

## Assessment of Five Heavy Metals in Water, Sediment and Catfish- *Clarias gariepinus* from River Benue at Ibi, Taraba State, Nigeria

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### Abstract

Water is also a vital resource for agriculture, manufacturing and other human activities. In urban areas, the careless disposal of industrial effluents and other wastes into rivers may contribute greatly to the poor quality of river water. This research is to assess the level of heavy metals (Cd, Cu, Mn, Ni, Pb and Zn) in Catfish-*Clarias gariepinus* and the sediment from River Benue at Ibi, Taraba state, Nigeria. The level of heavy metals in water, sediment and catfish from the study area were assess and the estimate contamination factor and pollution load index in the sediment of the study area was also access and compared with the WHO results and other relevant standards. The results shows that the concentration of heavy metal in fish was within the WHO permissible limits. Also the concentration of Pb, Zn and Ni in catfish were significantly ( $P \leq 0.05$ ) higher compared to the metals but they were within the WHO permissible limits except for Cd. Heavy metal concentrations in sediment were within the acceptable WHO and USEPA limits, except for Cd, and Mn. PLI values for sediment from all the sites were less than one, implying that the sediment was unpolluted. The persistence of heavy metals in water, fish and sediment samples from the studied areas over time might lead to potential health risk on both humans and aquatic lives via food ingestion. Changes in water and

sediment chemistry might be responsible for the variations in the chemical properties of sediment, water and fish.

**Keywords:** Catfish, Heavy Metals, Sediment, River

## INTRODUCTION

Anthropogenic activities continuously increase the number of heavy metals in the environment, especially in aquatic ecosystem. Pollution of heavy metals in aquatic system is growing at an alarming rate and has become an important worldwide problem [1]. Contamination of water by toxic heavy metal has been a major environmental problem since long. Some of the past episodes of heavy metal contamination in the aquatic environment have increased the awareness of the toxicity [2].

Anthropogenic sources of  $Cd^{2+}$  in the environment are derived from copper and nickel smelting, fossil fuel combustion and the use of phosphate fertilizers [3]. Cadmium is also present as a pollutant in non-ferrous metal smelters and the recycling of electronic waste [4]. An association between heavy metals exposure markers (blood and urine) and coronary heart disease, stroke, peripheral artery disease, and atherogenic changes in lipid profile was also observed [5].

Water is also a vital resource for agriculture, manufacturing and other human activities. In urban areas, the careless disposal of industrial effluents and other wastes into rivers may contribute greatly to the poor quality of river water [6]. Heavy Metals are reported to encourage tumor and mutations at greater amounts in animals [7]. They have capacity of producing genetic harm to germ cells of both male and female animals. They are observed as growing toxins which through biomagnifications in plants affect the health of humans [8].

There is need to adopt appropriate, continuous, effective and constant monitoring and evaluations of this River for heavy metal concentrations to avoid high deposits of these metals and their adverse effects on Human consumers. The results of the present study point out the need to implement common objectives, compatible policies, programs and proper sensitization on the public to stop or improve in the discharge of waste, dumping of refuse, industrial wastes and sewage into River body. Educate and sensitize the residents

living around these areas on the various ways of water treatment before use while government provides alternative portable water for their domestic uses.

## MATERIALS AND METHODS

### Study Area

The study was carried out by taken the mean value of four (4) different locations Nwonyo, Dampar, Ibi (Kwatan Badge) and Angwan Jukunawa for water, sediment and fishes along Benue River in Ibi local government area of Taraba state. Figure 1 is the map of areas of studies. Ibi is a town and the administrative district in Taraba State. The town is located in the southern back of the Benue River and lies between the latitude  $8^{\circ} 11' 52''N$  and Longitude  $9^{\circ} 45' 39''E$  with an area of  $2,672 \text{ km}^2$  (Bureau for land and Survey Jalingo, Taraba State). To the west, it shares boundary with Nasarawa State, to the East Gossol Local Government Area, to the South Wukari and to the North, Plateau State.

