Risk Assessment of Heavy Metals in Food Crops at Abandoned Lead-Zinc Mining Site at Tse-Faga, Logo, Lga, Benue State, Nigeria

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Abstract

Hundreds of children died in 2010 due to suspected lead poisoning from mining sources in Zamfara State among epidemiological concerns. Evaluating ecological and human health risks of heavy metals levels in sampled food crops harvested near two abandoned Lead-Zinc mining sites at Logo Benue State is crucial. *Abelmoschus esculentus*, *Carica papaya*, *Manihot esculenta*, and *Zea mays* were sampled, prepared, and analyzed for four heavy metals using the Atomic Absorption Spectrophotometric method. The mean data from the analysis of variance was subjected to ecological and health risk models. Pb means value ranged from *Carica papaya* Peel 0.46 ± 0.011 mg/kg to 1.30 ± 0.01 mg/kg in *Zea mays* seed. Zn was highest in *Carica papaya* flesh 0.50 ± 0.01 mg/kg, and lowest in *Manihot esculenta* peels and its flesh 0.12 ± 0.000 mg/kg. Hg and Cd were below detectable levels. *Zea mays seeds* (1.001) had the highest Pd bioaccumulation factor. BAF of zinc and ecological indices were <1. Daily Intake of Metals were all <1, however, Hazard Quotient (HQ) of Pb was ≥1 in *Manihot esculenta* flesh 1.143 and Zea mays at 1714. Cancer Risks were within permissible range (10^{-4} - 10^{-6}). Health Risk result indicates communities around the mining area may be at risk of lead poisoning therefore due to high contamination of samples, routine checks on heavy metals especially lead is recommended to prevent excessive bioaccumulation in the body.

Keywords

Mining, Food Crops, Heavy Metals, Ecological Risk, Health Risks, Lead Poisoning

1. Introduction

The environmental consequences of the human interactions with nature through mining are highly detrimental to both human and environmental health, lead poisoning, air, and water pollution are some of the risks associated with this venture across Nigeria [1] [2].

The revenue generated from this sector, however, has saved the country massive finances, some of these monies have been used in funding many government programs ranging from infrastructural design and development, education, health care, etc. [3]. However, informal miners and companies have become very active recently in the production of solid minerals without having a clearly defined policy, standard regulatory document as well as reforms [4]. About 223 small-scale mining operations, 195 mining leases, 845 artisanal mining cooperatives were documented and 2048 exploration licenses were issued in the country [5]. The operations of the above have resulted in widespread ecological impacts at the expense of adjacent communities. So many abandoned mines across the country have become major sources of environmental hazards [6]. The levels of toxic residues from zinc and geological hazards among other issues such as the destruction of flora and fauna are threats posed by mining [7]. These challenges are massively emanating from the activities of artisanal and small-scale mining.

Mining fields in Jos, Barkin-Ladi, Bukuru, Bossa and Riyom districts have generated hazards to the people of Plateau for many years now **Figure 1**. [8] [9] all agreed that mining ponds with high levels of radiation could be the cause of mysterious deaths in areas that used high levels of monazite-rich sand for building.

History has it that, there are about 1100 to 4000 tin and columbite mines,

Figure 1. Picture of artisan mining pits in northern Nigeria. Content source: [14].

which were abandoned after the mining boom of the 1960s, these mines now pose serious health hazards to almost 2 million residents in Jos [10] [11].

The residents of these communities are exposed to a whopping 325 km^2 of contaminated lands by carcinogenic radioactive materials through indiscriminate disposal of mining wastes with brain-damaging potentials in the Jos plateau [11] and [12]. In the year 2015, there were death occurrences caused by mining in the Madaka Rafi Local government of Niger State, and also along with the Kawo village near the lower stream of the River Kaduna known for the mining of gems and gold with more devastating effects [13].

