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SOME HEAVY METALS IN SURFACE WATER, SEDIMENT AND FISH (*Clarias gariepinus*) FROM IKPOBA RIVER BENIN-CITY, EDO-STATE, NIGERIA

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ABSTRACT

Fumes from high vehicular traffic dense areas combined with mixed effluent sources, and run-off waters from some industrial areas channelled into water bodies are possible sources of metal pollutions. Specimens of *Clarias gariepinus*, surface water samples and sediments from Ikpoba River were collected from two stations, on monthly basis for six months: They were analyzed for concentrations of some heavy metals, using Atomic Absorption Spectrophotometer (AAS). Metal absorption in all three samples revealed a decreasing order of concentration as follows: fish>sediments>surface water. Total mean concentration of metals in samples also showed a decreasing order Zinc>Lead > Copper>Cadmium>Chromiun. ANOVA results revealed that all metals except Chromium and Copper, were higher in fish harvested from station 1 than those from station 2. Samples of fish, water or sediment harvested in station 1, contained higher concentration of metals than those isolated from station 2. For instance, Zinc (45.03mg/l) had the highest total mean concentration from fish in stations 1. Surface water in station 1 (0.111mg/l) had higher concentration of lead than station 2 (0.106mg/l) whereas station 2 (0.154mg/l) recorded higher concentration of Copper than station 1 (0.137mg/l). All metals analyzed in sediment samples were higher in station 1 than in station 2 except for Chromium where the value in station 2 (0.29mg/l) exceeded that in station 1 (0.15mg/l). Lead and Zinc concentrations from sediments were highest at station 1 (28.71mg/l) and (24.11mg/l) respectively. The observed concentrations of Lead and Cadmium in fish samples exceeded the WHO maximum permissible limits for aquatic lives, while other metals did not. The results suggest that Ikpoba River is polluted and *Clarias gariepinus* fish from the river may not be fit for human consumption.

Keywords: Heavy metals, Surface Water sample, Sediment, *Clarias gariepinus*, Ikpoba River

INTRODUCTION

Samples of fish, water and sediments are notorious for their ability to concentrate heavy metals. They need to be screened to ensure that unnecessary high levels of toxic metals are not transferred to man through them (Igboanugo and Chiejine, 2012). Heavy metals occur in the environment as a result of natural processes as well as contaminants from human activities (Kishe and Machiwa, 2003). Those known as potentially toxic especially when found in high concentration include, Lead, Aluminium and Cadmium. Few others regarded as essentials are

Nickel, Zinc and Chromium. Heavy metals do not only have positive and negative effects on fish health but impacts on all other organisms in the environment (Abduijaleel, and Shuhaimi-Othman, 2011). Heavy metals are an important group of chemical pollutants that find their way into fish that search for food, through plankton grazing and sediment foraging. Some heavy metals are irreversibly bound to fish tissues. For instance, Cadmium is bound to kidneys and lead to bones (Kaplan *et al.,* 2011). High levels of metals in the environment when consumed or absorbed over the period by fish, man or other organisms, result in bio-concentration and bio-magnification in such organisms, thus causing harm (Al-Khateeb and Lellah, 2005).

Heavy metals pollution of the aquatic environment (lakes, rivers and sea) has been receiving worldwide attention due to the serious health risk it poses to aquatic life and man through food intake (Asegbeloyin and Ukoha, 2010). Oronsaye *et al*. (2010) reported the concentration of Iron, Copper, Manganese, Zinc, Nickel, Cadmium, Chromium and Lead in two benthic fish species (*Mormyrops deliciosus* and *Mormyrus macrophthalmus)* netted from two locations in Ikpoba River, Benin-city. The range of trace metal concentration in the fishes were Iron (39.60-41.07mg/kg), Copper (5.04-8.04mg/kg), Manganese (0.38-1.34mg/kg), Zinc (17.01-23.16mg/kg), Nickel (0.24-0.48mg/kg), Cadmium (0.79-0.98mg/kg), Chromium (0.38-0.91mg/kg) and Lead (2.67-3.53mg/kg). The levels of lead in the fish species exceeded the recommended limit by Food and Agricultural Organisation (FAO, 1985). Ekpo *et al*. (2008) also reported the mean concentration of some heavy metals (Lead, Cadmium and Mercury) in the muscles and organs of some common species: *Clarias lazera, Tilapia zilli and Citharinus citharus* from Ikpoba River, Benin-city. The mean concentrations of lead in the muscle, kidney and liver were in the range of 0.001-0.004mg/kg, 0.010-0.015mg/kg and 0.004-0.010mg/kg respectively. Cadmium concentrations were in the range of 0.001-0.002mg/kg in the muscle, 0.004-0.006mg/kg in the kidney and 0.002-0.004mg/kg in the liver. The levels of Mercury were 0.001-0.002mg/kg in the muscle, 0.004-0.006mg/kg in the kidney and 0.002-0.004mg/kg in the liver. This indicates that the kidney of fish was a better bio-accumulator of heavy metals than the liver and the muscle. The accumulation pattern of heavy metals contaminants in fish depended upon their uptake and elimination rate.

