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Distribution of heavy metals in fish organs, associated water and sediment from Ero Dam, Ekiti State, Nigeria

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ABSTRACT

An investigation into the distribution of lead, manganese, copper, zinc, mercury, iron, chromium and cadmium in the sediment, water and the organs of Oreochromis *niloticus, Tilapia zillii,* African catfish *(Clarias gariepinus)* and *Citharinus citerus* obtained from Ero Dam in Ikun-Ekiti, Ekiti State, Nigeria was undertaken. This was done to ascertain the presence of these metals in the three matrixes and to determine the bioaccumulation factors of these metals in the organs of these fishes. The three matrixes were differently digested and analysed for heavy metals using Atomic Absorption Spectrophotometer (Buck 200). Hg was determined via cold vapour generation. The levels of the metals in water were very much lower than their corresponding concentrations in the sediment. In the same vein, concentrations of the metals in the fish organs were higher than those recorded for the water except Cu and Mn that showed slight variations. The most concentrated metal in the organs of the four fish species was Zn which recorded concentrations (mg/kg) ranging from 7.36±0.03 in the head of *Clarias gariepinus* to 8.12±0.13 in that of *Citharinus citerus*. In *Clarias gariepinus,* Cr, Cd and Hg were only detected in its gills. On the contrary, all the metals were detected in the organs of *Oreochromis niloticus* and *Tilapia zillii.* Zn, Mn and Fe were the three most abundant metals in the organs of these fishes. The highly toxic metals (Pb, Cd and Hg) in this determination were either not detected or detected at low levels. It is obvious from this work that Zn was bioaccumulated most in the organs of each fish. It is certain that heavy metals are present in Ero dam but in low concentrations. This calls for constant monitoring because as industries are established in Ekiti State, Nigeria, the level of heavy metals in this dam may increase.

Keywords: *Oreochromis niloticus, Tilapia zillii, Citharinus citerus.*

INTRODUCTION

Metals are introduced into our aquatic system as contaminants via several ways which include weathering of rocks, dissolution of aerosol particles from the atmosphere and from several human activities (Adefemi et al., 2004). Once these metals get into the aquatic environment, they may be precipitated, adsorbed on solid surface, remain soluble, suspended in water or may be taken

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up and accumulated in the body part of aquatic organisms (Ipinmoroti et al., 1997a). Bioaccumulation and magnification is capable of leading to toxic level of these metals in fish, even when the exposure is low (Ipinmoroti et al., 1997b; Ekeanyawu et al., 2010).

Ero Dam, which was established in 1983, is located in Ikun-Ekiti (latitude7^0 59′N and longitude $5^0$12′E), Moba Local Government Area of Ekiti State, Nigeria. It covers a distance of about 11 km. The dam supplies over one hundred towns and villages in the state with pipe born water. Ekiti State, one of the youngest states in Nigeria, was carved out of the old Ondo State in 1996, and therefore has very low industrial activities. In fact, more than seventy percent of the inhabitants of this state are farmers (majority of which are on subsistent scale). The possible sources of heavy metals to Ero dam include: run off water, exhaust fumes from vehicles and different agricultural chemicals used by farmers.

Fishes are notorious for their ability to concentrate metals in their muscles (Okoye, 1991). Fish is valuable in the diet because apart from supplying good quality protein and vitamins A and D, it also contains several metals such as Ca, Fe, etc which are beneficial to man (Adeyeye, 1997). However, toxic metals such as Pb, Cd, etc may also be present especially if the environment of the fish is polluted. Considering the ability of fishes in concentrating metals in their bodies, their importance in human nutrition and the rate at which they are consumed, fishes need to be carefully screened. This will ensure that unnecessarily high levels of toxic metals are not being transferred to man through fishes.

Little attention has been paid to the comparative study of metal concentrations in the three matrixes of sediment, water and fish of any water reservoir. Reported works include those of: Adefemi et al., 2004; Gupta et al., 2009; Ekeanyanwu et al., 2010; Olowu et al., 2010; Ali et al., 2010. This work focuses on the determination of Zn, Mn, Cr, Cd, Hg, Fe, Pb and Cu in these three matrixes.

