Heavy metal contaminants in *Malapterurus electricus* (Gmeli, 1789), *Tilapia zillii* (Gervais, 1848) and water from Ikpoba Reservoir, Benin City, Nigeria

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Abstract

The study was carried out to evaluate the potential health risk associated with the consumption of fish and water from the Ikpoba Reservoir, with regard to heavy metal contamination. The concentrations of some heavy metals, Manganese (Mn), Zinc (Zn), Copper (Cu), Cadmium (Cd) and Lead (Pb) were determined in *Malpterurus electricus, Tilapia zillii* and water by Atomic Absorption Spectrometric Technique. A total of 8 *M. electricus* sp. (mean wet weight 59.75±2.37g; mean total length 17.50±1.94 cm) and 10 *T. zillii* sp. (mean wet weight 39.45±2.37g; mean total length 12.35±1.52 cm), were used. The mean concentrations of (Mn, Zn, Cu, Cd and Pb) in mg/kg in *M. electricus* were 11.4±0.96, 10.13±0.45, 10.03±0.13, 0.323± 0.181 and 0.045±0.003 mg/kg respectively while in *T. zillii,* the mean concentrations were 10.61±0.33 (Cu), 9.82± 0.18 (Zn), 8.66± 0.74 (Mn), 0.181± 0.001 (Cd) and 0.044± 0.003 (Pb). The mean concentrations (mg/L) of the metals in water were 29.87±0.09 (Mn), 19.01±0.07 (Zn), 23.43±0.03 (Cu), 0.13±0.01 (Cd) and 0.14±0.009 (Pb). The mean concentrations of the heavy metals in water exceeded the World Health Organization (WHO) recommended limits of 0.2 mg/L (Mn), 3.0 mg/L (Zn), 1.0 mg/L (Cu), 0.003 mg/L (Cd) and 0.01 mg/L (Pb), for potable drinking water , while the mean concentrations of Zn, Cu, Cd and Pb in fish fell within the Food and Agriculture Organization (FAO) recommended limits of 30 mg/kg (Zn/Cu/Mn) and 0.05 mg/kg (Cu/Zn) for food fish. The Relative Health Factor (RHF) values for the investigated heavy metals were below unity for the fish species confirming that these fish species were safe for human consumption. The study revealed that, while the fish species might be fit for eating, the water was unsafe for drinking as the WHO limits were exceeded. It was advocated that the reservoir be closely monitored for heavy metal contamination in order to avert serious health hazards.

Keywords: heavy metals, *Malapterurus electricus, Tilapia zillii*, Relative Health Factor, reservoir.

Accepted: 21 July, 2015

Introduction

Heavy metal pollution has been observed to pervade many parts of the world especially developing countries where it threatens the health of wildlife and man via the food chain (Zhiyuan *et al,* 2014). In recent years, some inland waters of Nigeria have been subjected to ecological degradation owing to pollution. Increase in industrialization, technological development, and growing human population, have led to an increase in the influx of anthropogenic wastes into the aquatic environment (Obasohan and Eguavoen, 2008). According to Idodo-Umeh (2002), pollution whether physical or chemical can cause changes to the quality of receiving waters. In this light, heavy metal pollution is a serious and widespread problem due to the toxic, persistent, non-biogradable and bio-accumulation properties of these contaminants (Yuan *et al,* 2004). Heavy metals are well known environmental pollutants that accumulate in the bodies of aquatic organism and their negative impacts have been documented (Endo *et al,* 2004).Waste water containing heavy metals are produced by many manufacturing processes and eventually find their way into the environment (Oguzie, 1996; Mohammad *et al,* 2013). The aquatic ecosystem is usually the final recipient of heavy metal pollution.

Toxicity of heavy metals occurs when excretory, metabolic, storage and detoxification mechanisms are unable to counter uptake. This capacity however varies between different species and different metals (Langston, 1990). Studies carried out with different fish species have revealed that both essential and non-essential metals can produce toxic effects in fish by disturbing physiological activities, biochemical processes, reproduction, and growth (Mance, 1987). The accumulation of heavy metals in the tissues of organisms can result in chronic illness and cause potential damage to the population of such organisms (Barlas, 1999). In the aquatic environment, heavy metals in dissolved form are easily taken up by aquatic organisms where they are taken up by aquatic organism where they are strongly bound with sulfhydril groups of proteins and accumulate in their tissues (Hadson, 1988). It is evident that a thorough assessment of any adverse effects of heavy metals on the future management of Nigerian fishery resources will require the availability of a broad based data. It is in this vein that the present study was undertaken. The Ikpoba Reservoir in Benin City, Nigeria, serves as a rich source of fish for human consumption and is in receipt of both domestic and industrial effluents. The study essentially monitored the level of contamination by heavy metals in two economically important fish species (*M. electricus* and *T. zillii*) and water from the reservoir.

