

## Estimation of Some Heavy Metals and Mineral Elements in Tissues of *Oreochromis niloticus* Collected from Goronyo Dam and its Two Tributaries in North-Western Sub-Sahara Nigeria

\*Muhammad, H.L.,<sup>1</sup> Shehu, R.A.,<sup>2</sup> Bilbis, L.S.,<sup>2</sup> Dangoggo S.M.<sup>3</sup>

<sup>1</sup>Department of Biochemistry, Federal University of Technology, Minna, Nigeria

<sup>2</sup>Department of Biochemistry, Usmanu Danfodiyo University, Sokoto, Nigeria

<sup>3</sup>Department of Applied Chemistry, Usmanu Danfodiyo University Sokoto, Nigeria

---

**Abstract:** The Nile Tilapia *Oreochromis niloticus* (a fish species) was collected from Goronyo Dam, its two tributaries and Rima River (an overflow of Goronyo Dam) in two seasons for comparative studies of metal contents in gills, muscles and bones. The samples were dissected, organs were collected and digested by FAO/SIDA methods of 1983. Atomic Absorption Spectrophotometer (AAS) was used for the estimation of metals and mineral elements in the samples as described in the Pye Unicam Atomic Absorption data book (1984). Only fishes collected in season II (August-September) of Goronyo Dam had lead (Pb) values in gills, muscles and bones higher than the World Health Organization standard of 2.0 µg/g in sea foods. *Oreochromis niloticus* species of season II consumed from Goronyo Dam can be a rich source of Pb to humans.