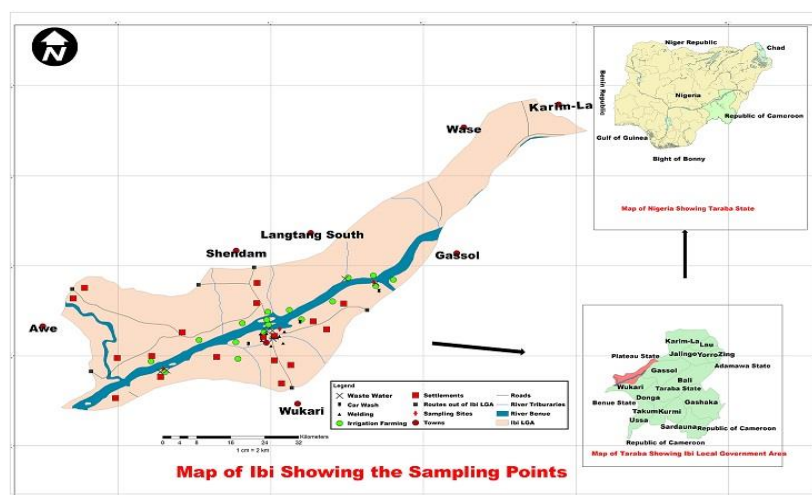


Figure 1: Map of Taraba Showing Study Area. (Source: Researcher's survey using arc map, 2023. (GIS)

### Equipment/Apparatus

Oven model HMF50050/60/50, Hot plate GMP model, Electrical Weighing balance model JA60002, Atomic Absorption Spectrophotometer AA6800 Shimadzu-automated.

### Sample Collection and Preservation

Plastic bottles were used to collect surface water sample from four (4) sampling Sites: Nwonyo, Dampar, Ibi (Kwatan Badge) and Angwan Jukunawa at a depth 5 – 25 cm along

the river during the rainy season (August, 2022) and dried season (March, 2023). The bottles were rinsed with few drops of nitric acid ( $\text{HNO}_3$ ) first before the samples were collected (WHO, 2006). Concentrated nitric acid ( $5 \text{ cm}^3$ ) was added in order to prevent hydrolysis of some chemical compounds, biological action and to reduce volatility of some chemical constituents, the samples collected was transported to Central Laboratory, Federal University Wukari, Taraba State. Sediment sample from the selected locations were collected into polyethylene bags using antirust scoop by scooping 10 cm of the bed sediment during the same period as for the water sample [9]. The fish sample of *Clarias gariepinus* (Cat fish) used for the analysis was caught at the same sampling locations using drag net, which was left over night in the river by local fishermen. The netted fish was covered the next morning in a picnic box with some quantity of river water to the laboratory. The fish was rinsed with distilled water to remove debris planktons and other external adherents. It was then drained under folds, weighed, wrapped in an aluminum foil and then frozen at  $-10^\circ\text{C}$  prior to analysis.

### **Sample Preparations and Treatments**

#### **Water Sample**

The water sample ( $100 \text{ cm}^3$ ) was transferred into a  $150 \text{ cm}^3$  beaker,  $10 \text{ cm}^3$  nitric acid was added and the beaker was covered with a watch glass and the content heated on a hot plate (GMP model) until there was a clear solution. The beaker and the glass walls were washed down with deionised water and the sample was filtered into a  $50 \text{ cm}^3$  volumetric flask in order to remove insoluble materials or particulate matters that could clog the atomizer. The volumes of the samples were made up to mark with de-ionized water. The digested sample was then preserved at  $4^\circ\text{C}$  in a refrigerator at the Laboratory for further analysis of heavy metals using Atomic Absorption Spectrophotometer (AAS) AA6800 Shimadzu-automated [10][11].

#### **Fish Sample**

The fish was dried in an electric oven (HMF50050/60/50 model) at  $70-80^\circ\text{C}$  for 2 days. The dried fish sample was pulverised using clean mortar and pestle to produce powdered form. Two grams (2 g) was weighed into a beaker and  $5.0 \text{ cm}^3$  of concentrated nitric acid was added and mild heat was applied until the solution of the minerals in sample is clear. The digest was filtered into  $50 \text{ cm}^3$  volumetric flask and made up to mark with the de-ionized water. The digest was analysed for heavy metal contents [12].