Materials and methods

The study-area

The study was conducted on the Ikpoba Reservoir in Benin City, Nigeria, which lies between Latitude 6.5′N and Longitude 5.8′E. The reservoir is situated some 3.75 km south-east of University of Benin. The reservoir at full capacity is 3.25 km long and 0.6 km wide with a water storage capacity of 1.5 million m^3 (Wangboje and Oronsaye, 2012). The Ikpoba Reservoir is located within the equatorial region, having two climatic regimes. The wet season spans from April to October while the dry season spans from November to March. Annual temperature ranges from 21^{o}C to 34^{o}C with humidity ranging from 68% to 96%. The marginal vegetation in the area includes *Commelina* sp., *Sida acuta, Mimosa pudica, Talinum triangulare* and *Ipomea* sp. The length of the Ikpoba River which feeds the reservoir, is flanked by thickets of *Bambusa* sp. and *Elaeis guinensis.* Samples of environmental matrices (fish and water) were collected fortnightly between June and August 2012 from the Okhoro Station (Station 1) and low lift pump station (Station 2) of the reservoir (Figure 1).The Okhoro Station is located adjacent to the Okhoro community of the city while the low lift pump station is located at the point where raw water is pumped out for treatment by authorities of the Edo State Urban Water Board, the Managers and Operators of the Reservoir.

Collection of bio-indicators

Fish samples were captured with the assistance of fishermen using local fish traps, cast nets and baited hooks. Fish were washed in flowing water to remove adhering debris before they were transported to the laboratory within 24 hours in an ice box. A total of eight (8) *M. electricus* (mean wet weight 59.75±2.37g; mean total length 17.50±1.94 cm) and ten (10) *T. zillii* (mean wet weight 39.45±2.37g; mean total length 12.35±1.52 cm), were used for the study.

Collection of water samples

A total of 12 water samples were collected at 30 cm depth into polyethylene bottles of 250 ml capacity. The bottles were pre-conditioned with concentrated nitric acid (HNO_3) and later rinsed with distilled water, 24 hours prior to sample collection. The water samples were acidified with nitric acid prior to preservation to ensure that heavy metals did not adhere to the walls of the bottles during storage. The samples were transported to the laboratory within 24 hours and stored at -5^{o}C in a Sonoko® freezer (Wangboje and Oronsaye, 2012).

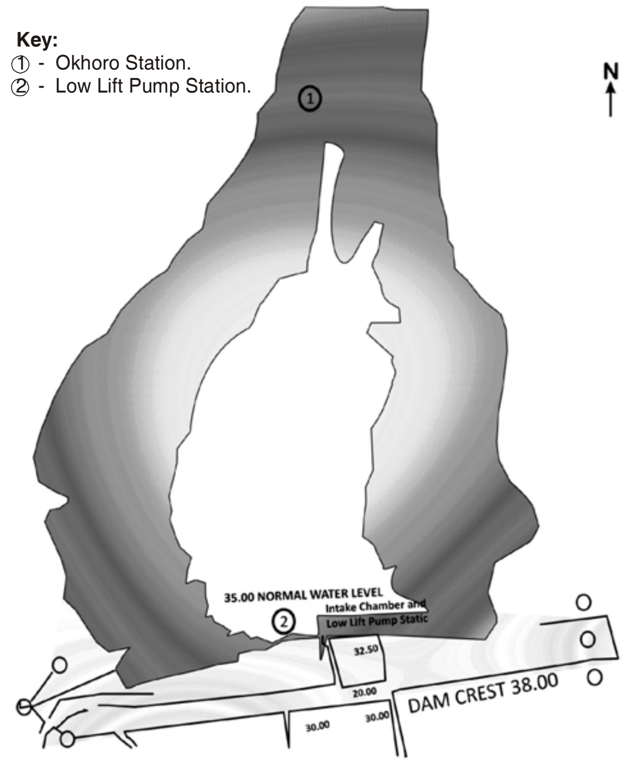

Figure 1. Ikpoba Reservoir showing sample Stations 1 and 2.
Source: Edo State Urban Water Board, Benin City, Nigeria.

