



Risk Assessment of Poisonous Metals in Water and Soil at Two Abandoned Lead-Zinc Mines at Yonov, Benue State

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Authors' contributions

This work was carried out in collaboration between both authors. Author BBB designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author SNP did field sampling, preparations, analysis, result discussions, managed the analyses of the study, managed the literature searches and prepared manuscript with author BBB. Both authors read and approved the final manuscript.

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ABSTRACT

Aim: The study was aimed at determining the risk assessment of toxic metal concentration in soil and water at two abandoned Lead-Zinc mines Yonov District, Logo, Benue State, Nigeria.

Study design: comparative cross-sectional study.

Place and duration of study: This study was carried out at the Bruce Powel Toxicology & Biodiversity Laboratory, Animal and Environmental Biology Department, University of Port Harcourt, Analysis at Giolee Global Services Limited Port Harcourt, Nigeria from 16th July to 30th October 2019.

Methodology: Eighteen composite water and soil samples were collected and analyzed using Atomic Absorption Spectrophotometer.

Results: The mean concentration of Lead (Pb) was higher than that of Zinc (Zn) in all eighteen

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samples, while, Mercury (Hg) and Cadmium (Cd) were below detection limit in all samples. Mean concentration for Pb in soil samples in the order Site II > Site I (1.29 ± 0.134 mg/kg > 1.26 ± 0.04 mg/kg) > control 0.82 ± 0.06 mg/kg. Zn was higher in site I, 0.70 ± 0.10 mg/kg than site II 0.66 ± 0.04 mg/kg, and control 0.42 ± 0.02 mg/kg. Pb values in water was similar in both sites at $0.46 \pm 0.04/0.02$ mg/L, while control 0.02 ± 0.001 mg/kg. Zn was higher in site II 0.05 ± 0.01 mg/L than site I 0.04 ± 0.01 mg/L, control was 0.004 ± 0.00 mg/L. Health risk assessment showed that Estimated daily intake of metals, hazard quotient, hazard index were all less than 1, Carcinogenic risk was within the stipulated ranged of 10^{-6} to 10^{-4} .

Conclusion: Ecological and health risk indices revealed non-contamination by Poisonous metals, however, routine assessment is recommended to forestall any sudden change in the concentration that may result to deleterious effects on human health.

Keywords: Mining; poisonous metals; ecological; health risk assessment.

ABBREVIATIONS

AAS	: Atomic Absorption Spectrophotometric
ANOVA	: One-Way Analysis of Variance
APHA 3030	: American Public Health Association
BAF	: Bioaccumulation Factor
B _n	: Geochemical Background Value
Cd	: Cadmium
CF	: Contamination Factor
CR	: Cancer Risk
CSF	: Cancer Slope Factor
DPR	: Department of Petroleum Resources
EDIM	: Estimated Daily Intake of Metal
GIS	: Geospatial Information Systems Data
Hg	: Mercury
HI	: Hazard Index,
HQ	: Hazard Quotient
IAEA	: International Atomic Energy Agency
IGEO	: The Geo-accumulation Index
NORM	: Naturally Occurring Radionuclides
OGP	: Oil and Gas Producers.
Pb	: Lead
PLI	: Pollution Load Indices
PTMs	: Potential Toxic Metals
RfDO	: Oral Reference Doses
SON	: Standard Organization of Nigeria
UNCEAR	: United Nations scientific committee on the effects of atomic radiation
US EPA	: United State Environmental Protection Agency

1. INTRODUCTION

Nigeria is blessed with abundant solid minerals under different categories made up of precious metals, stones including industrial minerals like coal, tin, gold, marble, limestone, and others [1] which are found in association with other

components such as poisonous metals etc. It is estimated that the contribution of metals from human activities in the soil is higher than contribution from natural sources [2]. Mining and smelting metalliferous ores among other anthropogenic activities is still a major source of toxic metal contamination in the environment [3].

Globally, mining activities have been established as a source of poisonous metals, comprising of non-renewable mineral and aggregate resources in measurable amounts, [4] Ofomata [5] considered mining operations as critical sources of poisonous metals.

Bhattacharya et al. [6] claimed that open cast mining has the ability to generate large amounts of sulfide-rich tailings which impacts the quality of soils as well as surface water. Vega et al. [7] and He et al. [8] reported that the mechanical, physical, chemical and biological composition of mined soils is seriously deficient due to instability and limited cohesion, these soils are known for low nutrients contents as well as organic matter with relatively high levels of poisonous metals. Verner and Ramsey [9] stressed that, apart from local disturbance of physical characteristics, potential toxic metals (PTMs) have the potential for widespread contamination of soil, sediments and nutritional crops which translate to a high loss of biodiversity and pose serious health risks to communities residing in proximity to the mining areas.