### **Sediment Sample**

The collected sediment samples (1 kg) were air-dried on a table surface in the laboratory for 2 days and further dried to a constant weight in an oven at a relatively low temperature (30 °C). The samples were ground using pestle and mortar, then sieved with 2 mm mesh to eliminate the effect of particle size and also to obtain a more homogenous grain distribution [9]. The sieved sediment samples (2 g) was weighed into 50 cm<sup>3</sup> beaker and 25 cm<sup>3</sup> aqua regia (3 : 1) of HCl : HNO<sub>3</sub> were added and digested for 2 hrs on a hot plate. The digest was diluted with de-ionized water and allowed to cool and then filtered into a 50 cm<sup>3</sup> volumetric flask using Whatman No.541 filter paper. The solution was made up to mark with de-ionized water. The prepared sample solution was transferred into pre-cleaned well labelled sample bottles and preserved for heavy metal analysis using Atomic Absorption Spectrophotometer (AAS) [9].

### **Analytical Quality Assurance**

In order to check the reliability of the analytical procedure employed for heavy metals determination, a certified reference material of similar composition was analysed in like manner to the samples and replicate analysis of samples together with blank were carried out.

### **Determination of Metals**

Trace elements concentration in the digests was determined using Atomic Absorption Spectrophotometer (AAS) AA6800 Shimadzu-automated equipped with Zeeman's background correction (SR-BDG).

### **Bio-concentration Factor (BCF)**

Bio-concentration factor can be expressed as the ratio of the concentration of a chemical in an organism to the concentration of the chemical in the surrounding environment. It is the measure of the extent of chemical sharing between an organism and the surrounding environment. The BCFs were calculated using the following equation [13].

$$\text{BCF} = \frac{\text{Concentration in Biota}}{\text{Concentration in Water}} \quad (1)$$

## **Determination of Contamination Factor and Pollution Load Index for Metal in Sediment Samples**

### **Contamination factor (CF)**

Contamination factor is the ratio of heavy metals concentrations to the background value.

CF gives an indication of the degree of contamination of sediment. The level of contamination factor of metal is expressed by a given equation.

$$\text{Contamination Factor (CF)} = C_s / C_b$$

(2)

$C_s$  is the given metal in the shore sediment;  $C_b$  is the background value of the metal. The background values for some heavy metals are: Zn (40), Pb (85), Cu (36), Cd (0.8), Mn (850), Ni (35) mg/kg [14][15].

### **Pollution Load index (PLI)**

The pollution load index measures the degree of overall contamination in a sampling site. In order to ascertain the pollution load index of heavy metals, contamination factors were calculated. The PLI of the place are calculated by obtaining the n-root from the n-CFs that was obtained for all the metal. Generally, Pollution Load Index (PLI) as developed by [16], which is a potent tool used in heavy metal pollution assessment:

$$\text{CF} = \text{metal concentration in water} / \text{metal concentration in polluted sediment}$$

$$\text{PLI} = \sqrt[n]{(\text{CF}_1 \times \text{CF}_2 \times \text{CF}_3 \times \dots \times \text{CF}_n)}$$

(3.3)

Where  $\text{CF}_1 \dots \text{CF}_n$  = Concentration of individual metals in the sample,  $n$  = Total number of metals under study.

### **Statistical Analysis**

Significant differences ( $P \leq 0.05$ ) in heavy metal concentrations in water, fish and sediments was determined using analysis of variance (ANOVA) and T-Test. SPSS (v.23) software was used for both analyses. Turkey Multiple Honestly Significant Different (HSD) was used to evaluate any significant difference in the concentrations of metals in Water, Fishes and Sediments samples at 95 % confidence limit.

## RESULTS AND DISCUSSION

### Heavy Metal Concentrations in water Samples

The results for the heavy metal (Cd, Cu, Mn, Ni, Pb and Zn) concentrations in water samples are presented in Tables 1. The presence of these heavy metals in the water could be attributed to discharge of agricultural effluents and municipal wastes, geology of river bed and catchment area [17]. It was also found that most of the elements varied significantly ( $P \leq 0.05$ ) between the sampling sites.

