

# **Title: Determination of Heavy Metals in Water and some selected Fish Species in River Ofin, Ado-Ekiti**

## **Abstract**

This study investigates the physico-chemical parameters of water and quantification of heavy metals (zinc, copper, lead, chromium and cadmium) in the gill, liver and flesh of *Oreochromis niloticus*, *Hemichromis fasciatus*, *Sarotherodon galilaeus* and *Oreochromis aureus* in River Ofin, from October to December, 2019, using Atomic Absorption Spectrophotometer. Mean values of the parameters were; Temperature;  $27.18 \pm 0.15^{\circ}\text{C}$ , pH;  $7.06 \pm 0.10$ , Turbidity;  $9.0 \pm 0.94\text{Ntu}$ , Conductivity;  $236.10 \pm 0.53\mu\text{s/cm}$ , DO;  $6.67 \pm 0.16\text{mg/l}$  and BOD;  $6.87 \pm 0.81\text{mg/l}$ . Mean values of the concentration of the heavy metals in the water were; Zn;  $0.31 \pm 0.01\text{mg/l}$ , Cu;  $0.26 \pm 0.01\text{mg/l}$ , Pb;  $0.13 \pm 0.01\text{mg/l}$ , (Pb in water was higher than the highest value  $0.12 \pm 0.003$  ( $P \leq 0.05$ ) recorded in fish) Cr;  $0.12 \pm 0.01\text{mg/l}$  and Cd;  $0.002 \pm 0.001\text{mg/l}$  while the concentration of heavy metals in fish varies from species to species as it displayed species differences. Heavy metal concentration in water is in this order: Zn>Cu>Pb>Cr>Cd. The presence of Zn, Cu, Pb, Cr and Cd were confirmed in all the fish species except Cd that was discovered only in the gill of *S. galilaeus*. Metals in fish gills is in the order of Zn>Cu>Pb>Cr>Cd for the four species, for liver and flesh/muscle in *O. niloticus* and *H. fasciatus* it is Cu>Zn>Cr. Pb was detected only in the gill of *O. niloticus*, the liver and flesh lack Pb. Other fish species parts showed different Pb concentrations with the highest value ( $0.12 \pm 0.003$ ) recorded in the gill of *O. aureus*. This study showed that Cd, Cr, Zn, and Cu were in the maximum acceptable limit range (Cr; 0.44, Zn; 5.04, Cu; 1.37 and Cd; 0.20) while Pb in water and fish was slightly above the maximum acceptable limit range (Pb; 0.04) by FAO/WHO. Lead poisoning is ranked among the most common environmental health hazard even at low levels. Periodic monitoring by relevant regulatory authorities is recommended to ensure safety of the water and fish consuming populace.

**Key words: Physico-chemical parameters, Water, Heavy metals, Fish species, River Ofin.**

## **1.0 INTRODUCTION**

The subject of heavy metal is receiving increasing popularity in food industry due to high incidence of contamination in agricultural and seafood products [1]. All heavy metals are potentially harmful to most organisms at some levels of exposure and absorption [2] The threat of toxic and trace metals in the environment is more serious than those of other pollutants due to their non bio-degradable nature, accumulative properties and long biological half-lives. It is difficult to remove them completely from the environment once they enter into it [3]. Heavy metal contamination may have devastating impacts on the ecological balance of natural water bodies including the loss of aquatic diversity [4]. With increased use of a wide variety of metals in industries and in our daily life, there is now a

greater awareness of toxic metal pollution of the environment. Many of these metals tend to remain in the ecosystem and eventually move from one compartment to the other within the food chain [5]

Fish are often at the top of aquatic food chain and when pollutants build up in the food chain, fish are widely used to evaluate the health of aquatic ecosystems. Fish may concentrate large amounts of metals from the water and therefore are responsible for adverse effects and death in the aquatic systems. Metal accumulation in fish tissues poses a direct threat for human being [6]. The distribution of metals varies between fish species, depending on age, development status and other physiological factors. The ingestion of food is an obvious means of exposure to metals, not only because many metals are natural components of food stuffs, but also environmental contamination and contamination during processing. The ingestion of heavy metals by fish via food and water may affect not only the productivity and reproductive capabilities of such fish, but ultimately affect the health of man that depends on these organisms as a major source of protein [7].