The health impacts of these poisonous metals to humans upon exposure can never be overemphasized, for example, Lead (Pb) ingestion in any form is highly toxic and chronic [10]. The weathering processes increase disturbance of the underlying rocks by miners thereby improving transmissivity, and thus moving potentially toxic metals (PTMs) to subsurface water, thus posing more risks to inhabitants and the ecosystem in general [11].



Fig. 1 Picture of an abandoned lead Zinc mining site in Yonov, Benue State

In Nigeria, Musa, [1] reported 223 small scale mines, 195 mining leases, about 845 artisanal mining cooperatives documented and 2,048 exploration permits issued. The operations of these mines have resulted in the spread of ecological impacts at the detriment of affected communities.

Lead toxicity has been reported by research as a serious concern for child development, by affecting the developing nervous system, which in turn leads to language cognition issues as well as fine motor skills [12,13]. Lead exposure is related to various health challenges leading to even deaths. In Zamfara State, in the Northern part of Nigeria, the death of more than 400 children was attributed to lead intoxication which originated from a mining site, research data

indicated that the lead poisoning had started since early in 2010. Oladipo et al. [14] also reported unconfirmed reports of high mortality of geese within these villages. [15]. It also affects growth and pubertal development in females, (delay) [16] renal impairment, [17] dental caries, [18], and hypertension. [19]. Flora, Flora, and Saxena [20] reported that, blood lead levels around 10 $\mu\text{g/dL}$, can lead to coma while levels more than 100 $\mu\text{g/dL}$ can result to death. According to Flora et al. [20] Pb at 70 $\mu\text{g/DL}$ has potentials of causing damage to the central nervous system (CNS) and kidney failure. Cadmium is a naturally occurring toxic heavy metal. It is an extremely toxic industrial and environmental pollutant classified as a human carcinogenic. Acute exposure to cadmium fumes may cause symptoms such as fever and muscle

ache, respiratory tract and kidney problems. Cadmium derives its toxicological properties from its chemical similarity to zinc an essential micronutrient for plants, animals and humans [21]. Severe exposure to Cd may result in pulmonary effects such as bronchiolitis, emphysema, and alveolitis [21]. Cd can also result in bone fracture, kidney dysfunction, hypertension and even cancer [22]. Obasi and Akudinobi [12] stated that Lead, cadmium, arsenic and mercury are very carcinogenic metals. He claimed that Exposure to elevated levels of metallic, inorganic and organic mercury can damage the kidney, brain as well as developing fetus, methyl mercury has very high potential to cause cancers.

2. MATERIALS AND METHODS

2.1 Study Area

Logo local government is located latitude 7° 29" and 7° 52" north of the Equator and longitude 9° 05" and 9°20" east of the Greenwich Meridian Fig 1. 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, [23].

According to the 2006 census exercise, the local government has an area of 1,408 km² and a population of 169, 570. The common occupation of the people is farming of grains and root crops while a negligible aspect of this population practices other occupations such as fishing, trading, among others.

2.2 Sample Collection

Eighteen (18) samples (soil and water) were collected from marked points from the abandoned Lead-Zinc mining sites in Tse-Faga and Tse-Vule Yonov District of Logo Local Government Area of Benue State for three months.

Samples were transported from the site in Benue State to the Bruce Powel Toxicology & Babs and Laboratory, Animal and Environmental Biology department, University of Port Harcourt, Choba, Rivers State for sample preparation and laboratory analysis.

2.2.1 Soil samples

Soil auger was used for collection of composite soil samples at a depth of 0-15 cm and placed

inside very clean plastic buckets, each composite sample was made up by soils from different sampling points. The soil was then mixed thoroughly and all foreign materials such as roots, wood, stones, pebbles, and gravel were removed. Quartering was performed to reduce soil quantity to about 1kg, after which they were transferred into a clean Ziplock bag and labeled accordingly.

2.2.2 Water samples

Two (2) liters of triplicate water samples were taken each at the sampling points using very clean water bottles.

The sampling position include;

- A stream which serves as a water source for the mining community,
- An abandoned mining pit and,
- A borehole water source about 1km from the mining area located on a hill to serve as a control for the research.

