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Assessment of the heavy metals in some fish species of Elemi River, Ado-Ekiti, south west Nigeria

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Abstract

This study deals with the quantification of some heavy metals (zinc, lead, cadmium and copper) in the flesh, liver and kidney of three fish species, (*Parachanna obscrura, Clarias gariepinus* and *Tilapia zilli*) in River Elemi, Ado Ekiti, during three months. The quantitative assessment confirmed the presence of zinc, lead, cadmium and copper in all fish samples. *C. gariepinus* had significantly higher (p<0.05) concentrations of zinc in all tissue and organs in comparison with the other fish species. Cd was found in the tissue and all the organs of *C. gariepinus* whereas it was detected only in some organs of *T. zilli* and *P. obscrura*. The pattern of occurrence of these metals in the fish flesh is in the order of Zn > Pb> Cu> Cd. For the liver, it is Pb >Zn >Cu. No Cd was detected. For the kidney, the pattern is Zn > Cu > Cd. No lead was detected. This study has revealed 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. 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 fish consuming populace.

Key words: heavy metals, fish, health, risk, Nigeria

Introduction

Fish are of tremendous importance as food for people around the world. Fish is a source of animal protein containing high level of protein, (17-20%), with an amino acid profile which is similar to meat (Aremu *et al.,* 2009). However, due to the continuous rise in the development of industries, several water creatures are contaminated or killed, because of pollutants. Historically, the monitoring of aquatic ecosystems has been based on chemical measures of water quality (Akan *et al.,* 2012). However, current views are that chemical monitoring does not provide sufficient information to enable meaningful conclusions to be drawn (Akan et al., 2012; Wright *et al.,* 1994). Consequently, there has been an increase in the use of biological approaches to water quality assessment. It is possible to use any group of organisms to examine the biological situation of a river, and many attempts have been made using both flora and fauna (Armitage *et al*., 1983). The bioaccumulation of heavy metals in aquatic organisms depends on the ability of the organisms to digest the metals, the concentration of the heavy metals in the surrounding soil sediments and the feeding habit of the organism (Eneji *et al.,* 2011).

Heavy metals such as lead (Pb) and cadmium (Cd) are the most common toxicant that can be found in the marine environment (Sireli *et al.,* 2006). Chromium is known to be a very toxic pollutant introduced into natural waters from a variety of sources including industrial wastes. When these heavy metals enter human body, through drinking water or consumption of aquatic organisms, it has a tendency to accumulate in particular organs (Even *et al*., 2011).These heavy metals can be toxic at high concentrations, when ingested over a long period of time (Sireli *et al*., 2006).

However, in fluvial environments, metal pollution can result from direct atmospheric deposition, geologic weathering or through the discharge of agricultural, municipal or industrial waste products (Dawson *et al.,* 1998). Apart from the natural sources, several anthropogenic activities also contribute to metal concentrations in the environment. Aquatic environment is one of the receiving ends for pollutants, particularly heavy metals which are ploughed back into the food chains through bioaccumulation in plankton and invertebrates to fishes and finally biomagnified in man (Edward *et al.,* 2013).

Heavy metal concentrations in aquatic ecosystems are usually monitored by measuring their concentrations in water, sediments and associated biota (Camusso *et al.,* 1995). These elements generally exist in low levels in water and attain considerable concentration in sediment and biota. Sediments are important sinks for various pollutants, like pesticides and heavy metals, and also play a significant role in the remobilization of contaminants in aquatic systems, under favorable conditions, and in interactions between water and sediments (Rashed, 2001). FAO and WHO (FAO (1983 and EC, 2001) permissible levels (mg kg^{-1}), above which human consumption is not encouraged are displayed in Table 1.