In the year 2010, over 400 children died from confirmed cases of lead poisoning from lead mining in Zamfara state northern Nigeria. Between April and May 2015, 3000 residents of in Kawo and Magiro villages have been exposed to the lead, while 28 children mysteriously died days after suffering symptoms of convulsions, insomnia and hallucinations [15]. Paul and Babatunde [16] (Table 1) reported high levels of leads in the water as a result of Lead-Zinc Mining from Yonov district in Logo Local Government area in Benue state. The need to carry out this research cannot be over-emphasized due to the devastating impact of lead poisoning on human health, which is translated to poor economies, over-stressed health delivery systems and subsequent death rates.

2. Materials and Methods

2.1. Scope of the Study

The scope of the present study was limited to the risk assessment of heavy metals (Pb, Cd, Zn, and Hg) in food crops at an abandoned lead-zinc mining site at Tse-Faga, in Logo Local Government Area of Benue State.

2.2. Study Area

Logo local government is located between latitude 7˚29" and 7˚52" north of the Equator and longitude 9˚05" and 9˚20" east of the Greenwich Meridian Figure 2. It is bonded to the East by Ukum, to the North-West by Guma, to the West by Buruku, to the south by Katsina-Ala Local Government Area of Benue State and to the North by Wukari Local Government Area of Taraba state, [17] according to the 2006 census exercise, the local government has an area of 1408 km^2 and a population of 169,570.

2.3. Sample Collection and Preparation

Food crops (Abelmoschus esculentus, Carica papaya, Manihot esculenta, and Zea mays) were collected randomly on the farms directly from the farmers around the abandoned Lead-Zinc mining site at Tse-Faga in Logo Local Government Area of Benue State and neatly packaged in zip-lock bags, labeled accordingly and conveyed to the and transported to the Powel and B Toxicology and Biodiversity Laboratory, Department of Animal and Environmental Biology University of Port Harcourt, Choba, Rivers State for sample preparation and laboratory analysis.
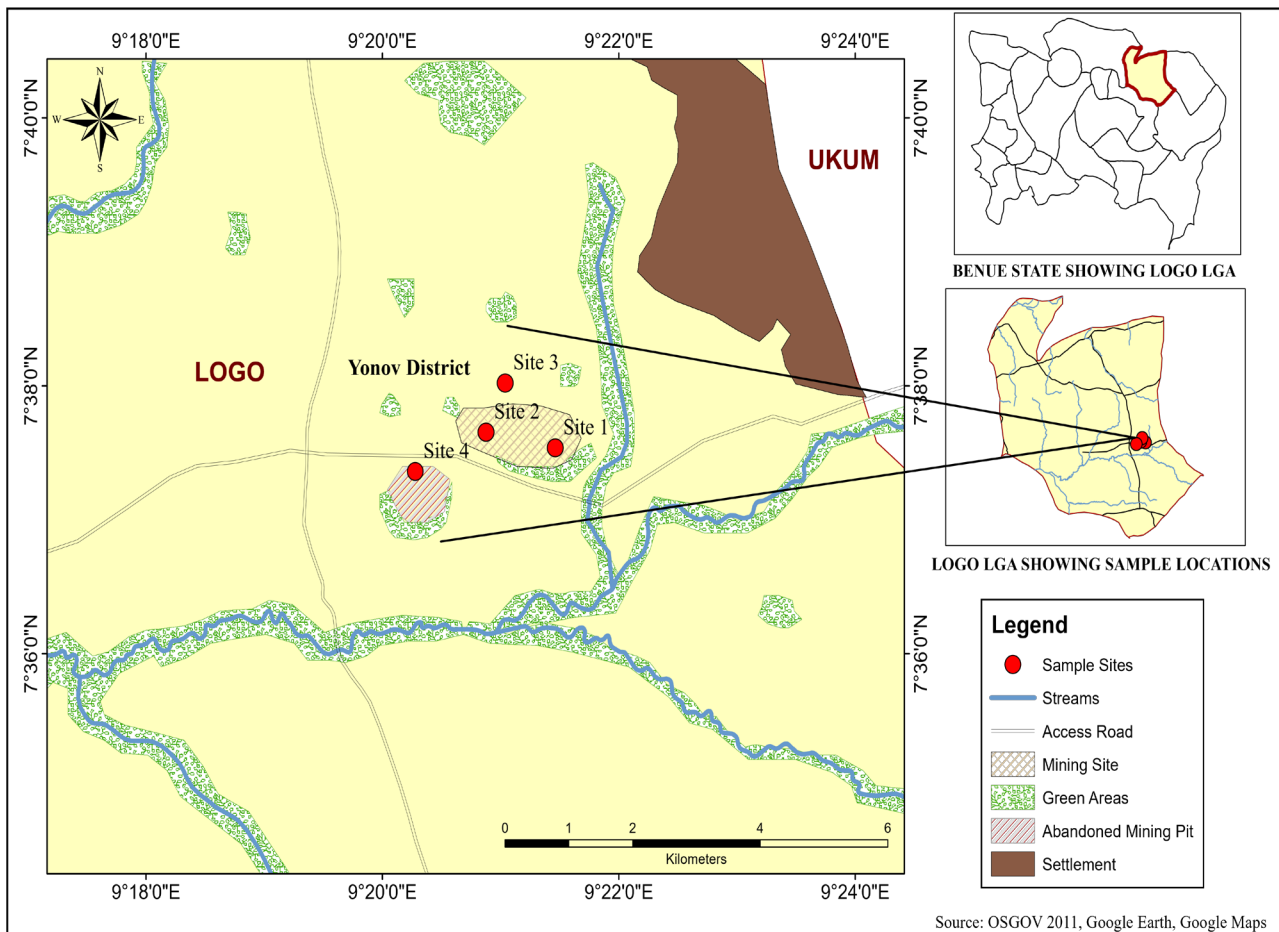
Figure 2. Map of study.