**Keywords:** *Oreochromis niloticus*, Heavy metals, Lead, Cadmium, Goronyo Dam

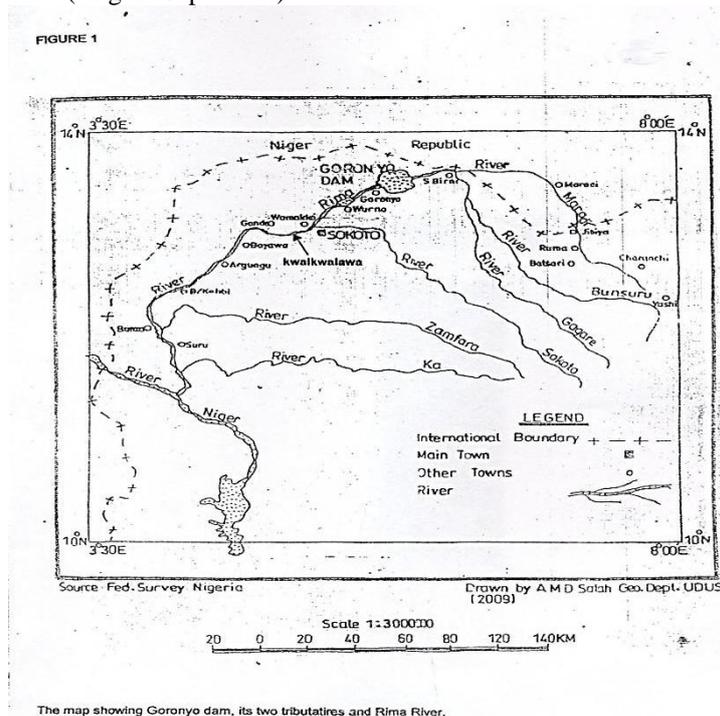
---

### I. Introduction

Human beings have been exposed to heavy metal toxins for an immeasurable amount of time. The domestic and industrial activities of human result in the production of materials, which are disposed of into the environment. These materials contain heavy metal toxins which accumulate faster in the body than can be eliminated (Goyer, 1991). All these contribute to human physiological and psychological decline (Kiffney and Clement, 1994). The heightened concern for reduction of environmental pollution that has been occurring over the past 20 – 25 years has stimulated active continuing research on the toxicology of heavy metals. While the toxic effects of these substances are a widespread concern in the modern industrial context, the human society has succeeded in poisoning itself with them repeatedly throughout recorded history. All ecosystems are affected by ubiquitous atmospheric deposition of organic and inorganic pollutants such as heavy metals (Reddy *et al.*, 1995). Today heavy metals are (abundant) in the drinking water, air and soil due to human's increased use of products containing these compounds. They are present in virtually every area of modern consumerism – from construction materials to cosmetics, medicines to processed foods, fuel sources to agents of destructive appliances and personal care products (Largewerff, 1972). Human population growth and technological advancement have contributed to increased complexity in types and amount of waste materials, which enter the ecosystems as products or by-products of industrial processes (Stewart *et al.*, 1974). It is very difficult for anyone to avoid exposure to any of the many harmful heavy metals that are so prevalent in the environment. *Oreochromis niloticus*, one of the major fish species consumed by people living around the study areas, some of it is also exported to the neighbouring Niger Republic. Heavy metals originate within the earth where they may be harmless until released by human interference. As the concentrations of heavy metals rise in the air, water and topsoil, they also rise within human bodies contributing to chronic diseases, learning disorders, cancer and premature aging (Keen *et al.*, 1981). Once in the body, they compete with and displace the essential minerals such as zinc, copper, manganese and calcium and bind their receptor sites causing diffuse symptoms by affecting nerves, hormones, digestion and immune functions. In general, heavy metals produce their toxicities by forming complexes or ligands with other organic compounds. These modified biological molecules lose their ability to function properly, and result in malfunction or death of the affected cells (Mouvet, 1984). The most important common elements involved in ligand formation are oxygen, sulphur and nitrogen. When metals bind to these groups they inactivate important enzyme systems, or affect protein structure. The degree to which a system, organ, tissue or cell is affected by a heavy metal toxin depends on the toxin itself and the individual's degree of exposure. Overtime, there have been continuous activities involving illegal mining of gold, and the dyeing of clothing materials by the community of the study area. The gold mining activity generates lead as a by-product because lead is found in combination with gold as ore. The dyeing of materials on the other hand makes use of chemical agents that are toxic to aquatic organisms at certain concentrations. The two activities produce effluents which get into the aquatic environment either by direct disposition or by run-off during rain fall.

## The Study Area

The Goronyo Dam is located near Keta village, some twenty five kilometres east of Goronyo town and ninety kilometres away from Sokoto town, in north-western region of Nigeria. The construction of the earth fill dam was completed across the Rima River in 1984, and has Gagare, Bunsuru and Maradi rivers as the main tributaries. The river Gagare comes from Kaura Namoda through Moriki to Birnin Yero in Katsina State. River Bunsuru on the other hand comes from Zurmi in Zamfara State through Bafarawa. Both rivers (Gagare and Bunsuru) have their confluence at Attalawa. Active fishing activities are going on in the two tributaries. The dam is made up of three embankments (main dam, secondary dam and saddle dam) with a reservoir area of 200 km<sup>2</sup> and capacity of 942 million cubic meters at 288 meters above sea level (M.A.S.L) full storage. The dam supplies raw water for Sokoto State Water Board, stream bank (Fadama) irrigation through lifting, Wurno and Falalia irrigation schemes and fishing activities. Some of the crops grown by these schemes are rice, cassava, vegetables and garlic. River Rima is an overflow of Goronyo Dam, active fishing activities are taking place in all the rivers, and the river waters are also for irrigation. The study area (comprising Sokoto, Zamfara, and Katsina states), is a semi-arid region with moderate rain fall, and all the weathers at the extreme. It was speculated that the mining activities might generate lead which may probably be held in drainages (if at all there are any), or the by-products may just be in the air and the immediate environment, and will likely be washed away into the aquatic environment during rain fall. Dry season is termed season I (January-February) while rainy season is termed season II (August-September).



It was in Zamfara state, Anka local government area that lead poisoning of children numbering over 600 took place between the year 2010 and 2011 WHO (2011). Lead was taken into various homes by illegal gold miners where their wives do the final processing of the ore to obtain the pure gold for onward transportation to the market to be sold to gold dealers. Lead poisoning took place because the villagers used same containers for processing the ore and for other domestic activities. Children were especially more vulnerable because the blood-brain barrier is still at the process of formation.

## II. Materials And Methods

### Chemicals and Reagents

All chemicals and reagents used for this work are of analytical grade. They include: concentrated HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, 0.01M CaCl<sub>2</sub>, MnSO<sub>4</sub>·4H<sub>2</sub>O, flouroboric acid, starch solution, 0.025M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O (sodium thiosulphate), 25 % (v/v) acetic anhydride, glacial acetic acid, absorption grade lanthanum oxide, dry NaCl, dry KCl, pH buffer, dry calcium carbonate, concentrated HCl, HClO<sub>4</sub>, lead metal, nickel metal, calcium metal, iron filings, chromium metal, copper metal, magnesium ribbon, NaN<sub>3</sub>, KI, and 40 % (v/v) hydrofluoric acid

### Sample Collection

Fresh specimens of *Oreochromis niloticus* weighing between 400 g- 700 g were collected in the years 2005 and 2006 as part of Ph.D research work from the local fishermen either at the time of fishing operations or as the fishermen landed on the shores. Five specimens were collected for each analysis. The fishes were kept in ice packed container for transportation to the laboratory where they were kept in the refrigerator till ready for digestion. Five tissues of gills, muscles and bones collected from each of the five specimens were digested for analysis.

