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Environmental and Health Risk Assessment of Heavy Metals in Water and Sediment along River IBI Trough

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ABSTRACT:

The study evaluated the environmental and health risk associated with heavy metals in river Ibi, Taraba state. The concentrations of cations such as Cd, Cr, Cu, Fe, and Zn were determined by ICP-OES (model Optima 4300 DV; PerkinElmer Life and Analytical Sciences, Shelton, CT, USA) using the standard procedure (APHA, 1995). The instrument is equipped with a cross-flow nebulizer, Scott spray chamber, echelle grating, and segmented array charge-coupled device detector. The result shows the presence of the following heavy metals; Fe, Zn, Cu, Pb, Cd, Cr, As, and Hg. The concentration of Fe varies between 20.829 ± 9.728 ppm to 39.178 ± 7.427ppm, while that of Zn in water at Ibi varies between 5.951 ± 2.779 ppm to 11.193 ± 2.121 ppm, Hg ranging from 0.002 ± 0.000 ppm to 0.004 ± 0.000 ppm, Cu varies between 3.409 ± 1.592 ppm to 6.413 ± 1.216 ppm in the water samples across all the sampling locations in Ibi. Also, the concentration of Cd in water at the river Ibi varies between 0.072 ± 0.014 ppm to 0.093 ± 0.038 ppm ,all these elements Fe, Zn, Cu, Cd, and Hg had higher concentrations above the acceptable limits recommended by WHO (2011). The concentration of Cr, Pb, and As in water from river Ibi had low concentrations respectively. Cr, varies between 0.001 ± 0.001 ppm to 0.002 ± 0.000 ppm, Pb varies between 0.025 ± 0.001 ppm to 0.051 ± 0.030 ppm, the concentration of As in water at the river Ibi varies between 0.020 ± 0.002 ppm to 0.026 ± 0.010 ppm in the water samples across all the sampling locations in river Ibi. Results for the analyzed heavy metal concentrations in sediment samples at the entire sampling site in Ibi revealed the concentration of Fe was highest at I site 2 while the lowest was observed at I site 1. For Zn, the values ranging from 22.004±10.276 ppm to 41.388±7.847 ppm. The value of Cu ranges from 6.744±3.150 ppm to 12.686±2.405 ppm. For Pb 0.022±0.010 ppm to 0.041±0.007 ppm while for Cd, the concentration ranges from 0.029±0.013ppm to 0.054±0.010ppm, the concentration of Cr ranges from 1.531±0.715 ppm to 2.881±0.546 ppm. Result for As indicated the concentration range at the different sites ranges from 0.060±0.028ppm to 0.113±0.021ppm. For Hg, the concentration ranges from 0.009±0.037 to 0.016±0.032 ppm. However, there is no significance in the concentration levels in the levels of Fe, Zn Cu in water samples from the two rivers. The result of the average concentration of heavy metals in water samples obtained from river Ibi shows the concentration varies between 70.003±22.85ppm to 0.0118±0.03ppm with Fe and Hg having the highest and lowest concentrations respectively. There is significance difference in the concentration of the following heavy metals between the two sampling locations; Zn, Fe, Cr, As, Hg and Cu. The concentrations of almost all the heavy metals analyzed in water across the sampling site posed health risks based on the CDI, HQ and HI method and USEPA criteria (2005). The human health risk assessment indicated that the water from the sampling locations are not recommended for human consumption. Non-healthy risk was determined in sediment; the risk to human health in the river water can be attributed to the dissolution of minerals, trace metals from direct sewage discharge, agricultural runoff, due to bioaccumulation downstream. Therefore, it can be established that the population living in the riverine landscape and using untreated surface water for drinking are vulnerable to the health risk from pollution due to heavy metals. Proper monitoring in the area should be implemented to control the pollution and to identify alternative sources of drinking water. Government should enforce a law that will ensure provision of wastewater treatment plants particularly at the lower point of the river where effluents are discharged into the river

Keywords: heavy metals, water, sediments, pollution, contamination, environmental, health risk.

Introduction

Heavy metals represent a distinct category of naturally occurring elements that persist in the environment over extended periods without undergoing biodegradation (Kanamarlapudi *et al*., 2018). Their introduction into the environment can be attributed to either natural processes or human activities (Emmanuel *et al*., 2023). Naturally occurring heavy metals are intrinsic to the environment, originating from the weathering of metal-bearing rocks and volcanic activity. Conversely, human-related sources encompass various industrial, mining, and agricultural practices (Dixit *et al*., 2015). Activities such as mining, smelting, industries, irrigation, urbanization, transportation, and the use of fertilizers have led to significant quantities of heavy metal contamination in the soil (Chaoua *et al*., 2019). Despite their persistence, heavy metals exert adverse effects on living organisms (Otitoju *et al*., 2020), manifesting as acute or chronic issues and posing a substantial threat to biota (Iornenge *et al*., 2024). The accumulation of heavy metals in marine environments has become a pressing concern due to global industrialization and human activities (Javed and Usmani, 2016). These metals infiltrate oceans through sources such as river inflow, atmospheric deposition, and human actions. Once in the ocean, heavy metals tend to settle within underlying sediments, posing risks as they accumulate in exposed biota (Emmanuel *et al*., 2023). Adverse health outcomes related to heavy metal exposure include growth inhibition, cancer, organ impairment, nervous system damage, and mortality at high concentrations (Yepe *et al*., 2018). Notably, copper, zinc, nickel, and manganese pose threats at elevated levels, while mercury, cadmium, lead, and arsenic exhibit toxicity even at low concentrations (Uluozlu *et al*., 2017). These pollutants negatively impact the air, water, soil, and living organisms. Exceeding permissible limits of heavy metal absorption can lead to severe health problems in humans (Akcali and Kucuksezgin, 2011; Iornenge *et al*., 2024). Certain metals like mercury and lead can induce autoimmune diseases that target the body's immune cells, resulting in conditions such as rheumatic calcification, kidney disorders, circulatory and nervous system complications, and developmental brain damage (Dural *et al*., 2017). It's crucial to recognize that the effects of heavy metals are not solely determined by their concentrations within living organisms. Instead, the impact varies based on the species of the organism and the specific characteristics of the metal ions (Hajeb *et al*., 2019). This is why maximum concentration limits are established for nutrients and food items cultivated in drinking water, soil, and sea, as these are frequently consumed (Turkmen *et al*., 2019).