2.4. Sample Preparation

All collected samples were separated accordingly, the outer parts such as peels ad shells were separated from the inner parts such as seeds, tuber, flesh respectively. The separation of samples into the various components was aimed at assessing the different concentration of the metals in the different sample components.

Samples were the oven dried to reduce moisture, grinded, and sieved properly using a 300 microns sieve for proper surface area for Laboratory analysis.

Atomic absorption spectrophotometric methodology was used for this analysis at Giolee Global Services Limited, Port Harcourt.

2.5. Sample Digestion

One gram (1 g) of each food crop was measured into a 250 ml conical flask, 10ml of well mixed (Perchloric, Nitric and Sulphuric acid) was introduced into the solution and allowed to soak. Digestions were done in a fume cupboard. The heated samples were cooled off, filtered and the filtrates introduced into a 100-ml laboratory volumetric flask and prepared for heavy metal analysis using an atomic absorption spectrophotometer (AAS) and the results were printed out in three decimal points.

2.6. Data Analysis Methods

Statistical analysis

The statistical analysis of data was done using SPSS 21 software (IBM) Corporation, Armonk, NY, USA). The means of the different results were analyzed using a one-way analysis of variance (ANOVA). Post-Hoc Tukey HSD test was done to verify statistically significant differences among individual means at $P \leq 0.05$.

2.7. Ecological Risk Assessment

Bioaccumulation Factor (BAF) of Metals in Biota Samples

The bioaccumulation factor (BAF) is the relative tendency of a substance to be accumulated by a certain species of plant or animal. It is the ratio of the concentration of heavy metal in a plant to the levels of such heavy metal in soil, which is described as [18]

$$\text{BAF} = \frac{\text{Concentration in crop}}{\text{Concentration in soil}} \quad [19] \tag{1}$$

where:

Concentration of Pb in soil was 1.30 mk/kg;

Zinc levels in soil were 0.67 [15].

Contamination Factor (CF)

C. Factor (CF) is basically used to assess the extent of sample contamination by heavy metals. It is expressed as the ratio of the concentration of the heavy to the background value. The background value used in this work is the standard value stipulated by USEPA 2011. The contamination factor does not have a unit of expression.

$$\text{CF} = \frac{C \cdot \text{metal}}{Bn} \tag{II}$$

where:

C metal is the metal concentration in polluted media;

Bn is the background value of that metal.

