Levels of some heavy metals in fish organs from Egbe Dam, Ekiti State, Nigeria

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This research studied the levels of cadmium, chromium, copper, cobalt, Iron, lead, nickel and zinc in the gill, liver, bone, and muscle of *Tilapia zilli, Oreochromis niloticus* and *Clarias gariepenus* and its associated water and sediment from Egbe dam in Ekiti – State. The levels of the metals in water were much lower than their corresponding concentrations in the sediment. Also, concentrations of the metals in the fish organs were higher than those recorded for the water except Cu, Zn and Fe in *Oreochromis niloticus*. It was observed that the mean concentrations of the metals in *Tilapia zilli* and *Clarias gariepinus* followed the order Muscle < Bone < Gills < Liver, while the order in *Oreochromis niloticus* was Muscle < Bone < Liver < Gills that showed that muscle possessed the lowest concentration of all the metals and that the metals varied among fish species and organs. Also, the highly toxic metals (Pb, Cd) detected fell below the Maximum Allowed Limit by Median International Standard. The result of this study, however, established the presence and bioaccumulation of these heavy metals in fish organs from water and sediment column hence, the need for continuous monitoring of the dam.

Keywords: Heavy, Metals, Fish, Organs, Egbe, Dam

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INTRODUCTION

Water bodies consist of foods that are rich in essential amino acids, fatty acids, protein, carbohydrates, vitamins, and minerals. Among sea foods, fish are commonly consumed and hence, are a connecting link for the transfer of several minerals and pollutants such as heavy metals from water bodies to human being. Heavy metals have the tendency to accumulate in various organs of marine organisms, especially fish, which may, in turn, enter humans through consumption, thus causing serious health hazards [1].

Pollution of heavy metals in aquatic ecosystem is growing at an alarming rate due to an increase in human activities and has become an important worldwide problem [2]. Heavy metals cannot be degraded but they are deposited, assimilated, or incorporated in water, sediments and aquatic biota causing pollution in water bodies [2, 3]. Heavy metals in water can originate both from natural sources, industrial, agricultural, and domestic activities in the drainage basin of a water system. As the metal levels in many aquatic ecosystems increase due to anthropogenic activities, they raise the concern on metal bioaccumulation through the food chain and related human health hazards [4 - 6]. Fish, being at the top of the aquatic food chain, may concentrate large amounts of metals from the water.

Fish analysis is often used as an indicator of heavy metals' contamination in the aquatic ecosystem because they occupy high trophic levels and are important food sources [7]. Analysing pollutants in living organisms is more attractive and