Study area

Ibi is a local government in Taraba state, east-central Nigeria, on the south bank of the Benue River, opposite the mouth of the Shemankar River. Ibi lies on both bank of River Ibi; within latitudes 5°65`N and longitudes 9°36`E, 8°36`E (Wikipedia, 2009). Most of the inhabitants of river Ibi are normally engaged in fishing. Ibi is a collecting point for sesame seeds and soybeans.

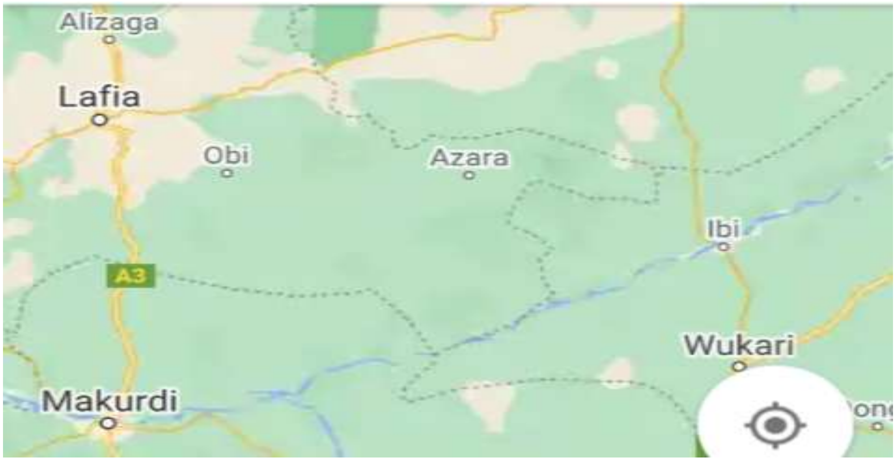

Figure 3.0: Map showing River Benue and River Ibi (Source: google maps/retrieved 2022)

Sample Collection

Both water and sediment samples were collected from five (5) sites along river Ibi 100m apart. 10-L sample (0-20 cm below the surface) were collected two times into glass sample bottles. Surface sediments were sampled in all cases to approximately 5-cm depth using a Van Veen grab (25 cm^2). Three replicates 10m apart, were randomly collected and pooled as one sample for each site on the same day (Di *et al*., 2014). Approximately 1.5 kg of the pooled wet sediment was placed in an aluminum foil bag, marked and transferred to the laboratory.

Materials and reagent

All materials, equipment and reagent used for this study were of analytical standard

Sample preparation and extraction

Water samples were filtered through 0.45µm fiber glass filters (Whatman) to remove suspended materials. Sediment samples were air dried and then sieved through a 250 µm stainless steel mechanical shaker. water and sediment samples was done according to the method developed by Therdteppitak and Yammang (2002) with some little modifications.

Determination of heavy metals in water and sediments samples

The water and sediment samples were digested using concentrated Analar Nitric acid according to Zhang (2007). The heavy metal analyses were done in the laboratory within 2 to 3 weeks of the sample collection. The concentrations of cations such as Cd, Cr, Cu, Fe, and Zn were determined by ICP-OES (model Optima 4300 DV; PerkinElmer Life and Analytical Sciences, Shelton, CT, USA) using the standard procedure (APHA, 1995). The instrument is equipped with a cross-flow nebulizer, Scott spray chamber, echelle grating, and segmented array charge-coupled device detector.

Principles: The fundamental principle underlying the operation of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) revolves around the unique energy emissions exhibited by various elements in a sample. Depending on the concentration of heavy metals present, each element emits energy at distinct wavelengths. However, it's common practice to select a single wavelength for each element based on the intensity of the emitted energy. The energy intensity emitted at this chosen wavelength is directly proportional to the concentration of the specific element within the sample.

Consequently, it becomes feasible to determine and quantify the concentration of the targeted element in the sample by comparing it to a reference standard using a calibration curve. Throughout the analysis process, a multi-elemental solution (Spex Certiprep, WP-15-500, from Spex, Metuchen, NJ, USA) was employed for calibration purposes. In addition, a process blank was meticulously prepared and analyzed alongside the actual samples. This blank serves to account for any potential matrix effects and is factored into the analysis to ensure accuracy and reliability (Subrata, 2020).

Statistical analysis

All the results were statistically analysed using single factor ANOVA and Least Significant Difference (LSD) test was performed to determine the location of significant differences.

