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Investigation of heavy metals in water and sediment from contamination sites between Rimi and Kabawa axis, Lower Benue River, Ibi, Taraba, Nigeria

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Abstract
This study investigated heavy metals in water and sediment from contamination sites between Rimi and Kabawa axis by Lower Benue River, Ibi, Taraba state. Heavy metal levels was investigated using atomic absorption spectrometer (AAS) Bulk Scientific Model 210 VGP using spectrometer techniques. The highest concentration of Zinc (Zn) in September/October, was (0.1667 mg/kg) while Cadmium (Cd) recorded a lower mean concentration value (0.0013 mg/kg) in December/January. Concentration ranking profile in water was found to be Zn>Pd>Cu>Cd. Results of heavy metal in sediments during the study from September 2022 to February 2023 revealed significant difference (p<0.05) among metals studied. Ranking profile in sediment was found to be Zn>Pb>Cu>Cd. Zinc (Zn) value show the higher concentration (2.2667 mg/kg) in November and recorded lower value (1.1000 mg/kg) for the month of January and February. Value recorded for Cadmium (Cd) was observed to be lower than those recorded other metals. Higher Cadmium (Cd) values (0.0020 mg/kg) were observed to be high in September, October and January and low value (0.0013 mg/kg) recorded for November, December and February. Mean heavy metals concentrations between water and sediment during the study showed sediment recorded higher value for Zinc (Zn) (2.2667 mg/kg) in November while lower value was recorded for Cadmium (Cd) (0.0013 mg/kg) in November, December and January. Mean concentrations of metals on water showed zinc (Zn) reported higher in September (0.1667 mg/l), October (0.1667 mg/l), November (0.1334 mg/l) and December (0.1334 mg/l), compared to January and February (0.1000 mg/l). The concentration of Lead (Pb) in water recorded higher value in December (0.5147 mg/l), January, November (0.3910 mg/l), and February (0.3497 mg/l), compared to October (0.1647 mg/l), and September (0.1237 mg/l). Result of important physico-chemical parameters measured in water samples during the study period showed total dissolved solid (TDS) recorded the higher value (134.25 mg/l) compare to other parameters**.** There were significant difference (p<0.05) in metals Variation between water and sediment. Findings from this study showed levels of metals were within WHO safe range and USEPA in drinking water and sediments except lead (Pb) values which was above the safe level. Thus, there is need for continuous monitoring of the contamination sites at Rimi and Kabawa districts by Lower River Benue and the general water body at large. If not controlled, it will contribute to general contamination of the river at Ibi and hinder its use for both commercial and household purposes.

Keywords: Heavy metals water, sediments, Lower Benue river, Taraba

1. Introduction

Aquatic ecosystem is a “receiver” of almost everything including heavy metals Contamination. Heavy metal is a growing problem worldwide currently reaching an alarming rate [21]. Estuaries and inland water bodies are major sources of drinking water in Nigeria, but often contaminated by urban population and industrial establishment [14]. We have various sources of heavy metals; some originates from manmade events like draining of sewage and dumping of wastes, conversely, metals occurring in small amounts naturally enters aquatic ecosystems through leakage, airborne dust and forest fires [3]. Other sources of contamination in our water ways include human activities such as, domestic waste, agriculture, aquaculture, shipping, block molding, fishing, and Industrial effluent are mainly discharge directly or indirectly through seepage into our waters with little or no treatment [13]. Since metals cannot be readily degraded, they are deposited and incorporated in water, sediments and aquatic organisms, resulting in contamination of water bodies [17].

Concentration of metallic contaminant are greatest near towns with urban storm water project runoff, landfills, leachates, boating activities [4]. Due to the aforementioned industrial contamination of water ways have advanced as major encounter in densely populated countries including Nigeria [14]. Presence of heavy metals in water might profoundly affect microalgae which constitutes main sources of food for bivalve, mollusks, zooplankton (rotifers, copepods, and brine shrimps) [25]. Also, bio concentration and magnification lead to high toxicity of metals in organisms, even when the exposure rate is low. Under such situation, toxicity of a moderately toxic metal could be enhanced by synergism resulting in decline in the fishery [5]. Contamination in form of heavy metals and crude oil spills in aquatic food web poses danger to public health and could a long term effect on ecological integrity and man [23, 15]. All wastes have prospect of causing environmental harm that will translate to global challenges, pressure of population growth produces stress causes environmental degradation especially in form of solid waste contaminants, affects water which life depends [6].