#### Cadmium (Cd)

The seasonal mean concentrations of Cd in Table 1 during the rainy season ( $0.25 \pm 0.02$  mg/L) and dry season ( $1.16 \pm 1.57$  mg/L) indicating that Cd was higher during the dry season due to anthropogenic activities around the sampling sites. There were statistically significant differences ( $P \leq 0.05$ ) in Cd concentrations along the sampling stations for both seasons. The concentration of Cd in this study were high compared to the study 0.02 to 0.09 mg/L reported for water sample from the vicinity of Oluosun Landfill in Ojota Lagos, [18] but lower than  $1.81 \pm 0.19$  mg/L reported for heavy metals in Zayandeh rood river, Isfahan-Iran, [19]. The levels of Cd recorded were above the 0.05 mg/L permissible limit in water [20]. About 15 mg/L of cadmium has been reported to cause these effects with target organs including the liver, placenta, kidneys, lungs, brain and bones [21].

#### Copper (Cu)

The seasonal mean concentrations of Cu in Table 1 during the rainy season ( $0.25 \pm 0.08$  mg/L) and dry season ( $0.61 \pm 1.17$  mg/L) indicating that Cu was higher during the dry season. Cu varied significantly different ( $P \leq 0.05$ ) between the sampling sites. The concentration of Cu in this study were higher compared to the study 0.01 to 0.09 mg/L reported for water sample from the vicinity of Oluosun Landfill in Ojota Lagos, [18] but lower than ( $1.81 \pm 0.19$  mg/L) reported for heavy metals in Gutter, Zayandeh rood river, Isfahan-Iran, [19]. The levels of Cu recorded were above the 0.02-0.5 mg/L permissible limit in water [20].

#### Manganese (Mn)

The seasonal mean concentrations of Mn were  $0.51 \pm 0.01$  mg/L and  $1.78 \pm 0.45$  mg/L for rainy and dry season respectively, the concentration of Mn in this study were lower than 14.36 mg/L recorded in water sample from Ajawere river in Oke-Osun farm settlement in

Osogbo, Nigeria, but higher than 0.02mg/L recorded for analysis of water samples from Gutter, Baghicha in Sindh, Karachi, Pakistan [22]. The concentration was higher than the permissible limit (0.05 mg/L) for drinking water [20]. Its exposure can cause decrease in body weight, heart and liver damage and skin irritation [23]. The higher concentration in dry season may be attributed to runoff from rice mills and residential areas into the river [24]. There was no significant difference ( $P \leq 0.05$ ).

### **Nickel (Ni)**

Seasonal comparison as seen in Table 1 showed that Ni highest concentration recorded  $0.50 \pm 0.33$  mg/L in rainy season as against the lowest concentration  $0.04 \pm 0.03$  mg/L in dry season. There was no significant difference ( $P \leq 0.05$ ). These values were lower than the concentration 3.75 mg/L reported for water from Ajawere River in Oke-Osun, Osogbo [25] but within the same concentration (0.05 mg/L) reported for analysis of water samples from Gutter, Baghicha in Sindh, Karachi, Pakistan [22] and 0.04 mg/L from water of River Tyume [26]. The levels in the present study were below the 0.07 mg/L [20] permissible limits. Higher concentrations of Ni in some sites could come from debris from mechanic and car wash shops through surface runoffs. Ni levels varied significantly in both seasons.

### **Lead (Pb)**

As presented in Table 1, Pb concentration recorded in both seasons were below detection limits. This indicates a low pollution of Pb in the water from this river or the equipment was not able to monitor that concentration. Concentration of Pb in this study was not similar to the concentration (0.06 to 0.27mg/L) recorded in river Mpape in FCT [15] and the 0.16 to 0.33mg/L reported for Tamda Dam [27].

### **Zinc (Zn)**

The seasonal comparison as in Table 1 indicated that the highest concentration of Zn  $3.23 \pm 1.44$  mg/L was in the rainy season while  $1.54 \pm 0.45$  mg/L in dry season, which may be due to high rainfall. Zn was significantly different ( $P \leq 0.05$ ). The values recoded in the present study were higher than the concentrations 0.04 mg/L and 0.10 mg/L reported in water samples from Gutter, Baghicha in Sindh, Karachi, Pakistan [22] and from Ebute Ogbo river in Ojo, Lagos [25] but lower than 14.63 mg/L for water from Ajawere River in Oke-Osun, Osogbo Nigeria [28]. However, Zn levels were lower than the permissible limit of 5 mg/L for drinking water [20]. It has been reported that zinc is able to damage nerve receptors in the nose, which can cause anaemia and recommended that consumers should

stop using zinc-based intranasal cold products and ordered their removal from store shelves [29].

