**Bioaccumulation of heavy metals in the fish species *Sarotherodon melanotheron* from Alaro Stream Ecosystem in Ibadan.**

Emmanuel Teryila Tyokumbur.

Department of Zoology, University of Ibadan, Ibadan, Nigeria.

Email: e.tyokumbur@mail.ui.edu.ng

**Abstract:** A study was carried out on the bioaccumulation of heavy metals in the fish species *Sarotherodon melanotheron* from Alaro Stream Ecosystem in Ibadan. Fishes have been identified as affordable protein source that are efficient bioaccumulators of organic and inorganic pollutants which depends on the age of the fish, lipid content in the tissue and mode of feeding that are significant factors that affect the accumulation of heavy metals in fishes. The objective of the study was to evaluate the bioaccumulation of the heavy metals and to compare it with international permissible limits for public health good. Twenty five (25) fish were collected from the Alaro stream and dissected to remove the gills, fins, gut, liver, bones and muscle. These organs were oven dried at 1050C for 6hours, pulverized and acid digested for heavy metal analyses. The results showed that the mean Ni and Se in the organs of *S. melanotheron* were above the World Health Organization (WHO) permissible limit guideline standard of 0.07 and 0.04ppm respectively. The mean Zn in the organs of *S.melanotheron* did not exceed the permissible limit of 1000ppm. It can be concluded that there is need for moderation in the consumption of fish obtained from Alaro Stream in Ibadan through monitoring of daily intakes even though some heavy metals that have physiological relevance have been found to exceed the recommended permissible limits since there is no massive fisheries output from the aquatic ecosystem that forms a major part of the diet in the populace.

[Emmanuel Teryila Tyokumbur. **Bioaccumulation of heavy metals in the fish species *Sarotherodon melanotheron* from Alaro Stream Ecosystem in Ibadan.** *N Y Sci J* 2016;9(2):83-88]. ISSN 1554-0200 (print); ISSN 2375-723X (online). <http://www.sciencepub.net/newyork>. 14. doi:[10.7537/marsnys09021614](http://www.dx.doi.org/10.7537/marsnys09021614).

**Keywords**: Bioaccumulation, heavy metals, fish, *Sarotherodon melanotheron,* Ibadan.

**Introduction**

The natural aquatic ecosystem can be extensively contaminated with heavy metals released from domestic, agricultural, industrial and other man-made activities (Velez and Montoro, 1998; Vinodhini and Narayanan, 2008). These heavy metals gain access into aquatic ecosystem through anthropogenic source and get distributed in the water body, suspended solids and sediments during the course of their mobility Eneji *et al*, 2011).This contamination of the freshwater ecosystems with a wide range of pollutants has become a matter of public concern in recent times due to the have devastating effects on the ecological balance which requires biomonitoring and mitigation (Dirilgen, 2001; Vutukuru, 2005, Farombi *et al*, 2007). Among animal species, fishes are the aquatic inhabitants that cannot escape from the detrimental effects of these pollutants (Olaifa *et al*., 2004). Several factors including time of the year (season), physicochemical properties of water play an important role in heavy metal bioaccumulation in diverse fish organs and tissues (Kargin, 1996). The gills and the skin which are in directly contact with the water reflects an elevated accumulation of heavy metals in relation to their concentration in water while the content in the liver represents active storage (Romeo *et al*., 1999).

The rate of bioaccumulation of heavy metals in aquatic organisms depends on the ability of the organisms to excrete the metals, the concentration of such metal in the water, the concentration of the heavy metal in the surrounding soil sediments as well as the feeding habits of the organism (Eneji *et al*, 2011). Fishes have been identified as efficient bioaccumulators of organic and inorganic pollutants which depends on the age of the fish, lipid content in the tissue and mode of feeding that are significant factors that affect the accumulation of heavy metals in fishes (King and Jonathan, 2003; Eneji *et al*, 2011). This is ultimately transferred to other animals including humans through the food chain when the fish is consumed as part of the diet (Tyokumbur, 2010). Toxic level of heavy metals has been shown to have apparent lethal or chronic effects on fish hence the fish does not only indicate pollution status of aquatic ecosystem but is one of the main sources of exposure to hazards in human nutrition (Kotze *et al*, 1999; Avenant-Oldewage and Marx, 2000; Wright and Welbourn, 2002; Qadir and Malik, 2011). The use of aquatic organisms as pollutant indicators has several advantages over the chemical analysis of abiotic comportments as it reflects a continuum of the chain of events following impacts by an environmental contaminant (Karadede-Akin and Unlu, 2007). In this study, the heavy metals sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), iron (Fe), vanadium (V), cobalt (Co), zinc (Zn), selenium (Se), molybdenum (Mo) and silver (Ag) will be assessed in the organs of *Sarotherodon melanotheron* from Alaro Stream Ecosystem in Ibadan, Nigeria. The objective of the study is to evaluate the bioaccumulation of the heavy metals and compare it with international permissible limits for public health good.

