0.0009	0.0043	0.0005	0.0023
<b>ΣEDI</b>	0.0053	0.0262	0.0321	0.16	0.0559	0.279	0.0279	0.1403
<b>Max</b>	0.0017	0.0073	0.0227	0.1133	0.0447	0.223	0.0173	0.087
<b>Min</b>	0.0013	0.0053	0.0015	0.0077	0.0009	0.0043	0.0005	0.0023
Hazard quotient of metals from Crop samples								
<b>Cu</b>	0.037	0.183	0.038	0.192	0.075	0.375	0.0933	0.467
<b>Cr</b>	ND	ND	0.0027	0.0136	0.0031	0.0153	0.0027	0.0133
<b>Zn</b>	0.0036	0.0178	0.0756	0.378	0.149	0.744	0.058	0.289
<b>Fe</b>	0.0086	0.0431	0.0129	0.0647	0.0157	0.0784	0.705	3.524
<b>Pb</b>	0.362	1.8095	0.457	2.29	0.248	1.238	0.133	0.667
<b>ΣHQ</b>	0.4112	2.054	0.586	2.938	0.491	2.451	0.992	4.9603
<b>Max</b>	0.362	1.8095	0.457	2.29	0.248	1.238	0.705	3.524
<b>Min</b>	0.0036	0.0178	0.0027	0.0136	0.0031	0.0153	0.0027	0.0133

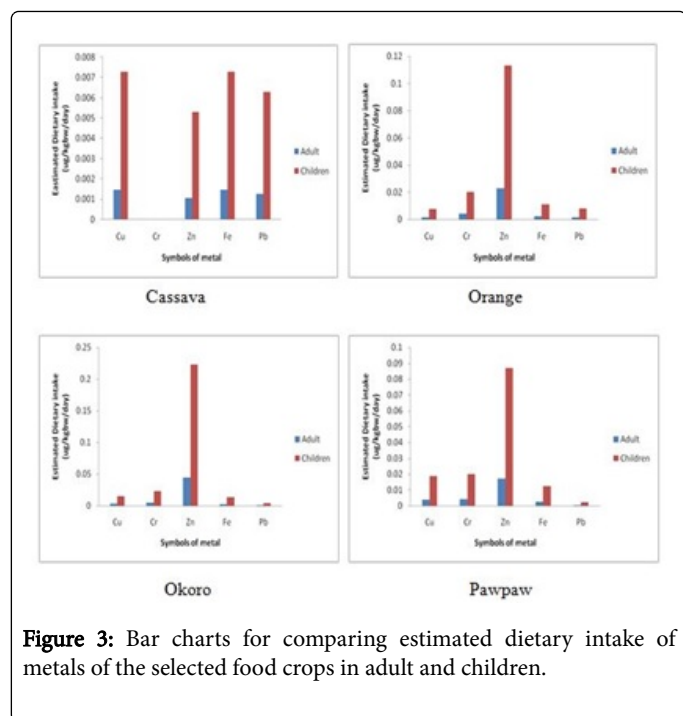
**Table 3:** Estimated dietary intake (mg/kg/BW day<sup>-1</sup>) and hazard quotient of metals from crop sample for adults and children.

The sum of the estimated dietary intake for the four fruit samples in adult followed the trend Okoro (0.0447)>Orange (0.0227)>Pawpaw (0.0173)>Cassava (0.0017) with Okoro being the highest and Cassava the lowest (Table 3). Sum of EDI for children Okoro (0.2230)>Orange (0.1133)>Pawpaw (0.0870)>Cassava (0.0073) had little slight changes but Cassava still remains the lowest in children with Orange having the highest level of EDI. Among the heavy metal toxic to living system, Pb showed the following trend in adult, Cassava>Orange>Pawpaw>Okoro with Cassava having the highest value of EDI with Okoro having the least value. The highest value of EDI was observed in Zn for children with value 0.223 mg/kg/BW day<sup>-1</sup> in Okoro. Though Zn is an essential element in both plant and animal system, in excess can pose serious health hazard when accumulated in the body. These values though low could constitute serious health hazard for consumers of fruit.