Preparation of fish samples

Whole fish samples were oven dried at 80^{o}C for 72 hours until a constant weight was attained. Each sample was milled separately for homogeneity using a porcelain mortar and pestle. Digestion of fish samples was achieved by organic extraction method (Streedevi *et al,* 1992). The digests were introduced into 100 ml plastic reagent bottles. Blanks were prepared using the same quantity of mixed acids but without the samples. All reagents used were of analytical grade (BDH, England).

Digestion of water samples

Water samples were digested using the pre-concentrated acid method (Parker, 1972). Each sample was stored in plastic reagent containers prior to analysis. Blank samples were prepared using the same quantity of nitric acid.

Analysis of fish and water digests for heavy metals

Fish and water digests were analysed for Mn, Zn, Cu, Cd and Pb by means of a Unicam 929 Series Atomic Absorbtion Spectrophotometer (Unicam, England) with a solar software using air acetylene flame. Heavy metal values in fish and water were expressed in mg/kg and mg/L respectively.

Calculation of bio-accumulation quotient (BQ)

The Bioaccumulation Quotient (BQ) expresses the ability of fish to accumulate heavy metals to levels above their ambient environment (Hilmy *et al,* 1987).

$$BQ = \frac{\text{Heavy metal concentration in fish}}{\text{Heavy metal concentration in water}}$$

Where BQ>1 = Bioaccumulation indicated.

Calculation of Relative Health Factor (RHF)

This is an index used to express the potential health hazard of consuming fish or water containing heavy metals (Gnandi *et al,* 2011).

$$RHF = \frac{\text{Heavy metal concentration in fish or water}}{\text{Maximum for heavy metal in fish or water}}$$

Statistical analysis

A GENSTAT® computer software (Version 8.1 for Windows) was used for statistical analysis. One-way analysis of variance (ANOVA) was used to test for significant differences between means at 5% probability level. Least Significant Difference (LSD) was used to separate significant means.

Results

Manganese (Mn) had the highest mean value of 29.96 mg/L at Station 2, while a lower mean value of 29.78 mg/L was recorded at Station 1 (Table 1). A similar trend was observed for Zn, Cd and Pb, where higher mean values were recorded at Station 2. As shown on Table 2, there was no significant difference (p>0.05) in the mean concentrations of the heavy metals between the stations. Table 3 shows no significant difference (p>0.05) in the mean concentrations of Cd and Pb between the months. The mean concentrations of Mn in *M. electricus* ranged from 10.08 mg/kg (Station 2) to 12.00mg/kg (Station 1), while the mean concentrations of Pb in the same fish species ranged from 0.0417 mg/L (Station 2) to 0.0483 mg/L (Station 1) (Table 4). The mean concentration of Cu in *T. zillii* ranged from 10.28 mg/kg (Station 2) to 10.95 mg/kg (Station 1), while the mean concentrations of Pb in the same fish species ranged from 0.0417 mg/kg (Station 1) to 0.0467 mg/kg (Station 2) (Table 5). Higher mean concentrations of Mn, Cd and Pb were recorded at Station 1 while higher mean concentration of Zn and Cu were recorded at Station 2 for both species. Table 6 showed no significant difference (p>0.05) in the mean concentrations of Zn, Cu and Pb between the investigated fish species, while on Table 7, there was a significant difference (p<0.05) in the mean concentrations of Cd between stations for *M. electricus.* As shown in Figures 2 a, b and Figure 3, Cd was bio-accumulated by the sampled fish species, with the highest Bio-accumulation Quotient (BQ) value of 2.48 recorded for *M. electricus*. The Relative Health Factor (RHF) values for heavy metals in water ranged from 3.8 for Zn to 59.74 for Mn while in *M. electricus* the range was from 0.09 for Pb to 0.65 for Cd. In the case of *T. zillii* the RHF values ranged from 0.09 for Pb to 0.36 for Cd as shown in Figure 3.

Table 1. Monthly variations in means of heavy metals in water (mg/L).