MATERIALS AND METHODS

Collection and treatment of samples

Water and sediment samples were collected and treated as described in literature (Adeyeye, 1997). Five of each of *Oreochromis niloticus*, *Tilapia zillii*, African Catfish (*Clarias gariepinus*) and *Citharinus citerus* (the four major fish species found in Ero dam) were caught from the dam with a net. Each fish was briefly washed with distilled water to remove any adhering substances. Each fish sample was drained under the fold of filter paper, wrapped in aluminum foil and deep frozen prior to analysis.

Analysis of samples

Five milliliter (5 ml) of concentrated HNO_3 (63%) was added to 250 ml of water sample and evaporated to 25 ml. The concentrate was transferred to a 50 ml standard flask and diluted to the mark with distilled water. The resultant solution was analysed for heavy metals using Atomic Absorption Spectrophotometer (Buck 200). The methods of AOAC (1990) were used for the treatment and digestion of the fish samples while the sediment was treated and digested using the methods of Adeyeye et al. (1996). Analysis of resultant solutions was done using Atomic Absorption Spectrophotometer (Buck 200).

Statistical analysis

Statistical analysis of data was performed using SPSS statistical package program. Duncan Multiple Range Test was carried out; means in the same column which are not significantly different ($p>0.05$) are indicated with the same superscript.

RESULTS

The result of heavy metals determined in the sediment and surface water is shown in Figure 1. The figure reveals the concentrations of the metals in water in the order Mn>Zn>Fe>Cu. Pb, Cr, Hg and Cd were not detected in the water. The values recorded for the metals, except for Mn, are all within the WHO standards for drinking water (Table 1). This, coupled with non detection of the highly toxic metals (Pb, Cd and Hg), shows that the water of this dam is safe for drinking. The levels of metals in the sediment also followed the same order Mn>Zn>Fe>Cu.

Table 2 indicates that Zn, Mn and Fe were the three most abundant metals in the organs of *Clarias gariepinus. Z*n values (mg/kg) ranged from 4.46±0.06 (eyes) – 7.36±0.03 (head), Mn had values ranging from 3.17±0.03 (head) - 4.84±0.06 (internal organs) and iron values ranged from 1.16±0.07 (body tissue) to 1.35±0.04 (gills). These three metals and Cu were the only metals detected in all the organs of this fish. The general order of distribution of heavy metals in the organs of *Clarias gariepinus* is Zn>Mn>Fe>Cu>Pb. Cr, Cd and Hg, which were only detected in the gills, all had the same concentration of 0.01 mg/kg.

Table 3 also reveals Zn, Mn and Fe to be the three most concentrated metals in the organs of *Oreochromis niloticus.* The head of *Oreochromis niloticus* recorded the highest concentrations of Zn (7.48±0.12 mg/kg) and Fe (3.25±0.01 mg/kg). This shows that the head of this fish (*Oreochromis niloticus*) is a good source of these beneficial elements. Zn, Mn and Fe were also observed to be the most abundant heavy metals in the organs of *Tilapia zillii* (Table 4). The highest concentrations of Zn (7.63±0.16mg/kg) and Fe (3.36±0.10) were found in the head. For Mn its highest concentration was detected in the gills. The levels of the highly toxic metals (Pb, Cd and Hg) in *Tilapia zillii* were very low.

Table 5 presents the results of heavy metals determined in the organs of *Citharinus citerus*. All the metals determined were detected in the organs of this fish except lead and chromium which were not detected in the internal organs and the head, respectively. The head of this fish had the highest levels of Zn and Fe as observed for *Tilapia zillii.* and *Oreochromis niloticus.* The order of bioaccumulation factors (Figures 2, 3, 4 and 5) for the various species of fish in this determination are as follows: *Clarias gariepinus* (Figure 2):- Zn>Cu>Fe>Mn, *Oreochromis niloticus*(Figure 3):- Zn> Fe>Mn>Cu, *Tilapia zillii* (Figure 4):- Zn>Fe>Cu>Mn and *Citharinus citerus* (Figure 5):- Zn>Fe>Mn>Cu.

