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HEAVY METAL CONTAMINATION IN THE TISSUES OF *CLARIAS GARIEPINUS* (BURCHELL) OBTAINED FROM TWO EARTHEN DAMS (ASA AND UNIVERSITY OF ILORIN DAMS), KWARA STATE, NIGERIA

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Abstract: This study determined the levels of heavy metal contamination in the tissues of North African catfish *Clarias gariepinus* (Burchell, 1822) obtained from two dams (Asa and University of Ilorin), Kwara State, Nigeria. *Clarias gariepinus*, between the mean weight of 149-154g and total length of between 28-34cm were investigated. Copper (Cu), zinc (Zn), cadmium (Cd), chromium (Cr) and lead (Pb) in flesh, heart, kidney and livers of species from the two dams were determined using Atomic Absorption Spectrophotometer (AAS). Tissues were digested for heavy metal concentration. The results showed that heavy metal contamination in the tissues sampled from Asa dam were in order of Zinc > Copper > Chromium. Cadmium and lead were not detected while those sampled from University of Ilorin were also in order of Zinc > Copper > Chromium. Lead was also not detected. The results show that *C. gariepinus* from Asa dam bioaccumulated heavy metals at higher concentrations than samples from Unilorin dam. The heavy metals concentration detected in *C. gariepinus* sampled from the two dams did not exceed the limits set by WHO and FAO thereby making the fishes wholesome for human consumption.

Key words: Heavy metals, Flesh, Heart, Heavy metals and Clarias gariepinus

INTRODUCTION

Arising from the numerous activities of man who discharge toxic substances including heavy metals into the aquatic environment, imbalance has been created in the earth's ecosystem. According to Meadows et al. (1992), pollution of the aquatic and terrestrial environments including other types of environmental degradation in any community or society are due to the combined effects of population increase, urbanization, affluence and technological developments. Apart from natural sources, anthropogenic sources have been reported to be the principal source of pollutants arising from municipal wastes, refuse heaps, agricultural practices and industrial waste water (Smith, 1985). Contamination of a river with heavy metals may have devastating effects on the ecological balance of the aquatic organisms (Sreedevi et al., 1992). Contaminants like Hg, Cd, As, Pb, Sr and Cr are toxic, nonbiodegradable and bioaccumulate in the human body and can cause damage to nervous system and internal

organs (Lohani et al., 2008). Other contaminants such as Cu, Fe, Mn, Ni and Zn that are essential micronutrients also pose detrimental effects to the functioning of living tissues at higher concentrations (Bruins et al., 2000). Metallic elements may exert beneficial or harmful effects on plants, animal life depending upon the concentration (Forstner and Wittmann, 1981). Since fish are located at the top of the aquatic food chain, they accumulate metals from both water and food chain and subsequently pass them to humans through food fish. The accumulation of metals in fish depends upon their intake and elimination from the body (Mansour and Sidky, 2002). In assessing environmental quality with respect to heavy metals in water the bio-available fraction is of major importance, because toxicity depends on the amount absorbed by an organism, which itself is based on bio-available exposure concentration (Fowler et al., 1993). This bioavailable fraction can be detected indirectly by determining the amount of metals incorporated in

organisms. As an indirect measure of the abundance and bio-availability of metals in the aquatic environment, the bioaccumulation of metals by the tissues of aquatic organisms is of great importance (Mance, 1987). Metals are naturally occurring elements that become contaminants when human activities increase their concentrations above normal levels in the environment (Unger, 2002). Trace heavy metals are environmentally ubiquitous, readily dissolved in and are transported by water and can be taken up by aquatic organisms due to bioaccumulation and biomagnifications in the food chain either as such or as their metabolites, thus causing concern on the animals at the top of the food chain (Papagiannis *et al.*, 2004).

Trace metal contamination is one of the major environmental issues in developing countries in recent times (Goher et al., 2014a). Trace metal contamination of fresh water is a major threat to environmental health and a factor in geochemical cycling of metals (Kabata-Pendias and Pendias, 1992). It is of great concern due to their long biological half-lives, non-biodegradability and potential toxicity to the environment (Goher et al., 2014b). Heavy metal pollution is a serious and wide spread environmental problem due toxicity. They enter the environment through various natural methods and human activities, and can accumulate in fish and other organisms (Kalay and Canli, 2000). There is increasing awareness of the potential hazards that exist due to the contamination of freshwater, especially by toxic metals associated with mining, industrial and agricultural practices (Du Preez et al., 2003). Fish are widely consumed in many parts of the world by humans due to high protein content, low saturated fat and sufficient omega fatty acids known to support good health (Forstner and William, 1981). Fish is widely used as bio-indicators of aquatic pollution by metals (Obasohan, 2007). It is generally believed that the aquatic environment and the organism itself determine bioaccumulation of heavy metals in fish. Metal distribution between the different tissues depends on the mode of exposure and metallic pathwayss, which serve as a pollution indicator (Obasohan, 2007). Nahle (2003) reported that acid rain is a form of pollutant caused by the emission of sulphur dioxide and nitrogen oxides to the atmosphere.