Table 1: The FAO/WHO permissible levels

Metal	Concentration (mg kg^{-1})
Cd	1.0
Pb	0.4
Zn	50
Cu	20

Source: (FAO, 1983, EC, 2001)

In recent times, Ado-Ekiti, the capital town of Ekiti state is witnessing a lot of developmental programs, especially road constructions. There has been massive landscape disturbance due to the construction processes and heavy vehicular activities. These activities coupled with expanding human population, intensive agricultural practices and discharge of massive amount of wastewater into rivers may result in the deterioration of water quality. The impact of these anthropogenic activities may be so extensive that the water bodies may lose their self-purification capacity, to a large extent. Elemi River is one of these receiving rivers, as it is located by the Ado-Ekiti – Iworoko road, under construction. This study was designed to monitor the amount of heavy metal present in the flesh and some organs of some of the fish species*; Parachanna obscrura, Tilapia zilli* and *Clarias gariepinus*, of Elemi River. Studying heavy metal contamination in fishes will help consumers in preventing many degenerative diseases (Colina, 2012).

Materials and Method

Sampling Area

This study was conducted at River Elemi (Fig.1), along Iworoko road, Ado Ekiti, Ekiti State, Nigeria. Elemi River is a fresh water body and running water moving to a lower level in a channel on land. Its center lies at latitude of 7, 37026 and longitude of 5, 17482 and it has an elevation of 355 meters above sea level. Elemi River is characterized with the availability of different fauna of fishes and it has high level of planktons and nektons which interpret its biological conditions. Several anthropogenic activities flank the course of the river, such as the presence of automobile repairing workshop, horticultural garden, cement block making factory and homestead farming.