### Sample Digestion

2.0 g (wet weight), each of gills, muscles, or bones were separately placed in respectively labelled reflux flasks. 20 ml of freshly prepared (1:1) HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> was added to each reflux flask in the block digester for two hours till volumes reduced to about 10 ml. The digest was allowed to cool and filtered through Whatmann no 1 filter paper, and the volume made up to 100 ml. The digest was further transferred to polythene bottle and stored till ready for use (FAO/SIDA, 1993). These tissues were chosen for analyses because they are the parts mostly consumed by the people living in the study areas, and man is the ultimately end receptor of the heavy metal being at the top of the trophic level in food chain.

### Estimation of Metals

Atomic Absorption Spectrophotometer (Philips model PU 9100) was used for the estimation of Pb, Cd, Cr, Ni, Fe, Mg, Ca, Cu, Na and K as described in the Pye Unicam Atomic Absorption data book (1984), and in the introduction to Atomic Absorption Spectrophotometry Scientific Analytical Equipment manual book by Whiteside (1987).

## III. Results

The results of metal analyses in tissues of *Oreochromis niloticus* collected from the study sites are presented in Tables 1- 4. With the exception of Goronyo Dam with season 11 lead (Pb) values in high concentrations above the World Health Organization (WHO) acceptable limit in sea foods, all other sites had values below the WHO limits. All the values reported are means of triplicate analyses of five specimens of gills, muscles, and bones from five samples of *Oreochromis niloticus*, results expressed as means with standard deviations. The data were statistically analysed using ANOVA with multiple comparisons. P<0.05 were considered significant (Duncan *et al.*, 1997).

TABLE 1  
Metal concentrations (µg/g) in *Oreochromis niloticus* Tissues of River Bunsuru

Season	Tissue	Pb	Cd	Ni	Fe	Mg	Cr	Cu	Ca	Na	K
Season I	Gills	0.33 <sup>a±</sup> 0.05	0.38 <sup>a±</sup> 0.12	0.34 <sup>a±</sup> .05	33.02 <sup>a±</sup> 2.80	35.65 <sup>a±</sup> 6.23	0.28 <sup>a±</sup> 0.07	1.13 <sup>a±</sup> 0.01	134.11 <sup>a±</sup> 6.88	3.45 <sup>a±</sup> 0.60	3.48 <sup>a±</sup> 0.33
	Muscles	0.31 <sup>a±</sup> 0.03	0.37 <sup>a±</sup> 0.11	0.34 <sup>a±</sup> .05	32.46 <sup>b±</sup> 3.28	34.36 <sup>b±</sup> 6.22	0.29 <sup>a±</sup> 0.07	2.12 <sup>b±</sup> 0.01	132.16 <sup>b±</sup> 8.47	3.63 <sup>a±</sup> 0.54	3.59 <sup>a±</sup> 0.34
	Bones	0.32 <sup>a±</sup> 0.04	0.37 <sup>a±</sup> 0.11	0.33 <sup>a±</sup> .05	32.03 <sup>c±</sup> 2.54	35.14 <sup>a±</sup> 6.32	0.30 <sup>a±</sup> 0.06	1.14 <sup>a±</sup> 0.01	138.86 <sup>c±</sup> 5.42	3.36 <sup>a±</sup> 0.52	3.76 <sup>a±</sup> 0.43
Season II	Gills	0.04 <sup>a±</sup> 0.02	0.03 <sup>a±</sup> 0.02	0.01 <sup>a±</sup> .005	30.27 <sup>a±</sup> 2.28	70.16 <sup>a±</sup> 5.82	0.13 <sup>a±</sup> 0.06	2.18 <sup>a±</sup> 0.11	144.87 <sup>a±</sup> 7.18	3.42 <sup>a±</sup> 0.36	2.92 <sup>a±</sup> 0.37
	Muscles	0.02 <sup>a±</sup> 0.01	0.03 <sup>a±</sup> 0.02	0.03 <sup>a±</sup> .02	40.90 <sup>b±</sup> 3.88	73.74 <sup>b±</sup> 4.27	0.13 <sup>a±</sup> 0.09	1.18 <sup>b±</sup> 0.12	132.45 <sup>b±</sup> 5.99	2.99 <sup>b±</sup> 0.54	2.45 <sup>a±</sup> 0.35
	Bones	0.02 <sup>a±</sup> 0.02	0.06 <sup>b±</sup> 0.02	0.05 <sup>b±</sup> .46	20.90 <sup>c±</sup> 3.70	53.86 <sup>c±</sup> 14.61	0.06 <sup>b±</sup> 0.04	1.23 <sup>b±</sup> 0.11	146.65 <sup>c±</sup> 13.70	3.06 <sup>c±</sup> 0.63	3.82 <sup>b±</sup> 0.33