Heavy metal affects freshwater organisms and induces certain harmful modifications at histological and morphological levels, also decreases the growth and developmental rates resulting in increase of death rate and the decrease of birth rate. Their potential toxic effects are given by the presence in water solution at concentrations exceeding certain threshold levels and their long persistence in the aquatic ecosystems and their bioaccumulation and biomagnifications in the food webs [8]. Trace elements assimilated from food are transported in the blood, deposited in various tissues and excreted or stored. Heavy metals having penetrated into human being through food chains might cause various disturbances or serious diseases [9]. Once heavy metals are ingested, numerous health problems will take place. Lead may cause learning disabilities, impaired protein and hemoglobin synthesis and shorten the lifespan of red blood cells which leads to severe anemia (hypochromic microcytic anemia) in children. The most common toxic effects of cadmium in human are renal failure, accumulation in the bone resulting in calcium loss and malfunctioning of peripheral and central nervous system. Nickel has different undesirable effects on human health such as impairing the biological activity of cells, lung and nasal cancer in long-term exposure; respiratory, nervous and digestive disorders and also psychological problems will be increased [10]

Many studies have been carried out on the eco-toxicological status of some inland water bodies in Nigeria; these include the work of [11].in River Elemi, Ekiti State. The authors reported that the investigated fish species in Elemi River presented no health threat to man, as the permissible heavy metal limits for human consumption, set by FAO/WHO, were not exceeded in the edible portions. However, the concentrations of the non-essential metals, lead and cadmium, in this present study calls for concern.

Odeyemi *et.al.*, [12] worked on assessment of heavy metals on sediments and Tilapia species from Ureje Reservoir, Ado Ekiti, Ekiti State Nigeria and observed that accumulation of metals were significantly higher ( $P < 0.05$ ) in gills than the liver and Muscle. The levels of metals accumulation in the gills, liver and muscle followed the order: Fe > Zn > Pb > As > Cd. The most concentrated metal in the organs of the fish samples was iron. Fe, Zn and Pb were the three most abundant metals in the organs of these fishes and the same trend was also seen in the sediment. Cadmium and Arsenic were detected at low levels in the fish organs and the sediment samples. The heavy metals assessed were a little above WHO/FEPA standard limit which suggests that the reservoir could be polluted with heavy metals. Other works on the heavy metals in aquatic environment include the works of the following authors; Joy *et. al.*, [13] in Ubeji, Warri, Delta State, Ojutiku and Okojevo, [14] in three selected fish species from Chanchaga River, Minna, Niger State, Bawuro *et. al.*, [15] in Lake Geriyo Adamawa State.

Studies have shown the heavy metal burden of several Rivers in different parts of the world but there remain paucity of information on the level of heavy metals in River Ofin. River Ofin is one of the major rivers in Ekiti State Nigeria that is rich in fisheries resources that are widely exploited as human food. This study is to specifically ascertain the concentrations of heavy metals in water and fish species from River Ofin in order to determine potentially hazardous levels of these heavy metals especially with regard to human health.

## **2.0. Materials and Methods**

### **2.1. Study Area**

The study took place in River Ofin in Ado-Ekiti, the capital city of Ekiti State. The city lies between Latitude  $7^{\circ} 34'$  and  $7^{\circ} 44'$  north of the Equator and Longitude  $5^{\circ} 11'$  and  $5^{\circ} 18'$  east of the Greenwich Meridian. It has a number of Satellite towns around it. To the North is Iworoko, about 16 kilometers away from the city; to the east are Are and Afao, about 16 kilometers; to the West are Iyin and Igede, about 20 km and to the South is Ikere, about 18 km. The vegetation around the study area is ever green rain forest type; this type of vegetation favors agricultural practices. In terms of fisheries development, there is no stocking of the river; hence, the fish in the river are naturally occurring.

### **2.2. Sampling Stations**

Sampling for the study was done in two different stations, the upper stream (station A) and downstream (station B). Activities going on in station A are bathing and watching why in station B; dumping of refuse, sewage and agricultural practices are the activities around the place

### **2.3. Sample Collection**

Fish species were caught by the local fishermen using gill nets. The fish samples were then ice-packed and transported to the laboratory where they were identified.

