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An Assessment of Heavy Metals in *Synodontis Clarias* (Linnaeus, 1766) from Ikpoba Reservoir, Benin City, Nigeria.

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***Key words**:* Heavy metals, *Synodontis clarias*, Ikpoba Reservoir, Nigeria.

ABSTRACT: This study determined the concentrations of Cd, Mn, Cu, Pb, Zn and Cr in *Synodontis clarias* (Linnaeus, 1766) and water from Ikpoba Reservoir, Benin City, Nigeria, in order to ascertain the magnitude of impact by these heavy metals on the resources of the investigated ecosystem. The mean concentrations of the heavy metals in fish were Cd (0.01mg/kg), Mn (2.38 – 2.54mg/kg), Cu (0.09 – 0.16mg/kg), Pb (0.03 – 1.25mg/kg), Zn (10.45 – 15.38mg/kg) and Cr (0.01 – 0.02 mg/kg). The mean concentrations of the heavy metals in water were Cd (0.01mg/l), Mn (0.02 – 0.03mg/l), Cu (0.19 – 0.32mg/l), Pb (0.05 – 0.08mg/l), Zn (98.70 – 132.38mg/l) and Cr (0.02 – 0.05mg/l). The mean concentrations of Pb and Zn in fish, were significantly different ($P < 0.05$) between stations while the mean concentrations of Cu and Zn in water, were significantly different ($P<0.05$) between stations. Manganese was bioaccumulated by the fish at all the stations while Pb was bioaccumulated by the fish at all the stations except at the low lift pump station. Heavy metal concentrations in fish and water were discussed with reference to the World Health Organisation (WHO) limits for food fish and water. It was advocated that regular monitoring of heavy metals in fish and water in the Reservoir be carried out in other to curtail further negative impacts

There is a growing concern about the impact of heavy metals on the aquatic environment around the world. Pollution of streams, rivers, lakes and other water bodies constitute great danger in that such polluted water finds its way into municipal drinking water sources thereby becoming a health hazard. It has been reported that in many African countries, considerable population growth accompanied by a steep increase in urbanization, industrial and agricultural land use has resulted in the discharge of pollutants into receiving waters, causing undesirable effects on the aquatic environment and its resources (Oronsaye *et. al.,* 2011)

The presence of heavy metals in aquatic ecosystems is the result of two main sources of contamination; natural processes or natural occurring deposits and anthropogenic activities. The main sources of heavy metals pollution to biotic forms are invariably the result of anthropogenic activites (Francis, 1994). Heavy metals cannot be destroyed through biological degradation as in the case of most organic pollutants and they are easily assimilated and can be bioaccumulated in the protoplasm of aquatic biota (Egborge, 1994). Heavy metals are considered hazardous to aquatic life because of their extreme persistence, high toxicity, tendency to bioaccumulated and because they are available through diverse anthropogenic sources (Atchison et al., 1987). It has been demonstrated that fish exposed to high levels of heavy metals in water can take up substantial quantities of these metals (Wangboje and Oronsaye, 2001)

Heavy metal concentrations in aquatic ecosystem are usually monitored by measuring their concentrations in environmental matrices such as flora, fauna, water and sediment (Camusso et al., 1995). Bioaccumulation and biomagnifications of heavy metals are two processes capable of leading to toxic levels of metals in fish even when the exposure is low. The presence of heavy metals in fresh water ecosystems above their respective natural background concentrations is known to disturb and to disrupt the delicate balance of aquatic ecosystems.

Fishes are notorious for their ability to concentrate heavy metals in their bodies and since they provide a source of quality protein to man, they need to be screened to ensure that unnecessary high levels of heavy metals are not being transferred to man through fish consumption (Ekeonyanwu *et al.,* 2011). The use of fish as bio-indicators of heavy metal pollution of aquatic environments and possible

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unfitness for human consumption from a toxicological view point has been documented (Kalay and Canli, 2000; Chale, 2002; *Ozturk et. al*., 2008). The Ikpoba Reservoir, situated in Benin City, Nigeria, is an important source of potable drinking water and fish to inhabitants of the City. *Synodontis clarias* is a popular freshwater fish used as human food. It is an omnivorous benthic feeder, feeding on detritus, insect larvae, and filamentous algae. It commonly inhabits rivers, creeks, lakes and dams. This study was geared towards investigating the concentrations of heavy metals in *Synodontis clarias*, in order to ascertain the potential ecological risk of these metals. The results obtained from the study are expected to provide valuable information on the concentrations and distribution of heavy metals in fish, contributing to the effective monitoring of the Ikpoba Reservoir ecosystem.