Common waste found in refuse dumps includes heavy metals, which enters into environment from both natural and manmade sources, unclean food source or agricultural products, soils and other components through water, air and soil [29, 15].

Sediments are major sinks of heavy metal released to the environment and accumulates from waste; municipal, medical/pharmaceutical, unlike other organic contaminants they are not readily oxidized to carbon (IV) oxide by microbial action [22]. Most metals do not undergo microbial or chemical degradation, and their total concentrations in soils persists for a long time after introduction [31]. Therefore the deployment of water and sediment as indicator of heavy metal contamination in aquatic environment, its suitability for human utilization is very important and have been documented [22, 27, 14].

Materials and Methods

Study Area

This study was conducted at Lower River Benue, ibi, between Rimi and Kabawa axis located in Taraba south bordering Shandam town of Plateau state. It is found within Latitude 8°18'N and 9° 51'E about 350 meter below sea level. The axis of the river receives effluents discharge from Agricultural fields, Block molding cottage industries and huge dump sites just by the river. The axis of the river is also utilized for commercial activities such as fishing, domestic purposes and as a commercial transportation route. The inhabitant are majorly farmers, fishermen and traders.

Samples collection

Water

Water samples were collected at 30cm depth below the water surface and acidified to pH 1.5 with Five (5) ml concentrated nitric acid *in situ* after collection to keep the metals in solution [9]. Afterwards, seal and kept in containers earlier washed and rinsed in distilled water. Sample was collected monthly for six (6) months between September 2022 and February 2023. All samples were transported to laboratory and kept in deep freezer at -5 °C, prior to further analysis method described by (Wangboje *et al*., 2014).

Sediment

Sediment sample were obtained using bottom grab sampler from a determined point of 50-100 cm and packed in polythene bags previously soaked in aqueous HNO_3 acid and rinsed in purified water. Samples were air-dried at temperature of 60 °C in moisture extraction oven to obtain constant weight. Thereafter kept in labeled polythene bags prior to digestion and analysis.

Samples digestion

Water

Water sample was allowed to defreeze at room temperature (27 °C) and digestion was carried out using pre-concentrated HNO_3 acid methods [26]. Blank were prepare using the same amount of mixed acids.

Sediment

The oven-dried sediments sample was sieved using a 160 µm mesh size screen. Sediments were weighed and 1 g of each was placed in a 250 ml flask and digested using $HCLO_4$ and HNO_3 (10 ml). Mixture was heated until milky precipitate appears suggesting complete digestion. The precipitate was allowed to cool and made to 25 ml mark in a volumetric flask with distilled water. The digest was kept in a labelled plastic bottle until analysis.

Statistical analysis

Data was presented as mean and standard deviation. Mean was subject to one way analysis of variance (ANOVA) using 9.0 statistical packages for the social sciences (SPSS) 2012 to ascertain significant differences at 5% level of probability. Significant mean were subject to Duncan Multiple Range Test (DMRT).

Results and Discussion

Results of investigation of metals concentrations in water and sediment from two contaminated sites, Rimi and Kabawa axis of Lower Benue River are shown in Table 1 to 4. The samples were collected monthly for six (6) month between September 2022 and February 2023.

Monthly Mean concentrations of heavy metals in water during study period.

Result of concentrations of heavy metals in water during the study are presented in Table 1. The result revealed heavy metals concentration for Zinc (Zn) was higher in September (0.1667 mg/l), October (0.1667 mg/l), November (0.1334 mg/l) and December (0.1334 mg/l), compared to January and February (0.1000 mg/l). While cadmium (Cd) recorded lower value (0.004 mg/l) in water. Cadmium (Cd) concentration in water showed November (0.0043 mg/l) recorded higher level of concentration compared to October, February (0.0020 mg/l) while December, January (0.0013 mg/l) and September (0.004 mg/l) recorded lower concentrations. Lead (Pb) Concentration (0.5147 mg/l), for water was higher in December, November (0.3910 mg/l), and February (0.3497 mg/l), compared to October (0.1647 mg/l), and September (0.1237 mg/l). Copper (Cu) concentrations were lower in September (0.0057 mg/l), December (0.0104 mg/l), and January (0.0177 mg/l), compared to October, November (0.0180 mg/l), and February (0.0204 mg/l).