Stations	Station 1 (Okhoro)					Station 2 (Low Lift Pump Station)				
	Heavy metals					Heavy metals				
Months	Mn	Zn	Cu	Cd	Pb	Mn	Zn	Cu	Cd	Pb
June	34.10± 1.14	20.07± 0.07	25.67± 0.08	0.150± 0.02	0.11± 0.02	34.17± 1.02	20.11± 0.18	25.71± 1.34	0.20± 0.05	0.140± 0.04
July	35.15± 2.05	21.00± 1.15	24.55± 1.22	0.160± 0.06	0.13± 0.01	35.56± 2.05	21.36± 1.09	24.24± 1.17	0.165± 0.11	0.150± 0.08
August	20.08± 0.11	15.71± 1.24	20.18± 2.06	0.060± 0.04	0.145± 0.04	20.14± 1.25	15.78± 2.11	20.21± 1.09	0.065± 0.02	0.150± 0.09
Mean	29.78± 6.86	18.93± 2.30	23.46± 2.37	0.123± 0.04	0.128± 0.01	29.96± 6.96	19.08± 2.39	23.39± 2.32	0.143± 0.05	0.1467± 0.0047

Table 2. Comparison of means of heavy metal concentrations in water (mg/L) at sampling stations.

	Heavy metals				
Stations	Mn	Zn	Cu	Cd	Pb
Station 1	29.78[a]	18.93[a]	23.46[a]	0.123[a]	0.128[a]
Station 2	29.96[a]	19.08[a]	23.39[a]	0.143[a]	0.147[a]

Means in vertical rows with the same superscripts are not significantly different at the 5% probability level.

Table 3. Cmparison of mean of heavy metal concentrations in water (mg/L) for different months.

	Heavy metals				
Months	Mn	Zn	Cu	Cd	Pb
June	34.14[a]	20.09[a]	25.69[a]	0.175[a]	0.125[a]
July	35.36[a]	21.18[a]	24.39[a]	0.163[a]	0.140[a]
August	20.11[b]	15.74[b]	20.19[b]	0.063[a]	0.147[a]

Means in vertical rows with the same superscripts are not significantly different at the 5% probability level.

Table 4. Monthly variations of means of heavy metals in *M. electricus* (mg/kg).

Stations	Station 1 (Okhoro)					Station 2 (Low Lift Pump Station)				
	Heavy metals					Heavy metals				
Months	Mn	Zn	Cu	Cd	Pb	Mn	Zn	Cu	Cd	Pb
June	14.16± 0.18	10.68± 0.23	10.12± 0.8	0.525± 0.03	0.05± 0.007	10.77± 1.15	11.91± 0.20	10.52± 0.59	0.335± 0.05	0.05± 0.007
July	13.11± 0.12	10.29± 0.06	10.00± 0.11	0.515± 0.13	0.05± 0.01	11.30± 0.76	11.83± 1.24	10.17± 2.14	0.315± 0.08	0.05± 0.003
August	8.74± 0.09	8.07± 1.02	9.56± 1.25	0.150± 0.08	0.045± 0.005	8.16± 1.25	8.04± 2.11	9.78± 1.56	0.100± 0.005	0.020± 0.006
Mean	12.00± 2.34	9.68± 1.14	9.90± 0.24	0.397± 0.17	0.048± 0.002	10.08± 1.37	10.59± 1.80	10.16± 0.30	0.250± 0.11	0.042± 0.01

Table 5. Monthly variations of means of heavy metals in *T. zillii* (mg/kg).

Stations	Station 1 (Okhoro)					Station 2 (Low Lift Pump Station)				
	Heavy metals					Heavy metals				
Months	Mn	Zn	Cu	Cd	Pb	Mn	Zn	Cu	Cd	Pb
June	11.17± 1.29	10.30± 1.67	12.46± 2.17	0.230± 0.006	0.065± 0.008	9.04± 2.61	11.52± 1.76	12.09± 1.85	0.240± 0.061	0.06± 0.004
July	10.30± 2.31	10.04± 0.93	11.36± 0.76	0.215± 0.05	0.05± 0.004	8.22± 1.53	10.18± 0.97	11.42± 1.62	0.200± 0.008	0.05± 0.003
August	6.72± 1.26	8.58± 2.11	9.02± 1.59	0.100± 0.006	0.010± 0.002	6.52± 1.47	8.32± 1.28	7.32± 1.44	0.100± 0.003	0.03± 0.007
Mean	9.40± 1.92	9.64± 0.75	10.95± 1.43	0.182± 0.06	0.0417± 0.02	7.93± 1.05	10.01± 1.31	10.28± 2.11	0.180± 0.06	0.047± 0.01

Table 6. Comparison of means of heavy metal concentrations (mg/kg) in fish species.