### **2.4. Study of water quality parameters**

Water samples for all the physico-chemical analysis were collected on bi-monthly schedule from the study area at sub-surface level. Water samples were collected within 8.30 to 10.30 am on each sampling day using 250cl sampling bottles (for determining DO and BOD) plastic kegs (for other parameters) in a manner that it is representative of all layers of the water column. Temperature was measured on the spot with a Celsius thermometer while the rest of the above parameters such as turbidity (Ntu), dissolved oxygen (mg<sup>l</sup>-1), pH, biochemical oxygen demand (BOD) (mg<sup>l</sup>-1) and conductivity (mg<sup>l</sup>-1) were analysed at the Biological Science Laboratory, Afe Babalola University, Ado-Ekiti according to [APHA, 2012]

### **2.5. Measurement of Water Parameter**

#### **Water Quality Determination Parameters of pH**

The PH value of the water sample was confirmed in the laboratory using an electrical pH meter (Phep HANNA model). The glass was immersed in the water sample collected and the potential difference between them measured.

#### **Preparation of Fish Samples**

Sufficient gram of sample (depending on the type and nature of sample) was weighed in a platinum crucible (Sample of 1- 10g) was used in the analysis; solids are finely ground and then carefully mixed to facilitate the choice of a representative sample. Then it was placed in a muffle furnace at 450 - 550<sup>o</sup>c until all the carbon is removed as evidence by a white ash, the ashing time is typically 2hours.

The ash is dissolved in 10ml 1:1HNO<sub>3</sub> +1ml of concentrated HNO<sub>3</sub>+ 1ml of concentrated HCl acid, gently warmed to speed up the dissolution of the ash then the dissolved ash solution is then brought to 100ml.

#### **Determination of Heavy Metals in Water Samples**

Water samples were analyzed directly without further digestion. A volume of 25ml of each water sample was measured using a measuring cylinder, aspirated into Buck scientific Atomic Absorption Spectrophotometer model 210 VGP and analyzed for the concentration of heavy metals; Lead(pb), Cadmium (Cd), Chromium (Cr), Zinc (Zn), Copper (Cu) that are present. Calibration of the machine was done using standard solution of known concentrations of the analyzed heavy metals. Samples were analyzed in replicates. Blanks were also run intermittently to confirm machine's performance. Heavy metal concentration

was expressed in mg/l. Results obtained were compared with national and international standards/guidelines for heavy metals in water.

### **Determination of Heavy Metals in Fish Samples**

The analytical method used for the analysis of metal concentration was spectrometry and the equipment used is Atomic Absorption Spectrophotometer (AAS) Buck Scientific model 210 VGP using the calibration plot method. Three processes were involved; standard preparation, equipment calibration and sample analysis. For each element, the instrument was auto-zeroed using the blank (distilled water) after which the standard was aspirated into the flame from the lowest to the highest concentration. The corresponding absorbance was obtained by the instrument and the graph of absorbance against concentration plotted. The samples were analyzed with the concentration of the metals present being displayed in parts per million (ppm) after extrapolation from the standard curve.

### **2.6. Analysis of data**

Data were entered in Microsoft Excel sheets uploaded to Statistical Package for Social (SPSS) and analyzed using min, max, mean and standard deviation. In addition, the Pearson correlation coefficient (a measure of linear association) was used to detect significant relationship between the physico-chemical parameter of water and heavy metals in fish samples from the two sampling points

### **3.0. Results**

#### **3.1. Physico-chemical Parameter of Water Samples from the Sampling Stations**

The average values of physico-chemical parameters determined in this study in the two sampling stations are reported in Table 1, Table 2 and Table 3. A total of 24 samples during this study were collected and analyzed for assessing the water quality with respect to surface water temperature, turbidity, conductivity, biological oxygen demand and dissolved oxygen. Water temperature in station A ranged between 26.5 °C to 28.3°C (Tab. 1) with a mean value of  $27.29 \pm 0.22^\circ\text{C}$  (Tab. 3) while for station B, temperature ranged from 26.5°C to 27.7°C (Tab. 2) with a mean value of  $27.08 \pm 0.15$  (Tab. 3). The pH values in station A ranged from 6.5 to 7.3 with an average value of  $6.99 \pm 0.16$  (Tab. 3). While in station B, the pH values ranged within 5.9 to 7.9 with an average value of  $7.13 \pm 0.33$  (Tab. 3). Average value of Electrical conductivity for the two stations is  $236.10 \pm 0.53$  and for DO it is  $6.67 \pm 0.16\text{mg/l}$

Table1. Mean Values of Physico-chemical parameters for station A of River Ofin in Ado Ekiti, Ekiti State, Nigeria between October to December 2019.