Season I (January- February)

Season II (August – September)

**Metal concentrations are compared among tissues within each season**

**ANOVA was used for data generated**

a = means on the same column, with same superscripts are not significantly different (P>0.05)

b, c = means on the same column, with different superscripts differ significantly (P<0.05)

**TABLE 2**  
Metal concentrations (µg/g) in *Oreochromis niloticus* Tissues of River Gagare

Season	Tissue	Pb	Cd	Ni	Fe	Mg	Cr	Cu	Ca	Na	K
Season I	Gills	0.23 <sup>a±0</sup> .04	0.15 <sup>a±0</sup> .02	0.18 <sup>a±0</sup> .02	47.56 <sup>a±3</sup> 73	26.96 <sup>a±5</sup> .75	0.27 <sup>a±0</sup> .09	1.60 <sup>a±0</sup> .10	254.93 <sup>a±1</sup> 2.18	4.35 <sup>a±0</sup> .52	2.99 <sup>a±0</sup> .71
	Muscles	0.24 <sup>a±0</sup> .06	0.14 <sup>a±0</sup> .02	0.18 <sup>a±0</sup> .02	43.75 <sup>b±6</sup> 33	26.52 <sup>a±3</sup> .28	0.30 <sup>a±0</sup> .10	2.40 <sup>b±0</sup> .11	234.81 <sup>b±1</sup> 2.34	2.97 <sup>b±0</sup> .42	3.27 <sup>b±0</sup> .68
	Bones	0.28 <sup>b±0</sup> .06	0.94 <sup>b±0</sup> .35	0.17 <sup>a±0</sup> .02	55.38 <sup>c±1</sup> 1.28	24.11 <sup>b±</sup> 6.32	0.26 <sup>a±0</sup> .08	3.70 <sup>c±0</sup> .10	268.07 <sup>c±1</sup> 3.02	3.18 <sup>c±0</sup> .66	3.05 <sup>c±0</sup> .38
Season II	Gills	0.38 <sup>a±0</sup> .17	0.40 <sup>a±0</sup> .11	0.36 <sup>a±0</sup> .12	30.37 <sup>a±2</sup> 53	42.59 <sup>a±1</sup> .67	0.37 <sup>a±0</sup> .18	1.06 <sup>a±0</sup> .03	275.39 <sup>a±2</sup> 5.69	3.78 <sup>a±0</sup> .48	2.89 <sup>a±0</sup> .38
	Muscles	0.23 <sup>b±0</sup> .18	0.17 <sup>b±0</sup> .08	0.24 <sup>b±0</sup> .05	30.90 <sup>a±3</sup> 84	58.02 <sup>b±</sup> 6.74	0.33 <sup>b±0</sup> .15	1.10 <sup>a±0</sup> .03	254.09 <sup>b±2</sup> 0.36	3.96 <sup>a±0</sup> .78	3.28 <sup>b±0</sup> .40
	Bones	0.27 <sup>c±0</sup> .05	0.17 <sup>b±0</sup> .04	0.32 <sup>c±0</sup> .08	30.94 <sup>a±3</sup> 33	58.52 <sup>b±</sup> 8.81	0.32 <sup>b±0</sup> .11	1.09 <sup>a±0</sup> .03	203.01 <sup>c±2</sup> 6.84	3.65 <sup>a±0</sup> .27	3.51 <sup>c±0</sup> .65

Season I (January- February)

Season II (August – September)

Metal concentrations are compared among tissues within each season

ANOVA was used for data generated

a = means on the same column, with same superscripts are not significantly different (P>0.05)

b, c = means on the same column, with different superscripts differ significantly (P<0.05)