2.3 Sample Preparation

Atomic absorptive spectrophotometric methodology was used as analysis at an ISO Certified Laboratory at Giolee Global Services Limited, Port Harcourt.

Soils samples were air-dried for one week to reduce the moisture content and sieved using a 300 microns sieve to ensure fine particulate for proper digestion.

After sieving, they were repackaged in new zip-lock bags, labeled and prepared for laboratory operation.

While for water samples, samples were scaled for required quantities and transferred into laboratory test bottles and taken for laboratory digestion.

2.3.1 Sample treatment

2.3.1.1 Water analysis

Sampled groundwater were acidified using HNO₃ to a highly acidic pH of less than 2, it was then shaken properly to homogenize after duplications. The samples were prepared using the procedure stipulated by APHA, [24] 50mL sub-samples were then taken and transferred into the digestion vessel (250 ml beaker) fitted

with a watch glass. $1.0 \pm 0.1\text{mL}$ of concentrated Nitric acid (HNO_3) and $0.50 \pm 0.05\text{mL}$ concentrated hydrochloric acid (HCl) were added to the sample. The solution was digested for 2.0 – 2.5 hrs and heated at $95 \pm 5^\circ\text{C}$. Samples were transferred from heat source and cooled for about 30 minutes to reduce any potentially harmful fumes. The watch glass was detached while samples were reconstructed to $50 \pm 1\text{mL}$ with distilled water and well shaken to mix. Samples were then analyzed using the atomic absorption spectrophotometer appropriately.

2.3.1.2 Soil analysis

The procedure for analysis of soil samples was done following the APHA 3030 standard procedure APHA, [24] All reagents were of analytical grades and glassware was Pyrex. One gram (1g) of each soil sample was scaled into a 250 ml conical flask, 10 ml 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 poisonous metal analysis using an atomic absorption spectrophotometer (AAS) and the results were printed out in three decimal points.

2.4 Data Analysis Methods

2.4.1 Statistical analysis

Results from the atomic absorption spectrophotometer were statistically analyzed using SPSS version 21 software (IBM) Corporation, Armonk, New York, USA). The means of different metals was generated using a one-way analysis of variance (ANOVA). Post-Hoc Tukey HSD test was done to verify statistically significance differences among individual means at $P \leq 0.05$ and represented as superscript alphabets in Figures.

