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Research Article

Heavy Metal Contamination of African Cat Fish (*Clarias gariepinus*) from Industrial Effluent and Domestic Waste-contaminated Rivers and Home bred sources in Zaria, Nigeria

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ABSTRACT

Clarias gariepinus is an important species of fish that is a major component and source of animal proteins in most diets of the people of Zaria in particular, and Nigeria in general. This work assessed the concentrations of some heavy metals; lead (Pb), manganese (Mn) and cobalt (Co) in different parts of *Clarias gariepinus* from rivers Galma and Kubani and fish farms in Zaria, using Atomic Absorption Spectrophotometer, after wet digestion. The concentrations of the metals differed significantly across the different parts of the fish, with Pb levels being the most worrisome. Across the different sources, the results showed that fish caught from the wild (river Galma and river Kubani) have their metal concentrations comparatively higher than those gotten from fish farm. Generally, the concentrations of the metals in the different parts of the fish, across the sources were significantly higher ($P<0.05$) compared to the FAO/WHO and EU permissible limits of these metals in fish. This shows a possible high risk of heavy metal toxicity consequent upon the consumption of this fish from these sources.

Keywords: Toxic elements, polluted waters, River Kubani, River Galma, Fish farm, *Clarias gariepinus*

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INTRODUCTION

The aquatic environment with its water quality is considered the main factor controlling the state of health and disease in both cultured and wild fishes. Pollution of the aquatic environment by inorganic and organic chemicals is a major factor posing serious threat to the survival of aquatic organisms including fish. Chemical substances that enter water bodies come from a variety of sources (Ayotunde, 2012). Until recently efforts towards the control of water pollutants have concentrated on point sources – easily identifiable sources such as effluent discharged pipes and other overflow devices. Non-point sources such as run-off from agricultural lands, roads, packing lots, mining sites and watersheds are increasingly being given more attention.

The contamination of the waters, sediments and organisms of our rivers and other surface water bodies with a wide range of pollutants has become a matter of great concern world over especially in the last few decades (Kori-Siakpere and Ubogu, 2008). Water containing levels of pollutants so low that the water is deemed potable (fit to drink) can still be a source of problems due to bio-magnifications, a phenomenon whereby chemical substances become increasingly more concentrated at successively higher trophic levels, which is a characteristic of substances that are fat soluble and difficult to be degraded to harmless substances (Kamaruzzaman *et al*., 2010). Metals are non-biodegradable and form part of environmental pollutants in which elevated concentrations pose threats to human health through food chain (Kusemiju *et al*., 2012).

Heavy metals are natural components of the marine environment, but their concentrations have increased due to domestic, industrial, mining and agricultural activities (Bakan and Büyükgüngör, 2000; Altas and Büyükgüngör, 2007; Bat *et al*., 2012). The discharge of industrial wastes containing toxic heavy metals into water bodies may have significant effects on fish and other aquatic organisms, which may endanger public health. Marine organisms such as fish accumulate heavy metals to concentrations many times higher than present in water or sediment (Bat *et al*., 2012). When metals enter aquatic environment, a great portion settles and is absorbed by the bottom mud (Ada *et al*., 2012; Ayotunde, 2012). They could be recycled by chemical, physical and biological processes such that some quantity remains dissolved in the water column and some part absorbed by the inhabitants (Ada *et al*., 2012; Kori- iakpere and Ubogu, 2008).

Fishes are at the apex of the marine food chain and can bioaccumulate some of these substances in their tissues (Ada *et al*., 2012; Olaifa *et al*., 2004). Fishes are therefore useful sentinel species and bio-indicators of metal pollution because they can help to understand the risk to aquatic ecosystem and to humans (Peakall and Burger, 2003). Many biological factors of the fish such as age, lipid contents, mode of feeding and body size could play a role in the bioavailability of metals (Peakall and Burger, 2003). The use of wild and cultured fishes as biomonitors of metal pollution in the aquatic ecosystem is becoming popular throughout the world (Indrajith *et al*., 2008). Generally, the higher the metal concentration in the environment, the more the amount taken up and accumulated by fish. The quantity of metal accumulated has been reported to be directly related to the concentration to which the organisms are exposed and the period of exposure (Kusemiju *et al*., 2012, Kamaruzzaman *et al*., 2010). Metals are also preferentially accumulated by different organs of the body (Kusemiju *et al*., 2012, Rauf *et al*., 2009).