**Table 1: Seasonal mean Concentrations (mg/L) of heavy metals in Water Samples**

Metals	Dry Season	Rainy Season	WHO, 2008	EPA, 2002
Cd	1.16±1.57 <sup>a</sup>	0.25±0.02 <sup>a</sup>	0.01-0.05	0.01
Cu	0.61±1.17 <sup>b</sup>	0.25±0.08 <sup>a</sup>	0.2-0.5	0.2
Mn	1.78±0.45 <sup>b</sup>	0.51±0.01 <sup>b</sup>	0.05	0.2
Ni	0.04±0.03 <sup>b</sup>	0.50±0.33 <sup>b</sup>	0.07	-
Pb	ND	ND	0.01-0.03	0.02-0.05
Zn	1.54±0.45 <sup>a</sup>	3.23±1.44 <sup>a</sup>	5	2

Mean levels with the same alphabet within the same row are significantly different ( $P \leq 0.05$ )

ND = Not Detected, a=significantly different, b=No significant different

### Concentrations of Heavy Metals in fish Samples

#### Cadmium (Cd)

Table 2 presents the seasonal mean levels that ranged from  $0.21 \pm 0.00$  to  $1.53 \pm 1.91$  mg/kg for Catfish which was lower than the reported levels of 1.52 mg/kg and 1.71 mg/kg for fish collected from Antau River in Keffi [30] and [31] but within the same level 1.00 mg/kg reported by Ambedkar & Muniyan [32]. Higher levels of Cd (1.506 mg/kg) were also reported by Ejike & Liman [33] in fish from River Kwalkwalawa, Dundaye, Sokoto, Nigeria. These values were within 1 mg/kg [20] permissible limits. When taken over a long period of time, Cd causes slight anaemia due to reaction between iron and cadmium in body resulting in iron deficiency [15], it causes inflammation of the liver and kidney, ovarian and prostate cancer [34]. Cd level varied significantly in both seasons ( $P \leq 0.05$ ).

#### Copper (Cu)

The mean levels of Cu in Catfish varies from  $0.00 \pm 0.05$  to  $0.24 \pm 0.10$  as in Table 2 and was lower than the level 0.46 mg/kg and 21.106 mg/kg reported for fish from River Gadilam, India, [32] and Kwalkwalawa river, Dundaye, Sokoto [33]. However, the levels of Cu from the present study were within the concentrations 0.15 mg/kg reported for fish from antau River Keffi. The concentrations recorded in the present study were lower than 36 mg/kg [20] permissible limits. Cu level varied significantly in catfish in both seasons ( $P \leq 0.05$ ).

### **Manganese (Mn)**

The mean levels of Mn in Catfish ranged from  $0.14\pm 0.01$  to  $2.06\pm 0.19$  mg/kg in Table 2 which were within the levels 1.25 mg/kg reported for fish from river Antau river in Keffi, [30]. The values were higher than the 0.03 mg/kg reported by Ambedkar & Muniyan [32] and lower than 46.606 mg/kg reported by Ejike & Liman [33]. The values recorded in the present study were lower than 500 mg/kg [20] permissible limits. Mn can cause a poisoning syndrome in mammals, with neurological damage which is sometimes irreversible. Mn level did not vary significantly in both seasons ( $P\leq 0.05$ ).

### **Nickel (Ni)**

Nickel is highly essential for growth and reproduction in man and livestock, however, could be carcinogenic in higher amounts in the body [35]. The mean levels of Ni  $0.33\pm 0.37$  to  $0.60\pm 0.51$  mg/kg for Catfish in Table 2 (rainy and dry season respectively) were lower and within the 0.40 mg/kg and lower than the 1.43 mg/kg reported for different fish from river Antau in keffi [30][32] respectively. The values in the present study were lower than 67.00 mg/kg permissible limits [20]. Ni level did not vary significantly in catfish in both seasons ( $P\leq 0.05$ ).