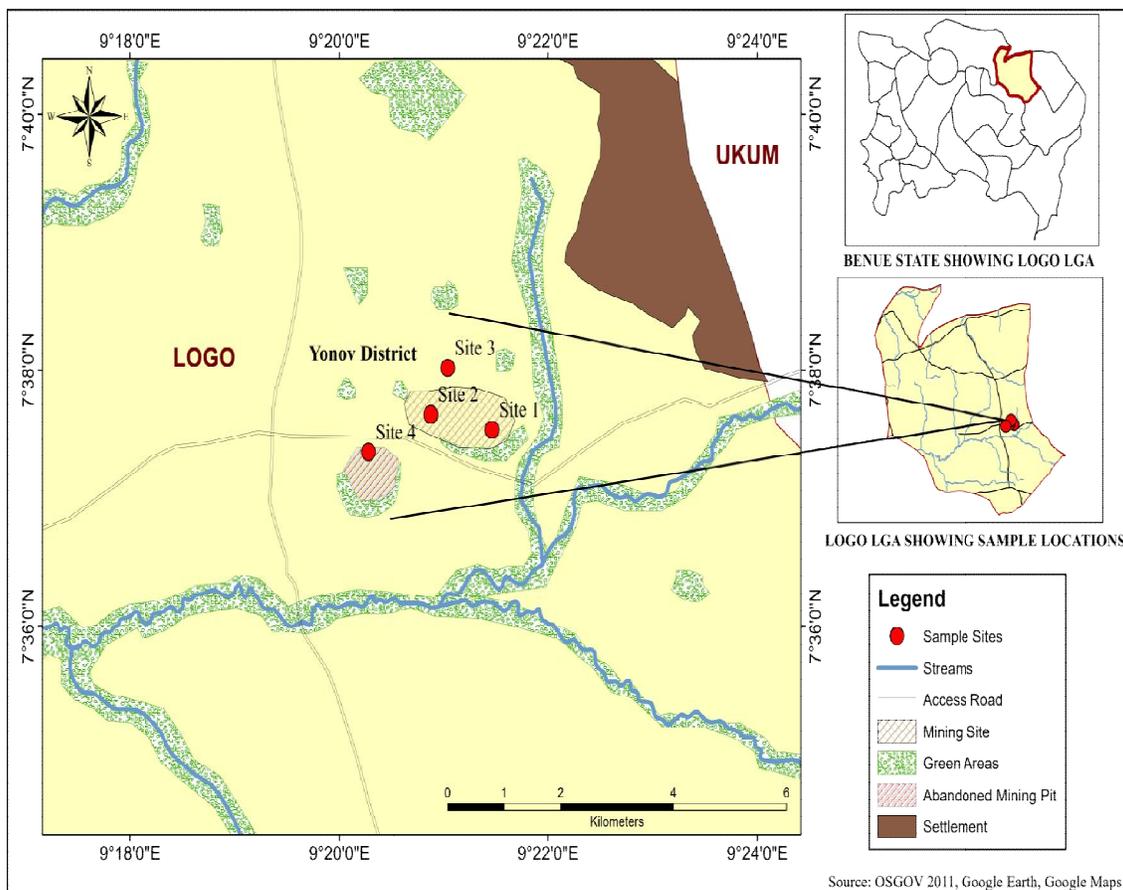


Fig. 2. Map of Yonov district (study area) showing the sampling sites

2.4.1.2 Ecological risk Indices

i. Contamination Factor (CF)

This contamination factor used to evaluate the level of sample contamination by poisonous metals. it is the ratio of the concentration of the poisonous metals in the sample to the reference value of the metals for such sample. [25].

$$CF = \frac{C_{metal}}{C_{ref}} \dots\dots\dots (I)$$

Background value of element according the Department of Petroleum Resources stipulates lead (Pb) 85 mg/kg/day, while Zinc (Zn) is 140 mg/kg/day [25].

ii. Pollution Load Index (PLI)

This Index (PLI) is used to check the levels of poisonous metal contamination and its impact on the microflora and fauna of soil. [26].

$$PLI = \sqrt[n]{(CF1 \times CF2 \times CF3 \dots\dots CFn)} \dots\dots\dots (Equation. II)$$

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

iii. The Geo-accumulation Index (Igeo)

The geo-accumulation factor is used to assess the presence and intensity of anthropogenic contamination. It is expressed as:

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5B_n} \right) \dots\dots\dots (Equation. III)$$

C_n = concentration of metal in the soil, B_n is the geochemical background for the element. Geochemical background value (B_n) for lead (Pb) is 20 mg/kg while Zinc (Zn) is 95 mg/kg [25].

2.4.1.3 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.

i. Estimated Daily Intake of Metal (EDIM)

$$EDIM = \frac{\text{Concentration of metal in crop} \times \text{Daily food intake}}{\text{Body Weight average}} \dots\dots (Equation V)$$

$$HQ = \frac{EDIM}{RfD} \dots\dots\dots (Equation VI)$$

Where:
Dfood intake = 0.3 mg/kg [27]
BWaverage = (62 kg assumed)
RfD is Oral slope factor in mg/kg/day according to USEPA guideline [28].
When *HQ* < 1 metal contamination is still within safe limits.

whereas *HQ* ≥ 1 means it has potential to cause disease [29].

ii. The hazard index (HI)

The hazard index (HI) is the sum total of hazards posed by the possible forms of pollutant absorption. It is calculated using the following equation

$$HI = \sum HQ_{1+}HQ_2 + HQ_{3+}HQ_4 \dots\dots HQ_n \dots\dots\dots (Equation VII)$$

iii. Carcinogenic risk (Cr)

$$Cr = EDIM \times CSF \dots\dots\dots (Equation VIII)$$

According to [30] 10⁻⁶-10⁻⁴ is the range of permitted assumed lifetime risks for carcinogens.

Reference values for different parameters

Parameter	ELEMENTS (mg/kg/day)		REFERENCE
	Pb	Zn	
Toxic reference factor	5	1	[31]
Geochemical background value (B _n)	20	95	[25]
Background value of element	85	140	[25]
Oral reference doses (RfD) mg/kg /day	0.3	0.004	[32,33]
Cancer slope factor	0.0085	-	USEPA (2011)