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<b>Water parameters</b>	<b>October</b>	<b>November</b>	<b>December</b>	<b>Range</b>
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<b>Temperature (°C)</b>	27.43± 0.90	27.4±0.26	27.03±0.38	26.5-28.3
<b>Ph</b>	6.83±0.38	7.00±0.16	7.14±0.18	6.5-7.3
<b>Turbidity (Ntu)</b>	12.5±2.89	7.5±2.89	9.0±3.46	5.0-15.0
<b>Conductivity (µs/cm)</b>	266.06±57.40	235.28±44.93	205.83±11.46	195.1-315.81
<b>DO (mg/l)</b>	6.05±1.47	6.85±0.42	7.43±0.30	4.5-7.8
<b>BOD (mg/l)</b>	7.60±2.26	6.23±1.71	8.50±0.14	4.7-9.7
<b>Zn (mg/l)</b>	0.27±0.06	0.36±0.01	0.33±0.05	0.21-0.37
<b>Cu (mg/l)</b>	0.28±0.03	0.27±0.06	0.25±0.01	0.21-0.31
<b>Pb (mg/l)</b>	0.14±0.05	0.08±0.02	0.16±0.01	0.06-0.18
<b>Cr (mg/l)</b>	0.15±0.01	0.10±0.03	0.10±0.01	0.07-0.16
<b>Cd (mg/l)</b>	0.002±0.001	0.001±0.001	0.003±0.002	0.00-0.01

Note: Data on the table is expressed in mean ± S.D at  $P \leq 0.05$

Table 2. Mean Values of Physico-chemical parameters for station B of River Ofin in Ado Ekiti, Ekiti State, Nigeria between October to December, 2019

<b>Water parameters</b>	<b>October</b>	<b>November</b>	<b>December</b>	<b>Range</b>
<b>Temperature(°C)</b>	27.0±0.52	27.25±0.42	26.98±0.33	26.5-27.7
<b>pH</b>	6.75±0.93	7.29±0.23	7.34±0.16	5.9-7.9
<b>Turbidity(Ntu)</b>	10.00±00	7.5±2.89	7.50±0.58	5.0-10.0
<b>Conductivity(µs/cm)</b>	216.7±29.45	255.22±48.05	237.5±1.60	191.2-297.15
<b>DO(mg/l)</b>	6.03±0.36	6.58±0.63	7.05±0.40	5.7-7.6
<b>BOD (mg/l)</b>	5.45±0.76	5.14±0.41	8.31±0.83	4.7-9.05
<b>Zn(mg/l)</b>	0.31±0.14	0.27±0.03	0.32±0.01	0.18-0.44
<b>Cu(mg/l)</b>	0.29±0.01	0.23±0.02	0.26±0.02	0.21-0.30
<b>Pb(mg/l)</b>	0.17±0.04	0.10±0.02	0.14±0.01	0.08-0.20
<b>Cr(mg/l)</b>	0.19±0.03	0.11±0.06	0.09±0.01	0.06-0.23
<b>Cd(mg/l)</b>	0.003±0.002	0.002±0.001	0.003±0.001	0.001-0.005

Note: Data on the table is expressed in mean ± S.D at P≤0.05

Table 3. Mean Values of Physico-chemical parameters studied from the 2 (two) sampling stations of River Ofin in Ado Ekiti, Ekiti State, Nigeria between October to December 2019.

Water parameters	Station A	Station B	Over-All	WHO STANDARD
Temperature( $^{\circ}$ C)	27.29 $\pm$ 0.22	27.08 $\pm$ 0.15	<b>27.18<math>\pm</math>0.15</b>	<b>20-35</b>
pH	6.99 $\pm$ 0.16	7.13 $\pm$ 0.33	<b>7.06<math>\pm</math>0.10</b>	<b>6.5-8.5</b>
Turbidity(Ntu)	9.67 $\pm$ 2.57	8.33 $\pm$ 1.44	<b>9.0<math>\pm</math>0.94</b>	<b>5.0</b>
Conductivity( $\mu$ s/cm)	235.72 $\pm$ 30.12	236.47 $\pm$ 19.28	<b>236.10<math>\pm</math>0.53</b>	<b>1000</b>
DO(mg/l)	6.78 $\pm$ 0.69	6.55 $\pm$ 0.51	<b>6.67<math>\pm</math>0.16</b>	<b>7.5</b>
BOD (mg/l)	7.44 $\pm$ 1.14	6.3 $\pm$ 1.75	<b>6.87<math>\pm</math>0.81</b>	<b>6.0</b>
Zn(mg/l)	0.32 $\pm$ 0.05	0.30 $\pm$ 0.03	<b>0.31<math>\pm</math>0.01</b>	<b>5.04</b>
Cu(mg/l)	0.27 $\pm$ 0.02	0.26 $\pm$ 0.03	<b>0.26<math>\pm</math>0.01</b>	<b>2</b>
Pb(mg/l)	0.13 $\pm$ 0.04	0.14 $\pm$ 0.04	<b>0.13<math>\pm</math>0.01</b>	<b>0.01</b>
Cr(mg/l)	0.12 $\pm$ 0.03	0.13 $\pm$ 0.05	<b>0.12<math>\pm</math>0.01</b>	<b>0.05</b>
Cd(mg/l)	0.002 $\pm$ 0.001	0.003 $\pm$ 0.001	<b>0.002<math>\pm</math>0.001</b>	<b>0.003</b>