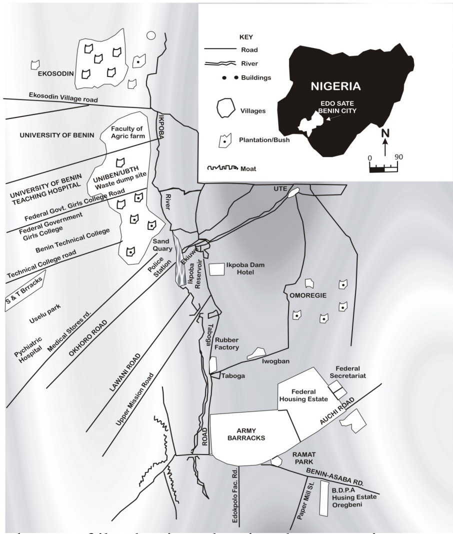

Fig. 1: map of ikpoba river showing the reservoir source: Edo state urban water board

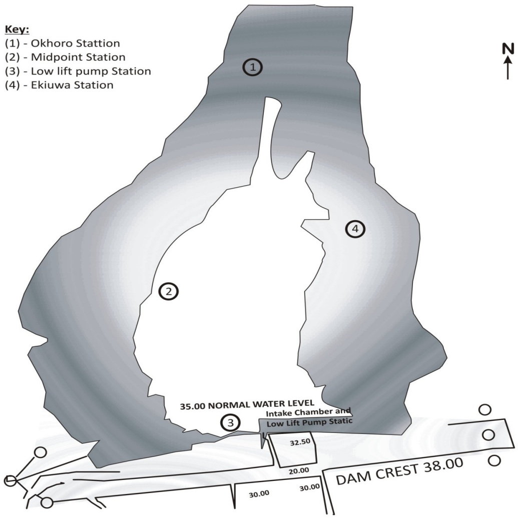

Fig.2: Aerial View Of The Reservoir Showing The Stations Source: Edo State Urban Water Board

MATERIALS AND METHODS

Study Area: Figure 1 shows the map of the Ikpoba River showing the Ikpoba Reservoir. The Ikpoba River was impounded in 1977 by a weir to form the Ikpoba Reservoir which seperates the downstream from the upstream sections of the river. The Reservoir is situated some 3.75 km South-East of the Ugbowo Campus of the University of Benin, Benin City. The climate of the area is typically tropical with wet (April – October) and dry (November – March) seasons. Rainfall is bi-modal, peaking in July and September with a brief break in August. Annual temperature ranges from 29^0C to 35^0C while annual humidity is between 67% and 96%. Human activities around the Reservoir include farming, bathing, laundry and fishing. In the vicinity are sawmills, a rubber processing factory and a quarry. The marginal vegetation includes *Commelina species, Sida acuta*, mimos*a pudica, Talinum triangulare and Ipomea species*. The length of the river is flanked by thickets of *Bambusa species and Elaeis guineensis*.

Sampling: The Reservoir covers a total surface area of about 1.1 million m^2 (107.5 hectares), within which four stations were established namely; Okhoro station, Midpoint station, Low-lift pump station and Ekiuwa station (Fig. 2).

There is a run-off drainage channel that empties into the Reservoir at the Okhoro station. Solid wastes including types, beverages cans, polythene bags and glass bottles are visible in the Reservoir at this station. It is at the low lift pump station that raw and unfiltered water from the Reservoir is pumped out and subjected to chemical treatment by the Edo state urban water Board Authorities, whom operate and manage the Reservoir. The midpoint station is approximately equidistant (0.075km) between the Okhoro and low lift pump stations. The Ekiuwa station is adjacent to the Ekiuwa community of the City. Duplicate samples of water and fish were randomly collected from the various stations between August 2005 and December 2005. Water samples were collected at a depth of 20cm below the water surface in 250ml capacity plastic bottles with screw caps. The bottles were treated with 10% nitric acid and rinsed with distilled water before use (Adams *et. al.,* 1980). The fish samples were caught using baited hooks and traps. Fish samples were washed in flowing water to remove adhering dirt. The fish were transported to the laboratory within 24 hours in ice boxes and stored in a deep freezer, prior to analysis.