### **Lead (Pb)**

The mean concentration of Pb was detected in catfish, Pb was not detected in dry season but  $1.58\pm 1.32$  mg/kg in rainy season. The mean in this study were higher than the 0.20 mg/kg and 0.38 mg/kg reported for fish from Antau river by Babalola & Tukura [30] and Gadilam river, Tamilnadu, India respectively. However, lower than 24.106 mg/kg reported by Ejike & Liman [33] from Kwalkwalawa river, Dundaye sokoto. Pb levels were lower than the 2 mg/kg [20] permissible limits. Pb level varied significantly in both seasons ( $P\leq 0.05$ ).

### **Zinc (Zn)**

Sources of Zn are runoffs from irrigation farmlands. Table 2 presents the mean concentrations of Zn in Catfish ranged from  $2.51\pm 0.46$  to  $3.41\pm 0.36$  mg/kg for which was higher than the concentrations that ranged from 0.30 to 31.90 mg/kg reported by Babalola & Tukura, [30] for fish in river Antau, keffi and 0.18 mg/kg from Gadilam river, India [32], however lower than 71.6 mg/kg reported by Ejike & Liman [33] from Kakwalawa river Dundaye Sokoto. Zn level varied significantly in both seasons ( $P\leq 0.05$ ).

**Table 2: Mean Concentrations (mg/kg) of heavy metals in Catfish in dry and rainy season**

Metals	Catfish		WHO, 2008
	Dry season	Rainy season	
Cd	1.53±1.91	0.21±0.00	1
Cu	0.00±0.05	0.24±0.10	30
Mn	2.06±0.19	0.14±0.01	500.00
Ni	0.60±0.51	0.33±0.37	67.00
Pb	ND	1.58±1.32	2
Zn	3.41±0.36	2.51±0.46	100

ND= Not Detected, a=significantly different, b=No significant different

### Bio-concentration factor

The higher the ratio, the more severe the bio-concentration of pollutants in this study. The Bio-concentration factor in fish in Table 3 varied with the highest BCF value recorded for Ni (19.33) in dry and rainy seasons while Pb (0.00) was not bio-concentrated by the catfish in both seasons. The non-bio-concentration of Pb by the aforesaid species may be attributed to low levels of Pb in water compared to the levels of the other metals in the same medium. Bio-concentration of metals can also be influenced by factors such as species type and seasons [36]. Heavy metals can be obtained by fish from the surrounding water, food and sediments. Nussey *et al.* [36] reported that when heavy metals are absorbed by fish, they are transported by the blood to either a storage point such as bones or to the liver for transformation and storage.

**Table 3 Mean Bio-concentration factor of Cat fish**

Metals	Catfish	
	Dry season	Rainy season
Cd	0.66	0.62
Cu	1.13	0.04
Mn	4	1.10
Ni	0.93	19.33
Pb	0.00	0.00
Zn	0.87	3.00

## Heavy Metal Concentrations in Sediment Samples

### Cadmium (Cd)

The seasonal comparison from Table 4 showed that highest concentration of  $1.05 \pm 0.12$  mg/kg was recorded in the dry season in contrast to the low concentration  $0.21 \pm 0.12$  mg/kg recorded in rainy season. There were no statistically significant differences ( $P \leq 0.05$ ) in both seasons. These values were higher than the concentration  $0.05 \pm 0.04$  mg/kg recorded for sediment from Mpape River FCT [15], but lower than the 8.08 mg/kg reported for sediment from Ajawere River on Oke-Osun farm settlement in Osogbo, Nigeria [28] and 1.36 mg/kg from Jabi Lake Abuja [37]. The values were higher than 0.03 mg/kg [20] and within 0.68-0.99 mg/kg. Cd levels did not vary significantly according to season ( $P \leq 0.05$ ).

### Copper (Cu)

The seasonal comparison as in table 4.4 showed that rainy season indicated higher concentration of Cu ( $0.54 \pm 0.19$  mg/kg) in contrast to the concentration  $0.07 \pm 0.05$  mg/kg in dry season. The concentration in both seasons were lower than concentration 4.10 mg/kg recorded for sediment from Jabi Lake Abuja [37], the 8.89 mg/kg recorded from Ajawere river in Oke-osun farm in Osogbo [28] and 0.57 mg/kg reported from Mpape river in FCT [15]. However, the levels were lower than the 2.00 mg/kg [20] and 18.7-31.7 mg/kg. The higher levels observed in rainy could be due to high levels of contaminants as a result of increase in anthropogenic activities. Cu levels vary significantly according to seasons ( $P \leq 0.05$ ).