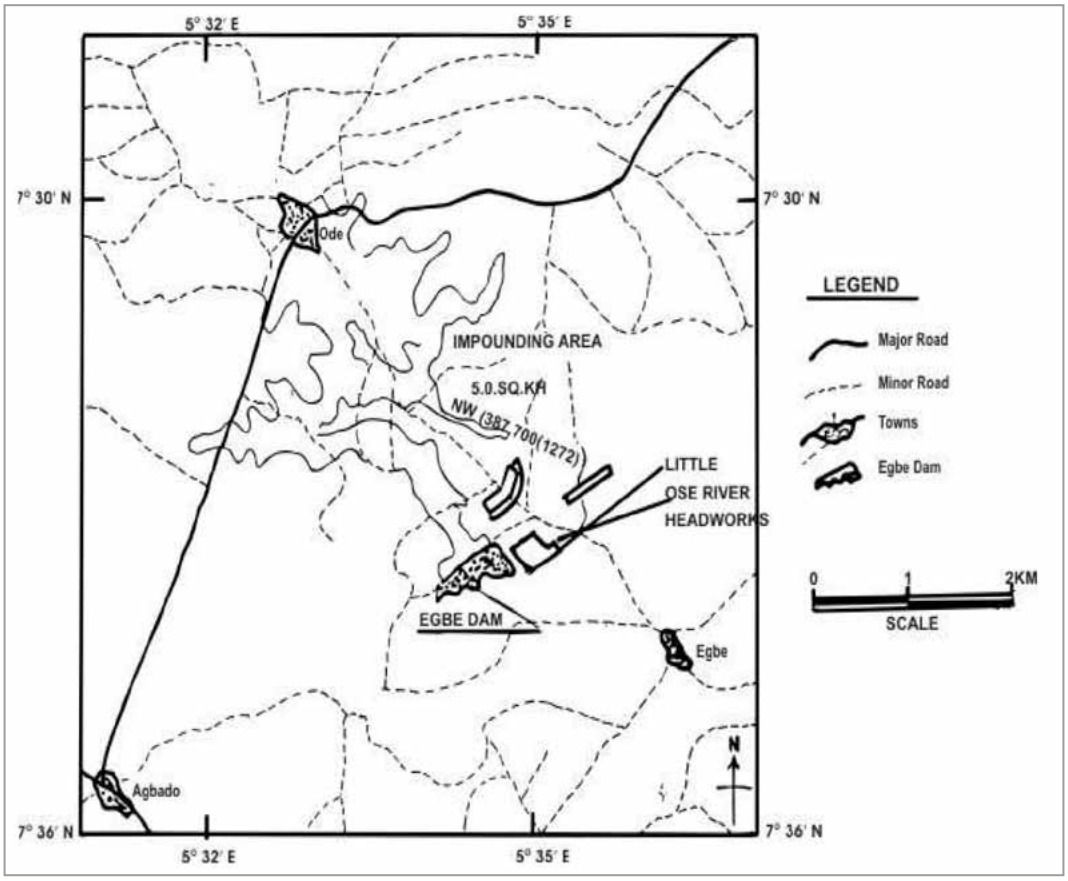

Figure 1 - Map of Egbe Dam

promising than analysing pollutants of the abiotic environment, as living organisms provide precise information on the bioavailability of pollutants [8]. This may assist in predicting pollutants transfer exposure and the health consequence to humans. In addition, such information is crucial in risk assessment for seafood safety purposes. In view of this, numerous studies have been carried out on metal pollution in different species of edible fish [9 - 13].

Egbe dam, which is one of the four major dams used for agricultural, artisanal fishing and domestic water supply in Ekiti - State was assessed for its fisheries potential [14]. The potential fish yield of the reservoir was predicted to be 413.9 metric tonnes per annum of the total reservoir area of 272.5 ha while the post-calculated (actual) annual fish yield is 126.58 kg ha^{-1}. This dam provides vital employment opportunities for the teaming youth within the surrounding communities such as Egbe, Ode and Aisegbe etc. all in Gbonyin Local Government Area of Ekiti State, Nigeria.

However, information concerning the level of heavy metal pollution in the dam is scanty or not available. Therefore, it is of great significance to assess and compare the concentration of heavy metals in fish and water samples from Egbe dam with the laid down maximum allowed limit by several monitoring organizations such as World Health Organisation (WHO) and the United States Environmental Protection Agency (USEPA). This will enable effective monitoring of both environmental quality and the health of aquatic organisms in the reservoir. It will also help the consumers of the fish from the dam to know how safe the fish they consume is.

EXPERIMENTS

STUDY AREA

Egbe reservoir is situated across Egbe River, which is in the suburb of Egbe Ekiti in Gbonyin Local Government Area of Ekiti State, South West, Nigeria. The reservoir takes its source from Kwara State and runs through Ekiti to Ondo State and eventually empty into the popular Osse River in Ondo state. The reservoir lies between latitudes 7° 36' N and 7° 39' N and longitude 5° 32' E and 5° 35' E of the equator. The entire length of the reservoir is 26.5 acres, and the depth is 64 m [14].