3. RESULTS AND DISCUSSION

3.1 Poisonous Metal Concentrations in Analyzed Soil Samples

The soil analysis results (Table 1 and Fig. 4), reveals that, abandoned mining site II had higher mean levels and standard deviation value for lead (Pb) 1.29 ± 0.13 mg/kg, compared to values recorded at abandoned mining site I (1.26 ± 0.042 mg/kg). This result is lower than the results of Nwabueze, [34] who reported a mean level range of 3198 mg/kg to 7881 mg/kg for all forty soil samples during his study on Lead (Pb) mining in Ebonyi State, Nigeria. This result is higher than the result of Abiya et al. [35] which was (0.216-0.278 mg/kg), during his study on "Assessment of Heavy Metal Pollution in a Gold Mining Site in Southwestern Nigeria". The results of the present study also indicated that, Cadmium (Cd) and mercury (Hg) had concentrations below detection limits the analytic method. This is similar to results reported by Ogbonnaya, [36] who also reported below detectable that, Cadmium (Cd), and mercury (Hg) were below detectable limits during his study to analyze the risks associated with the mining of Lead-Zinc minerals in some parts of the Southern Benue trough. However, Ogbonnaya reported a mean Pb concentration of 1,093.71 mg kg higher than the results of this study. Similarly, his study recorded a Zn concentration of 75–1,878.50 g/kg⁻¹ with a mean of 609.00 mg kg⁻¹ from the soils.

The mean levels and standard deviation range of zinc in the analyzed soil samples (Fig. 4) were 0.695 ± 0.099 - 0.66 ± 0.038 mg/kg. These results fall within the range reported by Abiya et al. [35] which was (0.628-0.70 mg/kg), but below the results of Edori and Kpee [37]. Zinc (Zn) 8.17 ± 96 - 14.33 ± 1.43 mg/kg Adanwo and Elechi [38] also reported Zinc levels in the soil to be 14.91 ± 0.197 mg/Kg, which is still higher than the results of this study. Relatively, the results of this study were lower than the regulatory standard level of zinc 300.0mg/kg [27].

Results in Fig. 4 above shows that there was no significance difference in the mean lead (Pb) concentration of at $P \leq 0.05$ in soils from mining site I and II, superscript "b", but there existed a significance difference between the control sample "a" and the soils from the mining areas.

In the mean concentration of Zinc (Zn), in Fig. 4 there was no significance difference in the mean concentration of Zinc (Zn), at $P \leq 0.05$ in soils

from mining site I and II, superscript "b", but there existed a significance difference between the control sample "a".

From all results, lead levels in soil fall far below the standard level of 10 mg/kg as stipulated by the World Health Organization [27].

3.1.1 Poisonous metal concentrations in analyzed water samples

Results from this research in Table 1 and Fig. 4. indicates that, mean concentration and standard deviation of lead (Pb) in the water samples from the sites is at 0.46 ± 0.04 mg/L, and 0.46 ± 0.018 mg/L for site I and site II respectively. The result of the present study is relatively higher than maximum permissible limit of 0.01mg/l for lead (Pb) in drinking water as stipulated by DPR, WHO and the NIS standard. These results are within the range reported by Babatunde et al. [39] for Pb concentrations of 0.2-0.6 mg/kg in 2011 and 0.2-0.9 mg/kg in 2012 respectively, however, these results is higher than the results of Edori and Kpee [37] who reported mean concentration and standard error of lead in their study to be 0.970 ± 0.00 mg kg and Ogbonnaya, et al. [36] who reported low concentration of Pb in water samples, he claimed that the low levels recorded were as a result of poor or limited dispersion pattern of Pb, hence its anomalies were restricted to the mineralized zones, he, however, recorded high concentrations of lead ($92 - \geq 1,700$ mg kg⁻¹) in stream sediments far away from mine sites, according to him, joint contributions of metal loads impacted by mining activities possibly increased levels of lead concentration in sediments. Oko, Aremu, Andrew, and Ecotoxicology [40] also reported lower Pb value of 0.1487 ± 0.2531 to 0.1086 ± 0.1846 mg/L in water source. The concentration of Pb in the present study is therefore an issue of concerned, considering the bioaccumulation and toxicity potentials of Pb as the most potent toxic metal amongst metals considered in this study [41].

Mean concentration and standard deviation of Zinc in water sampled from both abandoned sites at 0.04 ± 0.006 mg/L, 0.05 ± 0.013 mg/L for site I and site II (Fig. 5) respectively. Values of 0.04 ± 0.01 mg/L obtained from water from site I which is surface water source (stream) were higher than the reports of Ezeh and Anike [42] who reported Values of $0.008 - 0.023$ mg/L⁻¹ (mean of 0.01 mg/L-1) but lower than values reported by Ogbonnaya et al. [36]. Result

revealed even contamination by heavy metals, because this results y significant difference among the triplicate sample analyzed (Table 2), which reflects even contamination of Zinc in stream sampled water, the control sample underground) also show variation between outcomes of Ogonnaya et al. [36] in their study, they reported that levels of zinc contamination were below detectable limits in the control sample, however, the results of the present study revealed 0.004 ± 0.000 mg/L of Zn in the water (Fig. 5), this variation could be attributed to the differences in the nature soils in involved in their research, they attributed poor permeability/transmissivity nature of the underlying shale and clay as a major barrier to the contaminants from reaching the water table

[42]. This claim is different to the present study, the nature of soil in the present study is loamy stony soil that allowed for permissibility of the Poisonous metal down the water table.