Monthly mean concentration of heavy metals in sediments during study period

The results of concentrations of metals in sediment during the study is presented in Table 2. Results showed Zinc (Zn) recorded higher concentrations (2.2667 mg/kg) in November and lower value (1.1000 mg/kg) in January and February.

Cadmium (Cd) recorded lower concentrations throughout the study. Cadmium (Cd) values (0.0020 mg/kg) were generally observed to be higher in September, October and January and lower (0.0013 mg/kg). In November, December and February. Lead (Pb) Concentrations in sediment (1.9137 mg/kg) and (1.2347 mg/kg) was observed to be higher in October, November, follow by February (0.5970 mg/kg) compared to September (0.4940 mg/kg), December (0.4730 mg/kg), and January (0.3907 mg/kg). Copper (Cu) values were observed to be lower in September (0.1024 mg/kg), October (0.1100 mg/kg), November (0.1384 mg/kg), compared to February (0.1610 mg/kg), January (0.1737 mg/kg), and December (0.1757 mg/kg).

Comparison of heavy metal variation between water and sediments during the study

Variations of metals between water and sediments during this study period is presented in Table 3. Generally, sediments recorded higher mean concentration (2.2667 mg/kg) for Zinc (Zn) in November while Cadmium (Cd) value (0.0013 mg/kg) was lower in November, December and January. Higher mean value (0.1667 mg/l) for Zinc (Zn) in water was recorded in September and October. While Cadmium (Cd) recorded lower value (0.0013 mg/kg) in December and January. It was also observed that sediments value for Lead (Pb) (1.9137 mg/kg) recorded higher mean in October while Copper (Cu) recorded lower value (0.1024 mg/kg) in September. In water a higher mean value for Lead (Pb) (0.5147 mg/l) was recorded in December. While copper (Cu) value (0.0057 mg/l)
Recorded lower mean for sediments.

Correlation between heavy metal in water and sediments during study period

Correlation results of metals in water and sediments from Rimi and Kabawa axis during the study are presented in Table 4. Results revealed cadmium (Cd) and lead (Pb) reported positive correlation between water and sediment. There was significant difference between lead (Pb) value (0.259 mg/l) in water and cadmium value (0.143 mg/kg) in sediment, there was weak association (negative correlation) between zinc value (-0.037 mg/kg) in sediment and copper value (-0.238 mg/l) in water.

Table 1: Monthly variation of heavy metals (mg/l) in water from Rimi and Kabawa axis during study period.

	Months					
Metals	**SEPT**	**OCT**	**NOV**	**DEC**	**JAN**	**FEB**
W/Cd	0.004±0.0012 [a]	0.0020±0.0012 [a]	0.0043±0.003 [a]	0.0013±0.0007 [b]	0.0013±0.0007 [a]	0.0020±0.0012 [a]
W/Pb	0.1237±0.0355 [a]	0.1647±0.0544 [b]	0.3910±0.2698 [b]	0.5147±0.1088 [a]	0.3910±0.1606 [a]	0.3497±0.1647 [a]
W/Zn	0.1667±0.0334 [a]	0.1667±0.0334 [b]	0.1334±0.0334 [a]	0.1334±0.0334 [b]	0.1000±0.0000 [b]	0.1000±0.0000 [b]
W/Cu	0.0057±0.0024 [a]	0.0180±0.0050 [b]	0.0180±0.0069 [a]	0.0104±0.0024 [b]	0.0177±0.0027 [b]	0.0204±0.0027 [a]

KEY: W=Water. Data are presented as mean±S.E.M. Data with same letters are not significantly different (*p*>0.05).
Significance at (*p*>0.05)

Table 2: Monthly variation of heavy metal (mg/kg) in sediments from Rimi and Kabawa axis during study period.