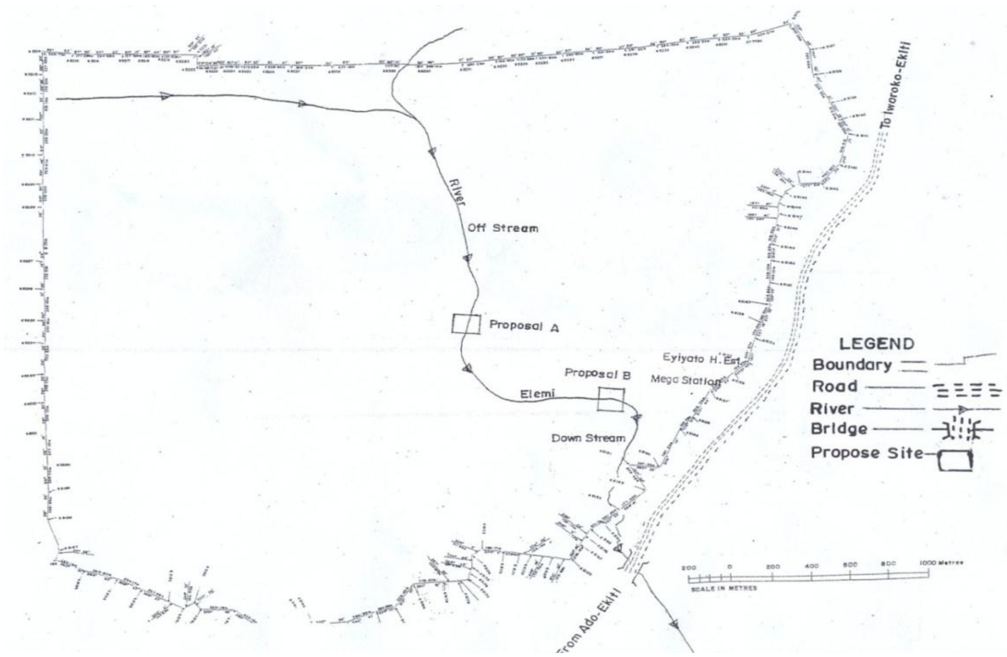

Fig. 1: Map showing the course of Elemi River

Sample Collection

The fish species (*T. zilli, C. gariepinus, P. obscura*) were caught using hook and line. The use of draw net was impossible, as sampling was done during the peak of the raining season, when the river flooded its banks. This preliminary sampling was exigent at this season, in order to provide a baseline data for the writing of the proposal for the feasibility study of erecting a power plant on this river. Twenty, uniform size, samples of each fish species were collected bi-weekly, for a period of three months, between July and September, 2015. Sampling was done at three sites (A, B and C) of the river, nearest to the proposed power plant. Properly labeled samples were transported to the laboratory on the same day for identification and dissection, to remove the liver, kidney and the fillets of each fish. To minimize contamination, all the materials used in the experiments were previously washed in ultra-pure water (Tuzen, 2003), and a stainless steel knife was used to sacrifice the fish and cut the tissues. The tissues/organs were kept in the freezer till use.

Biochemical Analysis

Digestion of samples

Two grams of the thawed tissues/organs of the fish were taken for analysis, according to the method of Storelli *et al.* (2005). Optimized microwave method was applied for the digestion of the samples. Triplicates of 0.5 g homogenates from each tissue/organ were placed in a Teflon digestion vessel, each with 7ml of concentrated nitric acid (HNO3) and 1 ml of hydrogen peroxide (H2O2). The samples in the vessels were digested and left to cool at room temperature. The digested products were then dissolved and diluted to 50 ml.

Heavy Metal Characterization

Heavy metals (Zn, Cu, Cd and Pb) analysis were determined by a Perkin-Elmer DV 4300 inductively coupled plasma-optical emission spectrophotometry (ICP-OES) (Binning and Baird, 2001). In the ICP-OES analysis, the following wavelength were used; Zn (213.9nm), Cu (324 nm), Cd (24.7 nm), Pb (248.3nm). The quality of the analytical process was also controlled by the analysis of NIST-CE278 certified standard reference materials of mussel tissue. Analysis of Cd was also performed by Hitachi 180-70, polarized Zeeman Atomic Absorption Spectrophotometer (AAS) equipped with a graphite furnace. A cadmium hollow cathode lamp was used. Calibration was performed by analyzing three standard solutions (10, 20, 40 µg/L).

Statistical Analysis

Data generated were subjected to one way analysis of variance (ANOVA) according to Duncan's Multiple Range Descriptive Test (Duncan, 1955) with mean at a significant level of $P<0.05$. Standard errors of means were also determined at 95% confidence limit using SPSS 13.0 package.

Results

Observations on the Site

Table 2 shows the various anthropogenic activities going on in the three sampled sites. The activities are illustrative of the observances in the tissues and organs of the fish

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Table 2: The various anthropogenic activities in the three sampled sites

Site	Activities
A	Location for block industry, mechanic workshop and horticulture garden
B	Farming and open defeacation
C	Upstream, Less activities, Washing of clothes

Heavy Metals in the Tissues and Organs of the Individual Fish

The comparisons of heavy metal contents of the organs of *C. gariepinus, P. obscrura* and *T. zilli* and among the fish species are shown in Table 3 and 4. The following are the concentrations in the tissues and organs in the fish in the order *C. gariepinus, P. obscrura* and *T. zilli.* The flesh of all the fish species recorded significantly higher ($p<0.05$) concentrations (32.10 ±12.01; 30.61±1.27; 22.34 ±8.13mg $100g^{-1}$) of Zn than the organs. The kidneys recorded the lowest ($p>0.05$) values (4.36 ±1.65; 2.68 ±0.29; 2.52 ±0.21mg 100g-1). Cadmium was present and significantly higher ($p<0.05$) in the kidneys of all the fish species sampled, while it was not detected in liver and flesh of *P. obscrura* and the flesh of T. zilli. The livers of all the fish species had significantly higher ($p<0.05$) concentrations (17.01 ±11.11; 15.88 ±2.67; 13.67 ±0.67mg $100g^{-1}$) of Pb than the flesh and kidneys. Lead was not even detected in the kidneys of *P. obscrura* and *T. zilli.* There were significant differences ($p<0.05$) in copper concentration in the liver compared to the other organs sampled, but there was no significant difference ($p>0.05$) in copper concentration between the flesh and kidney, and also there was no significant difference ($p>0.05$) in cadmium concentrations in the organs of *C. gariepinus*. The pattern of occurrence of these metals in *C. gariepinus* flesh was in the order of Zn > Pb> Cu>Cd. For the liver, it is Pb > Zn >Cu >Cd. For the kidney, the pattern is Zn > Cu > Pb>Cd.