Fish species	Mn	Zn	Cu	Cd	Pb
M. electricus	11.04±0.96[a]	10.13±0.45[a]	10.03±0.13[a]	0.323±0.07[a]	0.045±0.003[a]
T. zillii	8.66±0.74[b]	9.82±0.18[a]	10.61±0.33[a]	0.181±0.001[b]	0.0442±0.003[a]

Means in vertical rows with the same superscripts are not significantly different at the 5% probability level.

Table 7. Comparison of means of heavy metal concentrations (mg/kg) in fish species at the stations.

Fish species	*M. electricus*					*T. zillii*				
	Heavy metals					Heavy metals				
Stations	Mn	Zn	Cu	Cd	Pb	Mn	Zn	Cu	Cd	Pb
Station 1	12.00[a]	9.68[a]	9.90[a]	0.397[a]	0.048[a]	9.40[a]	9.64[a]	10.95[a]	0.182[a]	0.042[a]
Station 2	10.08[a]	10.59[a]	10.12[a]	0.250[b]	0.042[a]	7.93[a]	10.00[a]	10.28[a]	0.180[a]	0.047[a]

Means in vertical rows with the same superscripts are not significantly different at the 5% probability level.

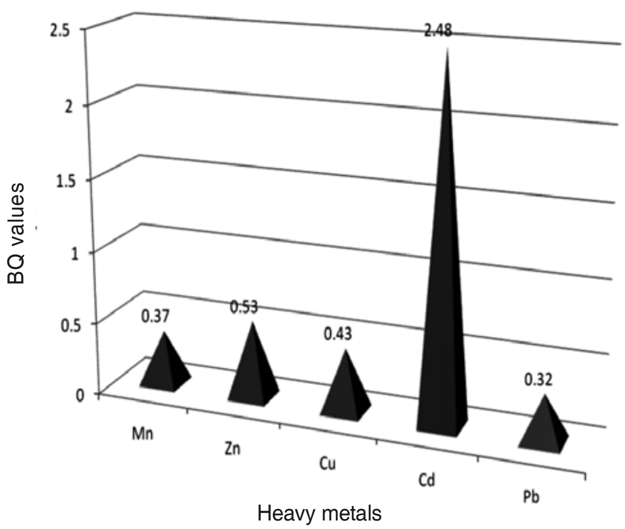

Figure 2a. Bioaccumulation Quotient (BQ) values for heavy metals in *M. electricus.*