Note: Data on the table is expressed in mean  $\pm$  S.D at  $P \leq 0.0$

### Heavy Metals in Water Samples from the Sampling Stations



The concentration of Lead (Pb) in water ranges between 0.06 to 0.18 mg/l and 0.08 to 0.20 mg/l with a mean concentration of  $0.27 \pm 0.02$  mg/l and  $0.26 \pm 0.03$  mg/l in Station A and Station B while the mean concentration of Copper (Cu) ranges was  $0.27 \pm 0.02$  mg/l and  $0.26 \pm 0.03$  mg/l ranging from 0.21 to 0.31 and 0.21 to 0.30 in Station A and Station B respectively (Tab. 3). The mean concentrations of Cadmium (Cd), Cr and Zn in Stations A and B were  $0.002 \pm 0.001$  mg/l  $0.12 \pm 0.01$  mg/l and  $0.31 \pm 0.01$  mg/l.

### 3.2. Heavy Metals in Fish Samples from the Sampling Stations

Five metals: Lead, Copper, Zinc, Cadmium and Chromium were analyzed in the fish species. The heavy metals were measured in gills, flesh/muscle and liver. The concentration of heavy metals in fish is shown in Tab. 4. Metal concentrations vary from species to species as it displayed species differences. Lead (Pb) was only detected in the gills ( $0.10 \pm 0.01$ ) of *Oreochromis niloticus* while it was not detected in liver and muscle/flesh of the species. In other fish species; the concentration was highest in the gills of *Oreochromis aureus* ( $0.12 \pm 0.003$ ), followed by *Sarotherodon galilaeus* ( $0.06 \pm 0.00$ ) and *Hemichromis fasciatus* ( $0.05 \pm 0.004$ ). In all the examined fish species copper was observed to be highest in the gills ( $0.59 \pm 0.01$ ) of *H. fasciatus* and followed by the muscle of *Oreochromis niloticus* ( $0.64 \pm 0.01$ ), and least value ( $0.31 \pm 0.003$ ) in *Oreochromis aureus*. Chromium (Cr) concentration was observed to be highest in the gills of *Oreochromis niloticus* ( $0.12 \pm 0.004$ ), followed by *Hemichromis fasciatus* ( $0.07 \pm 0.002$ ),. Cadmium was only detected in the gills of *Sarotherodon galilaeus* ( $0.002 \pm 0.001$ ). Zinc (Zn) was observed having its highest concentration in the gills of *Oreochromis niloticus* ( $1.38 \pm 0.002$ ) followed by the gill of *S. galilaeus* ( $1.15 \pm 0.01$  mg/l) and least in *Hemichromis fasciatus* ( $0.09 \pm 0.01$  mg/l). Comparing the values of heavy metals recorded for both fish and water samples, results showed that concentration of metals in fish samples were higher than in water samples except Pb that has higher value ( $0.13 \pm 0.01$  mg/l) in water than fish ( $0.12 \pm 0.003$  mg/l) species.

Table 4: Heavy metals content (mg/kg wet weight) of fish species from River Ofin in Ado Ekiti,

Ekiti State, Nigeria between October to December 2019.