**TABLE 3**  
Metal concentrations (µg/g) in *Oreochromis niloticus* Tissues of River Rima

Season	Tissue	Pb	Cd	Ni	Fe	Mg	Cr	Cu	Ca	Na	K
Season I	Gills	0.12 <sup>a±</sup> 0.10	0.32 <sup>a±</sup> 0.18	0.10 <sup>a±</sup> 0.03	45.89 <sup>a±</sup> 8.35	23.55 <sup>a±</sup> 4.80	0.11 <sup>a±</sup> 0.02	3.20 <sup>a±</sup> 0.06	164.64 <sup>a±</sup> 20.63	5.33 <sup>a±</sup> 1.37	4.67 <sup>a±</sup> 0.78
	Muscles	0.08 <sup>b±</sup> 0.06	0.11 <sup>b±</sup> 0.06	0.10 <sup>a±</sup> 0.03	38.00 <sup>b±</sup> 7.86	20.73 <sup>b±</sup> 3.12	0.12 <sup>a±</sup> 0.02	3.20 <sup>a±</sup> 0.06	136.31 <sup>b±</sup> 16.33	4.51 <sup>b±</sup> 0.86	4.35 <sup>b±</sup> 1.07
	Bones	0.07 <sup>b±</sup> 0.03	0.08 <sup>c±</sup> 0.04	0.10 <sup>a±</sup> 0.04	29.57 <sup>c±</sup> 2.72	19.85 <sup>b±</sup> 2.70	0.11 <sup>a±</sup> 0.03	3.11 <sup>a±</sup> 0.03	205.33 <sup>c±</sup> 22.46	6.83 <sup>c±</sup> 1.33	5.47 <sup>b±</sup> 1.08
Season II	Gills	0.08 <sup>a±</sup> 0.05	0.11 <sup>a±</sup> 0.11	0.16 <sup>a±</sup> 0.03	30.47 <sup>a±</sup> 2.60	60.05 <sup>a±</sup> 9.07	0.24 <sup>a±</sup> 0.10	1.05 <sup>a±</sup> 0.03	208.28 <sup>a±</sup> 18.29	3.24 <sup>a±</sup> 0.15	4.03 <sup>a±</sup> 0.14
	Muscles	0.13 <sup>b±</sup> 0.03	0.10 <sup>a±</sup> 0.10	0.14 <sup>a±</sup> 0.01	30.13 <sup>a±</sup> 3.78	50.08 <sup>b±</sup> 7.13	0.29 <sup>a±</sup> 0.15	1.04 <sup>a±</sup> 0.02	113.28 <sup>b±</sup> 3.75	3.18 <sup>a±</sup> 0.24	3.14 <sup>b±</sup> 0.33
	Bones	0.11 <sup>a±</sup> 0.03	0.09 <sup>a±</sup> 0.09	0.22 <sup>b±</sup> 0.04	30.31 <sup>a±</sup> 3.69	59.39 <sup>c±</sup> 8.82	0.37 <sup>b±</sup> 0.13	1.04 <sup>a±</sup> 0.02	165.75 <sup>c±</sup> 16.89	3.15 <sup>a±</sup> 0.29	3.90 <sup>c±</sup> 0.39

Season I (January- February)

Season II (August – September)

Metal concentrations are compared among tissues within each season

ANOVA was used for data generated

a = means on the same column, with same superscripts are not significantly different (P>0.05)

b, c = means on the same column, with different superscripts differ significantly (P<0.05)