Pollution Load Index (PLI)

The Pollution Load Index (PLI) evaluates the degree to which the soil sediment associated which heavy metal which might impact the microflora and fauna of soil. It can be used to check the levels of heavy metal contamination [20].

$$\text{PLI} = \sqrt[n]{\left(\text{CF}_1 \times \text{CF}_2 \times \text{CF}_3 \times \text{CF}_4 \cdots \text{CF}_n\right)} \tag{3}$$

where CF represent the contamination factor, n is the number of metals investigated, The PLI is scored using a scale from 0 - 6.

The Geo-Accumulation Index (Igeo) of Metals in Biota, Soil and Water Samples

The geo-accumulation factor is an indicator to assess the presence and inten-

sity of anthropogenic contamination. It is expressed as:

$$Igeo = \log 2\left(\frac{Cn}{1.5Bn}\right) \tag{4}$$

Cn = concentration of metal in the soil, Bn is the geochemical background for the element and 1.5 is a constant.

2.8. Human Health Risk Assessment of Heavy Metals

The estimated daily intake of metals is used to ascertain the health risk related to the intake of heavy metals from food crops, water, and exposure to soil. The Estimated Daily Intake (EDI) Hazard Quotient (HQ), Hazard Index (HI) and Cancer Risk (Cr) were also considered. The estimated daily intake of metals is expressed in $Mg/kg/day^{-1}$ Bw.

Estimated Daily Intake of Metal (EDIM)

$$EDIM = \frac{CM \times DFI}{BW} \tag{5}$$

where CM is the Concentration of metal in crop;

DFI is the Daily food intake = 0.3 mg/kg [21] [22];

BW is the Body Weight average (62 kg assumed).

The Hazard Quotient (HQ) of Heavy Metals in food-crops samples

$$HQ = \frac{EDIM}{RfD} \tag{6}$$

where:

RfD is Oral slope factor in mg/kg/day according to USEPA guideline [23].

When HQ < 1 metal contamination is still within safe limits. Whereas HQ ≥ 1 means it has potential to cause disease [22].

Carcinogenic risk (Cr)

$$Cr = EDI \times CSF \tag{7}$$

where Cr represents the cancer risk;

EDI is the estimated daily intake calculated in equation (V);

CSF is the cancer slope factor.

According to USEPA [24] 10^{-6} - 10^{-4} is the range of permitted assumed lifetime risks for carcinogens.

Table 1. Reference values for different parameters.

	ELEMENTS (mg/kg/day)		
REFERENCE VALUES	Pb	Zn	REFERENCE
Toxic reference factor	5	1	[25]
Geochemical background value (Bn)	20	95	[26]
Background value of element	85	140	[26]
Oral reference doses (RfD) mg/kg/day	0.3	0.004	[27] [28]
Cancer slope factor	0.0085	-	[29]

3. Results and Discussion

3.1. Heavy Metals Concentration the Food-Crops

Results in Table 2 below shows concentration of heavy metals in food crops, lead (Pb) was highest in maize seed (1.30 mg/kg) while the lowest mean concentration values were recorded in *Manihot esculenta* peel, *Carica papaya* peel, and with mean values of 0.46 ± 0.02 mg/kg, 0.46 ± 0.019 mg/kg, 0.46 ± 0.0164 mg/kg respectively. These results are relatively higher than the results of [30] 0.202 - 0.134 mg/kg for higher and lower limits respectively.

These results have revealed alarming levels of Lead in food crops such as *Zea mays* seeds as high as 130% to 45% and Carica papaya peel above the standard level of 0.1 mg/kg stipulated by World Health Organization [31].

Generally, zinc (Zn) concentration in all the food crops from the mining site revealed the highest concentration in *Carica papaya* with mean concentration and standard deviation of 0.50 ± 0.01 Mg/kg while the lowest mean concentration values were recorded in *Manihot esculenta* peel 0.122 ± 0.01 mg/kg (Table 2). [32] reported values of 1.205 - 1.017 mg/kg, [33] reported lead increase over a post spill event from NDL to 0.16 mg/kg over seasons. These results are relatively higher than the results of this work. All the concentrations of zinc in the food crops were below the stipulated standard by WHO. These results are significantly lower than the reports of [34] who report mean value of Iron, Copper, Manganese, Lead, Zinc, Chromium, Arsenic, and Cadmium in station 1 of his study area from 3.55 - 9454.0 mg/kg.