Note: Data on the table is expressed in mean  $\pm$  S.D at  $P \leq 0.05$

Heavy metals	<i>Oreochromis niloticus</i>			<i>Hemichromis fasciatus</i>			<i>Sarotherodon galilaeus</i>			<i>Oreochromis aureus</i>		
	Gills	Muscle	Liver	Gills	Muscle	Liver	Gills	Muscle	Liver	Gills	Muscle	Liver
Zn(mg/l)	1.38 $\pm 0.02$	0.41 $\pm 0.003$	0.15 $\pm 0.01$	0.64 $\pm 0.04$	0.30 $\pm 0.01$	0.09 $\pm 0.01$	1.15 $\pm 0.01$	0.72 $\pm 0.002$	0.56 $\pm 0.01$	0.87 $\pm 0.03$	0.80 $\pm 0.01$	0.24 $\pm 0.01$
Cu(mg/l)	0.41 $\pm 0.01$	0.64 $\pm 0.01$	0.52 $\pm 0.01$	0.59 $\pm 0.01$	0.54 $\pm 0.13$	0.29 $\pm 0.01$	0.73 $\pm 0.01$	0.79 $\pm 0.004$	0.51 $\pm 0.01$	0.29 $\pm 0.01$	0.31 $\pm 0.003$	0.13 $\pm 0.00$
Pb(mg/l)	0.10 $\pm 0.01$	-	-	0.05 $\pm 0.04$	0.01 $\pm 0.00$	0.00 $\pm 0.00$	0.06 $\pm 0.00$	0.01 $\pm 0.003$	0.00 $\pm 0.00$	0.12 $\pm 0.03$	0.06 $\pm 0.002$	0.03 $\pm 0.00$
Cr(mg/l)	0.12 $\pm 0.04$	0.06 $\pm 0.01$	0.02 $\pm 0.00$	0.07 $\pm 0.02$	0.06 $\pm 0.01$	0.01 $\pm 0.00$	0.01 $\pm 0.00$	-	-	0.07 $\pm 0.09$	0.01 $\pm 0.001$	0.00 $\pm 0.02$
Cd(mg/l)	-	-	-	-	-	-	0.002 $\pm 0.001$	-	-	-	-	-

Various degrees of correlations were observed between the water parameters and heavy metal in the water and fish samples of River Ofin. It can be observed from Tab. 5 that in the water

samples, Lead (Pb) had positive correlation with BOD (0.38), Turbidity (0.52) and Electrical conductivity (0.39) while Temperature (-0.68), pH (-0.32) and DO (-0.11) had negative correlation with Lead (Pb). Copper (Cu) had positive correlation with Temperature (0.05), BOD (0.01) and Turbidity (0.60) while pH (-0.85), DO (-0.57) and Electrical conductivity (-0.73) were negatively correlated with it. Cadmium (Cd) was positively correlated with DO (0.27), BOD (0.93), Turbidity (0.09), and Electrical conductivity (0.12) while it had negative correlation with Temperature (-0.21) and pH (-0.10). Chromium (Cr) had positive correlation with only Turbidity (0.43) while other parameters all had negative correlation with it. Zinc (Zn) correlated positively with DO (0.47) and BOD (0.10) and negatively with Electrical conductivity (-0.46), Turbidity (-0.41), pH (-0.11) and Temperature (-0.18).

Table. 6 showed that Lead (Pb) in the fish samples had positive correlation with Temperature (0.92) and Turbidity (0.12) while pH (-0.20), DO (-0.16), BOD (-0.05) and Electrical conductivity (-0.48) were negatively correlated with it. Copper (Cu) had a positive correlation with DO (0.01), BOD (0.09) and Turbidity (0.36) while Temperature (-0.34), pH (-0.60) and Electrical conductivity (-0.03) were negatively correlated with it. Cadmium (Cd) had positive correlation with DO (0.27), BOD (0.93), Turbidity (0.43) and Electrical conductivity (0.12) while it had negative correlation with Temperature (-0.21) and pH (-0.10). Chromium was positively correlated with Temperature (0.59), BOD (0.07) and Turbidity (0.54) while it was negatively correlated with pH (-0.76), DO (-0.25) and Electrical conductivity (-0.49). Zinc (Zn) had positive correlation with Temperature (0.61), BOD (0.05) and Turbidity (0.58) while pH (-0.77), DO (-0.30) and Electrical conductivity (-0.50) had negative correlation with it.