**TABLE 4**  
**Metal concentrations (µg/g) in *Oreochromis niloticus* Tissues of Goronyo Dam**

Season	Tissue	Pb	Cd	Ni	Fe	Mg	Cr	Cu	Ca	Na	K
Season I	Gills	0.07 <sup>a±</sup> 0.03	0.02 <sup>a±0</sup> .002	0.09 <sup>a±0</sup> 04	33.28 <sup>a±</sup> 2.45	20.03 <sup>a±</sup> 2.21	0.17 <sup>a±</sup> 0.02	2.08 <sup>a±</sup> 0.03	128.97 <sup>a±</sup> 3.54	21.56 <sup>a±</sup> 3.18	12.97 <sup>a±</sup> 0.71
	Muscles	0.06 <sup>a±</sup> 0.03	0.01 <sup>a±0</sup> .002	0.08 <sup>a±0</sup> 04	29.08 <sup>b±</sup> 1.97	17.44 <sup>b±</sup> 1.81	0.12 <sup>b±</sup> 0.02	2.07 <sup>a±</sup> 0.03	115.25 <sup>b±</sup> 3.17	18.04 <sup>b±</sup> 2.24	11.96 <sup>b±</sup> 0.47
	Bones	0.07 <sup>a±</sup> 0.03	0.02 <sup>a±0</sup> .003	0.09 <sup>a±0</sup> 05	21.60 <sup>c±</sup> 0.85	14.74 <sup>c±</sup> 1.63	0.16 <sup>a±</sup> 0.04	2.07 <sup>a±</sup> 0.02	154.66 <sup>c±</sup> 7.05	18.02 <sup>b±</sup> 2.33	12.03 <sup>c±</sup> 0.42
Season II	Gills	4.79 <sup>a±</sup> 0.57	0.45 <sup>a±0</sup> .10	0.003 <sup>a±</sup> 0.003	40.66 <sup>a±</sup> 2.55	90.87 <sup>a±</sup> 6.82	0.52 <sup>a±</sup> 0.15	1.20 <sup>a±</sup> 0.06	273.01 <sup>a±</sup> 12.67	4.75 <sup>a±0</sup> .36	4.38 <sup>a±0</sup> .77
	Muscles	5.12 <sup>b±</sup> 0.57	0.53 <sup>b±0</sup> .11	0.003 <sup>a±</sup> 0.003	50.89 <sup>b±</sup> 3.42	89.04 <sup>b±</sup> 4.38	0.56 <sup>a±</sup> 0.16	1.11 <sup>a±</sup> 0.07	287.27 <sup>b±</sup> 8.28	4.74 <sup>a±0</sup> .47	4.74 <sup>b±0</sup> .74
	Bones	4.42 <sup>c±</sup> 0.72	0.53 <sup>b±0</sup> .04	0.001 <sup>a±</sup> 0.001	50.26 <sup>c±</sup> 3.38	85.87 <sup>c±</sup> 6.92	0.62 <sup>b±</sup> 0.22	1.07 <sup>a±</sup> 0.03	259.24 <sup>c±</sup> 2.55	5.18 <sup>b±0</sup> .21	5.89 <sup>c±1</sup> .09

Season I (January- February)

Season II (August – September)

**Metal concentrations are compared among tissues within each season**

**ANOVA was used for data generated**

a = means on the same column, with same superscripts are not significantly different (P>0.05)

b, c = means on the same column, with different superscripts differ significantly (P<0.05)

#### IV. Discussion

The increasing concern with the roles and fates of heavy metals in Nigerian environment and their implication for human health has stimulated this work. There is little information on the concentrations of these metals in various locations where the samples were collected. There was also a remarkable case of lead poisoning of illegal gold miners and their families in Anka Local Government Area of Zamfara State, Nigeria (FMH, 2010). Elevated levels of some of the heavy metals in the aquatic environment can be a good indicator of human-induced pollution (Davies *et al.*, 1991). The discharge of heavy metals into rivers by domestic and industrial activities promoted their rapid association with particulates and incorporation in bottom sediments. And because of the bottom feeding habits of some fish species, including the Nile Tilapia, high levels are sometimes observed in fish tissues. The concentration of heavy metals, particularly Pb, may exceed the maximal permissible concentration of 2.0 µg/g recommended in fresh sea foods by the WHO. *Oreochromis niloticus* tissues bioaccumulated high levels of Pb during the rainy season sampling of Goronyo Dam (Table 4). No tissue (gills, muscles and bones) presented Cd concentration higher than the WHO standard of 2.0 µg/g. Since Cd, like Pb plays no role in enzyme activities, chronic discharge of Cd containing wastes to aquatic environment over time will lead to bioaccumulation. Whenever this happens, Cd replaces Zn in Zn binding proteins. Zn and Cd are in the same group on the periodic table, have the same common oxidation state (+2), and when ionized are almost of the same size. Due to these similarities, Cd readily replaces Zn in many biological systems, in particular, sulphur ligands. Cd can bind up to ten times more strongly than Zn in biological systems. Cd can also replace Mg and Ca in biological systems, although these replacements are rare (Lane and Morel, 2000). The metal -Cu, though required for some enzyme activities can be toxic at high concentrations. It is however present below the WHO standard of 3.0 µg/g (except for dry season sampling of Rima River). Cu, in its ionic forms Cu<sup>2+</sup>, CuOH<sub>2</sub><sup>2+</sup> and CuOH<sup>+</sup> are toxic to fish (Moore, 1991). The metals Ni, Fe, Mg, Cr, Ca, Na, and K are mineral elements and were present at tolerable limits and so do not cause threats to aquatic environment. Because *Oreochromis niloticus* gills, muscles, and bones had high levels of Pb in Goronyo Dam in the rainy season (as shown in Table 4), fishes consumed from this dam can be very rich source of Pb. Pb interferes with several enzymes in the haem pathway and decreases haem biosynthesis by decreasing α-aminolevulinic acid ferrochelatase activity. Pb is also sulphur seeking and easily binds to S-CH<sub>3</sub> and S-H (sulphydryl groups) in enzyme protein (Venugopal and Luckey, 1975). Such immobilized enzymes cannot function properly. In general, differential levels of heavy metals in different tissues may be attributed to some biological factors: nature of the body covering with respect to penetrability, availability of right type of enzymes and optimal physicochemical conditions, excretory capacity and the rate of elimination of by-products of metabolism, availability of body size and the sensitivity of the site of action, body size, age and life cycle stage as well as ecology with particular reference to location (Don-Pedro, 1997). Cadmium levels in the three organs