### Manganese (Mn).

The seasonal comparison of Mn in sediments as recorded in Table 4 indicated higher concentration of Mn  $45.02 \pm 9.01$  mg/kg in the dry season than the rainy season ( $1.58 \pm 0.02$  mg/kg). This may be due to reduced level of water volume and nature of activities [38] and increase in anthropogenic activities [39]. Concentration of Mn in this study was higher than the 10.97 mg/kg reported for sediment of Jabi lake in Abuja [37]. However, the values were lower than the 89.53 mg/kg for sediment in river Oke-Osun farm Osogbo Nigeria [28]. The concentrations in the study were higher than the 0.5 mg/kg [20] permissible limits for sediment. There is no significant difference according to season ( $P \leq 0.05$ ).

### **Nickel (Ni)**

As presented in Table 4, the presence of Ni may be attributed to nature and magnitude of anthropogenic activities in the study area [15]. The seasonal values showed that Ni had the highest recorded concentration  $1.42\pm 0.28$  mg/kg in dry season as against the lower concentration  $0.88\pm 0.45$  mg/kg in the rainy season. These values were higher than the concentration 0.17 mg/kg reported for sediment from Jabi Lake of Abuja metropolis [37] and 0.07 mg/kg for sediment of river Ekalu in Enugu. However, these levels were similar to the concentration  $0.16\pm 0.02$  mg/kg reported for sediment from Mpape river Abuja Jabi Lake [15] and 1.50 to 2.80 for sediment of river Ananaba in Algeria [39]. The level in the present study was higher than the 0.07 mg/kg [20] but lower than 22.7 mg/kg [40] permissible limits. Ni level varied significantly in both seasons ( $P\leq 0.05$ ).

### **Lead (Pb)**

As presented in Table 4, Pb concentrations recorded in both seasons was below detection limit. This indicates a low pollution of sediment from the river, Pb in this study was not similar to the 2.63 mg/kg reported for sediment samples from Mpape river [15] and 22.55 mg/kg reported from Ajawere river in Oke-Osun farm Osogbo [28].

### **Zinc (Zn)**

The seasonal comparison as in Table 4 indicated that the highest concentration of Zn  $5.08\pm 1.15$  mg/kg was in the rainy season and  $4.79\pm 0.51$  mg/kg in dry season. The values recorded in the present study were lower than the concentration  $155.10\pm 5.86$  to  $250.20\pm 30.6$  mg/kg reported for similar work done in sediment of Seyhouse River in Ananaba [39], the 89.91 mg/kg from sediment of Ajawere river in Oke-Osun farm settlement in Osogbo [28]. The concentrations of Zn were within the 5 mg/kg [20] and lower than the 121-124 mg/kg [40] permissible limits. It could be concluded that both anthropogenic and geochemical factors could have contributed to the level of Zn in the river sediment. Zn level varied significantly in both seasons ( $P\leq 0.05$ ).