**Materials and methods**

**Study site**

The study was carried out using fish samples from Alaro Stream which flows through the hydroecological

Area of the Oluyole Industrial Estate in Ibadan, Nigeria. It is impacted by effluents from diverse sources of heavy metal pollution. The Alaro stream flows into Oluyole Estate in a west to south east direction from its source at Agaloke near Apata in Ibadan, Oyo State. It forms a confluence with River Ona at the southeast tip of an animal farm as its main tributary. The stream receives effluents from diverse industries discharging effluents directly and indirectly into it. Effluents sources from natural and anthropogenic processes are discharged into Alaro stream through run-off, leaching and leachate or as windblown materials during the dry season. The Oluyole hydroecological system is located between Latitude 7o 21’N -7 o 22’N and Longitude 3 o 50’-3 o 52’E.

**Sample collection and processing**

Twenty five (25) fish were collected from the Alaro stream downstream of the industrial effluent discharge points. It was collected using cast nets with mesh size of 30-50mm of varying dimensional sizes. The nets were submerged for about three minutes before retrieving with a drawing string to check for any trapped fish. Gill nets with mesh sizes of 30-50mm were tied to stakes on each side of the shoreline with a lead weight suspended on the stream bed and maintained vertically in water overnight. Fish samples were identified using the textbook by Moses (1992).The fish were dissected to remove the gills, fins, gut , liver, bones and muscle. These organs oven dried at 1050C for 6hours .Each organ was then pulverized separately by using a porcelain mortar and pestle .The pulverized and powdered samples were stored in Ziploc bags prior to analyses.

Pulverzied samples were digested by adding 2mL trace metal grade HNO3 to 0.5-1g of each sample in Teflon digestion tubes and heated at 1050C for 1 hour in a heat block. The resulting clear solution was then allowed to cool followed by addition of 1ml H2O2. After the simmering reaction, it was boiled and left overnight. The digested sample was then diluted to the 10mL mark using MilliQ water and transferred into test tubes rinsed with deionized water for Inductively Coupled Plasma Mass Spectrometer (ICP-MS) analyses.

The Standard Reference Materials (SRM) used to assess accuracy, reproducibility of the results and metal recovery was bovine liver obtained from the National Institute of Standards and Technology (NIST-1577). The SRM is a sample that contains a sample that has been previously analyzed with values of a suite of heavy metals and other contaminants that is used to ensure accuracy and quality assurance of analytical results.

**Results and Discussion**

The results of the mean heavy metal concentration in the organs of *S. melanotheron* Fe).

**Figure 1: Mean Ni and Co concentration in the organs of *Sarotherodon melanotheron.***

All the mean nickel (Ni) concentration in the organs of *S.melanotheron* was above the World Health Organization permissible guideline limit of 0.07ppm (WHO, 2008). The highest mean Ni concentration in the organs was 1.72pp (gills) while the lowest was 0.1ppm (fins) in the increasing order: fins<gills<muscle<liver<bone<gut. The highest mean Co concentration in *S.melanotheron* was 2.64ppm (bone) while the lowest was in the gills (0.07ppm) in the increasing order: gills<gut<liver<muscle<fins<bone, however there is no set WHO permissible limit guideline for Co.

**Figure 2: Mean Mo and Se concentration in the organs of *Sarotherodon melanotheron.***

All the mean Se concentration in the organs was above the WHO permissible limit of 0.04ppm. The highest mean Se concentration in the organs of *S.melanotheron* was 5.49ppm (bone) while the lowest was in the gut (0.16ppm) in the increasing order: gut<fins<gills<liver<muscle<bone. The highest mean Mo was 0.44ppm (gills) while the lowest was 0.02ppm (muscle) in the increasing order: muscle<gut<liver<bone<fins<gills with no set WHO permissible limit guideline.