Results in Fig. 5 shows no significance difference in concentration of lead (Pb) in site I and II, superscript "b", but there existed a significance difference between the control sample "a" and the soils from the mining areas.

There was no significance difference in the level of Zinc (Zn), at $P \leq 0.05$ in water from site I and II, superscript "b", but there existed a significance difference between the control sample "a" and the soils from the mining areas.

Table 1. Concentration of Metals In Soil mg/Kg

Sample	Lead (Pb)	Mercury(Hg)	Cadmium(Cd)	Zinc (Zn)
Soil Control	0.872	<0.001	<0.002	0.418
Soil Control	0.702	<0.001	<0.002	0.371
MEAN	0.815	NDL	NDL	0.415
Soil Site I	1.298	<0.001	<0.002	0.608
Soil Site I	1.172	<0.001	<0.002	0.893
Soil Site I	1.298	<0.001	<0.002	0.585
MEAN	1.256	NDL	NDL	0.695
Soil Site II	1.047	<0.001	<0.002	0.634
Soil Site II	1.298	<0.001	<0.002	0.739
Soil Site II	1.511	<0.001	<0.002	0.617
MEAN	1.29	NDL	NDL	0.66



Fig. 3. Mean value Concentration of poisonous metals in soil samples of the mining sites; (where N=3). Presented as mean \pm Standard Deviation

The levels of mercury (Hg) and Cadmium (Cd) were all below lowest detectable limits of the equipment.

3.2 Risk Assessment of Poisonous Metals Concentration

3.2.1 Ecological indices of poisonous metals in water and soil

3.2.1.1 Contamination Factor (CF) of poisonous metals in water, and soil samples

The contamination factor (CF) of Pb and Zn revealed values that fall < 1, which is within the range described as low contamination factor as specified by Håkanson, [42]. These values are less than those reported by Edori and Kpee [37]. who reported a contamination factor range of 0.0114-0.0247 for lead (Pb) and zinc (Zn) 0.0583-0.102 for zinc respectively. the low contamination recorded in this study could be a result of the low scale of mining operations in the study area which is majorly small-scales artisanal which poses limited environmental risks.

3.2.1.2 Pollution load index

Results presented in Table 3 reveal the Pollution load index of samples to be highest in soil samples (0.00866), while water from Site I recorded the least PLI 0.0012. Yadav & Yadav [31] (2018), however, reported pollution load index from their study in some soil samples to range from 48.6880-74.3153. These values are grossly higher than the results recorded by the

present study, however, all values of PLI recorded in this study were below one (1), which signifies non-contamination according to PLI ranking.

3.2.1.3 Geo-Accumulation Factor (Igeo) of poisonous metals in water, and soil samples

All the results from this study were lower than the results reported by Edori and Kpee [37]. who report Igeo range of 0.00213-0.0194 in 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.

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 detectable limits of the atomic absorption spectrometer.

3.2.2 Human health risk assessment poisonous metals in water and soil

3.2.2.1 The estimated daily intake of heavy metals in water, and soil samples

The EDI of Pb through the drinking of water, 0.002 for Pb and 1.9 E-04 and 2.4 E-04 mg/kg (water site I&II) for Pb, while EDI Zn 3.1 E-05 and 1.9 E-04 mg/kg The of Pb and Zn via the ingestion, inhalation, or exposure to the soil from the study area ranged between 5.8 E-05 to 6.0 E-05 mg/kg for Pb, and 3.1 E-05 to 3.2 E-05 mg/kg for Zn respectively.