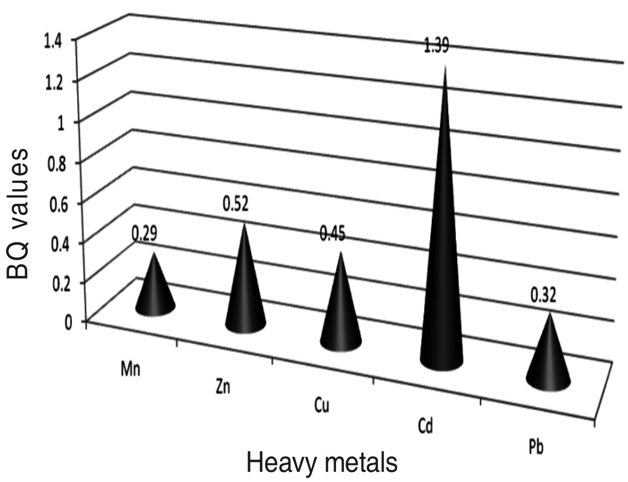

Figure 2b. Bioaccumulation Quotient (BQ) values for heavy metals in *T. zillii.*

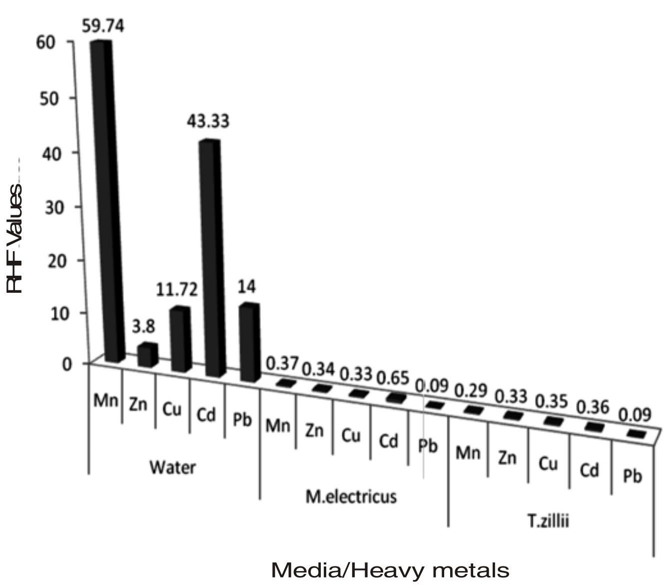

Figure 3. Relative Health Factor (RHF) values for heavy metals in water and fish species.

Discussion

The study reveals the presence of Mn, Zn, Cu, Cd and Pb in *M. electricus*, *T. zillii* and water of the Ikpoba Reservoir, with higher mean values in water than in the fish species. The mean concentration of Mn (29.87 mg/L) in water was higher than the mean value of 0.01 mg/L (Mn) reported for Ogba River by Obasohan *et al* (2006) and the mean value of 0.078 mg/L reported for the Ikpoba River dam by Oronsaye *et al* (2010) indicating a higher input and consequent presence of the metal in the Reservoir compared to the aforesaid studies. The high mean value of Mn recorded in water in this study may be attributed to the higher availability of Mn and its compounds in the effluents that reach the water body compared to the other heavy metals. The mean value of Mn in water exceeded the value of 0.5 mg/L recommended for potable drinking water by the World Health Organization (WHO, 2004).

The mean concentration of Zn (19.01 mg/L) in water was higher than the mean value of 0.63 mg/L reported for the Warri River by Okaka and Wogu (2011). Oguzie (2003), reported a lower mean value of 0.127 mg/L (Zn) for the lower Ikpoba River. The high Zn value recorded in this study may be attributed to leachates from farms and garbage dumps and other domestic wastes that may be washed into the reservoir through flood water. The mean value of Zn in water exceeded the WHO maximum permissible limit of 5.0 mg/L for potable drinking water (WHO, 2004). The mean concentration of Cu (23.43 mg/L) in water was higher than the mean value of 3.8 mg/L (Cu) reported for the Delimi River by Njoku and Keke (2003). The high mean Cu value recorded in this study may be attributed to a higher input of copper-rich effluents which the reservoir may be receiving from adjoining communities. The mean concentration of Cu in water exceeded the 2.0 mg/L benchmark for potable drinking water (WHO, 2004). The mean concentration of Cd (0.13mg/L) in water was higher than the mean value of 0.004 mg/L (Cd) reported for the Alaro River by Fakayode (2005) and was also higher than the mean value of 0.05 mg/L observed by Olatunji and Osibanjo (2012) for the Lower River Niger. The metal (Cd) had the lowest concentration in water compared to the other heavy metals in this study. The influx of Cd into the reservoir was therefore conceivably lower than the other heavy metals investigated. The mean value of Cd in water exceeded the 0.003 mg/L health benchmark recommended for potable drinking water (WHO, 2004).

The mean concentration of Pb (0.14 mg/L) in water was higher than the mean value of 0.024 mg/L (Pb) reported along the Nigerian Coast by Sadik (1990) and was much higher than the mean concentration of 0.0001 mg/L (Pb) reported by Muiruri *et al* (2013) for the Athi-Galana-Sabaka Tributaries, Kenya. The high mean Pb value recorded in this study may be attributed to the higher availability of Pb and its compounds in water as a result of received effluents enriched with the metal. The mean value of Pb in water exceeded the value of 0.01 mg/L recommended for potable drinking water

(WHO, 2004). The mean concentrations of Mn in *M. electricus* and *T. zillii* (11.04 mg/kg and 8.66 mg/kg respectively) in this study were higher than the mean value of 1.12 mg/kg reported for Mn in *Mormyrops deliciousus* by Oronsaye *et al* (2010) for the Ikpoba River dam. In this study, there was a significant difference (p<0.05) in the mean Mn values between the investigated fish species. This finding is in accordance with that of Heath (1991), who reported that different fish species have different tolerant levels for heavy metals and therefore their metal loads would vary. The variation could also be linked to the different levels to which each species of fish is capable of taking up and eliminating metals from their bodies. Manganese (Mn) was not bioaccumulated by the fish species, an indication that the rate of loss of the metal was conceivably greater than the rate of uptake.