Clarias gariepinus is a very important source of animal protein in human diet. It forms a significant percentage of captured fish from River Galma and River Kubani, Zaria, Nigeria, and is consumed in large quantities by the local inhabitants. *Clarias gariepinus* is a bottom feeder, and ingestion of sediment from industrial, municipal and domestic wastes will be reflected in the metal contents of their tissues (Udiba *et al*., 2013). Therefore this study was aimed at determining and comparing the concentrations of lead (Pb), manganese (Mn) and cobalt (Co) in organs of *Clarias gariepinus* obtained from River Galma, River Kubani and Fish farms in Zaria, with FAO/WHO standards in order to have an insight into the pollution status of the rivers and ascertaining the suitability or otherwise, of the fish for human consumption.

MATERIALS AND METHODS

Study Location: Zaria is located at latitude 1103'N and longitude 7040'E, 128km South- East of Kano and 64km North-East of Kaduna City. River Galma is located at the south-eastern part of Zaria and its source is the Jos Plateau. The Zaria dam is located on River Galma (Nnaji *et al*., 2007). Kubanni River originates in the precincts of the Ahmad Bello University (ABU) Main Campus, Zaria (Northern Nigeria), as a trench in an undulating agricultural land and is fed by a number of tributaries (Uzairu *et al.*, 2009). Kubanni river drains the northwest zone of the city of Zaria and receives effluents mainly from domestic activity and runoff from intense cropping located in the adjoining land. The ABU dam is on the river (Uzairu *et al*., 2009).

Sample collection and preparation: Ten *Clarias gariepinus* each (mean weight 130 ± 3g, Mean length 26.8 ± 2.6cm) were obtained on site from fishermen at the two Rivers (River Galma, River kubanni) and five each from two fish farms in Sabon Gari area of Zaria, Nigeria. They were stored in a cooler packed with ice block in order to maintain the freshness and latter transported to the Environmental laboratory of the National Research Institute for Chemical Technology (NARICT), Zaria, Nigeria for dissection of the organs after being washed thoroughly. During the dissection, the organs of the fish such as the Gills, Liver, Muscle and the Head were harvested and weighed separately. These weighed organs were digested separately and their heavy metals content determined using the AAS machine. As a result, there was determination of the heavy metals in the Head, Muscle, Liver and Gills separately. 5g (wet weight) of fish tissue was weighed and placed in a beaker, 10mL of freshly prepared concentrated nitric acid / hydrogen per oxide (1:1) was added and covered with a wash glass for initial reaction to subside. The beaker was placed on a water bath at a temperature not exceeding 800C for two hours to reduce the volume to 3-4mL. The digest was cooled filtered into 50ml volumetric flask and made up to the mark with distilled deionized water.

Metal analysis: Metal analysis was carried out using flame atomic absorption spectrophotometer AA-6800 (Shimadzu, Japan) at National Research Institute for Chemical Technology (NARICT), Zaria-Nigeria. The calibration curves were prepared separately for each of the metals by running different concentrations of standard solutions. The instrument was set to zero by running the respective reagent blanks. Average values of three replicates were taken for each determination and were subjected to statistical analysis. The metals determined included lead, manganese, and cobalt.

Analytical Quality Assurance: The result of the analysis was validated by digesting and analyzing Standard Reference Materials, animal blood coded; International Atomic Energy Agency (A-13) and Lichens coded; International Atomic Energy Agency (336) following the same procedure. The analysed values and the certified reference values of the elements determined were compared to ascertain the reliability of the analytical method employed. Double distilled and deionized water was used throughout the experimentation. All the reagents used in this work were of analytical grades from BDH Chemicals (UK).

Statistical Analysis

Data collected were presented as mean ± SD after calculation using Microsoft Office Excel 2008. The data was also subjected to analysis of variance (ANOVA) and post hoc (LSD) for levels of significance using SPSS version 16.0. A P-value of 0.05 or less was considered statistically significant

RESULTS

Distribution of toxic minerals in fish organs of *Clarias gariepinus* in studied areas

River Galma: The level of Manganese in the head is significantly higher ($P<0.05$) than that of Pb and Co, as presented in Table 1. The level of Lead in the gill, liver and muscle is significantly higher ($P<0.05$) than that of Mn and Co. Similarly, the level of Mn in the gill and liver was significantly higher compared with Cobalt. However, there was no significant difference between Mn and Co distributions in the muscle. The level of Mn distribution in the liver was significantly higher ($P<0.05$) than that in the head, gill and muscle. The level of Co distribution in the liver was significantly higher ($P<0.05$) than that in the gill, head and muscle. Comparatively, the level of Pb in the head was significantly lower than in the other organs while that of Mn and Co in the muscle were significantly lower than the other organs.