Table 1: WHO standards for drinking water.

Metal	**Mn**	**Pb**	**Cr**	**Cu**	**Cd**	**Hg**	**Fe**	**Zn**
WHO[a]	0.1	0.01	0.05	2.00	0.003	0.001	0.30	3.0

[a] (WHO, 1993)

Table 2: Concentration of heavy metals in the organs of African catfish (*Clarias gariepinus)* in mg/kg dry weight.

	Head	Eyes	Gills	Body Tissue	Internal Organs
Mn	3.17^{d}±0.03	3.78^{c}±0.12	4.45^{d}±0.005	3.96^{d}±0.05	4.84^{d}±0.06
Pb	ND	0.001^{a}±0.00	0.01^{a}±0.01	0.01^{a} ±0.01	ND
Cr	ND	ND	0.01^{a}±0.00	ND	ND
Cu	0.41^{b}±0.01	0.23^{a}±0.03	0.54^{b}±0.05	0.34^{b}±0.06	0.38^{b} ±0.03
Cd	ND	ND	0.01^{a}±0.00	ND	ND
Hg	ND	ND	0.01^{a} ±0.00	ND	ND
Fe	1.26^{c}±0.02	1.23^{b}±0.33	1.35^{c}±0.04	1.16^{c}±0.07	1.18^{c}±0.01
Zn	7.36^{e}±0.03	4.46^{d}±0.06	6.89^{e}±0.10	5.72^{e}±0.64	6.72^{e}±0.12

Mean± standard deviation for triplicate determinations; means with the same superscript in the same column do not differ ($p > 0.05$).

Table 3: Concentration of heavy metals in the organs of *Oreochromis niloticus* in mg/kg dry weight.

	Head	Eyes	Gills	Body Tissue	Internal Organs
Mn	2.75^{b}±0.06	1.25^{c} ±0.06	5.02^{d}±0.10	1.50^{c}±0.08	1.46^{b} ± 0.12
Pb	0.005^{a}±0.00	0.008^{a}±0.001	0.001^{a}±0.00	0.013^{a} ±0.002	0.003^{a}±0.00
Cr	0.004^{a}±0.001	0.001^{a}±0.00	0.007^{a}±0.001	0.001^{a}±0.00	0.004^{a}±0.00
Cu	0.05^{a}±0.001	0.001^{a}±0.00	0.007^{a}±0.01	0.008^{a}±0.01	0.012^{a}±0.00
Cd	0.002^{a}±0.00	0.003^{a}±0.00	0.007^{a}±0.00	0.009^{a}±0.00	0.006^{a}±0.00
Hg	0.006^{a}±0.00	0.003^{a}±0.00	0.12^{a}±0.02	0.007^{a}±0.00	0.01^{a}±0.00
Fe	3.25^{c}±0.01	1.035^{b}±0.032	1.05^{b}±0.062	1.1^{b}±0.01	2.51^{c}±0.09
Zn	7.48^{d}±0.12	4.06^{d}±0.08	4.63^{c}±0.33	3.42^{d}±0.00	6.10^{d}±0.10

Mean ± standard deviation for triplicate determinations; means with the same superscript in the same column do not differ ($p>0.05$).

Table 4: Concentration of heavy metals in the organs of *Tilapia zillii* in mg/kg dry weight.

	Head	Eyes	Gills	Body Tissue	Internal Organs
Mn	2.82^{b}±0.03	1.37^{b}±0.09	5.34^{d}±0.01	1.64^{c}±0.01	1.38^{b}±0.05
Pb	0.007^{a}±0.03	0.011^{a}±0.01	0.013^{a} ±0.02	0.016^{a}±0.00	0.005^{a} ±0.00
Cr	0.025^{a}±0.00	0.002^{a}±0.00	0.01^{a} ±0.006	0.013^{a}±0.00	0.004^{a} ±0.002
Cu	0.07^{a}±0.001	0.003^{a} ±0.00	0.11^{a} ±0.02	0.01^{a}±0.001	0.015^{a} ±0.01
Cd	0.003^{a}±0.00	0.005^{a} ±0.001	0.01^{a} ±0.00	0.011^{a}±0.003	0.01^{a} ±0.00
Hg	0.008^{a}±0.00	0.005^{a} ±0.01	0.015^{a} ±0.02	0.009^{a}±0.00	0.013^{a}±0.002
Fe	3.36^{c}±0.10	1.29^{b}±0.08	1.12^{b} ±0.04	1.32^{b}±0.06	2.65^{c}±0.15
Zn	7.63^{d}±0.16	4.13^{c}±0.11	4.81^{c}±0.043	3.96^{c}±0.06	6.24^{d}±0.06