SAMPLE COLLECTION AND TREATMENT

Life samples of three species of Fishes, *Clarias gariepinus, Oreochromis niloticus, Tilapia zilli* were obtained from the dam with the assistance of local Fishermen. The samples were transported live to the laboratory where each species was grouped into different sizes. After the grouping, the fishes were killed by asphyxia-

tion, weighed and scales removed from *fish* and washed with distilled water. The samples were kept in the freezer prior to analysis.
Samples of the dam water from randomly selected locations in the reservoir (four sampling points) were collected. At every sampling point, the sampling containers were thoroughly washed with the water sample before final collection. Water samples collected were stored in pre-washed 1litre polythene bottle and fixed to a pH of <2 by the addition of 5 ml conc. HNO_3. Sediment samples from the dam were also taken at the same point where the water samples were collected with the assistance of Divers. Collected samples were drained and put in pre-cleaned polythene bags. The samples were air dried prior to analysis. All samples were properly labelled.

SAMPLE ANALYSIS

Muscle, bone, liver, and gills of the different species of fish were wrapped in aluminium foil and oven dried at 103°C in a Gallenkamp moisture extraction oven until constant weight was obtained and then grinded into powder using laboratory mortar and pestle. 1 g of each sample were accurately weighed and digested using a 20 ml mixture of 68% concentrated nitric acid and 62% perchloric acid in ratio 5:2 in a fume cupboard until colourless liquid was obtained [15], [16]. The solutions were allowed to cool at room temperature, filtered into a 25 ml standard flask and diluted to the mark with distilled water. The water samples were removed from the refrigerator and 100 ml of the water samples in each case was measured into 250 ml beaker and digested on a hot plate with the addition of 10 ml concentrated nitric acid. The solution was heated to almost dryness, diluted with 20 ml of 10% HNO_3 and the solution filtered with Whatman No. 42 filter paper into 25 ml standard flask and diluted to mark with distilled water [17].
The air-dried soil sediment samples were grounded using laboratory mortar and pestle until obtaining fine powder and sieved using a 2.00 mm mesh sieve. 1g of the grounded sample was weighed in each case and digested with 20 ml mixture of 68% concentrated nitric acid and 62% perchloric acid in the ratio 5:3 on hot plate at temperature of 120°C in a fume cupboard until a clear solution was obtained. After cooling, the digest was filtered into 25 ml standard flask and made up to the mark with distilled water [18].
The levels of Pb, Zn, Fe, Cr, Ni, Cd, Co and Cu of all the digests and blanks were determined using Flame Atomic Absorption Spectrophotometer (F. A. A. S) Buck Scientific Model 200A. Each preparation of sample was carried out in triplicate.

STATISTICAL ANALYSIS

One way ANOVA and Duncan multiple range test were used to evaluate the significant difference in the concentration of different studied metals with respect to different organs of fish. A probability at level of 0.05 or less was considered significant [19]. Standard errors were also estimated (Fig. 1).

RESULTS AND DISCUSSION

Table I presents the mean concentrations of heavy metals analysed in the dam water. In the water samples, the mean concentration of heavy metals in mg/L was Cu (0.020), Cd (0.003), Cr (0.077), Zn (0.108), and Pb (0.055), Fe (0.400), Ni (Below Detection Limit), Co (Below Detection Limit). The order of the heavy metals concentration in the water was Fe > Zn > Cr > Pb > Cu > Cd > Ni = Co.
Table II shows the mean concentrations of heavy metals analysed in the sediment samples taken from the various water sampling locations. The mean values of heavy metals in mg/kg were Cd (0.046), Cr (0.969), Cu (0.678), Ni (0.257), Fe (0.804), Zn (0.801), Co (0.125) and Pb (0.330) respectively. The order of heavy metal concentrations in sediment was Cr > Fe > Zn > Cu > Pb > Ni > Co > Cd.

Table I - Heavy metal concentration (mg/L) in dam water sample

Metals	Mean	USEPA 2002	WHO 2008
Cu	0.020 ± 0.001	1	2
Zn	0.108 ± 0.012	2	3
Cr	0.077 ± 0.006	0.1	2
Cd	0.003 ± 0.007	0.01	0.003
Pb	0.055 ± 0.003	0.05	0.01
Fe	0.400 ± 0.033	.....	0.30
Ni	BDL	.....	.....
Co	BDL	.....	.....