Governing equations for health and environmental risk assessment

According to the USEPA, "a human health risk assessment is the process to estimate the nature and probability of adverse health effects in humans who may be exposed to chemicals in contaminated environmental media, now or in the future" (USEPA, 2016). Environmental Pollutants such as Heavy metals were selected in this study. The health risk assessment of each of these chemical contaminant in water is based on the estimation of the risk level. The methods delineated by the USEPA (USEPA, 2016) have been used to estimate the average chronic daily intake (CDI) from direct ingestion and dermal absorption routes, respectively. The governing equations are as follows:

Estimation of daily intake

$$\text{CDIingestion} = \frac{\text{Cw x IR x EF x ED}}{\text{Bw x AT}} \ldots\ldots\ldots\ldots 1$$

$$\text{CDIdermal} = \frac{\text{Cw x SA x ET x EF x ED x CF x ABS}}{\text{Bw x AT}} \ldots\ldots\ldots\ldots 2$$

CDI values were calculated to be utilized for both carcinogenic and Non carcinogenic risk analysis for heavy metals while that of pesticide residue was just for non-carcinogenic risk analysis

The hazard quotient (*HQ*) is an estimate of the toxicity potential posed by an element from direct ingestion or dermal absorption routes, which can be calculated using the relation:

$$HQingestion/dermal = \frac{\text{CDIingestion/dermal}}{\text{RfDingestion/dermal}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

where *RfDingestion/dermal* represents oral/dermal reference dose (mg/kg/day) (USEPA, 2016) of each contaminant under consideration. In general, *RfD* is an approximate estimate of daily exposure to the human (including sensitive subgroups) that is likely to have any noticeable risk of harmful effects during a lifetime (USEPA, 2016). The *RfD* estimate may have an uncertainty spanning perhaps an order of magnitude.

Hazard Index

The hazard index (*HI*) is the overall potential for non-carcinogenic effects posed by more than one contaminant via ingestion or dermal pathway, since more than one toxicant is present, the interactions are considered. The toxic risks due to potentially hazardous substances present in the same media are assumed to be additive. The HQs may then be summed to arrive at the overall toxic risk, the Hazard Index (Zeng *et al.*, 2010) which can be estimated from the relation:

$$HIingestion/dermal = \sum \text{HQingestion/dermal} \ldots\ldots\ldots\ldots\ldots 4$$

If, HQ>1, it represents adverse non-carcinogenic effects of concern while HQ<1 represents acceptable level (no concern).

Carcinogenic risk (*CR*) associated with the ingestion pathway can be estimated using the formula:

$$CRingestion = CDIingestion * CSFingestion \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 5$$

Pollution load index

Tomlinson first described the PLI, which is a comprehensive measure of the pollution by more than one element; it is expressed, as follows:

$$\text{PI} = \frac{\text{Cn}}{\text{GB}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots 9$$

$$\text{PLI} = \text{n}\sqrt{\text{PI1}x\text{PI2x} \ldots \text{Pin}} \ldots\ldots\ldots\ldots\ldots\ldots 10$$

where PI is the single pollution index, GB values of the geochemical background (mg/kg), and Cn is the content of heavy metal in soil (mg/kg). Additionally, n is the number of analyzed elements. PLI is the pollution load index of a sampling site and n is the number of evaluated elements.

Geoaccumulation Index (Igeo)

The Igeo allows for the assessment of PTE sediment contamination and can be used to evaluate the environmental pollution status compared with background values (Corami *et al*., 2020). The Igeo is calculated by Equation (6):

$$\text{Igeo} = \frac{\text{Log2(Cn)}}{\text{1.5 (Bn)}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots 11$$

where Cn is the content of elements in the sediment samples, Bn is the concentration of geochemical background for the same elements (n) and factor 1.5 is the background matrix correction factor due to lithological variations.

Results and discussion

Results

Heavy Metal Concentrations in Water Samples from river Ibi

The result of heavy metal concentrations in water samples from river Ibi is presented in Table 4.2 below. The result shows the presence of the following heavy metals; Fe, Zn, Cu, Pb, Cd, Cr, As, and Hg. The concentration of Fe varies between 20.829 ± 9.728 ppm to 39.178 ± 7.427ppm, while that of Zn in water at Ibi varies between 5.951 ± 2.779 ppm to 11.193 ± 2.121 ppm, Hg ranging from 0.002 ± 0.000 ppm to 0.004 ± 0.000 ppm, Cu varies between 3.409 ± 1.592 ppm to 6.413 ± 1.216 ppm in the water samples across all the sampling locations in Ibi. Also, the concentration of Cd in water at the river Ibi varies between 0.072 ± 0.014 ppm to 0.093 ± 0.038 ppm ,all these elements Fe, Zn, Cu, Cd, and Hg had higher concentrations above the acceptable limits recommended by WHO (2011). While the concentration of Cr, Pb, and As in water from river Ibi had a very low concentrations respectively. Cr, varies between 0.001 ± 0.001 ppm to 0.002 ± 0.000 ppm, Pb varies between 0.025 ± 0.001 ppm to 0.051 ± 0.030 ppm, the concentration of As in water at the river Ibi varies between 0.020 ± 0.002 ppm to 0.026 ± 0.010 ppm in the water samples across all the sampling locations in Ibi.

