



Assessment of Heavy Metal Pollution using *Mormyrus Rume*

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ABSTRACT

In this study, heavy metals Lead (Pb), Nickel (Ni), Mercury (Hg), Cadmium (Cd) and Selenium (Se) were determined to assess the pollution level of Opa Dam. The water of the dam and the liver, gills and fillet of six *Mormyrus rume* and six *Tilapia zilli* were analyzed by AAS. The order of the metals in the water and fillets of (*M. rume* and *T. zilli*) were $Pb > Ni > Se \geq Cd > Hg$, $Ni > Pb > Se \geq Cd \geq Hg$ and $Ni > Pb > Se > Cd \geq Hg$. Pb, Ni and Hg were higher above the standard permissible level (EPA2002, WHO2003, WPCL 2004 and SON 2007) in Opa Dam water while nickel was outrageous in the fillet above the FAO, 1983 and WHO 1985 limit of heavy metals in fish food. Thus, the dam needs periodical monitoring for the safety of the fish consumers and for water useage.

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Introduction

Fish are widely used for assessing the health condition of aquatic ecosystems because when pollutants are built up in the food chain, fish often top the aquatic food chain. Water reservoirs are collectors of all materials spread by human, industrial and agricultural activities. Heavy metals penetrate into water reservoirs via atmosphere, drainage, soil waters and soil erosion. As the concentration of heavy metals in the environment increases, the metals inevitably enter the biogeochemical cycle (Riget et al, 2004). Heavy metals are not biodegradable, they are assimilated and deposited in fish tissues while water and sediment could be a major source as aquatic animals are nourished through them (Linnik and Zubenko, 2000). Therefore, heavy metals can be bio-accumulated and biomagnified via the food chain and finally get to human being through consumption resulting in health risks (Agah et al., 2009).

Various metals are accumulated in fish body in different amounts, the concentrations of trace elements in liver and muscle may vary, depending on a number of factors. These differences result from different affinity of metals to fish tissues, different uptake, deposition and excretion rates. Many factors such as temperature, pH and acidity have been responsible for metal accumulation in fish tissues. Water temperature may cause the differences in metal deposition in various organs. Higher temperatures promote accumulation of cadmium especially in the most burdened organs: kidneys and liver (Yang and Chen, 1996). The temperature rise of the marine ecosystem helps in the increase of the metabolic rate, metal mobility and binding of metals to various tissues. Studies have shown that acidification of marine environment (lakes) increases the concentration of Pb and Cd (Haines and Brumbaugh, 1994; Horwitz et al., 1995). Acidity may enhance the solubility of the metals in the water body and hence allow free movement of the ions in solution, thus competitive uptake of H^+ ions may hinder the absorption of the metals into the fish or it could damage or weaken the epithelia and enhance easy passage of metals into the fish tissues (Barbara et al., 2006).

Materials and Methods

Study Area

The Opa Reservoir Basin, extends from Obafemi Awolowo University, Ile-Ife, Nigeria to as far away as Osu in the

Atakumosa Local Government Area. The area lies between latitudes $7^{\circ}27'N$ and $7^{\circ}35'N$ and longitudes $4^{\circ}30'E$ and $4^{\circ}40'E$ (Federal Survey Topographical Sheets, Ilesha S.W. 234 and Ondo N.W. 263).

The reservoir was created in 1979 by damming the Opa River for portable water supply and freshwater fisheries research. It has an embankment length of 233.3m, a crest width of 6.7m and is equipped with mechanical and auxiliary spillways. The climate of the area exhibits two distinct seasons, dry and wet (Lowenberg and Kunzel, 1992). The wet season spans between April and September and is marked by high rainfall, rise in water level in the reservoir and increased discharge through the auxiliary spillway. The mean water depth at the spillway exceeds 60cm at the peak of rains. The dry season on the other hand spans between October and March and characterized by low discharge and dryness. Consequently, the stream below the spillway shrinks into stagnant pools of water in the dry season. The pH of the water is in the range of 7.4-8.0, almost neutral but just very slightly basic showing that the reservoir will accommodate a lot of aquatic organisms' activities.