B.D.L = Below Detection Limit; Metal concentration recorded as means ± standard deviation; Mean value is the result of three replicates

Table II - Heavy metal concentration (mg/Kg) in dam sediment sample

Metal	Mean
Cd	0.046 ± 0.011
Cr	0.969 ± 0.020
Cu	0.678 ± 0.010
Pb	0.330 ± 0.003
Zn	0.801 ± 0.090
Fe	0.804 ± 0.010
Ni	0.257 ± 0.001
Co	0.125 ± 0.090

Metal concentration recorded as means ± standard deviation; Mean value is the result of three replicates

Table III shows the bioaccumulation index of heavy metals concentration in water and sediments. This is the ratio of heavy metal concentration in sediments to the concentration in surface water.

Tables IV - VI show the mean concentrations of cadmium, chromium, copper, nickel, iron, cobalt, lead and zinc in the bone, gill, muscle, and liver of *Tilapia zilli, Clarias gariepinus and Oreochromis niloticus* along with the results of statistical comparison of the metal concentrations.

Comparing the concentration of heavy metals in surface water and sediments gave the relative accumulation index of more than 1 for all the metals determined in this study (Table III). This clearly shows that the concentrations in sediment were much higher than that of surface water. This is in complete agreement with other literature [11], [20 - 22].

While weathering of rocks and farming activities has been the major source of heavy metals in natural water and sediments [25], higher concentration is expected in the sediment since it acts as repository for all contaminants and dead organic matter from the water column.

Apart for Pb that is slightly higher than the limit set by the United State Environmental Protection Agency (USEPA), the values of heavy metals recorded in the Dam water in this study were generally low when compared to the limit of chronic reference values suggested [23, 24] and as such safe for drinking (Table I).

Table III - Relative accumulation index of sediment/water

Metals	Water	Sediment	Bioaccumulation Index
Cu	0.020	0.678	33.9
Zn	0.108	0.801	7.4
Cr	0.077	0.969	12.6
Cd	0.003	0.046	15.3
Pb	0.055	0.330	6
Fe	0.400	0.804	2.01
Ni	BDL	0.257	…..
Co	BDL	0.125	…..

B.D.L = Below Detection Limit; Mean value is the result of three replicates

Table IV - Mean concentrations of heavy metal in *Tilapia zilli (mg/kg)*

Parts	*Cu*	*Zn*	*Cr*	*Cd*	*Pb*	*Ni*	*Fe*	*Co*
Muscles	0.010^{a}±0,091	0.850^{b}±0.010	0.068^{a}±0.030	0.190^{a}±0.020	0.723^{a}±0.090	0.014^{a}±0.100	1.484^{a}±0.110	BDL
Bone	0.107^{b}±0.102	0.900^{b}±0,001	0.293^{b}±0.130	0.178^{b}±0.083	1.577^{b}±0.180	0.041^{b}±0.140	1.648^{a}±0.101	0.104^{b}±0.901
Gills	0.041^{a}±0.130	0.390^{a}±0.020	0.341^{b}±0.104	0.169^{b}±0.020	0.720^{a}±0.132	0.059^{b}±0.170	3.210^{b}±0.110	0.130^{b}±0.110
Liver	0.280^{c}±0.100	1.635^{c}±0.900	0.555^{c}±0.130	0.096^{a}±0.140	2.087^{c}±0.100	0.084^{b}±0.020	5.460^{c}±0.110	0.110^{b}±0.020

Metal concentration recorded as means ± standard deviation; Mean value is the result of three replicates; Data on the same column with different superscripts are significantly difference ($P < 0.05$); BDL: Below Detection Limit