Table 1: Heavy Metal Concentrations in Water Samples from River Ibi

Parameters (ppm)	I SITE 1	I SITE 2	I SITE 3	I SITE 4	I SITE 5	AVERAGE	MRL(ppm) (WHO,2011)
Fe	20.829±9.728[a]	39.178±7.427[b]	22.548±6.004[a]	34.812±9.648[ab]	27.498±14.486[ab]	28.973±9.459	0.30
Zn	5.951±2.779[a]	11.193±2.121[b]	6.442±1.715[a]	9.946±2.756[ab]	7.856±4.139ab	8.2776±20.702	5.00
Cu	3.409±1.592[a]	6.413±1.216[b]	3.690±0.982a	5.698±1.579[ab]	4.501±2.371[ab]	4.7422±1.548	2.00
Pb	0.035±0.007[a]	0.025±0.001[a]	0.033±0.020[a]	0.045±0.001[ab]	0.051±0.030[ab]	0.038±0.013	0.1
Cd	0.074±0.007[a]	0.074±0.007[a]	0.093±0.038[a]	0.077±0.002[a]	0.072±0.014[a]	0.078±0.014	0.005
Cr	0.001±0.001[a]	0.001±0.001[a]	0.001±0.001[a]	0.001±0.000[a]	0.002±0.000[a]	0.0012±0.001	0.05
As	0.020±0.002[a]	0.021±0.002[a]	0.026±0.010[a]	0.020±0.003[a]	0.020±0.003[a]	0.0214±0.004	0.1
Hg	0.004±0.000[a]	0.003±0.000[a]	0.002±0.000[a]	0.003±0.000[a]	0.003±0.000[a]	0.003±0.000	0.002

Results presented as mean ± standard deviation. Results within the same row with the same superscript indicate no significance differences ($p>0.05$) while results with the different superscripts along the same row differ significantly ($p<0.05$)

Heavy Metal Concentrations in Sediment Samples from River Ibi

Results for the analyzed heavy metal concentrations in sediment samples at all the sampling site in Ibi is illustrated in Table 4.4 across the entire site in Ibi. The concentration of Fe was highest at I site 2 while the lowest was observed at I site 1. For Zn, the values ranging from 22.004±10.276 ppm to 41.388±7.847 ppm. The values of Cu ranges from 6.744±3.150 ppm. to 12.686±2.405 ppm. For Pb 0.022±0.010 ppm to 0.041±0.007 ppm while for Cd, the concentration ranges from 0.029±0.013ppm to 0.054±0.010ppm, the concentration of Cr ranges from 1.531±0.715 ppm to 2.881±0.546 ppm. Result for As indicated the concentration range at the different sites ranges from 0.060±0.028ppm to 0.113±0.021ppm. For Hg, the concentration ranges from 0.009±0.037 to 0.016±0.032 ppm.

Table 2: Heavy Metal Concentrations in Sediment Samples From River Ibi

Parameters (ppm)	I SITE 1	I SITE 2	I SITE 3	I SITE 4	I SITE 5	AVERAGE	MRL(ppm) (WHO,2011)
Fe	50.325±23.503[a]	94.659±17.946[b]	54.480±14.506[a]	84.112±23.311[ab]	66.439±35.001[ab]	70.003±22.85	20.00
Zn	22.004±10.276[a]	41.388±7.847[b]	23.821±6.342[a]	36.776±10.193[ab]	29.049±15.303[ab]	30.6076±9,99	5.0
Cu	6.744±3.150[a]	12.686±2.405[a]	7.302±1.943[a]	11.273±3.124[a]	8.904±4.691[a]	9.3818±3.06	2.00
Pb	0.022±0.010[a]	0.041±0.007[bc]	0.023±0.006[a]	0.037±0.105[ab]	0.029±0.015[ab]	0.0304±0.02	5.00
Cd	0.029±0.013[a]	0.054±0.010[b]	0.031±0.008[a]	0.048±0.0135[ab]	0.038±0.019[ab]	0.04±0.02	0.30

Cr	1.531±0.715[a]	2.881±0.546[b]	1.658±0.442[a]	2.56±0.709[ab]	2.022±1.065[ab]	2.1304±0.69	0.50
As	0.060±0.028[a]	0.113±0.021[b]	0.065±0.017[a]	0.101±0.028[ab]	0.079±0.042[ab]	0.0836±0.02	20.00
Hg	0.009±0.037[a]	0.016±0.032[bc]	0.009±0.026[ab]	0.014±0.040[abc]	0.011±0.061[abc]	0.0118±0.03	0.002

Results presented as mean ± standard deviation. Results within the same row with the same superscript indicate no significance differences (p>0.05) while results with the different superscripts along the same row differ significantly (p<0.05)

The average mean concentration of heavy metals from analyzed water samples obtained from river Ibi

The analysis of heavy metals in water samples obtained from both river Ibi as presented in Table 4.1. Result revealed the presence of the following heavy metals; Fe, Zn, Cu, Pb, Cd, Cr, As, and Hg. Result of the average concentration of heavy metals in water samples obtained from river Ibi shows the concentration varies between 28.973±9.459ppm to 0.0012±0.001ppm with Fe and Cr having the highest and lowest concentrations respectively. There is a significance difference in the concentration of the following heavy metals between the two sampling locations; Fe, Zn Cu Pb, Cd, Cr, As, and Hg .

Table 3: The average mean concentration of heavy metals from analyzed water samples obtained from river Ibi

Parameters (ppm)	River Ibi	(WHO,2011)
Fe	28.973±9.459	0.30
Zn	8.2776±20.702	5.00
Cu	4.7422±1.548	2.00
Pb	0.038±0.013	0.1
Cd	0.078±0.014	0.005
Cr	0.0012±0.001	0.05
As	0.0214±0.004	0.1
Hg	0.003±0.000	0.002

Results presented as mean ± standard deviation. Results within the same row with the same superscript indicate no significance differences (p>0.05) while results with the different superscripts along the same row differ significantly (p<0.05).