The mean concentrations of Mn in the fish species fell below the 30 mg/kg (Mn) benchmark recommended for food fish by the Food and Agriculture Organization of the United Nations (FAO, 1983). The mean concentrations of Zn in *M. electricus* and *T. zillii* (10.13 mg/kg and 9.82 mg/kg respectively) were higher than the mean value of 5.56 mg/kg reported for Zn in *Chrysicthys nigrodigitatus* by Obasohan *et al* (2006) for the Ogba River. The mean concentration of Zn in the experimental fish species in this study, did not exceed the FAO limits. The mean concentrations of Cu in *M. electricus and T. zillii* (10.03 mg/kg and 10.61 mg/kg respectively) in this study were higher than the mean value of 8.00 mg/kg reported for Cu in *Mormyrus macrophthalmus* by Oronsaye *et al* (2010) for the Ikpoba River Dam. The mean concentration of Cu in the fish species did not exceed the FAO limit for food fish.

The mean concentrations of Cd in *M. electricus and T. zillii* (0.323 mg/kg and 0.181 mg/kg respectively) were lower than the mean value of 0.62 mg/kg reported for Cd in *Oreochromis niloticus* by Ekeanyanwu *et al* (2011) for the Okumeshi River. Cadmium, was the only metal bioaccumulated by the investigated fish species, an indication that the metal was readily bioavailable to these fish species for uptake as corroborated by Anim-Gyampo *et al* (2013), whom reported the bio-accumulation of Cd in fish (*Sarotherodon galilaeus* and *Achenoglanis occidentalis*) from the Tono Irrigation Reservoir, Ghana.

It has been reported that bioaccumulation of heavy metals is capable of leading to toxic levels of these metals in fish even when exposure is low (Douben, 1989). However, the mean concentrations of Cd in the fish species did not exceed the FAO limit for food fish. The rational implication of this finding is that the fish species may be safe for human consumption, but are at risk of Cadmium poisoning.

The mean concentration of Pb in *M. electricus* and *T. zillii* (0.045 mg/kg and 0.044 mg/kg respectively) were lower than the mean value of 2.45 mg/kg reported for Pb in *Channa marulius* by Abida *et al* (2009) for the Madivala Lake. The mean concentration of Pb in the fish species did not exceed the FAO limits for food fish. The relative health factor (RHF) values of heavy metals were below unity for the fish species further confirming that these fish species are safe for human consumption. However the reverse was the case for water. The plausible deduction from this finding is that, while the fish species may be fit for consumption, the water is not good for drinking as the WHO regulatory limits for these metals in drinking water, were surpassed.

Conclusion

Results from this study confirmed the occurrence and concentrations of Mn, Zn, Cu, Cd and Pb in fish and water of the Ikpoba Reservoir. The mean concentrations of these heavy metals exceeded the WHO recommended limits for potable drinking water, implying that the water is unsafe for human consumption. In this study, the mean concentrations of Zn, Cu, Cd and Pb in fish were within the FAO recommended limits for food fish while Cd was the only heavy metal that was bioaccumulated by fish. There is thus an urgent need to closely monitor the Ikpoba Reservoir for heavy metals in order to avert human health hazards. Such monitoring efforts should include other heavy metals not covered in the present study and may include a complete sedimentology of the reservoir.

Acknowledgement

We thank Martlet Environmental Research Laboratory Limited for the use of their facilities for sample analysis.

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Citation: Wangboje, O. M. and Ekundayo, O. T.
Heavy metal contaminants in *Malapterurus electricus* (Gmeli, 1789), *Tilapia zillii* (Gervais, 1848) and water from Ikpoba Reservoir, Benin City, Nigeria.
The Zoologist, 13: 10-16 December 2015, ISSN 1596 972X.
Zoological Society of Nigeria.