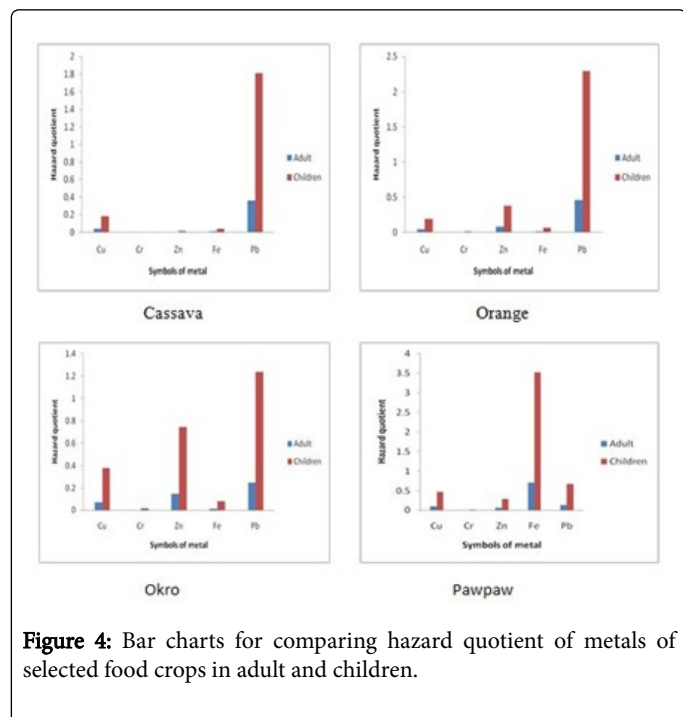
The bioavailable metals was the largest fraction is Cassava but largest in Okoro whereas Orange and Pawpaw show comparable values of bioavailable metal fraction. Amongst the three fractions the non-bioavailable metal fraction was smallest in Cassava and Okoro and had comparable values in Orange and Pawpaw.

It therefore means that consumption of much Okoro could possibly increase Zn concentration in the consumer. Okoro is seasonal and so its consumption is naturally regulated. This is not true about Pawpaw which is cultivated all year round, while Oranges equally seasonal and

have become expenses to afford by average income earners in Nigeria. The beauty in this result is that Zinc has lowest bioavailability in Cassava which constitutes the stable food of larger population in Nigeria thereby reducing possible Zn toxicity for most consumers.



**Figure 3:** Bar charts for comparing estimated dietary intake of metals of the selected food crops in adult and children.