Table 1.
Distribution of toxic minerals in fish organs of *Clarias gariepinus* from river Galma

Fish Organ	Head	Gill	Liver	Muscle
Lead	13.29 ±0.22$_{a}$	59.21 ±0.42$_{b}$	62.53 ±0.98$_{c}$	18.86 ±0.06$_{d}$
Manganese	39.69 ±0.91$_{e}$	31.38 ±0.89$_{f}$	56.72 ±0.94$_{g}$	3.72 ±0.32$_{h}$
Cobalt	5.29 ±0.55$_{i}$	12.66 ±0.24$_{j}$	31.76 ±0.78$_{k}$	3.71 ±0.10$_{h}$

Values are expressed as mean ± SD (n=3)
Values with different letters are significantly different at P<0.05

Table 2.
Distribution of toxic minerals in fish organs of *Clariasgariepinus* from river Kubani

Fish Organ	Head	Gill	Liver	Muscle
Lead	18.52 ±0.16$_{a}$	45.55 ±0.91$_{b}$	32.02 ±1.10$_{c}$	24.41 ±1.50$_{d}$
Manganese	0.96 ±0.05$_{e}$	8.03 ±0.04$_{f}$	6.31 ±0.60$_{g}$	5.32 ±0.38$_{h}$
Cobalt	2.92 ±0.14$_{i}$	4.36 ±0.58$_{j}$	19.54 ±0.35$_{k}$	0.78 ±0.07$_{l}$

Values are expressed as mean ±SD (n=3)
Values with different letters are significantly different at P<0.05

River Kubani: The distribution of toxic minerals in fish organs of *Clarias gariepinus* in river Kubani is given in Table 2. The level of Pb distribution in the head, liver and muscle was significantly higher ($P<0.05$) than that of Mn and Co. There was no clear cut pattern of Mn distribution in the organs when compared to Co, as it was significantly decreased in the head and liver. The level of Pb in the gill was significantly higher ($P<0.05$) than that in the liver, muscle and head. The level of Mn distribution followed a similar pattern as that of Pb, while that of Cobalt was higher in the liver and lower in the muscle comparatively.

Fish Farm: The distribution of toxic mineral in fish organ of *Clarias gariepinus* in fish farm is given in Table 3. The level of Pb distribution was significantly higher ($P<0.05$) in the gill, liver, head and muscle than that of Mn and Co. The level of Mn distribution was significantly higher ($P<0.05$) in the gill compared to Co and significantly lower ($P<0.05$) in the liver and head compared to the level of Co. There was no significant difference ($P>0.05$) between the level of Mn and Co in the muscle. The level of Pb was significantly higher ($P<0.05$) in gill than in the liver, head and muscle. The level of Mn was significantly higher (P<0.05) in the gill compared to the liver, muscle and head. The level of Co was significantly higher ($P<0.05$) in the liver than in the head, gill and muscle with no significant difference ($P>0.05$) between the levels of Cobalt in the gill and muscle.

Mineral absorption in Organs of *Clarias gariepinus* across the stations: The mineral absorption in organs of *Clarias gariepinus* across the stations is shown in Figure 1. There was no significant difference between the absorption of Pb and Mn in the head of *Clarias gariepinus* but there was significant difference in the absorption of Pb and Mn in the head compared to Co. The mineral absorption of Pb, Mn and Co in the gill of *Clarias gariepinus* was not significant. Also, in the liver, the absorption of Mn and Co showed no significant difference ($P>0.05$) between them. This pattern was followed for the absorption of mineral in the muscle of *Clarias gariepinus*

Table 3.
Distribution of toxic minerals in fish organs of *Clarias gariepinus* from fish farm

Fish Organ	Head	Gill	Liver	Muscle
Lead	10.42 ±0.43$_{a}$	53.66 ±0.94$_{b}$	18.73 ±0.36$_{c}$	4.08 ±0.10$_{d}$
Manganese	1.78 ±0.02$_{e}$	8.33 ±0.08$_{f}$	4.84 ±0.40$_{g}$	2.35 ±0.10$_{h}$
Cobalt	6.49 ±0.36$_{i}$	3.16 ±0.11$_{j}$	13.22 ±0.21$_{k}$	2.59 ±0.12$_{hj}$

