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Heavy metal profile of water, sediment and freshwater cat fish, *Chrysichthys nigrodigitatus* (Siluriformes: Bagridae), of Cross River, Nigeria

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Abstract: Cross River serves as a major source of drinking water, transportation, agricultural activities and fishing in Cross River State, Nigeria. Since there is no formal control of effluents discharged into the river, it is important to monitor the levels of metals contaminants in it, thus assessing its suitability for domestic and agricultural use. In order to determine this, three sampling stations designated as Ikom (Station I), Obubra Ogada (Station II) and Calabar (Station III) were randomly selected to study. For this, ten samples of the freshwater Silver Catfish (*Chryshchythys nigrogitatus*) (29.4-39.5cm SL, 310-510g), sediment and water were collected from each sampling Station from June 2009-June 2010. The heavy metals profiles of Zn, Cu, Fe, Co, Pb, Cd and Cr, in water, sediments and fish muscle were analyzed by atomic absorption spectrophotometry (AAS). In fish, the heavy metals concentration was found to be Cu>Fe>Zn>Cu>Pb>Cd>Co; the highest mean concentration of Copper (0.297±0.022 µg/g), Cadmium (0.011±0.007µg/g), Iron (0.371±0.489µg/g), Lead (0.008±0.008µg/g), were determined for the fish. In water, the order was found to be Fe>Pb>Zn>Cu>Cr>Cd>Co; the highest mean concentration of Iron (0.009±0.00µg/g), Copper (0.015±0.01 µg/g), Lead (0.0002±0.00µg/g) Cadmium (0.0006±0.001µg/g), Zinc (0.0036±0.003µg/g), were observed in the surface water, respectively. The highest mean concentration of Copper (0.037±0.03µg/g), Iron (0.053±0.04µg/g), Lead (0.0002±0.00µg/g), Cobalt (0.0002±0.00µg/g), Cadmium (0.0006±0.001µg/g) and Zinc (.009±0.0015µg/g) was observed in the bottom water. In sediments, the concentration order found was Zn>Fe>Cu>Pb>Co>Cd; the highest mean concentration of 0.057±0.04µg/g, 0.043±0.03µg/g, 0.0006±0.00µg/g, 0.0002±0.00µg/g, 0.0009±0.00µg/g, 0.099±0.00404µg/g in Iron, Copper, Lead, Cobalt, Cadmium and Zinc were observed in the sediment, respectively; Chromium was not detected in the sediment for the whole sampling area. Most of the heavy metals were below the maximum allowable levels set by the WHO, FEPA and USEPA, except Zinc which mean concentration of 0.099±0.00404µg/g was above the recommended limit of 0.0766µg/g of USEPA in the sediment at Ikom. This implies that the waste assimilation capacity of the river is high, a phenomenon that could be ascribed to dilution, sedimentation and continuous water exchange. This is an indication that an urban and industrial waste discharged into the Cross River has a significant effect on the ecological balance of the river. Thus fish species from the Cross River harvested are safe for human consumption. Rev. Biol. Trop. 60 (3): 1289-1301. Epub 2012 September 01.

Key words: Cross River, maximum limit, fish, water, sediment, heavy metals.

Water pollution has become a global problem. Water is essential to all living organisms and in all aspects of human life. Unfortunately, the availability and quality of water have been impacted upon by both natural and anthropogenic sources, leading to poor water quality and productivity of aquatic ecosystems (FAO 1992). Heavy metals are chemical elements with a specific gravity that is at least five times the specific gravity of water. The specific gravity of water is 1 at 4°C (39°F). Simply stated, specific gravity is a measure of density of a

given amount of a solid substance when it is compared to an equal amount of water. Heavy meals are one of the more serious pollutants in our natural environment due to their toxicity, persistence and bioaccumulation problems (Tam & Wong 2000). Most heavy metals have no beneficial functions to the body and can be highly toxic. If they enter into the body through inhalation, ingestion and skin they accumulate in the body tissue faster than the body's detoxification pathways can dispose of them (Ekpo *et al*. 2008). High concentration exposure is not necessary to produce a state of toxicity in the body tissue and, overtime, can reach toxic concentration at low levels (Prusty 1994, Khalid *et al*. 1978). Heavy metals belong to the group of elements whose hydro-geochemistry cycles have been greatly accelerated by man. The rapid industrialization, coupled with technological advances in agriculture, has introduced various pollutants (synthetic and organic) into the aquatic ecosystems, which serves as the ultimate sink for most metals (Ogbeibu & Ezeunara 2002). Harvey & Lee (1982) and Bradley & Morris, (1986) have also reported the significance of increased metal loadings in aquatic ecosystems coincidental with acidification, and concluded that fish population losses were a consequence of reproduction failures arising from both acid and metal stresses. Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis.