Table V - Mean concentrations of heavy metal in *Clarias gariepinus (mg/kg)*

Parts	*Cu*	*Zn*	*Cr*	*Cd*	*Pb*	*Ni*	*Fe*	*Co*
Muscles	0.033^{b}±0,004	0.206^{a}±0.031	0.047^{a}±0.100	0.061^{a}±0.360	1.110^{b}±0.290	0.023^{a}±0.310	1.988^{a}±0.100	BDL
Bone	0.164^{c}±0.220	0.839^{b}±0.060	0.090^{a}±0.220	0.150^{b}±0.100	1.807^{b}±0.310	0.009^{a}±0.070	2.922^{a}±0.006	0.072^{b}±0.310
Gills	0.009^{a}±0,111	1.697^{c}±0.310	0.212^{b}±0.110	0.292^{b}±0.290	2.433^{b}±0.160	0.030^{a}±0.220	3.509^{b}±0.810	1.020^{b}±0.110
Liver	0.062^{b}±0.110	3.974^{d}±0.310	0.549^{b}±0.290	0.619^{c}±0.340	0.383^{a}±0.220	0.280^{b}±0,009	4.789^{b}±0.310	1.760^{b}±0.710

Metal concentration recorded as means ± standard deviation; Mean value is the result of three replicates; Data on the same column with different superscripts are significantly difference ($P < 0.05$); BDL: Below Detection Limit

Table VI - Mean concentrations of heavy metal in *Oreochromis niloticus (mg/kg)*

Parts	*Cu*	*Zn*	*Cr*	*Cd*	*Pb*	*Ni*	*Fe*	*Co*
Muscles	0.064^{a}±0.060	0.510^{a}±0.360	0.198^{c}±0.040	0.092^{a}±0.074	1.06^{c}±0.092	0.023^{a}±0.111	1.934^{a}±0.913	0.048^{b}±0,011
Bone	0.078^{a}±0.160	0.813^{a}±0.260	0.312^{c}±0.231	0.247^{b}±0.652	0.78^{c}±0.063	0.101^{b}±0.092	2.036^{a}±0.992	0.101^{b}±0.093
Gills	0.454^{b}±0.090	2.765^{b}±0.110	0.028^{b}±0.062	0.090^{a}±0.061	0.009^{a}±0.001	0.210^{b}±0.191	1.908^{a}±0.381	BDL
Liver	0.430^{b}±0.070	3.908^{c}±0.140	0.009^{a}±0.001	0.021^{a}±0.043	0.102^{b}±0.061	0.314^{b}±0.084	5.672^{b}±1.901	BDL

Metal concentration recorded as means ± standard deviation; Mean value is the result of three replicates; Data on the same column with different superscripts are significantly difference ($P < 0.05$); BDL: Below Detection Limit