In *P. obscrura*, the flesh had the highest concentration of zinc with mean value of 30.60 ± 1.27mg $100g^{-1}$ and the highest in lead concentration with mean value of 16.42 ± 17.73mg $100g^{-1}$ but lowest in copper concentration. There was no indication of the presence of cadmium. The liver had the highest concentration of copper (3.05 ± 0.04mg 100g-1) and showed no indication of cadmium. The kidney had the highest concentration of cadmium (2.45 ± 0.65mg 100g-1) but showed no indication of lead. There were significant differences ($p<0.05$) in Zn, Cd, Cu and Pb concentrations in the tissue/organs (liver, flesh, kidney) sampled, but there was no significant difference ($p>0.05$) in cadmium concentrations in the liver and flesh of *P. obscrura*. The pattern of occurrence of these metals in *P. obscura* flesh is in the order of Zn > Pb> Cu. No Cd was detected. For the liver, it is Pb > Zn >Cu. No Cd was detected. For the kidney, the pattern is Zn > Cu > Cd. No lead was detected.

The flesh of *T. zilli* shows a high concentration of zinc (22.34 ± 8.13mg $100g^{-1}$), very low concentration of cadmium (0.56 ± 0.79 mg $100g^{-1}$), a moderately low copper concentration (4.24 ± 0.57 mg $100g^{-1}$), and Pb concentration value of 7.93 ± 11.22mg $100g^{-1}$. The pattern of occurrence of these metals in the fish flesh is in the order of Zn > Pb> Cu> Cd. For the liver, it is Pb > Zn > Cu. No Cd was detected. For the kidney, the pattern is Zn > Cu > Cd. No Pb was detected.

Among the fish species studied (Table 4), the flesh, liver and kidney of C. gariepinus had significantly highest ($p<0.05$) concentration of zinc (32.10 ±12.01; 7.62 ±1.01; 4.36 ±1.65 mg $100g^{-1}$) while T. zilli had the lowest (22.34 8.13; 5.77 0.50; 2.68 0.29 mg 100g-1). Cd was found in the tissue and all the organs of C. gariepinus whereas it was detected in some organs of *T. zilli* and *P. obscrura*. The quantity of Cd, where present, was not significantly different ($p>0.05$) among the species. The concentrations of Cu in *T. zilli* were significantly higher ($p<0.05$) than what were recorded for the tissues and organs of *P. obscrura*, but not significantly higher ($p<0.05$) than in C. gariepinus. Lead was not detectable in the kidney of *T. zilli* and *P. obscrura*, but present in the tissue and organs of C. gariepinus. The concentrations of Pb detected in *T. zilli* were significantly higher ($p<0.05$) than in all the other fish species.

Table 3: The heavy metal concentrations (mg $100g^{-1}$), in the tissues/organs of the fish species.