	Months					
Metals	**SEPT**	**OCT**	**NOV**	**DEC**	**JAN**	**FEB**
S/Cd	0.0020±0.0012 [a]	0.0020±0.0000 [a]	0.0013±0.0013 [a]	0.0013±0.0007 [b]	0.0020±0.0012 [a]	0.0013±0.0013 [a]
S/Pb	0.4940±0.0358 [b]	1.9137±0.5324 [a]	1.2347±0.214 [a]	0.4730±0.0742 [a]	0.3907±0.0207 [a]	0.5970±0.1793 [a]
S/Zn	1.2000±0.3056 [b]	2.2000±0.2082 [a]	2.2667±0.0882 [b]	1.3667±0.0334 [a]	1.1000±0.0578 [a]	1.1000±0.0000 [a]
S/Cu	0.1024±0.0024 [b]	0.1100±0.0296 [a]	0.1384±0.0154 [b]	0.1757±0.0074 [a]	0.1737±0.0169 [a]	0.1610±0.0179 [a]

KEY: S= Sediment. Data are presented as mean±S.E.M. Data with same letters are not significantly different (*p*>0.05).

Table 3: Heavy metal variation between water and sediment during the study period.

	Months						
Metals	**Sept**	**Oct**	**Nov**	**Dec**	**Jan**	**Feb**	**Safe Limit (WHO, 2008)**
W/Cd	0.004±0.0012 [a]	0.0020±0.0012 [a]	0.0043±0.003 [a]	0.0013±0.0007 [b]	0.0013±0.0007 [a]	0.0020±0.0012 [a]	0.05
S/Cd	0.0020±0.0012 [a]	0.0020±0.0000 [a]	0.0013±0.0013 [a]	0.0013±0.0007 [b]	0.0020±0.0012 [a]	0.0013±0.0013 [a]	0.99
W/Pb	0.1237±0.0355 [a]	0.1647±0.0544 [b]	0.3910±0.2698 [b]	0.5147±0.1088 [a]	0.3910±0.1606 [a]	0.3497±0.1647 [a]	0.05
S/Pb	0.4940±0.0358 [b]	1.9137±0.5324 [a]	1.2347±0.214 [a]	0.4730±0.0742 [a]	0.3907±0.0207 [a]	0.5970±0.1793 [a]	35.8
W/Zn	0.1667±0.0334 [a]	0.1667±0.0334 [b]	0.1334±0.0334 [a]	0.1334±0.0334 [b]	0.1000±0.0000 [b]	0.1000±0.0000 [b]	40
S/Zn	1.2000±0.3056 [b]	2.2000±0.2082 [a]	2.2667±0.0882 [b]	1.3667±0.0334 [a]	1.1000±0.0578 [a]	1.1000±0.0000 [a]	121
W/Cu	0.0057±0.0024 [a]	0.0180±0.0050 [b]	0.0180±0.0069 [a]	0.0104±0.0024 [b]	0.0177±0.0027 [b]	0.0204±0.0027 [a]	20
S/Cu	0.1024±0.0024 [b]	0.1100±0.0296 [a]	0.1384±0.0154 [b]	0.1757±0.0074 [a]	0.1737±0.0169 [a]	0.1610±0.0179 [a]	31.6

KEY: W=Water, S= Sediment. Value are presented as mean±S.E.M. Values with different superscript across each column indicates a level of Significance at (*p*>0.05).

Table 4: Correlation of metals between water and sediments during study period

Heavy metals	Cd (water)	Cd (sediment)	Pb (water)	Pb (sediment)	Zn (water)	Zn (sediment)	Cu (water)	Cu (sediment)
Cd (water)	1							
Cd (sediment)	0.143	1						
Pb (water)	0.259	-0.201	1					
Pb (sediment)	0.012	-0.39	-0.028	1				
Zn (water)	0.161	0.171	0.016	-0.244	1			
Zn (sediment)	-0.037	-0.056	-0.215	0.338	0.259	1		
Cu (water)	-0.238	0.096	0.296	0.02	-0.059	-0.296	1	
Cu (sediment)	0.353	-0.334	0.066	-0.066	-0.099	-0.062	-0.396	1

**. Correlation is significant at the 0.01 level (2-tailed).

Metal concentration in water and sediments from Lower Benue River

Contamination of aquatic environment with heavy metals is a worldwide problem due to its persistence and continuous accumulation in the environment [2]. Aquatic organisms are exposed to high levels of heavy metals and fishes are highly sensitive to changes surrounding their environment. Results from this study showed metals are concentrated in sediments than water, this corroborate findings of [1, 8].