Sample Collection, Pretreatment and Selection

Water samples at different points were collected at 10-15cm depth in separate pre-conditioned polyethylene bottles from the dam and the pH taken in situ. The collected samples were filtered with (Whatman no 42) and the filtrate acidified with concentrated HNO_3 to minimise precipitation and adsorption to container's wall. Two common species of fish (*Mormyrus rume* of the family of Mormyridae commonly called Eja Osan and *Tilapia zilli* of the family of Cichlidae locally called Tilapia) found at the peak of dry season (March 2012) in the dam (six samples from each species, labeled A - F and A2 - F2), were collected from the Opa dam with the help of the fisher men. *Tilapia* is a cultural fish and does not have feeding problems and therefore fit as an ideal species of aquatic organisms for assessment study on effects of heavy metal contamination in water bodies (Kalay and Canli, 2000; Mokhtar et al., 2009). *Tilapia zilli* displays high resistance to diseases, can survive low oxygen water and thus can withstand poor aquatic environment. (Zhou et al., 1998).

The fish were taken to the laboratory via an iced packed cooler, they were thoroughly washed with distilled water, each sample was weighed on a scale at Fish Laboratory, Department of Zoology, OAU, Ife and the standard and the total length were taken and recorded. The fishes were dissected to remove the liver and the gills before digestion. The quantity of fish were chosen in order to represent different sizes of fish species in the reservoir. Their fillet or flesh, liver and gills were digested and analyzed separately.

Sample Drying and Dissolution

0.2g of the liver and 0.5g of gills and fillet were weighed separately and transferred to Teflon beaker, 10ml of 1:1 HNO₃/H₂O₂ was added and the beaker was heated on a thermostatically controlled hot plate maintained at about 90°C for 20 minutes. The digested sample was transferred to a 100ml volumetric flask and the flask made up to mark with deionized water. The whole content was then transferred to a 120ml capacity Teflon bottle and stored at a temperature below 5°C prior to analysis. The water from Opa River was also digested for analysis. 5ml of the water was measured and digested through the same process and then made up to 100ml by dilution. This is done in order to know the level of heavy metal concentration in the water, and to ascertain the contamination source of the fish samples. The worked up samples above were analyzed for heavy metal concentration using Flame Atomic Absorption Spectrophotometry (FAAS) available at the International Institute for Tropical Agriculture, Ibadan. The FAAS were operated according to the manufacturer's manual.

Quantification of heavy metals in the sample

The heavy metal profile was done using the Buck Model 205 Atomic Absorption Spectrophotometer at the International Institute for Tropical Agriculture, Ibadan. Actual heavy metal concentration values in the samples were evaluated as follows:

$$M_i \times F_v$$

$$[M]_a = \frac{M_t}{F_v}$$

Where $[M]_a$ = actual heavy metal concentration in sample;

M_i = instrumental concentration obtained

Calibration of Instrument

The calibration of the FAAS used was done to evaluate the response of the analytical procedure with respect to known quantities of the standard solution of the heavy metals of interest, that the response to unknown quantities in the samples could be reliably estimated. Standard solution of concentration ranging from (20, 10, 6, 4, 2, 1) ppm were prepared by serial dilution for the determination of heavy metals in fish and water samples. These solutions were run to obtain the working calibration graph.

Validation of Analytical Procedure Adopted

The reliability of all the analytical procedures adopted in this study was in terms of sensitivity, precision and accuracy. The elements Lead(Pb), Nickel(Ni), Mercury(Hg), Cadmium(Cd) and Selenium(Se) were analyzed at the most sensitive wavelength viz; Pb (279Nm), Ni (233Nm), Hg (253.7Nm), Cd (228.9Nm) and Se(196Nm), the standard calibration curves obtained showed high linearity level with r^2 values between 0.999 and 1, these values are adjudged acceptable.

Results and Discussion

Variation of Heavy metals in fish species

The pH of Opa dam water ranged between 7.4 -7.5, this showed that the water is almost neutral. The concentration of the analyzed heavy metals in the Opa dam water. The heavy metal concentration of Pb, Ni and Hg were found to be higher than the permissible limit of the metals in raw water (EPA

2002, WHO 2003, SON 2007, WPCL 2004), hence, the water is said to be polluted with those metals. Selenium is within the limit of USEPA 2003. Heavy metals in fresh water are usually available to the fish in the soluble forms which may be labile and non-labile fractions. The labile fractions are readily released and made available for uptake by the aquatic organisms including fish, the amount assimilated largely depends on the environmental condition of the water (Kock et al., 1996; Barbara et al., 2006). In urban areas, the careless disposal of industrial/municipal effluents and other wastes in river and lakes may contribute greatly, to the poor quality of river water (Chindah et al., 2004; Emongore et al., 2005; Furtado et al., 1998 and Ugochukwu 2004).