**Figure 3: Mean Mg and Zn concentration in the organs of *Sarotherodon melanotheron.***

All the mean Zn concentration in the organs of *S.melanotheron* was below the WHO permissible limit guideline standard of 1000ppm. The highest Zn concentration was in the muscle (84.9ppm) while the lowest was 22.3ppm (bone) in the increasing order: bone<liver<gut<gills<fins<muscle. The highest mean Mg concentration was in the gills (1105ppm) while the lowest was in the gut (738ppm) in the increasing order: gut<bone<fins<liver<muscle<gills.

**Figure 4: Mean K and Ca concentration in the organs of *Sarotherodon melanotheron.***

The highest mean Na concentration in the organs of *S.melanotheron* was in the liver (16385ppm) while the lowest was in the fins (5704ppm) in the increasing order: fins<gills<bone<gut<muscle<liver. The highest Ca concentration in the organs was in the fins (75136ppm) while the lowest was 615ppm (liver) in the increasing order: liver<muscle<gut<bone<gills<fins.

The variation in the heavy metals found in the organs of *S.melanotheron* can be attributed to the contamination in aquatic environment, uptake, regulation and depuration from the fish body (Nussey, 2000). This depends on the route of exposure such as through diet or their elevated levels in surrounding environment (Alam *et al*, 2002). Comparatively, gills, liver and kidneys accumulate heavy metals in higher concentrations than the muscles which show the lowest levels of metals accumulation (Wepener *et al*, 2001). This study corroborates previous findings that have shown variations of heavy metals in fish organs sampled from impacted aquatic ecosystems. Karadede-Akin and Unlu (2007) found Cu, Fe, Mn and Zn values obtained from the muscle of fish sampled from the Tigris River in Turkey were variable but under the acceptable values. Vinodhini and Narayanan (2008) in their study from southern districts of Tamilnadu in India, concluded that the order of heavy metal accumulation in the gills and liver was Cd > Pb > Ni >Cr and Pb > Cd > Ni > Cr. Similarly, in the case of the kidney and flesh (muscle) tissues, the order was Pb > Cd > Cr > Ni and Pb > Cr> Cd > Ni. In all the heavy metals assessed, the bioaccumulation of lead and cadmium proportion was significantly increased in the tissues of *Cyprinus carpio* (Common carp). In a study along Ravi River in Pakistan, (Rauf *et al*, 2009) found that fish liver appeared to have significantly higher tendency for the bioaccumulation of cadmium and chromium (4.26 ± 1.57 and 6.23 ± 1.14 μgg-1), while gills had minimum concentrations (1.10 ± 0.53 and 1.46 ± 0.52 μgg-1) of these metals with *Catla catla* showing higher levels of metal concentrations than *Labeo rohita* and *Cirrhina mrigala.* Qadir and Malik (2011) discovered that measured concentrations of Pb, Cd, and Cr in muscles of species such as *Channa punctata, Labeo rohita, Oreochromis niloticus, Puntius sophore,* and *Wallago attu* from River Chenab in Pakistan were above permissible limits of heavy metals for human consumption, indicating potential health risks. Eneji *et al* (2011) in a study along River Benue in Nigeria asserted that *Tilapia zilli* gills contained the highest concentration (52.2%) of all the detected heavy metals, followed by the intestine (26.3%), while the muscle tissues appeared to be the least preferred site for the bioaccumulation of metals as the lowest metal concentration (21.5%) were detected in this tissue.

In this study, mean Ni and Se in the organs of *S.melanotheron* exceeded the World Health Organization’s permissible limit guideline standard of 0.07 and 0.04ppm respectively thereby making the fish unsuitable for human consumption or at best in moderation following nationally recommended daily intake. For most of the other macroelements like K, Mg and Ca, there is no set permissible limit guideline. However, the mean Zn in the organs of *S.melanotheron* did not exceed the permissible limit of 1000ppm, therefore the fish in this study sites are safe for human consumption. Other heavy metals like Mn, Co and Mo have had their permissible limit guidelines withdrawn due to their elevated levels in water and food sources that are being consumed over a long period of time without reported health hazards. It can be concluded that there is the need for moderation in the consumption of fish obtained from Alaro Stream in Ibadan through monitoring of daily intakes even though some heavy metals that have physiological relevance have been found to exceed the recommended permissible limits since there is no massive fisheries output from the aquatic ecosystem.

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2/13/2016