The average mean concentration of heavy metals from analyzed sediment samples obtained from river Ibi

The analysis of heavy metals in sediment samples obtained from both river Ibi and river Benue as presented in Table 4.2 revealed the presence of the following heavy metals; Fe, Zn, Cu, Pb, Cd, Cr, As, and Hg. Result of the average concentration of heavy metals in water samples obtained from river Ibi shows the concentration varies between 70.003±22.85ppm to 0.0118±0.03ppm with Fe and Hg having the highest and lowest concentrations respectively. There is significance difference in the concentration of the following heavy metals between the two sampling locations; Zn, Fe, Cr, As, Hg and Cu.

Table 4: The average mean concentration of heavy metals from analyzed sediments samples obtained from river Ibi

Parameters (ppm)	River Ibi	(WHO,2011) (ppm)
Fe	70.003±22.85	20.00
Zn	30.6076±9,99	5.0
Cu	9.3818±3.06	2.00
Pb	0.0304±0.02	5.00
Cd	0.04±0.02	0.30
Cr	2.1304±0.69	0.50
As	0.0836±0.02	20.00
Hg	0.0118±0.03	0.002

Results presented as mean ± standard deviation. Results within the same row with the same superscript indicate no significance differences (p>0.05) while results with the different superscripts along the same row differ significantly (p<0.05).

Adult Hazard Quatient (HQ) for Heavy Metal Concentrations in Water via Ingestion Route for Non Carcinogenic Evaluation

Hazard quotient (HQ) values for heavy metal concentrations in water samples in river lbi for non-carcinogenic evaluation via ingestion routes in adult is presented in Table 4.8. The HQ evaluated in water sample at river Ibi ranges between 12.19 to 0.01 with Hg (I site 5) and Cr (I site 2) having the highest and lowest values respectively. The hazard quotient of Fe, Cu, Cd and is greater than 1 across all the sampling sites in river Ibi while Hg greater than 1 at river Ibi. Cr, Zn, Pb and As had a hazard quotient lesser than 1 across all the sampling locations in river Ibi a there HQ's are greater than 1 at river Ibi site 3, 4 and 5.

Table 5: Adult HQ Values for Heavy Metal Concentrations in Water via ingestion Route for Non Carcinogenic Evaluation

Parameters	Fe	Zn	Cu	Pb	Cd	Cr	As	Hg
I site 1	0.84	0.56	2.4	0.28	2.09	0.01	0.04	0.06
I Site 2	1.58	1.05	4.52	0.2	2.09	0.01	0.03	0.03
I SITE 3	0.91	0.61	2.6	0.27	2.62	0.01	0.02	1.59
I SITE 4	1.40	0.93	4.01	0.360	2.170	0.009	0.029	5.18
I SITE 5	1.11	0.74	3.17	0.411	2.029	0.019	0.03	12.19

Hazard Quotient (HQ) >1 implies health risk**.** Where, I site: Ibi site

Adult HQ Values for Heavy Metal Concentrations in Water via Dermal Route for Non Carcinogenic Evaluation

Hazard quotient (HQ) values for heavy metal concentrations in water samples in river lbi for non-carcinogenic evaluation via dermal routes in adult is presented in Table 4.9. The HQ in water samples at the various sampling locations at river Ibi ranges between 54.531 to 0.017 with Hg (I site 5) and As (I site 3) having the highest and lowest values respectively. The hazard quotient of Fe, Zn and Cu is greater than 1 across all the sampling sites in river Ibi. Pb, Cr, Cd, and As had a hazard Quotient lesser than 1 across all the sampling locations in river Ibi. Ibi at site 1 and site 3, however, there HQ's are greater than 1 at river Ibi site 3, 4 and 5.

Table 6: Adult HQ Values for Heavy Metal Concentrations in Water via Dermal Route for Non Carcinogenic Evaluation

Parameters	Fe	Zn	Cu	Pb	Cd	Cr	As	Hg
I SITE 1	0.7989	1.3315	1.6950	0.1790	0.0662	0.0358	0.0358	0.2521
I SITE 2	1.5027	2.5044	3.1886	0.1279	0.0662	0.0358	0.0268	0.1261
I SITE 3	0.8649	1.4414	1.8347	0.1688	0.0832	0.0358	0.0179	7.0968
I SITE 4	1.3353	2.2254	2.8331	0.301	0.0689	0.0358	0.0268	23.1434
I SITE 5	1.0547	1.7577	2.2379	0.2608	0.0644	0.0716	0.0268	54.5306

Hazard Quotient (HQ) >1 implies health risk**.** Where; I site: Ibi site

Hazard Index for Adults in Non Carcinogenic Evaluation of Heavy Metal Levels at different collection sites

The evaluated hazard index (HI) in adult for non-carcinogenic evaluation for heavy metals at different sampling sites via dermal and ingestion route is presented in Table 4.10. The result of the analysis shows all the HI are above 1 thus indicating toxicity. The evaluated HI dermal of samples from river Ibi ranges between 60.13 to 4.75 with site 5 and site 1 having the highest and lowest HI respectively. Evaluated HI via the ingestion routes for water samples collected in river Benue ranges between 25.39 to 15.87 with site 1 and 3 having the highest and lowest HI respectively while that of samples obtained at river Ibi ranges between 20.90 and 9.96 with site 5 and 1 having the highest and lowest HI's respectively.