*Sample Treatment:*Frozen samples were thawed at room temperature (27^0C). Water samples were not given further treatment, but were mixed vigorously before aspiration into the flames of on Atomic Absorption Spectrophotometer (Varion Techtron Spectra B Model) for heavy metal analysis. Heavy metal values were expressed in mg/l. Fish samples were oven dried to constant weight at 105 ± 2^0C and thereafter milled using a porcelain mortar and pestle. Digestion of all milled samples was carried out according to the method as described by Streedevi *et. al*; (1992). One (1) gram of each sample was digested using 1:5:1 mixture of 70; perchloric acid, concentrated nitric acid and concentrated sulphuric acid at 80 ± 5^0C in a fume chamber until a colourless liquid was observed. Each digest was analyzed for heavy metal concentrations using an Atomic Absorption Spectrophotometer (Varion Techtron Spectra B Model). Levels of heavy metals were expressed in mg/kg. The study was laid out as a factorial experiment within a Randomized Complete Block Design.Tests of significance (at 5 % level of significance) between the stations were carried out using the Analysis of Variance (ANOVA) of the Statistical Package for Social Sciences (SPSS) Computer Programme , Version 16.0 for Windows.

Bioaccumulation Quotient (BQ) for heavy metals: Bioaccumulation Quotient (BQ) values for heavy metals were calculated to ascertain the bioaccumulation of heavy metals in fish based on the method by Adams *et. al.,* (1980)

$$BQ = \frac{concentration\ of\ heavy\ metal\ in\ fish}{concentration\ of\ heavy\ metal\ in\ water}$$

RESULTS AND DISCUSSION

Heavy Metals in Water: The heavy metals detected in water were Cadmium (Cd), Manganese (Mn), Copper (Cu), Lead (Pb), Zinc (Zn) and Chromium (Cr). The monthly variations of the respective heavy metals are presented in Table 1. The mean values for Cd was 0.01mg/l at the stations. The mean values for Mn were 0.03mg/l (Okhoro station and low lift pump station), out 0.02mg/L (Midpoint and Ekiuwa stations). The mean values for Cu were 0.27mg/l (Okhoro station), 0.19mg/l (Midpoint and Ekiuwa stations) and 0.32mg/l at the low lift pump station. The mean values for Pb were 0.08mg/l (Okhoro and low lift pump station station), 0.06mg/l (midpoint station) and 0.05mg/l (Okhoro station), 114mg/l (midpoint station), 121.13mg/l (low lift pump station) and 98.70mg/l (Okhoro station), 0.02 mg/l (midpoint and Ekiuwa stations) and 0.05mg/l (low lift pump station). Statistical analysis (ANOVA) showed that the mean values of Cd, Mn, Pb and Cr were not significantly different (P >0.05) between stations however the mean values for Cu and Cr were significantly different (P <0.05) between the stations.

Table 1: Monthly Variations of Heavy Metals in Water (Values in mg/l)

STATION	**OKHORO**						**MID POINT**						**LOW LIFT PUMP**						**EKIUWA**					
METALS	Cd	Mn	Cu	Pb	Zn	Cr	Cl	Mn	Cu	Pb	Zn	Cr	Cd	Mn	Cu	Pb	Zn	Cr	Cd	Mn	Cu	Pb	Zn	Cr
August	0.02	0.03	0.05	0.08	140	0.04	0.01	0.03	0.02	0.07	118	0.02	0.02	0.04	0.45	0.10	13.5	0.06	0.02	0.03	0.32	0.06	120	0.01
September	0.01	0.02	0.54	0.07	141.67	0.05	0.02	0.03	0.52	0.06	112	0.01	0.02	0.03	0.40	0.08	140.25	0.04	0.01	0.02	0.24	0.04	102	0.03
October	0.02	0.03	0.45	0.06	139.53	0.04	0.01	0.02	0.26	0.05	125	0.02	0.01	0.04	0.50	0.08	135.50	0.06	0.02	0.03	0.22	0.04	109	0.04
November	0.01	0.03	0.03	0.10	100.46	0.04	0.001	0.02	0.02	0.06	95.26	0.02	0.01	0.02	0.24	0.07	120.50	0.05	0.01	0.01	0.15	0.05	100	0.01
December	0.01	0.03	0.03	0.08	140.25	0.04	0.02	0.15	0.15	0.05	120.65	0.03	0.01	0.03	0.005	0.07	74.42	0.04	0.01	0.01	0.004	0.06	62.52	0.02
Mean	0.01	0.03	0.27	0.08	132.38	0.04	0.01	0.19	0.19	0.06	114	0.02	0.01	0.03	0.32	0.08	121.13	0.05	0.01	0.02	0.19	0.05	98.70	0.02