Table 2. Concentration Of Metals In Water Mg/L

SAMPLE CODE		Lead (Pb)	Mercury(H)	Cadmium(C)	Zinc (Zn)
Water	WC	0.023	<0.001	<0.002	0.004
Control	WC	0.021	<0.001	<0.002	0.003
(Mg/L)	WC	0.022	<0.001	<0.002	0.005
	MEAN	0.022	NDL	NDL	0.004
Water Site I	WS I	0.454	<0.001	<0.002	0.05
(Mg/L)	WS I	0.426	<0.001	<0.002	0.03
	WS I	0.488	<0.001	<0.002	0.04
	MEAN	0.456	NDL	NDL	0.04
Water Site II	WS II	0.533	<0.001	<0.002	0.049
(Mg/L)	WS II	0.456	<0.001	<0.002	0.036
	WS II	0.379	<0.001	<0.002	0.062
	MEAN	0.456	NDL	NDL	0.049
REG.	(Mg/L)	0.01	0.001	0.003	3
STANDARD	STD	NIS/DPR/WHO	NIS/DPR/WHO	NIS/DPR/WHO	NIS/DPR/WHO

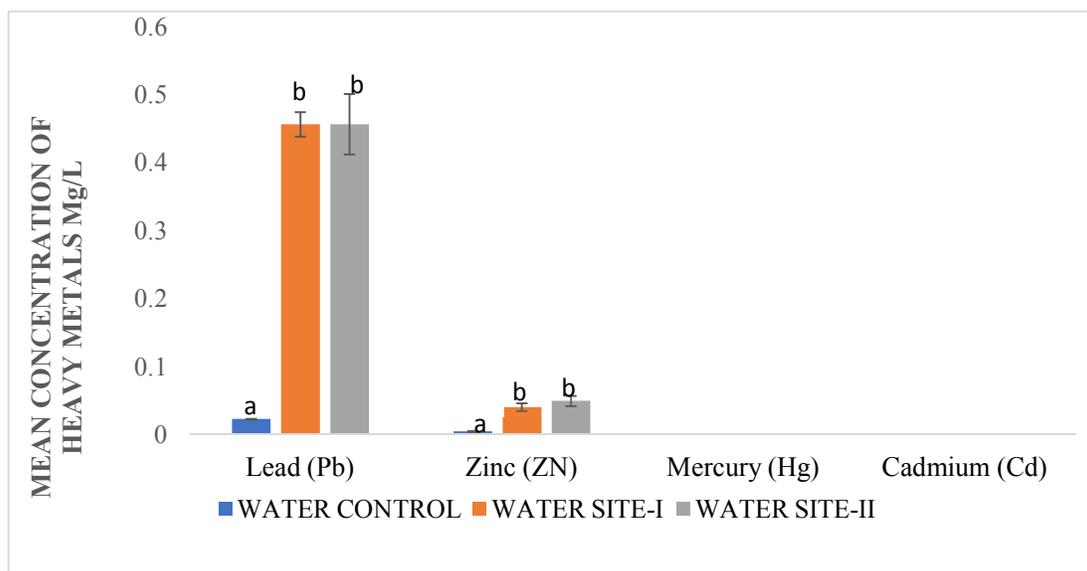


Fig. 4. Concentration of Poisonous metals in water samples from both abandoned mine sites Where (N=3), Data are presented as mean ± Standard Deviation. Values with different superscript characters indicate at P<0.05

Table 3. Contamination Factor (CF) and Pollution Load Index (PLI)

Samples	Contamination Factor		Pollution Load Index
	Pb	Zn	
Water site I	0.005	2.9 E-04	0.0012
Water site II	0.005	3.5 E-04	0.00132
Soil site I	0.015	0.005	0.00866

Table 4. Estimated Daily Intake (EDI), Hazard Quotient (HQ), and Carcinogenic Risk (Cr) of Heavy Metals in Water, and Soil samples

Estimated Daily Intake (EDI) of Heavy Metals in samples				
Samples	Pb	Zn	HG	Cd
Water site I	0.002	1.9 E-04	-	-
Water site II	0.002	2.4 E-04	-	-
Soil site I	5.8 E-05	3.2 E-05	-	-
Soil site II	6.0 E-05	3.1 E-05	-	-
RfDo	0.0035	0.3	-	-
Hazard Quotient (HQ) of Heavy Metals in samples				
SAMPLE	Pd	Zn		
Water site I	0.571	6.3 E-04		
Water site II	0.571	8.0 E-04		
Soil site I	0.017	1.1 E-04		
Soil site II	0.017	1.0 E-04		
Hazard Index	1.176	0		
Carcinogenic Risk (Cr) of Heavy Metals in samples				
Samples	Pb	Zn		
Water site I	1.7 E-05	-		
Water site II	1.7 E-05	-		
Soil site I	4.9 E-07	-		
Soil site II	5.1 E-07	-		
Standard	10-6 to 10-4			