The concentrations of lead in the different species of samples of fish liver ranged between 2.2µg/g (Mormyrus rume sample F) and 7.0µg/g (Tilapia zilli sample F2). Concentration of nickel is between 3.0µg/g (Mormyrus rume sample F) and 9.0µg/g (Tilapia zilli samples B2 and E2), mercury is between 0.5µg/g (Mormyrus rume sample E) and 3.0µg/g (Tilapia zilli sample F2), cadmium is between 1.0 µg/g (Mormyrus rume samples B, E and F) and 3.0µg/g (Tilapia zilli samples B2, D2, E2 and F2), and selenium is between 0.70µg/g (Mormyrus rume samples A) and 3.0µg/g (Tilapia zilli sample D2).

The concentrations of lead in the different species of samples of fish gills ranged between 2.2 µg/g (Tilapia zilli samples B2 and E2) and 3.0µg/g (Mormyrus rume sample B), of nickel is between 1.5µg/g (Mormyrus rume sample A) to 3.2 µg/g (Tilapia zilli samples A2, B2, D2, and F2), of mercury is between 0.6µg/g (Mormyrus rume sample E, Tilapia zilli sample E2) to 1.0µg/g (Mormyrus rume samples D and F, Tilapia zilli samples B2, C2 and F2), of cadmium is between 0.6µg/g (Tilapia zilli samples B2 and E2) to 1.2µg/g (Mormyrus rume samples B and D), and selenium is between 0.6 µg/g (Mormyrus rume samples D and F) to 1.2µg/g (Tilapia zilli sample D2).

The concentrations of lead in the different species of samples of fish fillet ranged between 1.8 µg/g (Tilapia zilli samples A, C and A2, C2 of M. rume) to 2.4µg/g (Mormyrus rume sample F), nickel is 2.2µg/g (Mormyrus rume sample B) to 3.0µg/g (Tilapia zilli sample D2), mercury is 0.4µg/g (Mormyrus rume samples A and C) to 0.8µg/g (Mormyrus rume sample F, Tilapia zilli samples C2 and E2), cadmium is 0.6µg/g (Mormyrus rume samples A, D, and E, Tilapia zilli samples A2, B2 and D2) to 0.8 µg/g (Mormyrus rume samples B, C and F, Tilapia zilli samples C2, E2 and F2), of selenium is 0.6 µg/g (Mormyrus rume samples B and C) to 1.2µg/g (Tilapia zilli sample E2).

Nickel has the highest accumulation than all the other metals in the liver, gills and fillet of the fish species, but higher in Tilapia zilli than in Mormyrus rume. Cadmium and mercury are high in the liver and gills of Tilapia zilli and selenium in Tilapia zilli. All the metals are more highly concentrated in Tilapia zilli than in Mormyrus rume. The order of heavy metal accumulation in the liver, gills and fillet of Tilapia zilli is Ni > Pb > Cd > Se > Hg, Hg, Cd and Se are almost the same in concentration; Ni > Pb > Se > Hg > Cd and Ni > Pb > Se > Cd > Hg, in most cases Hg and Cd were almost the same level of concentration. The order of heavy metal accumulation in the liver, gills and fillet of Mormyrus rume species are Ni > Pb > Cd > Se > Hg, Pb > Ni > Cd > Hg > Se and Ni > Pb > Se > Cd > Hg respectively. These results are supported by the reports of Ambedkar et al., (2012); Hogstrand and Haux, (1991) that the liver stores and transport most substances in the body. The order of heavy metal accumulation in the water of Opa reservoir is; Pb > Ni > Se and Cd have the same concentration > Hg.