Table 2: Monthly Variations of Heavy Metals in *Synodontis clarias* (Values in mg/kg)

Station	**Okhoro**						**Mid point**						**Low lift pump**						**Ekiuwa**					
METALS	Cd	Mn	Cu	Pb	Zn	Cr	Cl	Mn	Cu	Pb	Zn	Cr	Cd	Mn	Cu	Pb	Zn	Cr	Cd	Mn	Cu	Pb	Zn	Cr
August	0.01	0.23	0.07	1.51	30.64	0.03	0.01	0.15	0.03	0.09	25.02	0.02	0.01	0.45	0.04	0.08	10.25	0.03	0.01	0.43	0.03	0.07	9.24	0.01
September	0.01	11.21	0.45	1.62	39.63	0.02	0.02	9.25	0.26	1.49	35.46	0.01	0.01	9.25	0.36	0.06	17.95	0.03	0.01	10.21	0.17	0.07	35.27	0.02
October	0.00	0.00	0.00	0.00	0.00	0.00	0.01	2.92	0.02	0.04	4.36	0.02	0.01	6.30	0.08	0.08	10.55	0.01	0.00	4.35	0.06	0.07	5.37	0.02
November	0.01	0.25	0.22	1.41	5.25	0.02	0.001	0.23	0.11	1.38	4.29	0.01	0.01	0.33	0.09	0.07	11.25	0.01	0.01	0.33	0.15	1.25	6.34	0.02
December	0.01	0.23	0.07	0.08	1.36	0.01	0.02	0.15	0.04	0.06	1.42	0.01	0.01	0.25	0.09	0.06	2.24	0.03	0.01	0.01	0.02	0.04	1.96	0.01
Mean	0.01	2.38	0.16	1.25	15.38	0.02	0.01	2.54	0.19	0.61	14.23	0.01	0.01	3.32	0.13	0.07	10.45	0.02	0.01	3.07	0.09	0.30	11.63	0.02

Table 3: Bioaccumulation Quotient For Heavy Metals In *Synodontis Clarias*

Heavy metal	**Okhoro station**	**Midpoint station**	**Low lift pump station**	**Ekiuwa station**
Cd	1.00	1.00	1.00	1.00
Mn	79.33	127.00	110.67	153.50
Cu	0.04	0.47	0.41	0.47
Pb	15.63	10.17	0.88	6.00
Zn	0.12	10.12	0.09	0.12
Cr	0.50	0.50	0.40	1.00

Heavy Metals in Syndontis clarias: The monthly variations of heavy metals in *S. clarias* is shown in Table 2. The mean values for Cd did not exceed 0.01 mg/kg at the stations. The mean values for Mn were 2.38 mg/kg (Okhoro station), 2.54mg/kg (midpoint station), 3.32mg/kg (Low lift pump station) and 3.07mg/kg (Ekiuwa station).

The mean values for Cu were 0.16mg/Kg (Okhoro station), 0.09mg/Kg (midpoint and Ekiuwa stations) and 0.13mg/kg (low lift pump station). The mean values of Pb were 1.25mg/kg (Okhoro station), 0.61mg/kg (midpoint station), 0.07mg/kg (low lift pump station) and 0.30mg/kg (Ekiuwa station). The mean values of Zn were 15.38mg/kg (Okhoro station), 14.23mg/kg (midpoint station), 10.45mg/kg (low lift station) and 11.63mg/kg (Ekiuwa station). The mean values for Cr were 0.02mg/kg (Okhoro, low lift pump and Ekiuwa stations) and 0.01mg/kg (midpoint station).The concentration profile in descending order was Zn > Mn > Pb> Cu > Cr > Cd at the Okhoro station, Zn > Mn > Pb > Cu > Cr/Cd at the midpoint station and Zn > Mn > Cu > Pb > Cr > Cd at the low lift pump Station and Zn > Mn > Pb > Cu > Cr > Cd at

the Ekiuwa station. Statistical analysis (ANOVA) showed that the mean values of Cd, Mn, Cu and Cr were not significantly different ($P > 0.05$) between stations however mean values for Zn and Pb were significantly ($P<0.05$) different between stations.