Mean ± standard deviation for triplicate determinations; means with the same superscript in the same column do not differ ($p>0.05$).

Table 5: Concentration of heavy metals in the organs of *Citharinus citerus* in mg/kg dry weight.

	Head	Eyes	Gills	Body Tissue	Internal Organs
Mn	3.16^{b} ±0.003	1.43^{b}±0.012	4.91^{c}±0.16	1.74^{c}±0.009	1.53^{b}±0.18
Pb	0.005^{a}±0.00	0.01^{a}±0.005	0.11^{a}±0.03	0.02^{a}±0.00	ND
Cr	ND	0.004^{a}±0.00	0.007^{a}±0.002	0.011^{a}±0.00	0.006^{a}±0.00
Cu	0.09^{a} ±0.00	0.006^{a}±0.00	0.015^{a}±0.00	0.016^{a}±0.003	0.02^{a}±0.01
Cd	0.005^{a}±0.001	0.008^{a}±0.002	0.006^{a}±0.001	0.008^{a}±0.001	0.11^{a}±0.03
Hg	0.087^{a}±0.001	0.004^{a}±0.00	0.015^{a} ±0.002	0.013^{a} ±0.003	0.17a±0.03
Fe	4.43^{c}±0.19	1.35^{b}±0.14	1.38^{b}±0.11	0.38^{b}±0.01	2.89^{c}±0.04
Zn	8.12^{d}±0.13	4.62^{c} ±0.15	5.32^{d}±0.09	4.12^{d}±0.03	6.33^{d}±0.26

Mean ± standard deviation for triplicate determinations; means with the same superscript in the same column do not differ ($p>0.05$).