Table 5. Correlation Coefficient between the Physico-chemical parameters and heavy metals of River Ofin in Ado Ekiti, Ekiti State, Nigeria

Temp	pH	DO	BOD	Turbidity	EC	Pb	Cu	Cd	Cr	Zn
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<b>Temp</b>											
<b>Ph</b>	-0.27										
<b>DO</b>	-0.34	0.71									
<b>BOD</b>	-0.24	0.25	0.56								
<b>Turbidity</b>	-0.03	-0.74	-0.63	0.17							
<b>EC</b>	-0.29	0.56	0.46	0.39	-0.03						
<b>Pb</b>	-0.68	-0.32	-0.11	0.38	0.52	0.27					
<b>Cu</b>	0.05	-0.85	-0.57	0.01	0.60	-0.73	0.39				
<b>Cd</b>	-0.21	-0.10	0.27	0.93	0.09	0.12	0.54	0.38			
<b>Cr</b>	-0.31	-0.85	-0.86	-0.43	0.43	-0.37	0.51	0.70	-0.11		
<b>Zn</b>	-0.18	-0.11	0.47	0.10	-0.41	-0.46	-0.11	0.26	0.14	-0.22	

Significant level of  $P \leq 0.05$

Table 6. Correlation between the Physico-chemical parameters and heavy metals in fish samples from River Ofin in Ado Ekiti, Ekiti State, Nigeria

	<b>Temp</b>	<b>pH</b>	<b>DO</b>	<b>BOD</b>	<b>Turbidity</b>	<b>EC</b>	<b>Pb</b>	<b>Cu</b>	<b>Cd</b>	<b>Cr</b>	<b>Zn</b>
<b>Temp</b>											
<b>Ph</b>	-0.27										
<b>DO</b>	-0.34	0.71									
<b>BOD</b>	-0.24	0.25	0.56								
<b>Turbidity</b>	-0.03	-0.74	-0.63	0.17							
<b>EC</b>	-0.29	0.56	0.46	0.39	-0.03						
<b>Pb</b>	0.92	-0.20	-0.16	-0.05	0.12	-0.48					
<b>Cu</b>	-0.34	-0.60	0.01	0.09	0.36	-0.03	-0.37				
<b>Cd</b>	-0.21	-0.10	0.27	0.93	0.43	0.12	-0.01	0.26			
<b>Cr</b>	0.59	-0.76	-0.25	0.07	0.54	-0.49	0.63	0.47	0.29		
<b>Zn</b>	0.61	-0.77	-0.30	0.05	0.58	-0.50	0.64	0.44	0.28	0.99	

Significant level of  $P \leq 0.05$

## 4.0. Discussion

### 4.1. Physico-chemical parameters and Heavy metal in water sample

The results obtained from the analysis of water sampled from the two sampling stations indicated that the quality of water varies greatly between the two stations. The BOD in this study were

consistent with the results obtained by [17] in Omi Dam, [18] in Eleyele Lake, [19] in Kontagora Reservoir, and [20] in Moro Lake. However, this result implied that dissolved oxygen which is an important factor for aquatic life and the chemical characteristics of the environment was completely satisfactory for aquatic life in the river. This viewpoint is corroborated by many authors including [21,22] who established that the minimum dissolved oxygen should not be less than  $5 \text{ mg l}^{-1}$  for aquatic life in inland ecosystems.

The mean temperature and pH recorded during the study were within the normal range for growth and survival of aquatic organisms. These results compared well with other water bodies as reported by Idowu *et al.* [23] in Ado-Ekiti Reservoir, Akindele and Adeniyi [24] in Opa Reservoir, Anago *et al.* [25] in Awba Reservoir, Idowu and Ugwumba [26] in Eleyele Lake, all in Southwestern Nigeria. Conductivity range for the entire reservoir compares well with the ranges recorded for other rivers [27,28]

Also, there is marked high conductivity in the river and this could be attributed to high influx water which contains a lot of suspended and dissolved materials. Turbidity levels are dependent on the amount of suspended particles present in the water. Suspended particles act as a substrate for microorganisms in the water, thus promoting growth of the microbial populations [28]. Shittu *et al.* [29] opined that water turbidity is very important because high turbidity is often associated with higher level of disease-causing microorganisms such as bacteria and other parasite and lower primary productivity. The increase in the values of the turbidity of the rivers under study is an indication of pollution

The mean concentration of lead (Pb)  $0.13 \pm 0.04 \text{ mg/l}$  and  $0.14 \pm 0.04 \text{ mg/l}$  in Station A and Station B respectively was higher than the SON and WHO acceptable limits ( $0.01 \text{ mg/l}$ ). The high concentrations of Pb recorded in this study may be as a result of the direct disposal of domestic waste containing Pb from human activities at the river bank and vehicular exhausts. Pb has been implicated in the ethiology of functional diseases such as microcytic anaemia, inhibitory effects on delta-aminolevulinic acid dehydratase and in neurological damage in young children. It is therefore very important for rivers to be treated and managed so that the Pb level meets these standards before it could be safe for drinking and use for domestic activities [30]