Sawmill wastes are contaminated with wood preservatives such as pentachlorophenol, resin acids, dioxins and other toxic substances (Addision et al., 1991). These wastes when degraded or burnt emit toxic materials rich in various toxic chemicals including heavy metals. These hazardous substances eventually end up in inland water bodies through surface run-off water, wind-blown and deposited materials or as leachates from underground water sources (Forstner and Prosi, 1979). The metals could be absorbed by the fish and their accumulation may occur in various fish organs and tissues. Initially, early accumulation may take place in soft tissues but with prolonged exposure, they may bioaccumulate in the harder tissues and organs (Amiard, 1975). The bioaccumulation of metals is therefore an index of the pollution status of the relevant water body and is a useful tool for studying the biological role of the metals present at the elevated levels in fish. Due to their different roles in bioaccumulation process, fish tissues e.g. muscle, liver and gills are those more frequently used for analyses (Evans et al., 1993). Flesh (muscle) is preferred because it is one of the important final target tissues for metal storage and in addition, the main edible part of fish and its study, therefore constitutes the tool for the protection of public health (Reinfelder et al., 1998). The aim of this study was to determine the heavy metal contamination of tissues in Clarias gariepinus obtained from two earthen dams (Asa and University of Ilorin dams), Kwara State, Nigeria.

MATERIALS AND METHODS Study Site (Fig. 1)

Asa dam and University of Ilorin dam are located in Ilorin, the capital of Kwara State, Nigeria. Asa dam is located on River Asa (8°44' N; 4°56' E) at approximately 5 km from the city centre. The dam has an overall length of 597 m and storage capacity of 43 million m³ with lake extension of 18 km. The length and breadth of the spillway are about 65 m and 14 m respectively with discharge capacity of 79,000 cm³ (Araoye, 2009; Ayanshola, 2013). The University of Ilorin dam (Unilorin dam) is located on River Oyun (8°46' N; 4°67' E), providing water for the University community. The dam has a reservoir capacity of 1,800,000 m³, live storage capacity of1, 540,000 m³ and the length of the river

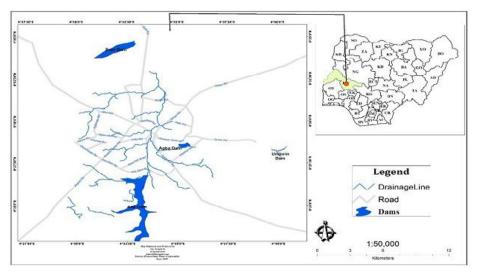


Fig. 1. Map of Ilorin showing the location of the two dams. Inset: map of Nigeria showing the states (Source: Clement *et al.*, 2015)

is 48 km. The spillway has 14,000 m³/day (Ayanshola, 2013).

Sample Collection and Transportation

Fish samples were collected from the two dams (Asa and Unilorin). Two hundred *Clarias gariepinus* weighing between 149-154g (mean = 152g) and total length of between 28-34cm (mean = 31cm) were obtained from each of the two dams using drag nets with the help of the local fishermen. The fish samples were tagged and put in separate sterile polythene bags and kept in an ice-chest for onward transportation to the laboratory where they were washed in flowing water to remove dirt. They were thereafter packed into clean plastic bags. All the fish samples were stored in deep freezer at 20°C prior to preparation for analysis.

Extraction of Tissues from Samples

Seventy-five fish samples were selected at random from the two dams. The weight of each fish sample was measured on a digital scale. As dam samples weighed $151\pm5.07g$ while Unilorin samples weighed $153\pm0.54g$. The fishes were dissected; the tissues of interest (flesh, heart, kidney and livers) were isolated. The tissues collected were cleaned and sterilized with Saline water (sodium chloride) and weighed before being packed in sachets and stored in a refrigerator while awaiting digestion.

Digestion

Frozen samples of flesh, heart, kidney and liver were allowed to thaw at room temperature. An average wet weight of 0.5g was used for each sample. Each tissue sample was duplicated to make a total of 12 samples for each fish being digested and a blank for control. Making up a total of 49 tissue samples with blank being digested. Each sample was pulverized in a mortar. Each pulverized sample (0.5g) was mixed with 6ml HNO₂ (ANALAR) (65% Suprapur, Merck, Darmstdt, Germany) and 2ml H₂O₂(Suprapur grade, Merck, Darmstdt, Germany). The mixtures were allowed to stand overnight in a beaker with a lid in a fume cupboard. The samples were then allowed to heat lightly the next day on a hot plate in a fume cupboard until the mixtures turned colourless. The digest was then allowed to cool at room temperature. The cooled digest was filtered using Whatman Type 1 filter paper into a 100ml Standard Flask. The filtered samples were then diluted with distilled water in the standard flask to reach the 100ml mark. The diluted samples were stirred vigorously and a portion of the stirred sample was collected in pre-washed transparent plastic bottles. The bottled digested samples were finally stored in a refrigerator to await metal analysis.