Table 2, revealed a trend of higher mean concentrations of lead (Pb) in the inner parts of the food crops than in the outer parts. [35] reported that lead/zinc mining areas accumulate significant levels of Cadmium, he noted that, vegetables have higher tendencies to accumulate Cadmium and lead (Pb) than the other heavy metals, however, the results in Table 2 and Figure 1 of this study contrasted this claim hence concentration of cadmium was below detectable limits. Figure 1 revealed higher centration of lead Pb in all analyzed food-based samples, with maize seeds accumulating the highest level of lead (Pb) (1.30 mg/kg).

The presence of heavy metals in food crops and plants, in general, has been

Table 2. Mean concentration of metals in food crops.

SAMPLE CODE	Pb Mg/Kg	Hg Mg/Kg	Cd Mg/Kg	Zn Mg/Kg
Manihot esculenta Peels	0.46	<0.001	<0.002	0.12
Manihot esculenta Flesh	0.89	<0.001	<0.002	0.12
Carica papaya Peels	0.46	<0.001	<0.002	0.46
Carica papaya Flesh	0.89	<0.001	<0.002	0.50
Zea mays Husk	0.67	<0.001	<0.002	0.26
Zea mays Seed	1.30	<0.001	<0.002	0.46
Abelmoschus esculentus	0.67	<0.001	<0.002	0.48

confirmed to be of deleterious effects due to the very critical roles they play in the food chain. Herbivorous animals take in these metals thereby, transferring the metals through higher organisms in the food chain as these higher animals such as humans, while some omnivores feed directly on the plants.

There was no significance difference in the mean concentration of lead (Pb) at $P \leq 0.05$ in *Manihot esculenta* tuber flesh, *Carica papaya* flesh, and *zeal mays* seeds, also, no significance difference was observed in the mean concentration of lead (Pb) at $P \leq 0.05$ in Zea mays husk and *Abelmoschus esculentus* and finally no significance difference in the mean concentration of lead (Pb) at $P \leq 0.05$ in *Manihot esculenta* peel, and *Carica papaya* peel.

In the mean concentration of Zinc (Zn), there was no significance difference at $P \leq 0.05$ in *Manihot esculenta* peel, and *Manihot esculenta* tuber flesh, *Carica papaya* peel, *Carica papaya flesh*, and *Abelmoschus esculentus* while there was a significance difference between *Zea mays* husk, *Zea mays* seeds and the other samples.

3.2. Bioaccumulation of Heavy Metals

Transfer factor is the ability of a metal to be accumulated by a particular species of plant. It is the ratio of the concentration of heavy metal in a plant to the concentration of heavy metal in soil. The bioaccumulation factor (BAF) of heavy metals from soil to plants of the study area is represented in Figure 3. The highest bioaccumulation factor of lead (Pd) was revealed *Zea mays seeds* (1.001) while *Manihot esculenta* tuber peel and *Carica papaya* peels with BAF value of 0.358 was the lowest.