The mean concentration of Zinc (Zn)  $0.32 \pm 0.05 \text{ mg/l}$  and  $0.30 \pm 0.03 \text{ mg/l}$  in Station A and Station B respectively obtained in this study falls within the acceptable SON and WHO limits ( $5.04 \text{ mg/L}$ ). Zinc is a micronutrient which at appropriate level helps in the regulation of vitamin A concentration in the blood. It is also a major component of insulin and is essential in the formation of protein. Likewise, copper is an important micronutrient associated with many metalloenzymes especially cytochrome-c oxidase. Cytochrome-c oxidase plays an essential role in oxidative metabolism. On this basis, this river can support aquatic life if other conditions are favourable, hence may not pose any danger to the community. It was also observed that the concentration of Cadmium, Chromium and Copper in water were lower than the maximum

recommended limit values recommended by FAO and WHO and agrees with the report of [27, 11,12]

#### **4.2. Heavy Metals in Fish Samples**

Heavy metals are one of the more serious pollutants in our natural environment due to their toxicity, persistence and bioaccumulation problems [11]. Most heavy metals have no beneficial functions to the body and can be highly toxic if they enter into the body through inhalation, ingestion and skin. They accumulate in the body tissue faster than the body's detoxification pathways can dispose them off [31]. Waste water streams containing heavy metals are produced by many manufacturing processes and find their way into the environment [32] Metals persist in the environment and become bio-concentrated and bio-amplified along the food chain. This may be responsible for high concentrations of Pb in gill of *O. aureaus* species. Some research findings have shown that heavy metals in aquatic environment could accumulate in biota especially fish as they are the most common aquatic organisms at higher tropic level [33] Fish are often at the top of the food chain in the river and have the tendency to concentrate heavy metals from water [34]. Therefore, bioaccumulation of metals in fish can be considered as an index of metal pollution in the aquatic bodies that could be a useful tool to study the biological role of metals present at higher concentrations in fish [35]. Concern about heavy-metal contamination of fish has been motivated largely by adverse effects on humans, given that consumption of fish is the primary route of heavy metal exposure. In order to effectively control and manage water pollution due to heavy metals, it is imperative to have a clear understanding of their distribution pathways, fate and effect on biota [36]

Fish bioaccumulates trace metals in considerable amounts of metals and store it over a long period of time in the bone, liver and gills as a result of their different physiological roles. The high accumulation of heavy metals in these components can result in serious ecological changes. One of the most serious results of the persistence of these metals is their biological amplification in the food chain [34]. The bioaccumulation of heavy metals varied between species, ages, sex and organs. In general, the target tissues of heavy metals are metabolic active ones which accumulate high levels of metal in fish such as liver and gills, this is not surprising in this study as higher concentration of lead was recorded in the gills of the fish species whereas in muscles where the metabolic activity is relatively low accumulates less level of heavy metals. Similar observation was made by [36]

In this study, higher level of Lead (Pb) and Copper (Cu) were recorded in the gills and muscles of *Sarotherodon galilaeus* respectively as compared to other fish species while the gills of *Hemichromis fasciatus* had higher concentration of Cadmium (Cd) as compared to other fish species and the gills of *Oreochromis niloticus* recorded higher concentration of Chromium (Cr) and Zinc (Zn) respectively. Although some metals such as Zn and Cu were high in the tissues and gills of the fish, they are very low and below the detected limits in the water from where the fish samples were collected. This, however, is in agreement with a study by [37] where the

concentration of heavy metals in fish was high even though the concentration of heavy metals in the water was low. It was also reported by [38] that Ca, Mg, Fe, Cu, Zn and Pb exhibited bio-accumulation from water to fish. These authors reported higher concentrations of metal in fish than in water, which indicates the bio-accumulation. The main reason is the long-term disposal of sewage treated water into the river, which resulted in the accumulation of toxic heavy metals in river water. This may adversely affect the growth of various aquatic vertebrates and invertebrates including fishes.

#### 4.3. Conclusion and Recommendation

The study show that the concentrations of the studied heavy metals are within the recommended values by WHO except Pb that was slightly higher in both water and fish samples. It is therefore recommended that further study should be carried out on the assessment of the quality of the reservoir. Also the community should be sensitized on proper disposal of waste and also the use of biological control of pest to avoid the use of pesticides in the farm and subsequently possible harmful chemicals into the water bodies.

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