**Figure 4:** Bar charts for comparing hazard quotient of metals of selected food crops in adult and children.

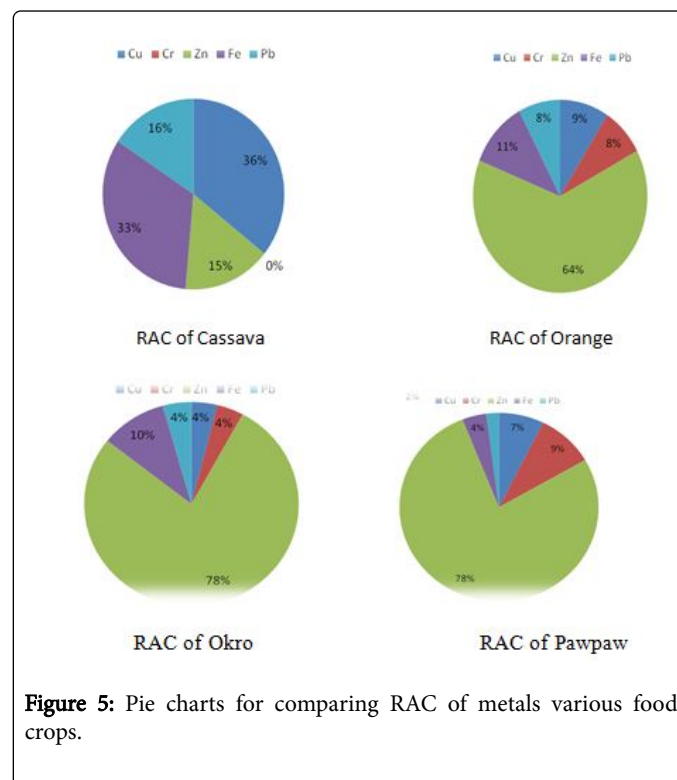
Values of HQ for all fruit samples analyzed were compared in Figures 3 and 4 for both children and adults. Considering Pb as most toxic element in the list, HQ for Pb for the four fruit sample was found to be greater than one, ( $EDI_{Pb} > 1$ ). Other metals with significant HQ include Fe in Pawpaw and Zn in Okoro both occurring in children. This is an indication of possible adverse health effect when consumed by children. The rest of the metals had HQ less than 1 and in particular, values of EDI for same metal in adult were less than 1 and so consumption of these fruit crops by adults could be considered to

have no risk. The trend of increasing EDI for Pb in the four fruit samples was as follows: (Pawpaw > Okoro > Cassava > Orange).

Generally, the HQ value for metals analyzed in the four fruit samples were found to be higher in children when compared to the values observed in adult. The trend of decreasing HQ in children was observed to be  $HQ_{Pawpaw} (4.9603) < HQ_{Orange} (2.938) < HQ_{Okoro} (2.4510) < HQ_{Cassava} (2.0540)$ . In adults decreasing values of HQ was observed to be  $HQ_{Pawpaw} (0.9920) < HQ_{Orange} (0.5860) < HQ_{Okoro} (0.4910) < HQ_{Cassava} (0.4120)$ .

### Risk assessment code

The model assumes that the most bioavailable fractions are likely to be absorbed into the body system hence cause toxicity to the consumer. Therefore summing the first three fractions and expressing them as a percent risk is the basic tenet of RAC. Five categories are employed in the interpretation of the model results In Table 2 as follows; no risk:  $RAC > 1$ , low risk:  $1 < RAC < 10$ , medium risk:  $11 < RAC < 30$ , high risk:  $30 < RAC < 50$ , very high risk:  $RAC < 50$  [28].



**Figure 5:** Pie charts for comparing RAC of metals various food crops.

Among all four food crops there was no risk of Cr only in Cassava (Figure 5). There were generally low values of RAC for Cassava compared to other fruit crops. Okoro showed highest values of RAC with Zn (1260) being the most risky metal while all metals Okoro and Orange showed very high risk. There were cases of medium risk in Pb and Fe in Pawpaw and Cassava respectively. The order of decreasing risk associated with consuming these four fruit crops in terms of summation of RAC was found to be Okoro (1620) > Pawpaw (1021) > Orange (861) > Cassava (178).

### Conclusion

Among all the four fruit samples analyzed, Pawpaw was found to have the highest HQ value in children. As expected values of HQ

obtained in the current study were higher in children compared to those for adult. However children are most at risk as confirmed with the HQ value of the present study. On the basis of RAC Okoro was adjudged the most risky fruit overall while Cassava was the lowest. The consumption of these fruits by children in the area should be highly minimized so as to prevent adverse health effect. It is therefore recommended that fruit crops from the study area be consumed majorly by adults.