The highest bioaccumulation factor (BAF) of zinc was recorded in *Carica papaya* flesh 0.754, Manihot esculenta tuber peels and flesh 0.181 was the lowest.
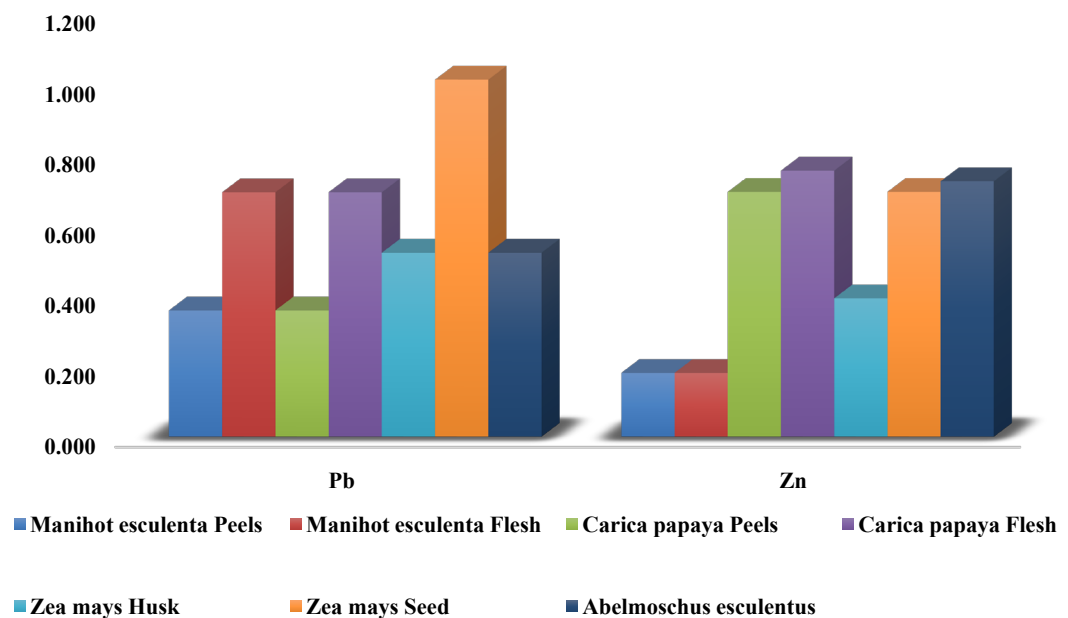

Figure 3. Bioaccumulation of Heavy metals in food crops from study area.

All the results of transfer factor of Zinc from soils to food crops were below the stipulated standard of BAF > 1, according to [33]. However, Zea Mays with BAF 1.011 was recorded the highest BAF, we can therefore conclude that, among all food crops under study, *Zea Mays* had the highest bioaccumulation factor.

3.3. Ecologicl Risk Assessment Risk

3.3.1. Contamination Factor (CF) and Pollution Load Index (PLI)

Results are presented in Table 3. Reveal the Pollution load index (PLI) of the analyzed samples. PLI recorded in this study were below one (1), which signifies that, even though the contamination of the individual sample by lead (Pb) was high in all food crops samples, the pollution load index for all the samples showed non-contamination according to the pollution load index ranking. The results of the present study are in agreement with the findings of [35] who report PLI value of <1 in station 1 of his study, however, he reported PLI value > 1 in the remaining two stations of his study area.

3.3.2. Geo-Accumulation Index (Igeo)

Figure 4 below shows the geo-accumulation index of food-crops as follows: *Manihot esculenta* peel 0.00026, *Manihot esculenta* tuber flesh 0.00026, *Carica papaya* peel 0.00096, *Carica papaya* flesh 0.00011, *Zea mays* husk 0.00055, *Zea mays* seed 0.00097, *Abelmoschus esculentus* 0.0001 for Zinc (Zn), while geo-accumulation of lead (Pb) was as follows: *Manihot esculenta* peel, 0.00458, *Manihot esculenta* tuber flesh, 0.00893, *Carica papaya* peel, 0.00458, *Carica papaya* flesh, 0.00893. *Zea mays* husk, 0.00675, Zea *mays seed*, 0.013, *Abelmoschus esculentus*, 0.00675.

Geo-accumulation index of Mercury (Hg) and Cadmium (Cd) was not calculated for, hence their concentrations in the biota (food crops) were all below lowest detectible limits of the atomic absorption spectrometer.

All the results from this study were lower than the results reported by [36] who report Igeo range of 0.00213 - 0.0194 for lead (Pb) and 0.0247 - 0.0172 for zinc. Hence all figures fall below the stipulated values of <1 signifies that these samples are safe from contamination according to this ranking.

Table 3. Contamination factor (CF) and pollution load index (PLI) of heavy metals in biota, water and soil samples.