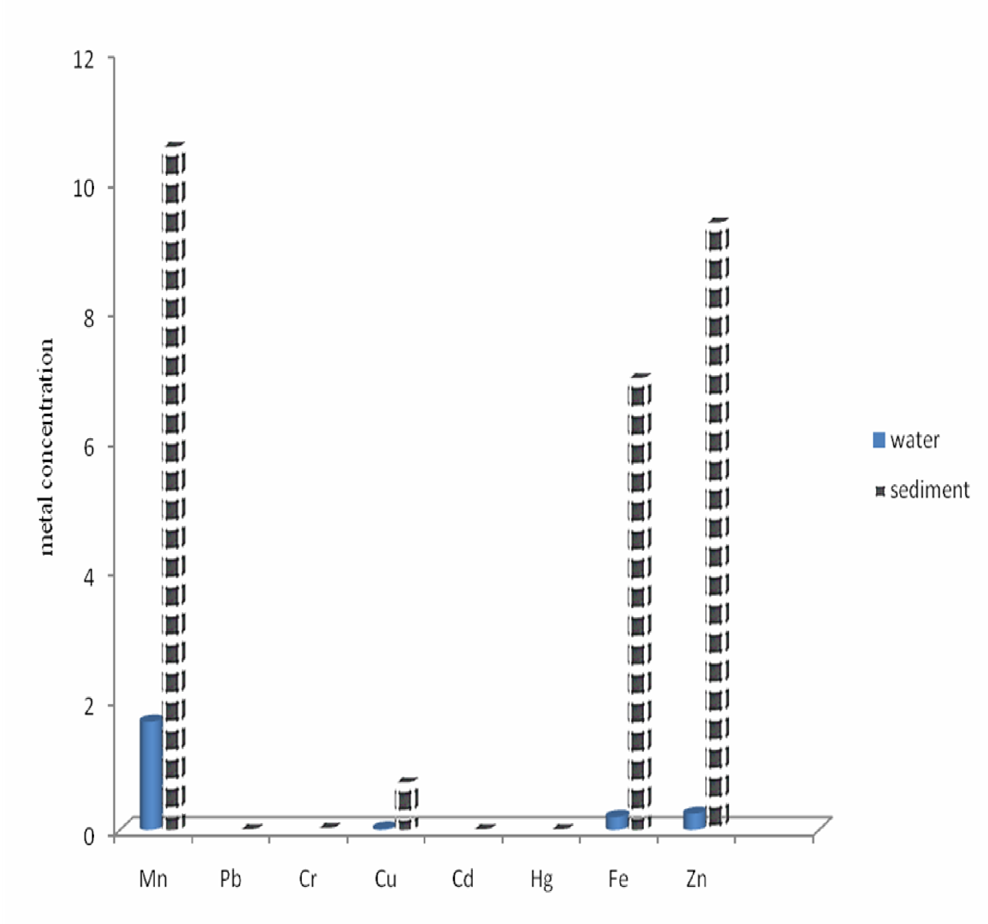

Figure 1: Concentration of heavy metals in water (mg/L) and sediment (mg/kg).

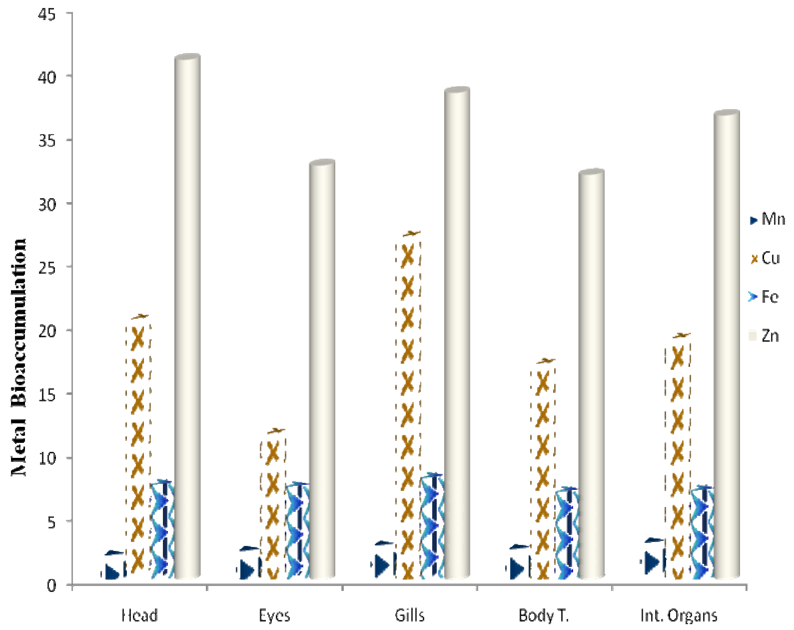

Figure 2: Bioaccumulation factors of heavy metals in the organs of *Clarias gariepinus.*