Bioaccumulation Quotient for heavy metals in *Synodontis clarias:* Table 3 shows the Bioaccumulation Quotient (BQ) for heavy metals in *S. clarias.* The BQ values for Cd did not exceed unity at the various stations. The BQ values for Mn ranged from 79.33 (Okhoro station) to 153.50 (Ekiuwa station) while the BQ values for Cu ranged from 0.04 (Okhoro station) to 0.47 (mid point and Ekiuwa station).The BQ value for Pb ranged from 0.88 (low lift pump station) 15.63 (Okhoro station) while the BQ value for Zn ranged from from 0.09 (low lift pump station) to 0.12 (Okhoro, midpoint and Ekiuwa stations). The BQ value for Cr ranged from 0.40 (low lift pump station) to 1.00 (Ekiuwa station). Generally, the highest BQ values were recorded for Mn while the least BQ values were recorded for Zn. Manganese was bioaccumulated by *Synodontis clarias* at all the stations while Pb was bioaccumulated by *S. clarias* at all the stations with the exception of the low lift pump station.

Heavy metals have been used as indices of pollution because of their high toxicity to human and aquatic life (Okaka and Wogu, 2011). Elevated concentrations of heavy metals in aquatic ecosystems have been linked with effluents from industries, refuse and sewage (Ezemonye, 1992). A mean concentration of 0.01mg/l was recorded for Cd in water in this study. Okoye (1991), recorded a higher mean Cd value of 2mg/l in water of the Lagos Lagoon while Okaka and Wogu (2011) recorded a lower mean Cd value of 0.0074mg/l in water of the Warri River. The mean concentration of Cd in water in this study, did not exceed the World Health Organisation (WHO) limit of 0.01mg/l. The mean concentration of Cd in *S. clarias* (0.01mg/kg), was exceeded by a mean value of 7.23mg/kg reported for Cd in *Oreochromis niloticus* in Madivala lake, India by Abida *et al.,* (2009). The mean Cd value in

S. clarias did not exceed the WHO limit of 2.0mg/l for food fish. The mean concentration of Cd in both water and *S. clarias* were the same. This phenomenon could be as a result of an equilibrium between the uptake and loss of Cd by *S. clarias* in the ambient water, as reflected in the non-bioaccumulation of the metal.

Bioaccumulation of heavy metals has been described as an equilibrium process involving the acquisition and loss of heavy metals between an organism and the surrounding water (Obasohan and Oronsaye, 2004). The mean concentration of Mn in water ranged from 0.02 to 0.03mg/l. Obasohan et. *al.,* (2006) recorded a range of 0.001 to 0.075mg/l in water from Ogba river, Benin City, Nigeria. Fonge *et. al.,* (2011), recorded a higher range of 0.04 to 0.54mg/l in water from the Douala Estuary in Cameroon. The mean concentrations of Mn in water in this study, did not exceed the WHO limit of 0.50mg/l. The mean concentrations of Mn in *S. clarias* ranged from 2.38 to 3.32mg/kg. A lower mean value of 1.12mg/kg was recorded for Mn in *Mormyrops deliciousus* from the Ikpoba river dam, Benin City by Oronsaye *et. al.,* (2010). The mean Mn values in *S. clarias* exceeded the WHO limit of 0.50mg/kg for food fish. The metal was bioaccumulated at all the stations by *S. clarias.* This finding can be attributed to the fact that *S.clarias* readily accumulated the metal from water or from ingested food at the various stations. Forstner and Prosi (1981), reported that aquatic organisms are capable of accumulating metals from their surrounding medium or food by absorption or ingestion. The mean concentrations of Cu in water ranged from 0.19 to 0.32mg/l. Saad and Kandeel (1988), reported a much higher mean Cu value of 5.1mg/l for the Red Sea in Egypt. The mean concentrations of Cu in water in this study, did not exceed the WHO limit of 1.0mg/l.