The Ikpoba River is one of the numerous rivers in Edo-State. The river is a notable source of African catfish (*Clarias gariepinus*) of great commercial importance because it is the most widely consumed fresh-water fish in Edo-State, Nigeria based on its large size at maturity (Olaifa and Ayodele, 2004). This study therefore investigated the concentrations of some heavy metals in *Clarias gariepinus*, sediments and surface water from Ikpoba River to assure their suitability for human consumption and aquatic life.

MATERIALS AND METHODS

Ikpoba River lies within latitude 6^{0}.20'N and longitude 5^{0}.31'E of the Equator (Fig. 1). It flows through Benin-city, Edo State, Nigeria and receives effluent discharges from a rubber processing factory, a brewery and other mini-factories around. Fish samples were collected from two station of the river, fortnightly for six months (June to November, 2012). The fish ranged in size from 6.0 to 18.0 cm total length and 18.8 - 60.1g body weight. A sterilized one litre plastic bottle and Van Veen Grab were used to collect surface water and sediment samples respectively. Samples collected on each sampling day, were transported to Quality Analytical Laboratory, located in Benin City for metal isolation using Atomic Absorption Spectrophotometer (AAS) according to (Idodo-Umeh and Oronsaye 2006).

In the laboratory, fish samples were measured for total lengths and body weights, to the nearest centimetres and gram respectively. About 2-5g of fish samples collected on monthly basis were placed inside a crucible and dried inside the muffle furnace at a temperature of 150^{0}C for three hours using AAS method according to Idodo-Umeh and

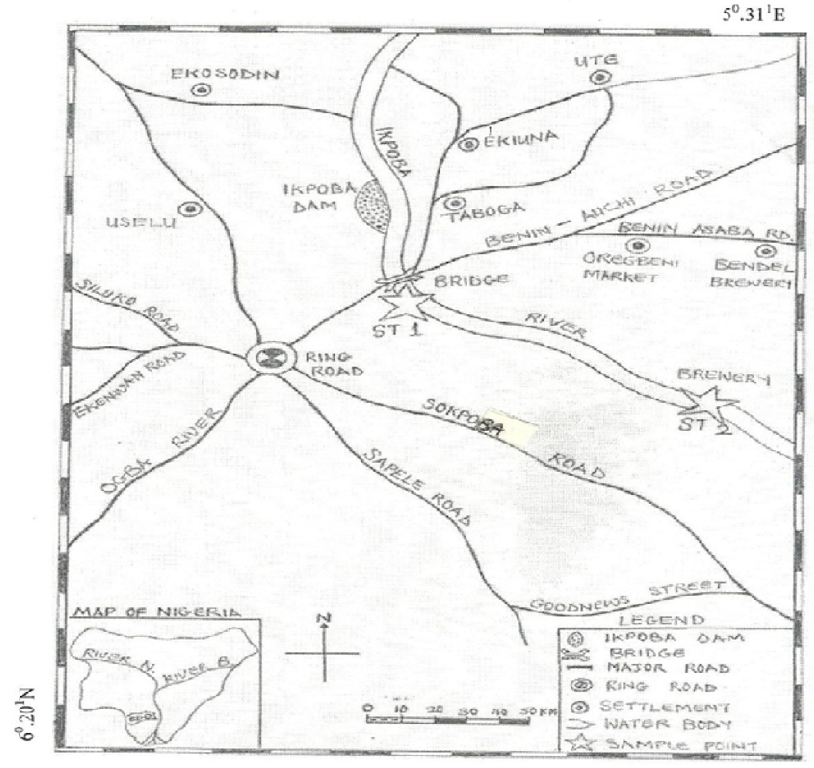

Fig. 1: Map of Ikpoba River and its environs showing sampling stations 1 & 2.