Values are expressed as mean ± SD (n=3)
Values with different letters are significantly different at P<0.05

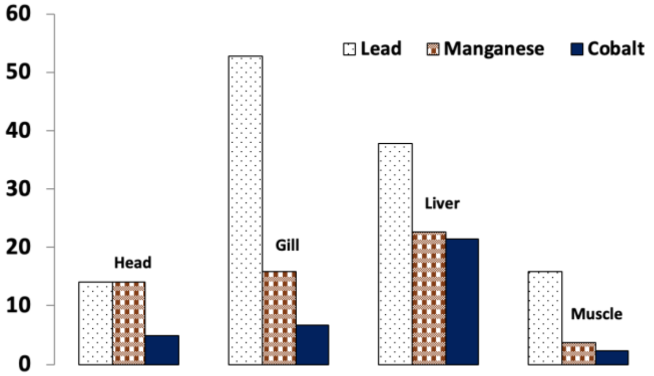

Figure 1.
Mineral absorption in Organs of *Clarias gariepinus* across the stations

DISCUSSION

The result of the present study showed that different parts of the fish have different ability to sequester heavy metals. This was indicated by the significantly high Pb concentration in the different parts of the fish compared to Mn and Co. Also, the results show that the concentrations of these metals are higher in the gill and liver compared to other parts of the fish.

This is a good pointer to the fact that the gill is in frequent contact with the environmental water, and being studded with blood vessels, have the tendency to absorb more of the heavy metals from the environment. The liver on the other hand, is the principal storage organ for these metals, compared to other tissues (Ayotunde, 2012). Particularly troubling is the fact that *Claria gariepinus* is among the few fishes that are consumed wholly, and the tendency for complete ingestion of these metals, irrespective of their organ of storage is imminent.

The concentrations of the metals in the fish from the various waters (Kubani, Galma and fish farm), was also significantly higher than the FAO/WHO permissible limits of heavy metals in fish of 0.1mg/kg (FAO/WHO, 2007), and the European union permissible limit of 0.5mg/kg (EU, 2009). This is a reflection of the fact that the effluents from the wet industries and domestic wastes occasionally dumped into the rivers may be the major contributors of heavy metals in this aquatic environment, while for the fish gotten from fish farm, it is likely that the feeds fed to the fish are contaminated with these metals. Comparatively, the concentrations of metals in the different organs of fish gotten from fish farms were lower than those from the wild.

Lead is classified as one of the most toxic heavy metals. There is no exposure limit below which Pb appear to be safe. WHO has recently withdrawn the Provisional Tolerable Weekly Intake (PTWI) value for Pb on the grounds that it is not possible to set an intake level that is protective for health (Joint UNEP/OCHA, 2010). Lead is number two on the Agency for Toxic Substances and Disease Registry (ATSDR) top 20 list, and accounts for most of the cases of pediatric heavy metal poisoning (ATSDR, 2008). It interferes with the normal development of a child's brain and nervous system. Children are therefore at greater risk of Pb toxicity. On the other hand, the effect on the peripheral nervous system is more pronounced in adults. Lead absorption constitutes serious risk to public health. It induces reduced cognitive development and intellectual performance in children, increases blood pressure, and cardiovascular diseases in adults as well as liver and kidney dysfunction (Udiba *et al.*, 2012). Manganese is biologically beneficial in trace amount. However, at elevated amount above the WHO permissible limits, it could become harmful. The primary targets of Mn toxicity are the brain and central nervous system.

Manganese has been shown to be deposited in certain regions of the brain, and exposure to high concentrations have been associated with permanent damage, with symptoms of impaired neurological and neuromuscular control, mental and emotional disturbances, muscle stiffness, lack of coordination, tremors, difficulties with breathing or swallowing, and other neuromuscular problems (Sharma and Pervez, 2005). Cobalt in trace amount is beneficial to health, being a major component of the B12 vitamin, Cyanocobalamin. However, with prolong exposure to elevated levels, Co is toxic (Udiba *et al.*, 2014). Cobalt poisoning that occurs from constant contact with the skin will likely cause irritation and rashes that go away slowly. Ingesting a large amount of absorbable Co at one time is very rare and is likely not very dangerous. It may cause nausea and vomiting. However, absorbing a large amount of Co over longer periods of time can lead to serious health problems, such as cardiomyopathy, deafness, nervous problems, tinnitus, thickening of the blood, thyroid problems among others

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