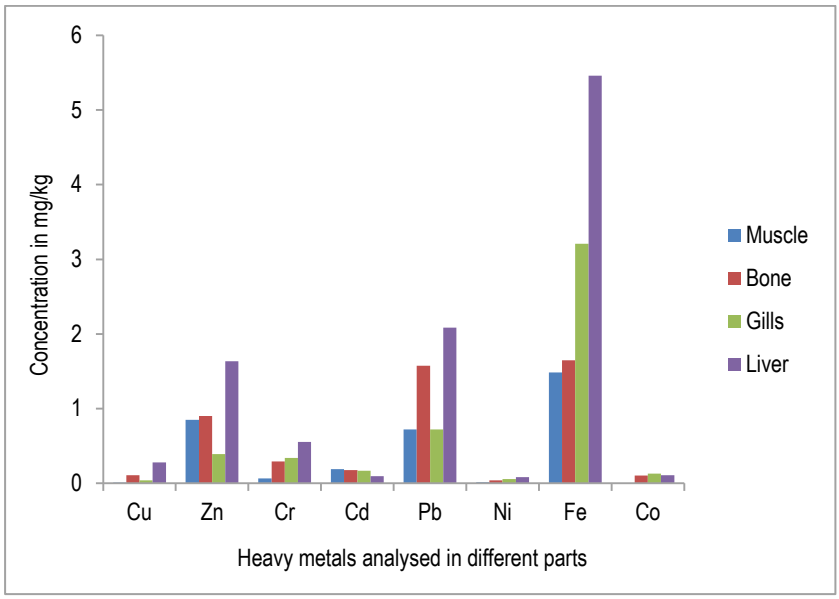

Figure 2 - Concentration of heavy metals in different organs of *Tilapia zilli*

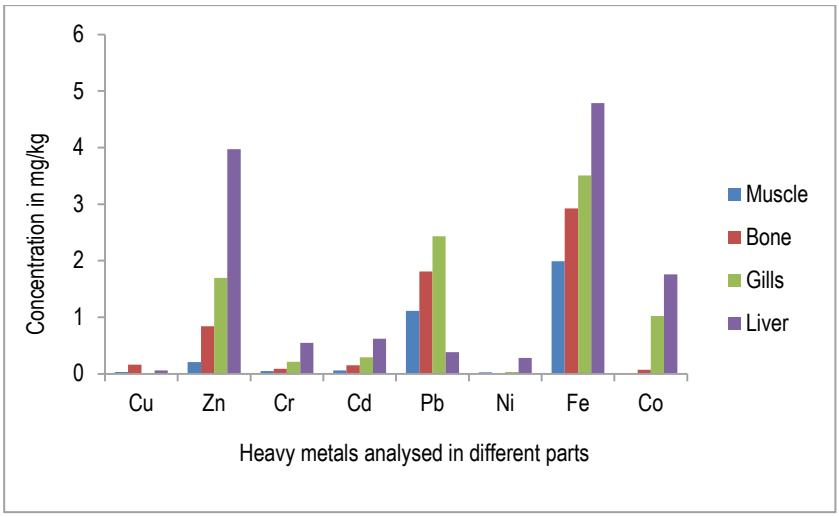

Figure 3 - Concentration of heavy metals in different organs of *Clarias gariepinus*

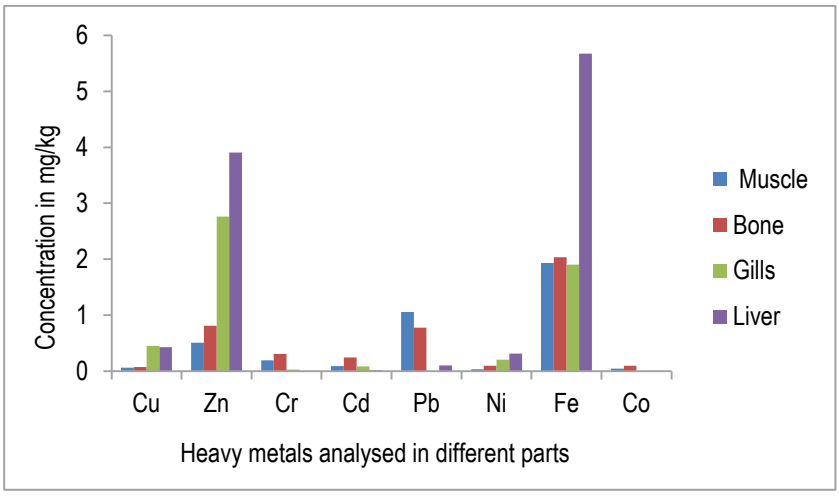

Figure 4 - Concentration of heavy metals in different organs of *Oreochromis niloticus*

Similar report has been attributed to water from Ero dam [11].

The relative distribution of heavy metals in the fish tissues are shown in Figures 2 - 4 for the 8 metals analysed. It was observed that the mean concentrations of the metals in the three fish species followed the order Muscle < Bone < Gills < Liver in *Tilapia zilli and Clarias gariepinus*, while the order in *Oreochromis niloticus* was Muscle < Bone < Liver < Gills. This result shows that the muscle and bone tissues of these fishes are not active in accumulating heavy metals compared to liver and gills in accumulating heavy metals.

Cadmium and lead are non-essential micronutrients accumulated in human tissues and are harmful to human health. The mean levels of all the metals vary for all the different organs of the different species. The respective levels of lead and cadmium in the muscles were 0.723 mg/kg and 0.190 mg/kg for *tilapia zilli;,* 1.110 mg/kg and 0.061 mg/kg for *Clarias gariepinus;* and 1.060 *mg/kg* and 0.092 mg/kg for *Oreochromis niloticus*.