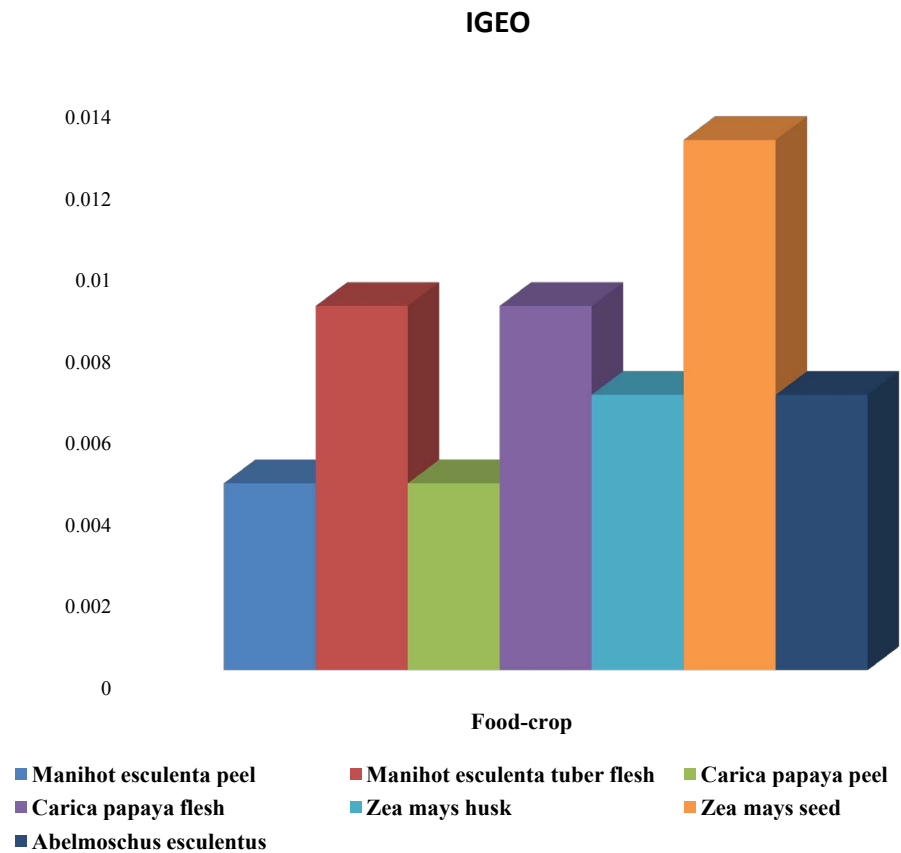| Samples	Contamination Factor		Pollution Load Index
	Pb	Zn	
Manihot esculenta peel	0.005	8.7E−04	0.00209
Manihot esculenta tuber flesh	0.01	8.7E−04	0.00295
Carica papaya peel	0.005	0.003	0.00387
Carica papaya flesh	0.01	0.004	0.00632
Zea mays husk	0.008	0.002	0.004
Zea mays seed	0.015	0.003	0.00671
Abelmoschus esculentus	0.008	0.003	0.0047

IGEO

Figure 4. Geo-accumulation index (Igeo).

3.4. Human Health Risk Assessment of Heavy Metals

3.4.1. The Estimated Daily Intake of Heavy Metals in Food-Crops Samples

The EDI of Pb through the consumption of Biota foodstuffs as represented in **Table 4** to range from, 0.002 to 0.006 mg/kg (*Manihot esculenta* peel, *Carica papaya* peel & flesh *Zea mays* seeds), while Zn was 5.9E−04 (*Manihot esculenta* peel and *Manihot esculenta* tuber flesh) to 0.002 mg/kg (*Carica papaya* Peel, *Carica papaya* Flesh, *Zea mays* Seed and *Abelmoschus esculentus*).

It is deduced from the values in **Table 4** below that, the daily intake of heavy metals via food crops of the study area is nearly free of potential risk hence the values of the estimated daily intake of the metals in food fall far below set standards. The results here are lower than reports of other studies including that of [37].

3.4.2. The Hazard Quotient (HQ) of Heavy Metals in Food-Crops Samples

The HQ of Pb in revealed in **Table 5** showed a range from *Zea mays* seed 1.714, cassava flesh 1.143, *Abelmoschus esculentus* 0.857 *Zea mays* husk 0.857, *Manihot esculenta* peel, *Carica papaya* peel and *Carica papaya* Flesh all at 0.571. *Zea mays* seeds and *Manihot esculenta* peel with HQ above recommended standard value of 1. These results were higher than the report of [38]. Who reported the maximum value of HQ in biota to be 1.111.