## References

1. Young I, Crawford J (2004) Interactions and Self-Organization in the Soil-Microbe Complex. *Science* 304: 1634-1637.
2. Enyoh CE, Ihionu EA, Ngozi VE, Ebosie PN (2017) Physicochemical Parameter of Palm Oil and Soil from Ihube Community, Okigwe, Imo State Nigeria. *International Letters of Natural Sciences*, 62: 35-43.
3. Kabata-Pendias A, Mukherjee AB (2007) Trace Elements from Soil to Human. Springer-Verlag, Berlin.
4. Chen TB, Wong JWC, Zhou HY, Wong MH (1997) Assessment of trace metal distribution and contamination in surface soils of Hong Kong. *Environmental Pollution* 96: 61-68.
5. Ure AM (1991) Trace element speciation in soils, soil extracts and solutions. *Microchimica Acta*, Austria 104: 49-57.
6. Lima MC (2001) Speciation of copper and lead in sediment of the shark river (SC) by the Tessier method. *Química Nova*, São Paulo 24: 734-742.
7. Barra CM (2000) Especificação de arsênio - Uma revisão. *Química Nova*, São Paulo 23: 58-70.
8. Reis LS, de Andrade Gonçalves ECB (2015) Chemical speciation: An instrument for evaluation of mineral bioavailability. *Rural Santa Maria* 45: 1126-1132.
9. Gleyzes C, Tellier S, Astruc M (2002) Fractionation Studies of Trace Elements in Contaminated Soils and Sediments: A Review of Sequential Extraction Procedures. *Trends in Analytical Chemistry*, Netherlands 21: 451-467.
10. Jain CK (2004) Metal fractionation study on bed sediments of River Yamuna, India. *Water Research*, United States 38: 569-578.
11. Yao Z, Gao P (2007) Heavy metal research in lacustrine sediment: A review. *Chinese Journal of Oceanology and Limnology*, China 25: 444-454.
12. Garcia-Barrera T (2012) Biological responses related to agonistic, antagonistic and synergistic interactions of chemical species. *Analytical and Bioanalytical Chemistry*, Germany 403: 2237-2253.
13. Bacon JR, Davidson CM (2008) Is there a future for sequential chemical extraction? *Analyst*, United Kingdom 133: 25-46.
14. Rao CRM (2008) A Review of the Different Methods Applied in Environmental Geochemistry for Single and Sequential Extraction of Trace Elements in Soils and Related Materials. *Water Air & Soil Pollution*, Germany 189: 291-333.
15. Tack F, Verloo M (1995) Chemical Speciation and Fractionation in Soil and Sediment Heavy Metal Analysis: A Review. *International Journal of Environmental Analytical Chemistry* 59: 225-238.
16. McLaren RG, Clucas LM, Taylor MD, Hendry T (2003) Leaching of macronutrients and metals from undisturbed soils treated with metal-spiked sewage sludge 1. Leaching of macronutrients. *Australian Journal of Soil Research* 41: 571-588.
17. McLaughlin MJ, Smolders E (2001) Background zinc concentrations in soil affect the zinc sensitivity of soil microbial processes—a rationale for a metalloregion approach to risk assessments. *Environmental Toxicology and Chemistry* 20: 2639-2643.
18. Speir TW, Van-Schaik AP, Percival HJ, Close ME, Pang LP (2003) Heavy metals in soil, plants and groundwater following high-rate sewage sludge application to land. *Water, Air and Soil Pollution* 150: 319-358.
19. Zarcinas BA, Ishak CF, McLaughlin MJ, Cozens G (2004) Heavy metals in soils and crops in Southeast Asia: 1. Peninsular Malaysia. *Environmental Geochemistry and Health* 26: 343-357.
20. Fernandes JC, Henriques FS (1991) Biochemical, Physiological and Structural Effects of Excess Copper in Plants. *The Botanical Review* 57: 246-273.
21. Elbagermi MA, Edwards HGM, Alajtal AI (2012) Monitoring of Heavy Metal Content in Fruits and Vegetables Collected from Production and Market Sites in the Misurata Area of Libya. *International Scholarly Research Network Analytical Chemistry*, Article ID 827645, 5 pages.