Metals	Fish parts	Concentrations (mg $100g^{-1}$)		
		C. gariepinus (Av. Wt=60.7g±1, SL=16.5cm±2)	*P. obscura* (Av. Wt=56.5g±3, SL=15.5cm±0.5)	*T. zilli* (Av. Wt=30.4g±0.7, SL=6.6cm±0.5)
Zn	Liver	7.62 ± 1.01^{a}	5.77 ± 0.50^{a}	3.67 ± 0.77^{b}
	Flesh	32.10 ± 12.01^{b}	30.61 ± 1.27^{b}	22.34 ± 8.13^{a}
	Kidney	4.36 ± 1.65^{c}	2.68 ± 0.29^{c}	2.52 ± 0.21^{b}
Cd	Liver	0.03 ± 0.86^{b}	ND	ND
	Flesh	0.45 ± 1.02^{a}	ND	0.56 ± 0.79^{b}
	Kidney	0.49 ± 1.10^{a}	0.45 ± 0.65	0.22 ± 0.03^{b}
Cu	Liver	3.85 ± 1.57^{a}	3.05 ± 0.45^{a}	3.41 ± 1.00^{ab}
	Flesh	1.89 ± 1.02^{b}	0.72 ± 0.54^{b}	4.24 ± 0.57^{a}
	Kidney	2.29 ± 0.91^{b}	2.25 ± 0.19^{a}	2.14 ± 1.10^{b}
Pb	Liver	17.01 ± 1.11^{a}	15.88 ± 2.67^{a}	13.67 ± 0.67^{a}
	Flesh	9.43 ± 1.28^{b}	16.32 ± 4.71^{a}	7.93 ± 1.22^{b}
	Kidney	0.90 ± 1.51^{c}	ND	ND

ND = Not detected

Means with the same superscripts in the same column are not significantly different at P>0.05, while those with different superscripts in the same column are significantly different at same level.

Table 4: Comparison of the heavy metal concentrations, (mg $100g^{-1}$), among the fish species.

Site	**Metal**	***C. gariepinus***	***P. obscrura***	***T. zilli***
A	Zn	14.17 ± 1.41^{a}	12.56 ± 1.49^{a}	-
	Cd	0.001 ± 0^{a}	0.001 ± 0^{a}	-
	Cu	2.44 ± 1.24^{a}	1.57 ± 1.26^{a}	-
	Pb	13.89 ± 1.42^{a}	16.19 ± 1.77^{a}	-
B	Zn	14.61 ± 1.96^{a}	13.25 ± 1.39^{a}	8.09 ± 0.44^{a}
	Cd	0.18 ± 0.03^{a}	0.001 ± 0.0^{a}	1.12 ± 0.84^{a}
	Cu	3.18 ± 1.23^{a}	2.23 ± 1.04^{a}	4.65 ± 2.18^{a}
	Pb	8.64 ± 1.03^{b}	8.05 ± 0.95^{b}	5.89 ± 0.95^{a}
C	Zn	15.28 ± 1.60^{a}	-	10.59 ± 1.22^{b}
	Cd	0.49 ± 0.10^{a}	-	ND
	Cu	2.61 ± 1.74^{a}	-	3.83 ± 0.81^{b}
	Pb	4.62 ± 1.08^{c}	-	0.005 ± 0.003^{b}

ND = Not detected

Means with the same superscripts in the same column are not significantly different at P>0.05, while those with different superscripts in the same column are significantly different at same level.

Comparative Heavy Metal Contents of the fish in the various Sampling Sites

The comparison of heavy metal contents of the fish in the various sites are shown in Table 5. In the site A, only two fish species were sampled (*P. obscrura* and *C. gariepinus*), in site B, three fish species were sampled (*T. zilli, P. obscrura* and *C. gariepinus*) and in site C, two fish species were sampled (*T. zilli* and *C. gariepinus*).