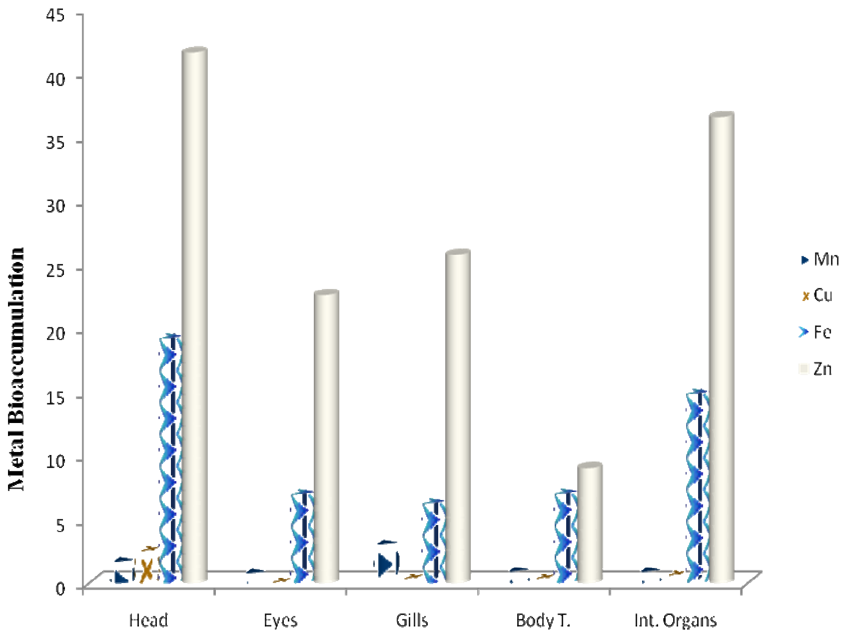

Figure 3: Bioaccumulation factors of heavy metals in the organs of *Oreochromis niloticus.*

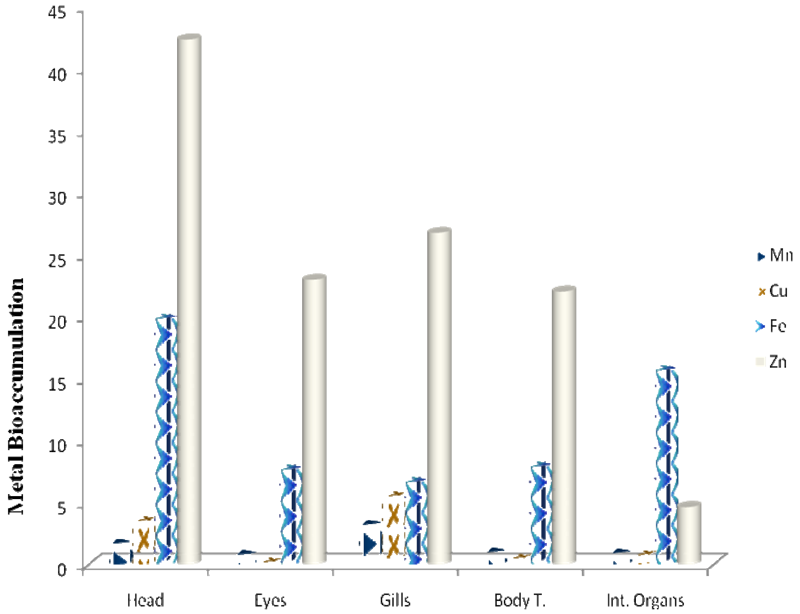

Figure 4: Bioaccumulation factors of heavy metals in the organs of *Tilapia zillii.*

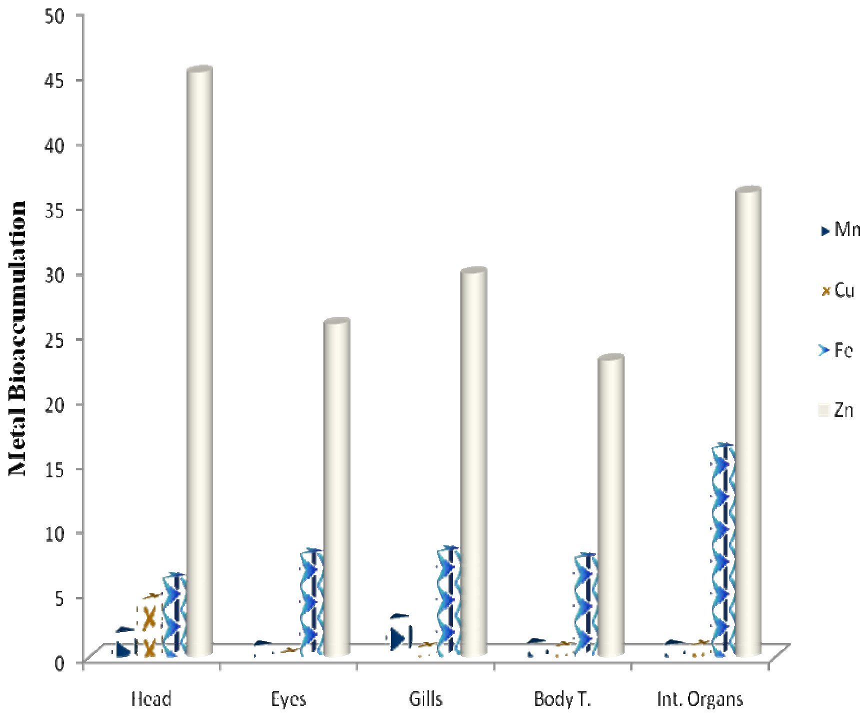

Figure 5: Bioaccumulation factors of heavy metals in the organs of *Citharinus citerus.*