Higher concentrations of metals in Sediment occur as result of discharge contaminants into aquatic environment and are absorbed into the sediment [1]. Heavy metals (Zn, Cu, Pb, and Cd) found in water and sediment were lower compared to the [28] safe limit recommend in fresh water. The higher concentration of zinc in October (2.200 mg/kg) and November (2.2667 mg/kg) in sediments may be as result of excessive effluent deposit from contamination into the water from nearby maize fields and petroleum products used in powering rice milling machines and automobiles, additionally, use of boats for transportation across the river may increases concentrations of the metals in water and soil [18]. Zinc (Zn) is essential in animals its deficiency may lead to decreased fertility [25].

Cadmium (Cd) target tissues include liver, placenta, kidney, lungs, brain and bone. Cd poisoning could lead to cancer, anemia .and in fish may causes gills damage [21] result of this study shows that Cd was low in water and sediment compared to WHO permissible limits 0.5 mg/l and 0.99 mg/l [28]. The level of lead (Pb) in this study may be as result of the inhalation of dust particles arising from ongoing bridge project construction. However, level of Pb in water and sediment shown in Table 1 and 2 is below the recommended limit of 35.8 mg/kg [32]. Reports have shown that adults absorbed 35 to 50% of lead (Pb) through drinking water while absorption rate for children may be greater than 50% influenced by factors like age and physiological status., in human body greatest percentage is adsorbed into the kidney, followed by liver and other soft tissues like heart and brain [10].

Copper (Cu) in aquatic environment could result from domestic and agricultural wastes, though it aid body functions and is necessary for synthesis of hemoglobin [25]. Copper (Cu) values reported in this study is less than the 20.00mg/l for water and 31.60 mg/kg for sediments recommended by WHO [28], excessive intake may cause health issue to aquatic life. The result from this present study shows variation from values of metal in water and sediment reported in Ovia River by [14]. Variations may be ascribed to l effluent discharge from domestic waste, runoff from pesticide, fertilizer and diesel accumulated with time [11]. Concentrations of Cd, Cu, Pb, Zn. in river and sediments were generally low during the study.

Correlation of heavy metal between water and sediment during the study

In aquatic environment, sediments have been widely used as environmental indicator for assessing metal contamination [16]. Carriage of metals is a function of the suspended sediment structure and water understanding in natural water [19]. Sediment is an essential part of the river, with the variation of environment [20]. The investigation of heavy metals in water and sediment could be used to assess impacts posed by waste discharges to river ecosystem [24]. The correlation analysis carried out to see the relationship of concentrations of heavy metals (Zn, Cd, Pb, and Cu) in water and sediment, shows significant positive correlation in Cadmium (Cd) and Lead (Pb). But Zinc (Zn) in sediment and copper (Cu) in water showed negative correlation as shown in Table 4. In general heavy metals (Zn, Cd, Pb and Cu) concentrations obtained in sediment were higher compared to heavy metals in water. This confirms the ability of sediment to serve as sinks for heavy metals [16]. The correlation values are indicatives of the origin of individual's metals showing that their sources were closely related. Copper (Cu) recorded higher correlation in sediment compared to Lead (Pb) in water respectively. The result emphasis that heavy metal in water and sediment might be from contaminated sources, consequences of anthropogenic activities such as effluent from industries, surface run-off and domestic wastes [7]. The positive correlation in water and sediment reported in Lower river Benue could be accounted for by geology of the area, domestic waste and surface run-off from agricultural fields [31].

Conclusion

Results from this research provide base line information on heavy metals in water and sediment along Rimi and Kabawa axis of Lower Benue River, Ibi, Taraba State. The study ascertained occurrence of metals in water and sediment along the axis of the contaminated sites at lower river Benue. The study also showed sediment recorded higher concentrations of heavy metal compared to water. Concentrations of metals were within the recommended limits for drinking water and sediment by WHO and FMENV except values for Lead (Pb). This present research work provides valuable baseline data on heavy metals in water and sediment from contaminated sites along Rimi and Kabawa axis of Lower River Benue, Ibi, Taraba State, Nigeria. Concerted effort must be put in place to avoid environmental and health hazards with time.

Recommendation

Therefore, it is recommended that routine heavy metals check should be sustained, the dumping of waste contaminants close to the river should be discouraged along Rimi and Kabawa area. Also setting up of cottage industries along the river bank should be discontinued at Rimi and Kabawa Areas. This will improve on water quality and reduce drastically heavy metal levels of the river.

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