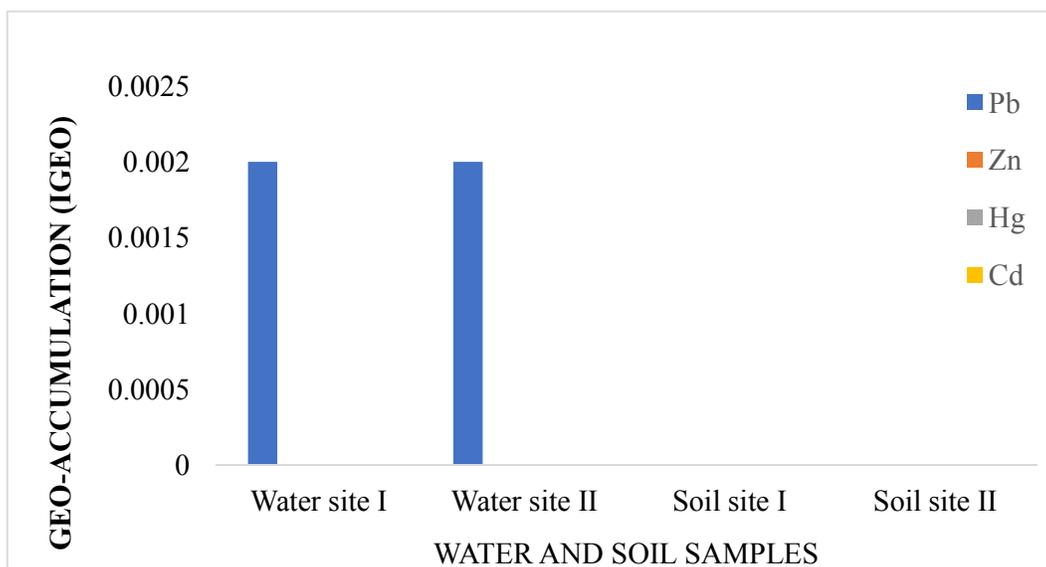


Fig. 5. Geo-accumulation Index (Igeo) in soil and water samples

It is deduced from these values that, the daily intake of, water, and exposure to the soil of the study area is nearly free of risk hence the values of the estimated daily of the metals in food and other exposure situations fall far below set standards. The results here are lower than reports of other studies including that of Ftsum and Abraham, [43].

3.2.2.2 The Hazard Quotient (HQ) of heavy metals in, water, and soil samples

Adanwo and Elechi [38], reported HQ value of 41.47 in soil samples which is extremely higher than the results of this study which is 0.571, 0.017 for soil and water respectively for lead (Pb), 6.3E-04 and 1.0 E-04 for water and soil respectively. (USEPA, 2004; Jolly *et al.*, 2013)

3.2.2.3 Hazard quotient for Zn in the analyzed samples ranged

The Hazard Index (HI) Pb and Zn emanating from water, and soil samples were 1.176 and 0 for Pb and Zn respectively. It is glaring here that, Pb has a relatively higher hazard index than zinc. Thus, the major risk or threat at the study area Pb.

3.2.3 Cancer Risk (Cr) of heavy metals in water, and soil samples

The data for the cancer risk of Pb in water and soil of the study area was within the range (10^{-6}

to 10^{-4}) USEPA (2011) of predicted lifetime risk for cancer-causing substances

4. CONCLUSION

Results obtained for water samples from this study were above regulatory standard for permissible limit of 0.01mg/l stipulated by WHO, PDR, and NIS. This shows that there was lead contamination in water samples. However, all samples analyzed revealed non contamination by zinc. The soil of the study area was not contaminated by any of the poisonous metals under study, while mercury and cadmium were undetectable in all samples.

All Ecological indices revealed non pollution of samples by metals. However, routine evaluation on the concentrations of poisonous metals around the abandoned mining site.

Poisonous metal contamination by lead at very increased levels ($\times 10$) order of magnitude compared to regulatory limit is also an issue of concern.

The EDI of Pb and Zn in the analyzed soil samples were below the oral reference dose of Pb and Zn respectively, this is an indication that the ingestion, inhalation or exposure to the soil by the populace is within the safe limit which may not result to health risk or toxicity.

Effective water purification methods are highly recommended as a way of preserving the health

of the residents of the host community to the abandoned Lead-Zinc mining is preserved.

We also recommend that the levels of this potentially toxic metals be kept in close check to prevent the probability of impacting the health of the people living around the mining area.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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