Table 7: Hazard index for Adults in Non Carcinogenic Evaluation of Heavy Metal levels at different Collection sites

Total hazard index of heavy metals at different site			
	Dermal	Ingestion	Total hazard index
I SITE 1	4.75	9.96	14.71
I SITE 2	7.88	12.7	20.58
I SITE 3	11.70	10.20	21.90

I SITE 4	30.13	16.43	46.56
I SITE 5	60.13	20.90	81.03

Note; Hazard Index (HI) and Hazard Quotient (HQ) >1 implies health risk**.** Where, and I site: Ibi site

Children HQ Values for Heavy Metal Concentrations in Water via Ingestion Route for Non Carcinogenic Evaluation

Result of hazard quotient (HQ) values for heavy metal concentrations in water samples obtained from river Ibi for non-carcinogenic evaluation in children via ingestion is presented in Table 4.11. For river Ibi, HQ values for I site 1 ranges between 2.24 to 0.01 with Cu and Cr having the highest and lowest HQ values respectively. HQ values for I site 2 ranges between 4.09 to 0.01 with Cu and Cr having the highest and lowest HQ values respectively. HQ values for I site 3 ranges between 2.36 to 0.01 with Cu and Cr having the highest and lowest HQ values respectively. I site 4, the HQ values ranges between 3.64 to 0.01 with Cu and Cr having the highest and lowest HQ values respectively while that of I site 5, HQ values ranges between 2.36 and 0.02 with Cu and Cr having the highest and lowest HQ values respectively.

Table 8: Children HQ Values for Heavy Metal Concentrations in Water via Ingestion Route for Non Carcinogenic Evaluation

Parameters	Fe	Zn	Cu	Pb	Cd	Cr	As	Hg
I site 1	0.78	0.52	2.24	0.26	1.95	0.01	0.04	0.05
I Site 2	1.43	0.95	4.09	0.18	1.89	0.01	0.03	0.03
I SITE 3	0.82	0.55	2.36	0.24	2.38	0.01	0.02	1.44
I SITE 4	1.27	0.85	3.64	0.33	1.97	0.01	0.02	4.70
I SITE 5	1.01	0.67	2.88	0.37	1.84	0.02	0.03	11.06

Hazard Quotient (HQ) >1 implies health risk**.** Where, I site: Ibi site

Children HQ Values for Heavy Metal Concentrations in Water via Dermal Route for Non Carcinogenic Evaluation

Results of hazard quotient (HQ) values for heavy metal concentrations in water samples obtained from river Ibi for non-carcinogenic evaluation in children via the dermal routes is presented in Table 4.12. For river Ibi, HQ values for I site 1 range between 2.288 to 0.008 with Cu and Cd having the highest and lowest HQ values respectively. HQ values for I site 2 ranges between 31.886 to 0.268 with Cu and As having the highest and lowest HQ values respectively. HQ values for I site 3 ranges between 18.347 to 0.179 with Cu and As having the highest and lowest HQ values respectively. I site 4, the HQ values ranges between 28.331 to 0.268 with Cu and As having the highest and lowest HQ values respectively while that of I site 5, HQ values ranges between 22.379 and 0.269 with Cu and As having the highest and lowest HQ values respectively.

Table 9: Children HQ Values for Heavy Metal Concentrations in Water via Dermal Route for Non Carcinogenic Evaluation

Parameters	Fe	Zn	Cu	Pb	Cd	Cr	As	Hg
I SITE 1	0.7989	0.5326	2.2882	0.2685	1.9868	0.0089	0.0358	0.0537
I SITE 2	15.0272	25.0437	31.8860	1.2785	0.6623	0.3580	0.2685	1.2605
I SITE 3	8.6485	14.4136	18.3470	1.6877	0.8323	0.3580	0.1790	71.0095
I SITE 4	13.3525	22.2536	28.3310	2.3014	0.6891	0.3580	0.2685	231.5180
I SITE 5	10.5472	17.5774	22.3794	2.6082	0.6444	0.7160	0.2685	545.3903

Hazard Quotient (HQ) >1 implies health risk. Where I site is Ibi site, Fe: Iron; Zn: Zinc; Cu: Copper; Pb; Lead; Cd; Cadmium; Cr: Chromium; As: Arsenic; Hg; Mercury

Hazard Index in Children for Non Carcinogenic Evaluation of some Heavy Metals at Different Collection Sites

The evaluated hazard Index (HI) in children for non-carcinogenic evaluation for heavy metals at different sampling sites via dermal and ingestion route is presented in Table 4.13. The result of the analysis shows all the HIs' are above 1 thus indicating toxicity. The evaluated HI dermal for samples collected from Ibi river ranges between 601.34 to 9.47 with site 5 and site 1 having the highest and lowest HI respectively. Evaluated HI's via the ingestion routes for water samples collected from river Ibi ranges between 18.99 and 9.24 with site 5 and 1 having the highest and lowest HI's respectively.

Table 10: Hazard index in children for non carcinogenic evaluation of some heavy metals at different collection sites

Total hazard index of heavy metals at different site			
	Dermal	Ingestion	Total hazard index
I SITE 1	9.47	9.29	18.76
I SITE 2	78.84	11.51	90.35
I SITE 3	117.02	9.24	126.26
I SITE 4	301.42	14.91	316.33
I SITE 5	601.34	18.99	620.33

Hazard Index (HI) >1 implies health risk.