Table 4. Estimated daily intake (EDI) of heavy metals in food crops.

Samples	Pb	Zn	Hg	Cd
Manihot esculenta Peel	0.002	5.9E−04	-	-
Cassava tuber Flesh	0.004	5.9E−04	-	-
Carica papaya Peel	0.002	0.002	-	-
Carica papaya Flesh	0.002	0.002	-	-
Zea mays Husk	0.003	0.001	-	-
Zea mays Seed	0.006	0.002	-	-
Abelmoschus esculentus	0.003	0.002	-	-
RfDo	**0.0035**	**0.3**	**-**	**-**

Table 5. Hazard quotient (HQ) of heavy metals in food crops.

SAMPLE	Pd	Zn
Manihot esculenta peel	0.571	0.002
Manihot esculenta flesh	1.143	0.002
Carica papaya peel	0.571	0.007
Carica papaya Flesh	0.571	0.007
Zea mays husk	0.857	0.003
Zea mays seed	1.714	0.007
Abelmoschus esculentus	0.857	0.007

Table 6. Carcinogenic risk (Cr) of heavy metals in food crops.

Samples	Pb	Cd	Hg	TCR
Manihot esculenta peel	1.7E−05	–	–	1.7E−05
Manihot esculenta tuber flesh	3.4E−05		–	3.4E−05
Carica papaya peel	1.7E−05	–	–	1.7E−05
Carica papaya flesh	1.7E−05	–	–	1.7E−05
Zea mays husk	2.6E−05	–	–	2.6E−05
Zea mays seed	5.1E−05	–	–	5.1E−05
Abelmoschus esculentus	2.6E−05	–	–	2.6E−05
STANDARD	**10^{-6} to 10^{-4}**			

Hazard quotient for Zn in the analyzed samples ranged from 0.002 to 0.007 (*Manihot esculenta peel*, *cassava to Carica papaya peel and Carica papaya* Flesh, *Zea mays* seeds *and Abelmoschus esculentus*) for Zn respectively (Table 5). It is worthy of note that, the hazard quotient of Zn in all the analyzed samples was less than 1, which simply means, the probability of health risk or toxicity to the residents originating from the ingestion of Zn via the consumption, ingestion, or exposure to the food crops by the populace very low compared to Pb.

3.4.3. Cancer Risk (Cr) of Heavy Metals in Food Crops Samples

Table 6 shows the cancer risk of Pb was within the range (10^{-6} to 10^{-4}) USEPA (2011) of predicted lifetime risk for cancer-causing substances, which indicates that, the risk of developing cancer from consuming Pb via the consumption of the food crops by populace.

4. Conclusions

Results obtained from this research revealed significantly high levels of lead in all sampled food crops, all concentrations were above the standard recommendation of 0.01 mg/kg as stipulated by the WHO. *Zea Mays* seeds which recorded the highest concentration levels of Lead also recorded the highest values of bioaccumulation factor. Zinc levels in all samples were at safe levels as determined by the WHO. Ecological risk assessment revealed no contamination, however, human risk assessment revealed high non-carcinogenic risk in hazard quotient (HQ). This is an indication that the consumption of food crops cultivated around the abandoned mining areas may significantly increase the risk of non-carcinogenic diseases associated with lead poisoning. The probability of people exposed to heavy metals via the consumption of these food crops to develop cancer is low hence, carcinogenic risk values were within the stipulated range of (10^{-6} to 10^{-4}) by the United State Environmental Protection Agency.

Data on ecological indices as revealed by this research is not an indication of safe levels of the contaminants, it only reveals significantly low potential ecological risks associated with the levels of the contaminants. Results of human health indices have clearly demonstrated significant potential human health risk of exposure via consumption of food crops contaminated by lead levels which can result in non-carcinogenic diseases such as lead poisoning.

We, therefore, recommend regular and strict quality evaluation of food crops produced from the areas around the abandoned mining sites to prevent possible food poisoning by lead.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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