Analysis of heavy metal

The metals, Cu, Zn, Cr, Cd and Pb in the tissues (flesh, heart, kidney and liver) of fish samples from Asa and Unilorin dams were analyzed using a spectra AA-10 Varian atomic absorption spectrophotometer. The atomic absorption spectrophotometer was standardized using stock standard solutions from the respective metals. Accuracy of the method employed was assessed by analysis of three replicate samples, which yielded standard deviations less than 5% for Cu, Pb and 1% for Cd. Mean recoveries were in excess of 92%. Blank samples were run with each set of experiments.

Statistical analysis

Data were analyzed by one-way analysis of variance (ANOVA) using Statistical Product for Service Solution (SPSS version 16.0) for window. Statistical significance of differences between means was compared using Turkey (HSD) test.

RESULTS

Among the heavy metals detected in the tissues sampled from Asa and Unilorin dams were Copper (Cu), Zinc (Zn) and Chromium (Cr). The mean concentration of heavy metals in the tissues of fish samples from Asa and Unilorin dams is given in Table 1.

Copper

The highest mean concentration of copper in the sample from Asa dam was found in the liver while the lowest mean concentration was in the flesh. However, in the sample from University of Ilorin dam, the highest mean concentration was detected in the kidney while the lowest mean concentration was also in the flesh. The overall highest mean concentration of copper was found in the liver of fish samples from Asa dam samples with value0.553±0.19mg/L while the overall least was found in the flesh of the sample from University of Ilorin dam with value 0.141 ± 0.01 mg/L. There was significant difference (P<0.05) in the bioaccumulation of copper between the flesh, heart, kidney and liverof fish samples from Asa dam and University of Ilorin dam respectively.

Zinc

The highest mean concentration of zinc in the samples from Asa dam was found in the kidney while the lowest mean concentration was observed in the flesh. In the fish samples from University of Ilorin dam, the highest mean concentration was also in the liver while the lowest mean concentration was in the flesh. The overall highest mean concentration of zinc was found in the kidney of the samples from Asa dam $(3.270\pm0.13 \text{ mg/L})$ while the overall least was found in the flesh of the samples from University of Ilorin dam $(1.200\pm0.16 \text{ mg/L})$. There was a significant difference (P<0.05) in the concentration of zinc in the samples from Asa dam and samples from University of Ilorin dam.

Chromium

The highest mean concentration of chromium in the samples from Asa dam was found in the kidney while

Essential heavy Metals	Tissues	Asa dam Mean ± Std (mg/L)	Unilorin dam Mean ± Std (mg/L
COPPER (Cu)	Flesh	$0.203 \pm 0.07^{\mathrm{a}}$	$0.141 \pm 0.01^{\circ}$
	Heart	$0.462 \pm 0.14^{\mathrm{a}}$	$0.255 {\pm}~0.11^{\text{d}}$
	Kidney	$0.517{\pm}0.04^{\rm a}$	$0.320{\pm}0.03^{\rm f}$
	Liver	0.553 ± 0.19^{d}	0.212±0.02 ^b
ZINC (Zn)	Flesh	2.102±1.04ª	1.200±0.16 ^b
	Heart	2.039±0.60ª	1.909±0.23°
	Kidney	3.270±0.13b	2.142±0.16 ^e
	Liver	3.124±0.05ª	2.508±0.51b
CHROMIUM	Flesh	0.044±0.03b	0.034 ± 0.01^{f}
	Heart	0.063±0.06°	0.051 ± 0.16^{b}
	Kidney	0.171±0.05ª	0.151±0.11 ^d
	Liver	0.148±0.14 ^e	0.122±0.20°

Table1. Mean concentration of heavy metals in the tissues of fish samples from Asa and Unilorin dams.

Mean with the same superscript along the column are not significantly different at p<0.05

the lowest mean concentration was observed in the liver. However, in the sample from University of Ilorin dam, the highest mean concentration of chromium was also detected in the kidney while the lowest mean concentration was in the flesh. The overall highest mean concentration of chromium was found in kidney of the Asa dam samples with the value 0.171 ± 0.05 mg/L while the overall least was found in the flesh with value 0.034 ± 0.01 mg/L. There was also a significant difference (P<0.05) in the bioaccumulation of chromium in the flesh, heart, kidney and liver of fish samples from Asa dam and University of Ilorin dam respectively.