Geoaccumulation for Heavy Metals in Sediment Samples from River Ibi

Results analysis of geoaccumulation factor for heavy metals in sediments at the various sampling site at river Ibi is presented in Table 4.14. Geoaccumulation of heavy metals in the various site in river Ibi, For I site 1, the geoaccumulation factor ranges between 5.03 to 0.01 with Fe and Hg having the highest and lowest geoaccumulation factors respectively. At I site 2, the geoaccumulation values ranges between 9.46 to 0.01 with Fe and As having the highest and lowest geoaccumulation factors respectively while that of I site 3 ranges between 5.44 to 0.01 with Fe and Hg having the highest and lowest geoaccumulation factors respectively while that of I site 4 ranges between 8.41 to 0.01 with Fe and Hg having highest and lowest accumulation factors respectively. For I site 5, the geoaccumulation factor ranges between 6.62 to 0.01 with Fe and Hg having the highest and lowest geoaccumulation factors respectively.

Table 11: Geoaccumulation for Heavy Metals in Sediment Samples from River Ibi

Parameters	Fe	Zn	Cu	Pb	Cd	Cr	As	Hg
I SITE 1	5.03	2.23	2.67	0.02	0.03	1.53	0.050	0.01
I SITE 2	9.46	4.13	1.27	0.05	0.05	2.80	0.01	0.02
I SITE 3	5.44	2.38	2.73	0.02	0.03	1.65	0.06	0.01
I SITE 4	8.41	3.67	1.12	0.04	0.05	2.56	0.01	0.01
I SITE 5	6.62	2.91	2.89	0.02	0.04	2.02	0.07	0.01

Where, M site: Benue site and I site: Ibi site. <0; Unpolluted, 0–1; Pristine to moderately contaminated, 1–2; moderately contaminated, 2–3; moderately to strongly contaminated, 3–4; strongly contaminated, 4–5; strongly to extremely strongly contaminated, >5; extremely strongly contaminated

Discussion

Because of the bioaccumulation and biomagnification characteristics of heavy metals in the food chain, heavy metal pollution of the environment is directly linked to a risk to public health (Hussain *et al.*, 2012). The analysis of heavy metals in water, sediments and fish samples obtained from both river Ibi and river Benue as presented in various individual tables revealed and confirmed the presence of the following heavy metals; Fe, Zn, Cu, Pb, Cd, Cr, As, and Hg. Consuming sea- foods contaminated with heavy metals can seriously deplete the body of some vital nutrients, impairing psychosocial functioning, reducing immune system defenses, increasing the risk of upper gastrointestinal cancer, and causing intrauterine growth retardation. It can also result in other severe health issues including renal illness, nerve damage, impaired mental function, heart disease, bone fractures, and even death (Otitoju *et al*., 2014). Due to their significant accumulation in the food chain, toxicity, nonbiodegradable nature, and environmental permanence, environmental managers and policy makers have been concerned about them for the past 20 years. (Badr *et al.,* 2020). The result of metals analysis in the River Ibi showed that the mean value of iron (Fe) in water and sediment was above WHO (2011) set standards. Fe is naturally present in the earth's crust in high concentrations, and its abundance in soil that runs off may have a big effect on surface water (Asare *et al.,* 2018). High concentration of Fe in surface water as recorded in this work is typical of a tropical aquatic ecosystem as reported by Iornenge *et al*. 2024. The mean concentration of Fe obtained in this study is in consonance with the findings of Nwankwoala and Ekpewerechi (2017) in Aba River. The sources of Fe in this water body could be attributed to domestic wastes, air particles, insecticide, and refuse from dumpsites which were carried into the stream as runoff (Iornenge *et al*., 2024).

Zn is essential to life since it performs several physiological tasks for cells, but when it rises over a certain threshold, it may be harmful to humans and other living things. (Edokpayi *et al*., 2017). The values of Zn obtained in both surface water and sediment sample from river Ibi pose danger since it is not within the permissible acceptable limit of Zinc by WHO (2011) required for surface water and sediment. Arsenic is associated with various diseases, including skin cancer, circulatory disorders, heart failure, chronic poisoning, extreme fatigue, and cancer. It accumulates by binding to thiol groups in the liver and then in tissues rich in keratin (Habibun *et al*., 2016). Hexavalent chromium, which is more toxic, alters human physiology, accumulates in the food chain and causes severe health problems ranging from simple skin irritation to lung cancer (Habibun *et al*., 2016). Exposure to some metals, such as mercury and lead, causes autoimmunity diseases that attack their own cells in the immune system. This may lead to conditions such as rheumatic calcification, kidney disorders, circulatory and nervous system problems, and damage to the fetal brain (Otitoju *et al*., 2023). High concentrations of Hg causes the impairment of pulmonary and kidney function, chest pain and dyspnea (Habibun *et al*., 2016). The concentrations of Chromium (Cr) as shown revealed that the mean values obtained in surface water and sediments were within WHO (2011) set standard limit. This is in conformity with the findings of Ighariemu *et al.* (2019) in Ikoli Creek and Nwankwoala and Angaya (2017) in New Calabar River, Eastern Niger Delta. One potentially harmful metal that can cause mutations in humans and other living things is Cr. It can affect both the neurological and circulatory. The increase in value of Cr above the recommended limits can lead to damage of sensitive organs like liver, kidney and brain (Bazrafshan *et al*., 2015). The low Cr levels observed in both surface water and sediment samples are an indication that the river is not polluted with Cr ion, attributed to fewer anthropogenic activities within the water source.