Generally, the order of accumulation of metals in the fish tissues irrespective of weight and length is; liver>Gill> fillet both in the *M. rume* and *T. zilli*. This result is similar to other researchers work as evident in (Adeyeye et al., 2012, Abdel-Baki 2011; Akan et al., 2009; Dimari et al., 2008; Farombi et al., 2007 and Zyadah, 1999) in which metals in the liver and gills were higher relative to other organs. Since liver and gills are good target organs of bioaccumulation of heavy metals, they are seen as vital organs for monitoring water pollution, because of the high correlation between metal in the liver and that of the water environment. The levels of heavy metals in the gills reflect the concentrations of metals in the waters, where the fish live, while the concentrations of metals in liver represent storage of metals in the fish body (Yilmaz, 2009; Roméo et al., 1999). It is well known that fish muscles is not an active tissue, that is why the concentration of metals in it is usually low as seen in the above trend and supported by the work of (Adeyeye et al., 2012, Yilmaz, 2009; Canli and Kalay, 1998).

The liver of *T. Zilli* accumulated more Pb than the liver of *M. rume* and this Pb concentration is higher in the gills and fillet of the two species. Samples A, C, D, E, E2 and F store more Ni at significantly higher level in the fillet than the gill. This indicates that *M. rume* fillet has strong affinity for Ni. Studies have shown that liver accumulate more metals than other organs in fish because of the high coordination of metallothionein protein in it with metals, it also detoxify, transport and stores most substances in the body. It is an active site of pathological activities for contamination of tissues, since it send/transport all the toxic substances to other parts of the body (Ambedkar et al., 2012; Hogstrand and Haux, 1991).

It is evident from these results that the concentration of these metals in the fish tissues were higher than the concentration in the dam, bioaccumulation over times might have been responsible and in accordance with the fact that aquatic animals usually show a higher level of accumulation of heavy metals than their habitat, Opa dam is one of the main source of these metals. *Tilapia zilli* are omnivorous with juveniles being more carnivorous, consuming a number of different zoobenthos, because they are bottom dwellers. Adults are especially herbivorous, consuming mainly aquatic plants, algae, photoplankton. Studies on the feeding habits of *T. zillii* within Lake Kinneret (Israel), showed that the main source of food was Chironomida pupae (Diptera) in the spring and winter and zooplankton in the summer and autumn with algae supplementing the diet throughout the year (Spataru, 1978). Thus, the feeding habit of *Tilapia zilli* might have made the metal accumulation to be more than *M. rume* because they live on all kinds of food.

Nickel tends to accumulate more in fillet (the commonly eaten part) life, hence shows the highest concentration in all species. The transfer factor/bioaccumulated ratio of Ni from water to the fillet ranged from 34.67 in C2 to 46.67 in F, A2 and F2 while that of Pb is between 25.7 in A,C, A2 and C2 to 34.28 in F. The remaining metals ranged from 30- 80. The concentrations of Nickel, Lead and Cadmium are above the maximum permissible concentration which poses risk upon continuous consumption. Anthropogenic activities such as farming and in flow of run-off that scavenges all manner of environmental contaminants and settles as sediments in water bodies led to the high concentrations of these metals in the dam and fish tissues. These contaminants settled and act as a repository for heavy metals. The time of sampling (dry season) could contribute to increase in the concentration of the metals in the water and the fishes as a result of reduction in the volume of

water. Nickel has high concentrations both in the water and the fish species; this could lead to heart failure and liver damage. The level of lead may pose serious damage to the nervous system, decreased sperm production and renal dysfunction over time by continuous consumption of the fish and use of the untreated water.

Conclusion

This study has revealed that the different twelve samples of the fish species (*Mormyrus rume* and *Tilapia zilli*) from the Opa dam were contaminated mainly with Ni and Pb now at the verge of pollution, the water is contaminated with Pb, Ni and Hg. The extent of contamination had actually reached pollution levels because they are above standard organization permissible level at the time of sampling.

Fish consumers may be exposed to relatively higher levels of Ni by eating heavy metals contaminated fish from the dam. The water and the fish might have been contaminated due to agricultural technology, run off, solid metal waste such as tins, sewage drainage, reduction in the water level at the time of sampling and other unknown sources, which could affect human health and cause chronic diseases. Therefore, since heavy metal pollution is less visible but its effects on man and ecosystem are extensive and intensive (Edem et al., 2009), regular monitoring of the dam should be put in place for the safety of the human and aquatic ecosystem.

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