The Maximum Allowed Limit for lead and cadmium in food fish specified by the E.U is 0.20 mg/kg and 0.05 mg/kg wet weight respectively [5], [26] while the tolerable levels by the Median International Standards (MIS) for lead and cadmium in food are 2 mg/kg and 0.3 mg/kg respectively [27]. The values of lead and cadmium obtained in the muscle were lower than the median international standard but were all higher than the E.U standard.

Iron, copper, chromium, nickel, cobalt, and zinc are essential metals in the biota and are regulated by physiological mechanism in most organisms. However, occurrence of excessive concentrations of these metals is regarded as a potential hazard that could endanger both the fish and human health [4]. The mean values of the metal in mg/kg in the muscles of the different fish species from the dam were Fe (1.484), Cu (0.010), Zn (0.850 mg/kg), Cr (0.068 mg/kg), Ni (0.014 mg/kg) and Co (not detected) for *Tilapia zilli, Fe (1.988),* Cu (0.033), Zn (0.206 mg/kg), Cr (0.047 mg/kg), Ni (0.230 mg/kg) and Co (not detected) for *Clarias gariepinus;* and Fe (1.934), Cu (0.064 mg/kg), Zn (0.510 mg/kg), Cr (0.198 mg/kg), Ni (0.023) and Co (0.048) for *Oreochromis Niloticus.*

The Median International Standard (MIS) values of Cu, Cr and Zn in food for human consumption are 20 mg/kg, 1.0 mg/kg and 45 mg/kg wet weight [27]. The levels of Cu, Cr and Zn recorded in fish are far below the Median International Standard. Hence, the observed metal levels posed no threat to the consumption of fish muscles from the dam.

The health quality of fish bone is becoming increasingly important due to its application in the production of food additives such as Gelatine [28]. Therefore, its health quality is becoming more important. The maximum value of lead in fishbone was found in *Clarias gariepinus* with a concentration of 1.807 mg/kg but still within the maximum allowable level of 2 mg/kg, while the maximum value for cadmium in fishbone (0.247 mg/kg) was found in Oreochromis niloticus, which is also below the MIS value, but all are above the EU value. Though little work has been done on the concentration of heavy metals in fishbone, the report of heavy metals concentration in fishbone was higher than the muscle in Lithuania freshwater fish species [29]. This is consistent with the findings in the present study.

Liver and gill are the major organs with high metal storage in fishes. Gill accumulates heavy metal in the head, while liver is found in the trunk as the major active site for metal storage. The concentration of Pb (2.433 mg/kg) in gill of *Clarias gariepinus* was higher than the Median International Standard of 2.00 mg/kg.

This result also showed that liver accumulated the highest concentration of metals in all fish species except Cadmium and Cobalt in *Tilapia zilli*, Lead in *Clarias gariepinus*, Copper and chromium in *Oreochromis niloticus* where the gills accumulated the highest concentration. This shows that gills and liver have high tendency to accumulate metals, thus should be avoided when consuming fish. The observed results are consistent with what was previously reported in the liver of freshwater fishes [5, 22], [29 - 31]. Thus, gill and liver are considered suitable as a control mechanism in monitoring heavy metal pollution of the aquatic habitat [7].

Figure 5 shows the ratio of investigated heavy metal levels in fish relative to their concentrations in the water column. It was observed that higher concentrations of the metals were detected in fish instead of water suggesting the bioaccumulation of these metals in the fish organs except for copper, zinc, and Iron of which the concentration in water was higher than in the fish organ of *Oreochromis niloticus*. Similar observation was reported by Wadi Hanifah, Saudi Arabia [31].