The analysis of water and sediment samples at River Ibi revealed the presence of Lead (Pb) in both water and sediment, with mean values that are below WHO (2011) standard limits. Because lead has detrimental effects on living cells, it is a non-essential metal that should never be present in any level in aquatic environments (Mgbemena, 2014). The low concentration of Pb observed in the river Ibi is typical of area with low anthropogenic activities. The low concentration of Pb observed in this study is similar to the finding of Bhuyan *et al.* (2019) in Old Brahmaputra River, Bangladesh, but is in variance with the report of Otene and Alfred-Ockiya (2019) in Elechi. Creek. the presence of Cd in the aquatic system (water and sediment) is of great concern due to its non-biodegradable and persistent nature in an ecosystem (Badr *et al*., 2020). Although cadmium is not necessary for life, even minute amounts of metal can have harmful effects such as food poisoning, which can alter human arteries and kidneys. (Hussain *et al.,* 2021). Therefore, it is good to avoid food or water that contains Cd (Ipeaiyeda and Onianwa 2011). The presence of Cd in the river Ibi could be attributed to fertilizer applied in the nearby farm lands which may have been washed into the water body. The low concentration of Cd as observed in sediment samples of the river Ibi is similar to the values reported by Ighariemu *et al.* (2019) in IkoliCreek, Bayelsa State, but varies from the higher Cd levels observed by Howard *et al.* (2006) in an oilfield in Niger Delta. The high Cu concentration obtained in water and sediment samples at river Ibi is not similar to the finding of Mgbemena (2014) in Aba River, Although copper is one of the essential metals required for human metabolic processes, drinking water or eating food that has higher than allowed levels of copper in it can have detrimental effects on the nervous and circulatory systems (Hussain *et al*., 2021). The average mean concentration of heavy metals Fe, Zn, Cu, Cd, and Hg in sediments and water obtained from river Ibi are above WHO (2011) set maximum permissible limits of heavy metals in sediments and water.

Non-Carcinogenic Risk Evaluation in Adults and Children (HQ and HI)

In this study, non-carcinogenic risk was determined by Estimating the Daily intake index (EDI), which represents the daily exposure of a population to contaminants, Hazard Quotient (HQ), to estimate the non-carcinogenic risk of toxic elements, and cumulative Hazard Index (HI). Exposures to multiple chemicals may contribute to increased health risks. Therefore, a measure of cumulative risk, HI is estimated. HI represents the overall potential for non-carcinogenic effects posed by more than one contaminants via ingestion or dermal pathway, which can be estimated using equation (Vetrimurugan *et al*., 2017). Since more than one toxicant is present, the interactions are considered. The toxic risks due to potentially hazardous substances present in the same media are assumed to be additive. The HQs may then be summed to arrive at the overall toxic risk, the Hazard Index (Zheng *et al.,* 2010). The studied exposure pathways were ingestion and dermal absorption in children and the adult population; the receptors were categorized in children (<6 years old) and adults (>30 years old). Non carcinogenic risk for adults and children were calculated based on reference dose (RfD) values. These results for the ingestion and dermal pathways are all presented in terms of Hazard Quotients (HQs) and hazard index (HI). When HQ and HI values are less than 1, there is no obvious risk to the population, but if these values exceed one, there may be concern for potential non-carcinogenic effects (United State Environmental Protection Agency, 2004). For both adult and children population, the calculated HQ values for majority of the heavy metals evaluated from river Ibi were greater than 1, thus indicating non-carcinogenic risk. However, the HQ values for children in water from Ibi were far greater than adult HQ values. Findings from this study are in consonance with findings of Ekere *et al*., 2014 who reported HQ greater than 1 for some heavy metals. These findings are also in consonance with findings of Ayantobo *et al*., (2014), and Maigari *et al*., (2016). In this study, all the HI values calculated for heavy metals consumption through water by children and adults were all above unity (greater than 1), indicating that high toxic risks are associated with them. HI values for adult exposure through dermal routes exposure are significantly lower compared to the ingestion exposure route. Comparatively, HI values for adult were slightly below that of the HI of children. Findings from this report are not similar to that of Prassad *et al*., 2020 who reported a high HI among heavy metals evaluated in river Ganga in India.

Geoaccumulation Factor of Heavy Metals in Water

Geoaccumulation index (Igeo) values are summarized in Table. The values and categorization of geoaccumulation is presented in Table <0; unpolluted, 0-1; pristine to moderately contaminated, 1-2; moderately contaminated, 2-3; moderately to strongly contaminated, 3-4; strongly contaminated, 4-5; strongly to extremely strongly contaminated and >5 extremely strongly contaminated. The Igeo values of Cu, and Cr at all sampled locations were less at moderately to strongly contaminated, Pb, Cd, As, and Hg according to Igeo value categorization depict a pristine to moderately contaminated across all the site from river Ibi. Zinc (Zn) was strongly to extremely contaminate across the entire sampling site at the various sampling locations in river Ibi. Fe had the greatest influence on the contamination of the river sediments, since they present the highest contamination values of the Igeo.

Conclusion

The concentrations of the following heavy metals were determined; Fe, Zn, Cu, Pb, Cd, Cr, As, and Hg. The concentrations of almost all the heavy metals analyzed in water across the sampling site posed health risks based on the CDI, HQ and HI method and USEPA criteria (2005). The human health risk assessment indicated that the water from the sampling locations are not recommended for human consumption. Non-healthy risk was determined in sediment; the risk to human health in the river water can be attributed to the dissolution of minerals, trace metals from direct sewage discharge, agricultural runoff, due to bioaccumulation downstream. Therefore, it can be established that the population living in the riverine landscape and using untreated surface water for drinking are vulnerable to the health risk from pollution due to heavy metals. Proper monitoring in the area should be implemented to control the pollution and to identify alternative sources of drinking water. Government should enforce a law that will ensure provision of wastewater treatment plants particularly at the lower point of the river where effluents are discharged into the river

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