There was no significant difference ($p>0.05$) in zinc, cadmium and copper concentrations in the tissues and organs of C. gariepinus in all the sites, but the lead concentration in the samples of *C. gariepinus* in site B is significantly higher ($p<0.05$) than in site A and C. *P. obscrura* in site A and B had mean values of 12.56 ± 1.89 mg $100g^{-1}$, 13.25 ± 1.39 mg $100g^{-1}$ respectively in zinc concentration, 0.001 ± 0.004mg $100g^{-1}$, 0.001 ± 0.004 mg $100g^{-1}$ respectively in cadmium concentrations, 1.57 ± 1.26 mg $100g^{-1}$, 2.23 ± 1.04 mg $100g^{-1}$ respectively in copper concentrations and 16.19 ± 1.77mg $100g^{-1}$, 8.05 ± 0.95mg $100g^{-1}$ respectively in lead concentrations. There was no significant difference ($p>0.05$) in zinc, cadmium, copper concentrations in the body of *P. obscrura* from site A and B, but there was significant difference ($p<0.05$) in lead concentration in the body of *P. obscrura* from site A compared with those from site B. *T. zilli* in site B and C had 8.09 ± 0.44mg $100g^{-1}$, 10.59 ± 0.22mg $100g^{-1}$ zinc concentrations respectively, 1.12 ± 0.84mg $100g^{-1}$ and undetectable cadmium concentrations, 4.65 ± 2.18mg $100g^{-1}$, 3.83 ± 0.81mg $100g^{-1}$ copper concentrations, 5.89 ± 0.95mg $100g^{-1}$, 0.005 ± 0.003mg $100g^{-1}$ lead concentrations. There was significant difference ($p<0.05$) in zinc, copper and lead concentration in the body of T. *zilli* from site B compared to those from site C. Cadmium was not present in the body of T. *zilli* from site C.

Table 5: Comparison of the heavy metal concentrations (mg $100g^{-1}$) in the fish sampled from the various sites

Site	Metal	*C. gariepinus*	*P. obscrura*	*T. zilli*
A	Zn	14.17 ± 1.41[a]	12.56 ± 1.49[a]	-
	Cd	0.001 ± 0[a]	0.001 ± 0[a]	-
	Cu	2.44 ± 1.24[a]	1.57 ± 1.26[a]	-
	Pb	13.89 ± 1.42[a]	16.19 ± 1.77[a]	-
B	Zn	14.61 ± 1.96[a]	13.25 ± 1.39[a]	8.09 ± 0.44[a]
	Cd	0.18 ± 0.03[a]	0.001 ± 0.0[a]	1.12 ±0.84[a]
	Cu	3.18 ± 1.23[a]	2.23 ± 1.04[a]	4.65 ± 2.18[a]
	Pb	8.64 ± 1.03[b]	8.05 ± 0.95[b]	5.89 ± 0.95[a]
C	Zn	15.28 ± 1.60[a]	-	10.59 ± 1.22[b]
	Cd	0.49 ± 0.10[a]	-	ND
	Cu	2.61 ± 1.74[a]	-	3.83 ± 0.81[b]
	Pb	4.62 ± 1.08[c]	-	0.005 ± 0.003[b]

Discussion

This study revealed that zinc and lead were highly concentrated in the tissues and organs of all the investigated species, while cadmium was least detected. The flesh of *T. zilli* accumulated lower concentration of zinc and lead compared to the flesh of *C. gariepinus* and *P. obscrura*. This result showed that in all the tissues/organs of the fish species sampled, the flesh and liver accumulated more of zinc and lead than any other organs while they accumulated less copper and relatively smaller amounts of cadmium. The kidney accumulated more cadmium than any other organs and accumulated lesser zinc and lead. This result also showed that accumulation ratio of any metal is different for each fish organs (Yang et al., 2007). A lot of researchers (Demirak *et al*., 2006; Yang et al., 2007; Al-Yousuf *et al*., 2000 and Usero *et al.,* 2004) have reported that metals accumulate in high concentrations in the liver, because the organ has relatively higher potential for metal accumulation than the muscle. The liver is the metabolizer and major detoxifier of the body. Al-Yousuf et al. (2000) and Usero *et al*. (2004) reported that the higher accumulation ratios of metals in the liver could be due to the greater tendency of the elements to react with the oxygen carboxylate, the amino group, the nitrogen and/or the sulphur of the mercapto group in the metallothionein protein of the liver.