On the other hand, Figure 6 shows that the sediment sample contained higher concentration of metals than the fish organs in *Oreochromis niloticus* and *Clarias gariepinus* with the exemption of Iron which contains higher concentration in *Clarias gariepinus*. However, the concentration of zinc, lead, cadmium, and iron were higher in the fish organs of *Tilapia zilli* than in the sediment due to low deposition of these metals in the sediment, or higher in their exchangeable or labile form in the sediment matrix, thus having low resident time in the sediment, or are more bioaccumulated in the fish organs [31 - 33].

This result shows that the metal concentrations in organs of the different fish species are strongly associated with the distribution and levels of the analysed metals in water and sediment.

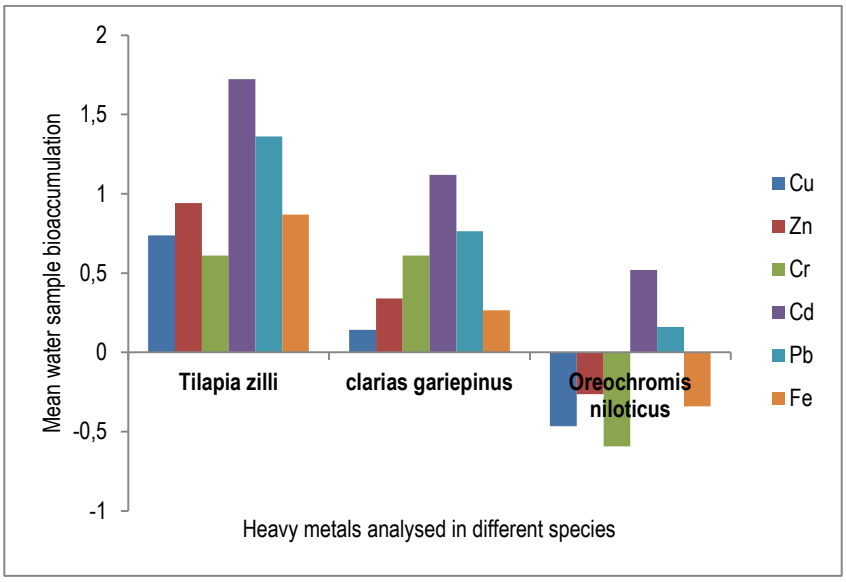

Figure 5 - A plot of the log ratio of mean concentrations of metals in fish and water column.

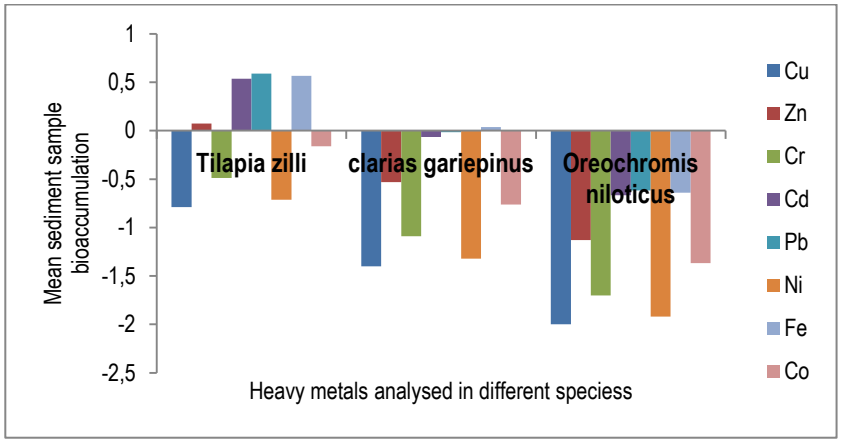

Figure 6 - A plot of the log ratio of mean concentrations of metals in fish and sediment column.

CONCLUSION

This research confirmed the presence of heavy metals in Egbe dam of Ekiti State that could arise from both natural and anthropogenic impacts from various farming activities. However, the presence is not harmful to consumption by the populace since the level of heavy metals studied in water and the edible parts of the fish do not exceed the Maximum Allowed Limit (MAL) by different standards.

Nonetheless, there is still need for continuous monitoring of this dam. The liver and gills of the fish species could serve this purpose since all the metals studied were detected in higher concentrations in both liver and gills of all the fish species.

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