**Table 4: Seasonal Mean Concentration of Heavy metals in Sediment samples (mg/kg)**

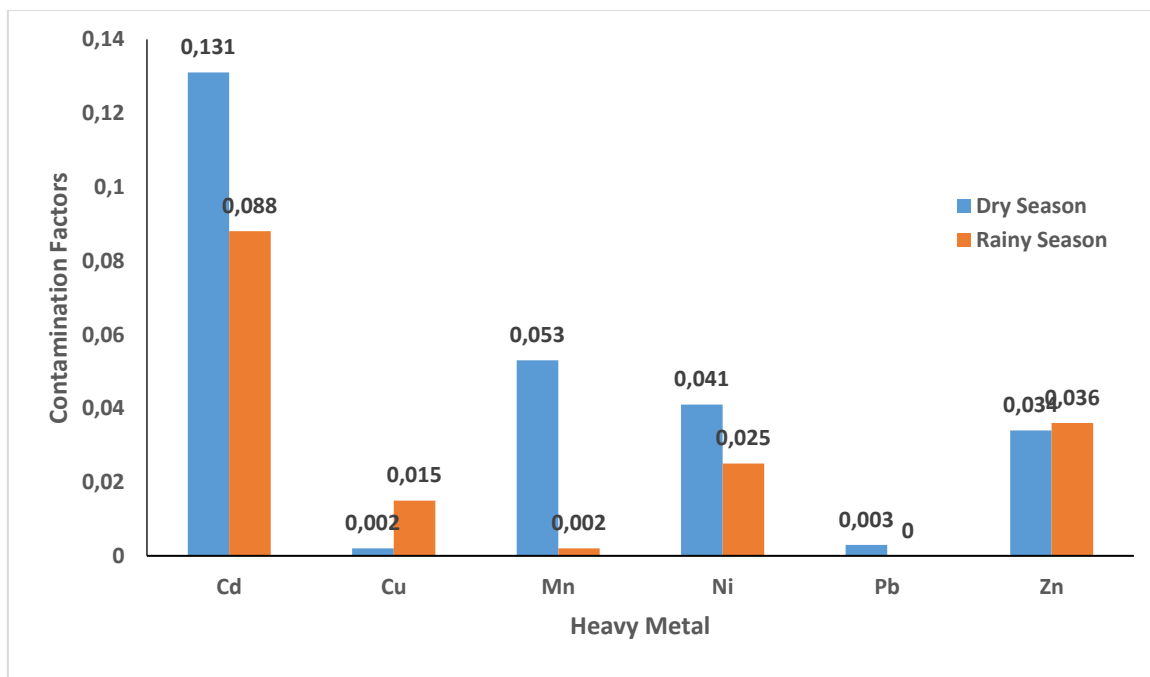
Metals	Dry Season	Rainy Season	WHO, 2008	USEPA, 2010
Cd	1.05±0.12 <sup>a</sup>	0.21±0.12 <sup>a</sup>	0.03	0.68-0.99
Cu	0.07±0.05 <sup>a</sup>	0.54±0.19 <sup>a</sup>	02.00	18.7-31.6
Mn	45.02±9.01 <sup>b</sup>	1.58±0.02 <sup>b</sup>	0.5	-
Ni	1.42±0.28 <sup>a</sup>	0.88±0.45 <sup>a</sup>	0.07	22.7
Pb	0.22±0.07 <sup>a</sup>	ND	0.01-0.03	35.8
Zn	4.79±0.51 <sup>a</sup>	5.08±1.15 <sup>a</sup>	5	121-124

Mean levels with the same alphabet within the same row are significantly different  $P \leq 0.05$

ND = Not Detected, a=significantly different, b=No significant different

#### **Pollution Load Index (PLI) in sediment samples**

Figure 2 presents the result for the pollution load index of sediment samples. To appraise the pollution load index of the metals in the sediment, contamination factors were calculated, which express the levels of pollution of the sediment by metal, using contamination factors classification categories [15]. The contamination factors for all the metals from the four sampling sites varied from 0.088 to 0.131 for Cd, 0.002 to 0.015 for Cu, 0.002 to 0.53 for Mn, 0.025 to 0.041 for Ni, 0.000 to 0.003 for Pb, 0.034 to 0.036 for Zn. Using the contamination factor classifications, sediment from the four sites were not contaminated by any of the heavy metals except for Cadmium in Dry season. The pollution Load Index (PLI) were measured based on the pollution index classifications categories of Eze *et al.* [15]. From the results, the PLI for sediment from the four sites varied from 0.0000608 to 0.0001460 which were generally far below 1. This also indicated no pollution of the sediment samples from the river by heavy metals.



**Figure 2: Pollution Load Index (PLI) in sediment samples**

## CONCLUSION

The values of concentration of all the heavy metals in water sample were higher than the WHO permissible limits except for Zn, Pb and Ni. The different levels of some metals in the fish samples suggested that the fish were capable of bioaccumulating the metals in their bodies from the aquatic environment. The difference noticed in the levels of concentration in different fish could be attributed to the differences in their physiological roles toward maintaining homeostasis, feeding habits, regulatory ability and behaviour of each fish. Accumulation of heavy metal in fish may be considered as an important warning signal for fish health and human consumption. The present study shows that precaution measures need to be taken in order to prevent future heavy metal pollution.

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