The mean concentrations of Cu in *S. clarias* ranged from 0.09 to 0.16mg/kg. Fonge *et. al.,* (2011) recorded a higher mean values for Cu ranging from 0.346 to 0.361mg/kg in *Arius heudelotii* from the Douala Estuary in Cameroon. The mean Cu concentrations is *S. clarias* did not exceed the WHO limit of 10mg/kg for food fish. Copper was not bioaccumulated by *S. clarias* at the various stations. This finding can be attributed to the greater rate of loss of the metal compared to the rate of uptake by the fish. Organisms with high food intake have been reported to accumulate more heavy metals (Ademoroti, 1996). The mean concentrations of Pb in water ranged from 0.05 to 0.08mg/l. Okaka and Wogu (2011) reported a lower mean value of 0.0001mg/l for Pb in water from the Warri River, Delta state, Nigeria. The mean concentrations of Pb in water were above the WHO limit of 0.05 mg/l at the various stations except at the Ekiuwa station. The mean concentrations of Pb in *S. clarias* ranged from 0.03 to 1.25mg/kg. Ekeanyanwu *et. al.,* (2011), recorded a lower mean concentration of 0.01mg/kg in *Tilapia nilotica* from Okumeshi river, Delta state, Nigeria. The mean Pb values in *S. clarias* exceed the WHO limit of 0.2mg/kg for food fish at the Okhoro and midpoint stations. The metal was bioaccumulated at all the stations by *S. clarias* except at the low lift pump station even through the highest mean value of 0.08mg/l was recorded for water at the low lift pump station. This finding could be adduced to the different metabolic rates exhibited by *S. clarias* at the various stations, for the metal.

The mean concentrations of Zn in water ranged from 98.70 to 132.38 mg/l. Okoye (1991), recorded a lower mean value of 15mg/l for Zn in water from the Lagos, Lagoon, Nigeria. The mean concentrations of Zn in water in this study exceeded the WHO limit of 5.0mg/l. The mean concentrations of Zn in *S. clarias* ranged from 10.45 to 15.38mg/kg. A higher mean value of 18.53mg/kg was recorded for Zn in *Mormyrus macrophthalmus* from the Ikpoba river dam, Benin City, by Oronsaye *et. al.,* (2010). The mean concentrations of Zn in *S. clarias* exceeded the WHO limit of 5.0mg/kg for food fish. The metal was not bioaccumulated by *S. clarias,* indicating that the dynamics of uptake and loss of the metal was at play, in which case the fish was effectively able to lose the metal faster than its uptake. The mean concentrations of Cr in water ranged from 0.02 to 0.05mg/l. Obasohan *et al.,* (2006) recorded a lower range of 0.001 to 0.008mg/l for Cr in water from Ogba river, Benin City, Nigeria. The mean concentrations of Cr in water in this study, did not exceed the WHO limit of 0.05mg/l. The mean concentration of Cr in *S. clarias* ranged from 0.01 to 0.02mg/kg. Abida *et al.,* (2009), recorded a higher range of 1.50 to 5.63mg/kg in *Channa marulius* from the Madivala lake, India. The mean Cr values in this study, did not exceed the WHO limit of 1.3mg/kg for food fish. The metal was not bioaccumulated by *S. clarias*, just like Cd, Cu and Zn. *Synodontis clarias* was thus able to effectively metabolize Cr, Cd, Cu and Zn.

The results from this study indicate that the heavy metals of significant ecological importance are Mn, Pb and Zn. Manganese and Zinc are essential elements while lead is a non- essential element. Manganese (Mn) is contained in batteries, fertilizers, varnish, fungicides and livestock feeding supplements. The metal is capable of bioaccumulating in phytoplankton, algae, molluscs and fish. Manganese toxicity has been reported to be related to several heart diseases in man (Akan *et al.,* 2010). Lead (Pb), can be found in batteries, rust inhibitors, ammunition, solder, alloys and plastic stabilizers. Lead toxicity leads to anaemia and it depresses spermatogenesis in man. It also causes damage to various organs including the kidney and liver and can lead to low intelligent quotient in children and high blood pressure in adults (Ottaway, 1978). Excessive intake of Zn may lead to vomiting, dehydration, abdominal pain, nausea and dizziness. The metal can be found in alloys, batteries, fungicides and pigments (Akan *et al.,* 2010). Zinc is an essential growth element for plants and animals but at elevated levels it is toxic to some species of aquatic life (WHO, 2004).

This investigation showed that the heavy metal content in water and *Synodontis clarias* varied. In order to avert further negative impacts by heavy metals on the Reservoir, especially by Mn, Pb and Zn, it is advocated that regular monitoring of heavy metals in fish and water within the Reservoir be carried out. Such monitoring would ensure that safety limits for heavy metals in water and fish are not exceeded in order to safeguard the health of people who depend on the water body for their source of water and fish supplies. A sedimentology of the Reservoir, is also suggested as sediments serve as repositories for heavy metals and are thus a potential source of contamination.

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