Oronsaye 2006). Fish samples were cooled to room temperature, while their dried weights were taken. The mass formed was then transferred into the cooled muffle furnace where the temperature was slowly raised to 500 ± 50 ^{0}C for 11 hours. The samples were removed and cooled inside the desiccators to room temperature. A volume of 2.0 ml concentrated HNO_3 was dispensed into the crucible and swirled, to acidify. It was gently warmed on a hot plate till evaporation of NO_2 ceased and heating continued, a little longer to evaporate the acid completely. The mass formed was transferred into the cooled furnace once again. The furnace was gradually heated to a range of 450-500^{0}C for two hours and the mass, cooled to room temperature. The process was repeated once again until white -ash colour of the residue was obtained. About 1.0 ml of 1.0N HCI was added and the mixture gently warmed until a clear solution was obtained. The mixture was then cooled and transferred into 25 ml volumetric flasks. Distilled water was added up to the mark and stored inside an incubator at 20^{0}C for metal analysis using Atomic Absorption Spectrophotometer according to (Idodo-Umeh and Oronsaye, 2006).

Bottom sediments collected from the river were dried at 80 ± 10^{0}C for ten hours in the oven, homogenised and the dried ash sieved for extraction of metals (Lead, Zinc, Cadmium, Chromium and Copper) using (AAS) according to (Anderson, 1974; Idodo-Umeh and Oronsaye, 2006). About 1.0±0.05 g dry weight of ground sediment was placed inside a crucible and ignited in a muffle furnace at 500^{0}C for three hours. The ignited mass was cooled inside a desiccator before transferring into a 100 ml suspension for swirling. The suspension was kept inside a thermostat controlled water bath within a temperature range of 70-80^{0}C for one hour. The supernatant was decanted and kept inside a 100 ml volumetric flask. This contains mostly alkaline earth metals. To the residue in the beaker, 10 ml each of concentrated Hydrochloric Acid and $HClO_4$ (concentrated 70% pure) and few porous beads were added and the mixture evaporated to dryness over a hot plate.

This process was repeated whenever necessary. The dried residue was dissolved completely by using minimum amount of concentrated HCI. This solution was then transferred to the same volumetric flask where previous extract containing alkaline earth extract was stored. The content of the flask were made up to the mark with distilled water, before storing inside a refrigerator. These extracts were analysed for heavy metals as earlier stated.

About one litre of surface water sample collected from the river was filtered through Whitman 0.45 μm glass fibre filter and transferred to acid cleansed polypropylene bottles and then acidified with concentrated Nitric acid to a pH not exceeding 2.0. Again the Atomic Absorption Spectrophotometer was used to isolate the metal contained in water samples according to (Idodo-Umeh and Oronsaye 2006).

All data collected were analyzed with analysis of variance at p=0.05 and significant means separated using Duncan Multiple Range Test (DMRT).

RESULTS

Fish, surface water and sediment samples examined had absorbed some heavy metals. Their bio-concentration revealed that all metals except copper and Chromium were higher in fish harvested from station 1 than those from station 2. However, the concentration of Lead and Cadmium at both stations were higher than FAO permissible limits, although station 1 concentration of both metals were higher than those from station 2

Table 1: Mean concentration (mg/l) of metals in fish samples compared with those of the maximum permissible limits.

Metal Types	Station 1	Station 2	FAO, 1985 Maximum Limit
Lead	*40.89	*16.86	1.50
Cadmium	*4.99	*3.36	1.00
Zinc	45.03	39.39	75.00
Chromium	00.02	00.06	13.00
Copper	07.28	12.65	20.00

***Concentration above FAO recommended limits.**

Surface water sample had higher concentrations (0.111mg/l) of Lead in station 1 than station 2 (0.106mg/l). Station 2 recorded higher value (0.154mg/l) for Copper than station 1, whose value was 0.1378mg/l. The concentration of Chromium and Cadmium at both stations were lower than WHO limits, whereas Zinc concentration at station 1 was slightly higher than that of WHO limits (Table 2).

Table 2: Mean concentration (mg/l) of heavy metals in surface water compared with WHO maximum permissible limits.

Metal Types	Station 1	Station 2	WHO, 1985 Maximum Limit
Lead	*0.111	*0.106	0.050
Cadmium	0.007	0.007	5.000
Zinc	*0.018	0.004	0.010
Chromium	0.012	0.012	0.050
Copper	0.137	0.154	1.000

*Concentration above WHO recommended limits.

Concentration of metals in sediment samples revealed that they were higher in station 1 than in station 2, except for Chromium where the value (0.29mg/kg) in station 2 was higher than the value (0.15mg/kg) in station 1, (Table 3).

Table 3: Mean concentration (mg/kg) of heavy metals in sediment samples

Metal Type	Station 1	Station 2	FAO, 1985 Maximum Limit
Lead	28.71	7.22	-
Cadmium	2.75	0.48	10.00
Zinc	24.11	12.95	-
Chromium	0.15	0.29	11.0
Copper	3.87	0.76	250.0

The concentrations of metals in fish, surface water and sediment samples were significantly ($P<0.05$) different from each other and at the stations. For instance, the concentrations of metals in fish were the highest, followed by concentrations in sediment and the least was in surface water.