analysed from *Oreochromis niloticus* from all the study areas and for both seasons did not exceed the WHO standard of 2.0 µg/g.

Baron (1995) views bioaccumulation as a result of the competing rate of a chemical uptake and elimination. Thus, bioaccumulation may likely occur if the fish is able to continuously absorb the metals from the surrounding aquatic environment. As with Pb, Cd plays no role in metabolism, but it is also sulphur-seeking. It binds to S-CH<sub>3</sub> and S-H groups in enzymes proteins. Cd<sup>2+</sup> and Zn<sup>2+</sup> are similar in their chemical properties including size. Cd<sup>2+</sup> replaces Zn<sup>2+</sup> in enzymes that contain the latter. It has been observed that Cd-Containing enzymes do not perform the same function as Zn-containing enzymes. Presence of Cd in tissues when bound to metallothioneins allows it to be transported to the blood by the erythrocyte or bound to large muscular weight proteins (Nordberg, 1972). In contrast to Pb and Cd, Ni and Cu are essential for enzyme activities. Ni is essential particularly in urease and dehydrogenase activities, absence of which retards growth or cause the death of the living organism. Ni is highly tolerable by organisms except the divalent state Ni<sup>2+</sup> (Weast, 1998). Ni has been found to be bioavailable in all tissues and from all the locations during the two seasonal harvests. The Ni<sup>2+</sup> binds strongly to the gills rendering it less functional. Fishes however, have developed mechanisms to control and regulate their nickel burdens. Cu, like Ni is essential for enzyme activities, but the divalent (Cu<sup>2+</sup>) state is also biotoxic. Other metals (Fe, Mg, Cr, Ca, Na and K) investigated, though not present at toxic levels, can pose some threat to the fish tissues through bioaccumulation and biomagnification (WHO, 1992). The concentration of the heavy metals in the tissues may be dependent on the sediment and water concentration. The concentrations will likely increase in future as a result of increased human activities. This can be explained on the basis that some of these metals that were held in stagnant stream must have been channelled away with floods during rainfall. Pb, Cd, Cr, and Cu featured more prominently during the rainy season sampling from River Gagare. The reason may be that, though River Gagare is a tributary to Goronyo Dam, it may likely be receiving waste discharges from some sources during the rainy season. If these wastes contain some heavy metals, they may be incorporated in water bodies and bottom sediment which some fishes feed on. River Rima and Goronyo Dam tissue specimens presented higher Pb and Cd values in the rainy season than in the dry season. As with River Gagare, floods might have contributed to this increase. Mg appeared in high concentrations in all the locations and in all tissues during the rainy season in contrast to Fe that have lower values in the same season. The reason for lower Fe level may be due to the fact that some tissues have bioaccumulated Pb, and Pb displaces Fe in some enzyme reactions, causing anaemia.

#### Acknowledgements

We appreciate the assistance of laboratory staff of Departments of Agriculture and Biochemistry, Usmanu Danfodiyo University, Sokoto, Nigeria. The chief Technologist, Department of Analytical Chemistry, Sheda Science and Technology Centre (SHESCO) Abuja, in whose company the metal analysis was carried out is also acknowledged.