22. Yang B, Shu W, Ye Z, Lan C, Wong M (2003) Growth and Metal Accumulation in Vetiver and two Sesbania Species on Lead/Zinc Mine Tailings. *Chemosphere* 52: 1593-1600.
23. Orisakwe OE, Nduka JK, Amadi CN, Dike DO, Bede O (2012) Heavy metals health risk assessment for population via consumption of food crops and fruits in Owerri, South Eastern, Nigeria. *Chem Central J* 6: 77-82.
24. Akinola MO, Adenuga AA (2008) Determination of the levels of some heavy metal in African pear (*Dacryodesedulis*) marketed in Lagos metropolis, Nigeria. *J Appl Sci Environ Manage* 1: 33-37.
25. Dhiman A, Nanda A, Ahmad S (2011) Metal Analysis in Citrus Sinensis Fruit Peel and Psidium Guajava Leaf. *Toxicol Intl* 18:163-168.
26. Philip SO, Adeniran OM, Odedairo AA, Kajihusa OE (2010) Heavy metal levels of some fruits and leafy vegetables from selected markets in Lagos, Nigeria. *African Journal of Food Sci* 4: 389-393.
27. Daili Mahmud NJ, Oniye SJ, Balarabe ML, Anta J, Caudugi AS (2012) Toxicological Implication of polluted water from Makara Drain.
28. Ngozi VE, Wirnkor VA, Louis U (2015) Seasonal Variation of Heavy Metals in Playgrounds of Public Schools within Owerri Metropolis, Imo State, Nigeria. *International Letters of Chemistry, Physics and Astronomy* 50: 61-70.
29. Yekeen TA, Toluwade TO (2012) Evaluation of some Heavy Metals in Soils along a Major Road in Ogbomoso, South West Nigeria. *Journal of Environmental and Earth Sciences* 2: 71-79.
30. Diet, nutrition and prevention of chronic diseases. Report of a joint FAO/WHO expert consultation Geneva, World Health Organization, 2003 (WHO technical report series, No.916).
31. Zazouli MA, Shokrzadeh M, Izanloo H, Fathi S (2008) Cadmium content in rice and its daily intake in Ghaemshahr region of Iran. *Afr J Biotechnol* 7: 3686-3689.
32. U.S. Environmental Protection Agency (US EPA) (2010) Integrated risk information system.
33. World Health Organization (WHO) (1993) Evaluation of Certain Food Additives and Contaminants. In: Forty-First Report of the Joint FAO/WHO Expert Committee on Food Additives, WHO, Geneva, Switzerland. (WHO Technical Series, 837).
34. USEPA (2011) USEPA Regional Screening Level (RSL) Summary Table: November 2011.
35. Divrikli U, Horzum N, Soylak M, Elci L (2006) Trace Heavy Metal Contents of Some Species and Herbal Plants from Western Anatolia, Turkey. *Int J Food Sci Technol* 41: 712-716.
36. Taupeau C, Poupon J, Nome F, Lefevre B (2001) Lead Accumulation in the mouse ovary after treatment-induced follicular atresia. *Reproductive toxicology* 15: 385-391.
37. Verla EN, HM Jnr, Orubite KO (2016) Total extractible concentration of Manganese, Cobalt, Nickel, Copper and Zinc in Soils of Children's playground within Owerri Metropolis, Imo State, Nigeria. *Research Journal of Chemical Sciences* 6: 38-47.
38. Akinyele IO, Osibanjo O (1982) Levels of trace elements in hospital diet. *Food Chem* 8:247-251.
39. World Health Organization (2010) Codex Alimentarius Commission. Food Additives and Contaminants. Joint FAO/WHO food standards programs, ALINORM 01/12A: pp. 1-289.



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40. Colak H, Soyak M, Turkoglu O (2005) Determination of trace metal content of herbal and fruit teas produced and marketed in Turkey. *Trace Elem Elec* 22: 192-195.
41. Deshpande JD, Joshi MM, Giri PA (2013) Zinc: The Trace Element of Major Importance in Human Nutrition and Health. *Int J Med Sci Public Health* 2: 1-6.