DISCUSSION

Heavy metals concentrations in surface water

The mean concentration of heavy metals at surface water decreased in the following sequence: Cu>Pb>Zn>Cr>Cd. There were no significant differences ($p>0.05$) of these metals observed between the stations. Copper recorded the highest mean value of 0.1536mg/l at station 2, while Cadmium concentration with a value of 0.0073mg/l was the lowest in station 1. The high levels of metals at surface water observed at station 2 could be attributed to the combined effects of the effluents from the breweries, and the petroleum products depots, which were discharged into the river close to that station; similar conclusion was drawn by Obasohan and Oronsaye (2000).

The levels of Zinc, Copper, Chromium and Cadmium recorded at both stations during this investigation were lower than the maximum acceptable limits for aquatic life as recommended by WHO (1985). The levels of Lead at the stations exceeded the recommended standard. These observed high levels of Lead may be due to the presence of surface runoffs and municipal waste discharges into the water bodies indicating that the water of Ikpoba River is not safe for aquatic lives.

Heavy metals concentrations in sediment

The mean concentration of heavy metals in sediment samples decreased in the following sequence: Pb>Zn>Cu>Cd>Cr. There were significant differences ($p>0.05$) in the heavy metals concentrations in sediment at both stations. Zinc recorded the highest mean value: 28.7100mg/kg at station 1, while Chromium mean concentration 0.1472mg/kg at station 1 was the lowest. The mean metal concentrations were generally higher in the sediments than in surface water. Such observation may have resulted from metal deposition/absorption in sediment particles as they serve as reservoir for heavy metals. It has been reported that in the aquatic environment, permanent and temporary storage of metals takes place in the sediment (Luoman and Bryan, 1978; Biney and Beeko, 1991 and Nwabueze, 2011). The distribution of the metals in sediment at the stations follow similar pattern as in surface water. Metal concentrations were higher at station 1 than in station 2, although with no significant differences, in regards to their concentrations in surface water.

Heavy metals concentrations in Fish

The mean concentration of heavy metals in fish sample decreased in the following sequence: Zn>Pb>Cu>Cd>Cr. There were significant differences ($p>0.05$) in the heavy metal concentration between both stations. Zinc recorded the highest mean value: (45.03mg/kg) at station 1 indicating bio-concentration, while Chromium mean concentration (0.0158mg/kg) was the lowest at station 1. Both concentrations were higher than those recorded by (Ekpo *et al*., 2008) in Ikpoba River. Generally metal concentration was higher in station 1 than in station 2. The high level of Lead and Cadmium metals in fish samples could be due to their release from local sources such as car wash, bathing and laundering taking place close to the stations (Asegbeloyin and Ukoha, 2010; Oronsaye *et al*., 2010). Station 1 was the largest depository of all manner of wastes from the city centre. Hence, it contained relatively higher concentrations of metals, than station 2. The station is the leading centre for trade and mini-factory activities that generate wastes rich in heavy metals from duplicating and printing houses, market wastes, paints and dyes for clothing items and fumes from high vehicular traffic. The concentration of metals in fish tissues may also be the product of equilibrium between the concentration of the metal in an organism's environment and its rate of ingestion and excretion (Oronsaye, 1987). Fish has been reported to accumulate metals from water by diffusion via skin and gills as well as oral consumption, through drinking of water (Nussey *et al.,* 2002). The result obtained in this study showed that Cadmium and Lead had maximum values that were greater than the recommended value by FAO (1985) indicating that *Clarias gariepinus* of Ikpoba River is unfit for human consumption. The level of heavy metals recorded in this study was generally low except Cadmium and Lead, when compared to FAO (1985) recommended limits for human consumption. Fish has been reported to accumulate large amounts of some metals from the water, because they are often at the top of the aquatic food chain (Mansour and Sidky, 2002).

CONCLUSION

The results of this investigation show that some toxic metals' contamination in surface water and fish (*Clarias gariepinus*) of Ikpoba River have reached hazardous levels. This observation renders both fish and surface water unsafe for aquatic life and human consumption. The fish was contaminated with Lead and Cadmium. Both metals may be toxic to other organisms and humans that depend on the river, especially when such metals are consumed in large quantity.

The observed levels for Copper in this study exceeded the WHO maximum permissible limit for surface water, while Cadmium, Zinc, Lead and Chromium were within the limits for surface water. This finding is worrisome in view of the health implications for the human population depending on the river water for domestic usage and fish supply for consumption. Considering the short period covered by the study, further research for a longer period should be conducted, to assess the health risks to aquatic organisms and humans within the catchment area of such polluted environment.

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