The levels of Zn and Pb in the tissues and organs of the bottom dwelling fish species, *C. gariepinus* and *P. obscrura,* were higher than in *T. zilli* species. The bioaccumulation tendency of the organs of *C. gariepinus* and *P. obscrura* may be due to their ecological demands as these species depend on the sediment for food and burrow into the mud, thereby exposed to both water and sediment loads of heavy metals. Yarkwan and Apeh (2015) are of the opinion that since catfish has a longer life span than tilapia, the former is capable of accumulating larger quantities of these metals within its tissues than tilapia fish.

Looking at the fish from the different sites sampled, site A showed higher metal concentrations. This is probably due to the various anthropogenic activities, such as the block industry and a mechanical workshop located by the side of the stream. This was followed by site B where farming and open defecation is done. Site C has less anthropogenic activities compared with the rest. This section of the river is used by the villagers for washing clothes and bathing. It has been indicated that BAFs changes according to the type of chemical available in the environment, the degree of pollution in the environment and the metabolite properties of the tissues (Ayas, 2007; Bashir *et al*., 2013, Ojebah and Emumejaye, 2015).

Findings by other researchers showed that the levels of heavy metals in fish depend on habitats (Canli and Atli, 2003), the durations of exposure of the fish to contaminants, their feeding habits (Canli and Kalay,1998), the age and the size of the species (Rashed, 2001; Fernandes *et al.,* 2007). Cu concentrations of all edible organs of the species were considerably lower than the permissible levels set by FAO and WHO. Although, copper is essential for good health but very high intakes can cause health problems such as liver and kidney damage (Agency for Toxic Substances and Disease Registry, 2004). In all species, Zn concentrations in the kidney, and the main edible portion of fish, were lower than the maximum limit. Zn is recognized as an essential element as required by a wide variety of enzymes and other cell components having vital functions in all living things. But excessive Zn will damage the health of animals as well as humans. The permissible limits for Cd (1mg kg^{-1}) were exceeded in some of the edible tissues of the species analyzed in this study. Akan et al. (2013) and Vos et al., (1987) stated that cadmium may accumulate in the human body and may induce kidney dysfunction, skeletal damage and reproductive deficiencies. The Pb levels in all the fish species were also higher than the tolerable levels (0.4mg kg^{-1}). Lead is known to induce reduced cognitive development and intellectual performance in children and increased blood pressure and cardiovascular disease in adults. Lead is toxic by substituting zinc in heme synthesis and obstructing the function of heme-synthesizing enzymes (Goyer and Clarkson, 2001). Lead poisoning is ranked among the most common environmental health hazard even at low levels.

Ingestion of heavy metals leads to numerous health challenges (Ayeloja *et al.,* 2014). Some heavy metals are potentially toxic (aluminiun, arsenic, cadmium, antimony, lead and mercury), some semi-essential (nickel, vanadium, cobalt) and while copper, zinc, selenium, manganese, iron, etc are essential (Szentmihalyi and Then, 2007). Even the essential metals can be toxic when excessively taken (Tüzen, 2003; Ellias, 2009). The investigated species presented no hazard for human consumption. The concentrations of the non-essential metals, lead and cadmium, in this present study however calls for concern considering their toxic nature, therefore periodic monitoring by relevant regulatory authorities is recommended to ensure safety of the fish consuming populace.

Conclusion

This research has highlighted the presence of heavy metals (Cd, Cu, Zn and Pb) in the fish species (*T. zilli, C. gariepinus* and *P. obscrura*) available in Elemi river. The various anthropogenic activities that are carried out along the river have pre- disposed the aquatic biota to bioaccumulation of these metals in the tissues and organs of the fish species. Bottom dwelling species, (*C. gariepinus* and *P. obscrura*), were found to accumulate more metals than the pelagic tilapia fish species. Although cadmium, zinc, lead and copper are vital in metabolic processes, efforts should be made to ensure that they and other heavy metals do not exceed the prescribed World Health Organization (WHO) and Federal Environmental Protection Agency (FEPA) acceptable limits for human consumption. All environmental policy should be enhanced and campaigns carried out to educate the public on the importance of protecting and preserving aquatic systems and their resident biota.

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