DISCUSSION

The result of heavy metals determined in the sediment and surface water (Figure 1) shows clearly that the concentrations of metals in the water were lower than those obtained for the sediment. This is in complete agreement with earlier literature reports (Adefemi et al., 2004; Ali et al., 2010; Ekeanyawu et al., 2010). Metals like Cr, Hg, Pb and Cd which were not detectable in the water were detected at very low level in the sediment (Figure 1). These observations could be attributed to the fact that sediments form the major repository of heavy metals in aquatic system (Adeniyi and Yusuf, 2007). The higher concentration of heavy metals in the sediment may be linked to the activities of farmers (which may include the use of pesticides, and herbicides) who have farms close to the dam. Manganese, zinc and iron, the three most abundant heavy metals in the water of Ero dam are comparatively non-toxic. For example, Fe is not toxic in water but can produce some annoying effects such as stains on clothing and giving water an undesirable colour and taste. These three metals have been reported to be the most abundant heavy metals in soil and water of Ekiti (Adefemi et al., 2004; Adeyeye, 2005).

The highly toxic metals in this study (Pb, Cd and Hg) were not detected in the organs (head and body tissue) of *Clarias gariepinus* that are usually consumed by man. It is worthy of note to observe that while all other organs of this fish had 3 or 4 heavy metals not present, the gills had all the metals present. Furthermore, the gills seemed to contain higher concentrations of metals than other organs except the internal organs and the head that had higher concentrations of Mn and Zn, respectively (Table 2). The fact that metal uptake in fish occurs through absorption across the gills surface or through the digestive tract during food intake (Adefemi et al., 2004) could have accounted for this observation. This observation could make one suggest that the gills of C*larias gariepinus* could be used to monitor the level of pollution of this dam.

The highly toxic metals (Pb, Cd and Hg) which were not detected in most of the organs of *Clarias gariepinus* were all detected in *Oreochromis niloticus* (Table 3). Of these, Hg recorded the highest value and this was detected in the gills. Pb and Cd recorded their respective highest concentrations in the body tissue. Each of these highly toxic metals had an approximate concentration of 0.01 mg/kg in the body tissue. The body tissue of this fish seemed to concentrate Pb and Cd more than other organs. This calls for attention because this is the part of the fish mostly consumed by man. It is obvious from this determination that Zn was the most bioaccumulated metal in the organs of the four fish species (Figure 2 – 5). The head of each fish specie bioaccumulated Zn more than any other organ. This shows that the heads of fish in Ero dam are a good source of this beneficial element. Bioaccumulation factors could not be determined for Cr, Cd, Hg and Pb because they were not detected in water.

Generally, for the detected metals in the three matrices of water, sediment and fish organs, Zn, Mn and Fe were found to be the most abundant. The high concentrations of manganese iron and zinc in the fish organs could be associated with the fact that these metals are naturally abundant in Nigeria soils (Olowu et al., 2010). Since these metals are beneficial to man, the four fish species will complement the supply of Zn, Fe and Mn in food. Zn is involved in nucleic acid synthesis, iron in the synthesis of haemoglobin and manganese functions as an essential constituent of bone structure, for reproduction and normal functioning of the nervous system (Adeyeye, 1997). The concentrations of heavy metals recorded for the water of Ero dam are within the WHO standards for drinking water. This shows that the dam is not polluted with heavy metals.

It is hoped that as Ekiti State industrialises, the level of heavy metals in this dam may increase. This, therefore, calls for continuous monitoring of this dam and others that supply water for public consumption in the state. The gills of any of the fish species could be used for this monitoring, since all the metals determined were detected in the gills of all the fish species.

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