DISCUSSION

Heavy metals are easily absorbed by aquatic life forms and accumulation may occur in higher concentration (Omoregie *et al.*, 2002). Fish can take up heavy metals in their diets and bioaccumulate them at different rates in their muscles and organs (Phillips and Rainbow, 1994). According to Rainbow *et al.* (1990), the rate of accumulation and ability of the fish to detoxify particular metals differ greatly. This might account for the variation in the concentration of heavy metals found in the *Clarias gariepinus* obtained from Asa dam and University of Ilorin dam respectively. The mean concentrations of heavy

Toxic heavy metals	TISSUES	Asa dam	Unilorin dam
		Mean ± Std (mg/L)	Mean ± Std (mg/L)
CADMIUM (Cu)	Flesh	0.056±0.09ª	0.111±0.14 ^b
	Heart	0.147±0.04°	0.411 ± 0.21^{d}
	Kidney	0.204±0.06b	0.102 ± 0.10^{f}
	Liver	0.236±0.050ª	0.231±0.28ª
LEAD (Pb)	Flesh	ND	ND
	Heart	ND	ND
	Kidney	ND	ND
	Liver	ND	ND

Table 2. Mean concentration values of toxic heavy metals (cadmium and lead) in the tissues of fish samples from Asa dam and Unilorin dam

Mean with the same superscript along the column are not significantly different at p<0.05 NB: ND means Not Detected.

metals in the flesh of C. gariepinus obtained from the two dams are higher than those from other tissues (heart, kidney and liver), thus supporting the idea of bioaccumulation in the flesh (muscle). This finding is in agreement with the findings of Murphy (1978) who reported that edible flesh of fish accumulated more metals. The concentration of Zn was higher in the flesh of C. gariepinus samples obtained from Asa dam. This is in line with the findings of Senthil et al. (2008) who reported significant bioaccumulation of metals in fish flesh. The concentration of Cu was significantly the same in the flesh of both samples (Asa dam and Unilorin dam). The highest concentration of Zinc (3.270mg/l) was observed in the samples from Asa dam. This finding may not be unconnected with effluents from dungs, which are transported to the dam through run-off water. According to Forstner and Prosi (1979), Zinc is a

product of animal food and is readily concentrated in excretions with adult animals excreting an average of 7 and 20mg Zn daily. Copper was significantly higher in the heart of Asa dam sample. Zinc was significantly the same in both samples. Chromium was higher in the heart of Asa dam sample than those from University of Ilorin dam. This is in agreement with the work of Dahunsi et al. (2012) who found similar trend of heavy metals in the heart of fish species that he worked on. Copper bioaccumulation was significantly higher in the kidney of the sample from Asa dam than the kidney of sample from University of Ilorin dam. Zinc bioaccumulated significantly in the kidney than in the other tissues which might be based on specific metabolism process and co-enzyme catalyzed reactions in the kidney. Zinc bioaccumulated significantly higher in the liver of Asa dam than those from University of Ilorin dam.

The high concentration of copper in the liver can be ascribed to the binding of Copper to metallothionein in the liver, which serves as a detoxification mechanism. Copper, though essential in the diet can be harmful when taken in large amounts. The harmful toxicity is largely attributed to its cupric (Cu²⁺) forms (Olaifa et al., 2004). Low levels of chromium and cadmium in both samples may be attributable to the fact that the fish feeds on aquatic plants. Aquatic plants have been reported to take up quantifiable levels of heavy metals (Ndiokwere, 1984). Lead was not detected which might be due to the fact that the two dams are not polluted by lead. Low levels of lead has been reported in some water bodies by Idodo-Umeh and Oronsaye (2006). The concentrations of heavy metals observed in this study are lower than values recommended for portable drinking water by World Health Organization (WHO, 1985). The values recorded are within the recommended levels for fish food by the Food and Agricultural Organization of the United Nations (FAO) (Nauen, 1983).

CONCLUSION

The heavy metals concentration detected in *C. gariepinus* sampled from the two dams did not exceed the limits set by WHO and FAO thereby making the fishes better for human consumption. Thus, *C. gariepinus* obtained from Asa dam and Unilorin dam are safe for human consumption.

In view of the importance of the two dams in Kwara State, the following recommendations are forwarded: (i) More research should be conducted on heavy metal pollution of Asa and Unilorin dams; (ii) Fisheries unit of Kwara State Ministry of Agriculture should collaborate with Department of Aquaculture and Fisheries, University of Ilorin to show case the natural endowments of the two dams; (iii) Kwara State Ministry of Agriculture, Kwara State Ministry of Water Resources, Kwara State Environmental Protection Agency (KWASEPA) and University of Ilorin should ensure that findings from this research are widely circulated among the inhabitant of the state on the safety level of the fishes in the two dams for human consumption; and (iv) Appropriate authorities should ensure that the current trends of heavy metals from the two dams are not exacerbated.

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