#### References

- [1]. Baron MG (1995). Bioaccumulation and Biomagnification in Aquatic Organisms In: Handbook of Ecotoxicology pp 652-662. (Hoffman DH, Rattner BA, Burton BA Jr, Cairns GA Jr. Eds). CRS Press Inc- Lewis Publishers. London. Tokyo. Pp 652-662.
- [2]. Davis CA, Tomlinson K, Stephenson T (1991). Heavy metals in River Tees Estuary Sediments. Environ Technol. 18: 961-972.
- [3]. Duncan RC., Knapp RG., and Miller MC (1997). Test of hypothesis in population means. In: Introductory Biostatistics for health sciences. John Wiley and Sons Inc. NY pp 71-76.
- [4]. Don –Pedro OP (1997). Differential Responses of Perennial Salt Marsh Plants to Oil Pollution. Ph.D Thesis Imperial College of Science and Technology University of London. pp 258
- FAO/WHO (1993). World Health Organization Report of the 36th Session of the Codex Committee on Food Additives and Contaminants. 28th session. The Hague, Netherlands. p 22-24  
Tfp://fop.org/codex/ccfac38/fa3:18e.pdf cited 15th June 2011.
- [5]. FMH (2010). Federal Ministry of Health. Zamfara state lead poisoning epidemic. In: US CDC Report June 2010.
- [6]. Goyer RA (1991). Toxic Effects of Metals. In Amdur M.O., Doull, J.D., and Klaasen C.D. (Eds). Casarett and Doull' Toxicology 4th ed. Pergamon Press. New York pp 625-680.
- [7]. Keen CL, Leonard BO, Fisher GL (1981). Age- Related Variation in Hepatic Iron, Copper, Zinc and Selenium Concentrations in Beagles. Am J. Vet Res. 42: 1884-1887.
- [8]. Kiffney PM, Clement WH (1994). Effects of Heavy Metals on a Macroinvertebrate Assemblage from a Rocky Mountain Stream in Experimental Microcosms. J. Am Bent Soc. 13: 511-523.
- [9]. Lane TW, Morel FMM (2000). A Biological Function in Marine Diatoms. Procedures in Nat. Acad of Sci. 9: 4627-4631.
- [10]. Langerweff JN (1972). Lead, Mercury, and Cadmium as Environmental Contaminants. In JJ Mortredt PM, Giodano WL, Lindsay P. Eds. Micronutrients in Agriculture. Soil Sci Soc Am. Madison. 50: 593- 636.
- [11]. Moore JW, Sutherland DJ (1991). Distribution of Heavy Metals and Radionucleotides in Sediments, Water, and Fish in an Area of Great Lake Contaminated with Mine Wastes. Archives of Environmental Contamination and Toxicology. 10: 329-338.
- [12]. Mouvet C (1984). Accumulation of Chromium and Copper by Aquatic Moss, *Fontinalis antipyretica* L. ex Hedw Transplanted in a Metal Contaminated River. Environmental Technology Letters. Moore J.W (1991). Inorganic Contaminants of Surface Water. New York: Spring Verlag 5: 541- 548.
- [13]. Nordberg K (1972). Fish Mercury Distribution in Massachusetts USA Lakes. Environmental Toxicology and Chemistry. 18: 1358-1389.
- [14]. Reddy KJ, Wang L, Gloss SP (1995). Solubility of Copper, Zinc, and Lead in Acidic Environment. Plant and Soil. 171: 53-58.

- [15]. Stewart EA, MaxGrimshaw H, John AP, Christopher Q (1974). Chemical Analysis of Ecological Materials. Institute of Terrestrial Ecology. Merlewood Research Station, Grange –Over- Sands, Cumbria. pp 97.
- [16]. Venugopal B, Luckey TP (1975). Toxicology of non-radioactive heavy metals and their salts: In Heavy metal toxicity, safety and hormology. TD Luckey, B Venugopal, D Hutchenson (Eds). George Theime, Stuttgart. pp 85.
- [17]. Weast B (1998). Heavy metal distribution in different fish species from the Mauritanian coast. *Science Total Environment*. 232: 169-175
- [18]. Whiteside, PJ (1987). An Introduction to Atomic Absorption Spectrophotometry. Published by Pye Unicam Ltd, First Edition. pp 25
- [19]. WHO (1992). World Health Organization. Report of the 36<sup>th</sup> session of the Codex Committee on Food Additives and Contaminants, Rotterdam, The Netherlands, 22-26, March. pp
- [20]. WHO (2011). World Health Organization. Lead poisoning recorded in 43 Nigerian villages. A report from United Nations Public Health Arm. pp 22