Waste water streams containing heavy metals are produced by many manufacturing processes and find their way into the environment (Soon *et al*. 1980, Higgings & Dasher 1986, Oguzie 1996, Ogbeibu & Ezeunara 2002). Metals persist in the environment and become bioconcentrated and bioamplified along the food chain. This may be responsible for high concentrations of these metals in predators such as sharks and eagles (Broda 1972, Martins & Coughtry 1975). Some research findings have shown that heavy metals in aquatic environment could accumulate in biota especially fish as they are the most common aquatic organisms at higher tropic level (Olaifa *et al.* 2004). Bio-accumulation in fish has been reported by many researchers (Jernelov & Lann 1971, Goldwater 1971, Mathis & Cummings 1973, Chernof & Dooley 1979, Bull *et al*. 1981, Biney *et al*. 1991, Law & Singh 1991). The uptake of heavy metals in fish was found to occur through absorption across the gill surface or through the gut wall tract (Mathis & Cummings 1973).

Diffusion facilitated transport or absorption in gills and surface mucus are the mechanisms of uptake from water (Oguzie 1996). The concentrations of heavy metals in fish have been reported to depend upon the rate of uptake through the gut from food and the rate of excretion (Bull *et al*. 1981). Fish production is an important industry in Nigeria where riverine settlements are established (Ako & Salihu 2004). Fish is a valuable and cheap food item and source of protein to man. Concern about heavy-metal contamination of fish has been motivated largely by adverse effects on humans, given that consumption of fish is the primary route of heavy metal exposure (Nsikak *et al*. 2007). In order to effectively control and manage water pollution due to heavy metals, it is imperative to have a clear understanding of their distribution pathways, fate and effect on biota (Sabo *et al.* 2008).

Sediments can be sensitive indicators when monitoring contaminants in aquatic environments. The sediments were polluted with various kinds of hazardous and toxic substances, including heavy metals. These accumulate in sediments via several pathways, including disposal of liquid effluents, terrestrial runoff and leachate carrying chemicals originating from numerous urban, industrial and agricultural activities, as well as atmospheric deposition. Sediments effectively sequester hydrophobic chemical pollutants entering water bodies such as lakes. Lake sediments provide a useful

archive of information on changing lacustrine and watershed ecology (Cohen 2003). Core sediments provide useful information on the changes in the quality of the lake from a past period. Many researchers had studied the pollution history of aquatic ecosystem by core sediments (Karbassi *et al.* 2005, Lopez & Lluch 2000, Mohamed 2005). Many researchers have used sediment cores to study the behavior of metals (Bellucci *et al.* 2003, Bertolotto *et al.* 2003, Borretzen & Salbu 2002, Lee & Cundy 2001, Weis *et al.* 2001).

Cross River serves as a major source of drinking water and fishing in Cross River State. The river is also being use for transportation and agricultural activities. Since there is no formal control of effluents discharged into the river, it is important to monitor the levels of metals contaminants in the river, thus assessing its suitability for domestic and agricultural use. This work is to assess the heavy metal profile in Cross River Water, Sediment and common fish consumed (Silver Catfish *Chryshchythys nigrodigitatus*) in Cross River State, and compare the results with USEPA, FEPA, WHO water quality criteria and recommend the standard methods of disposing waste in Cross River State.

MATERIALS AND METHODS

Study area: The study site is the Cross River, a floodplain river located at the South Eastern part of Nigeria (Fig. 1) on Latitude 4º25´ - 7º.00´ N, Longitude 7º15´ - 9º30´ E. It is bounded in the South by the Atlantic Ocean, East by the Republic of Cameroun, the Nigerian states of Benue in the North, Ebonyi and Abia in the West and Akwa Ibom in the South West. Climate of the study area is defined by dry season and wet season. The wet season (April-October) is characterized by high precipitation (3050±230mm), while the dry season (November-March) is marked by low precipitation (300±23mm). Mean annual temperature ranged from 15.5 ± 7.6ºC (wet season) to

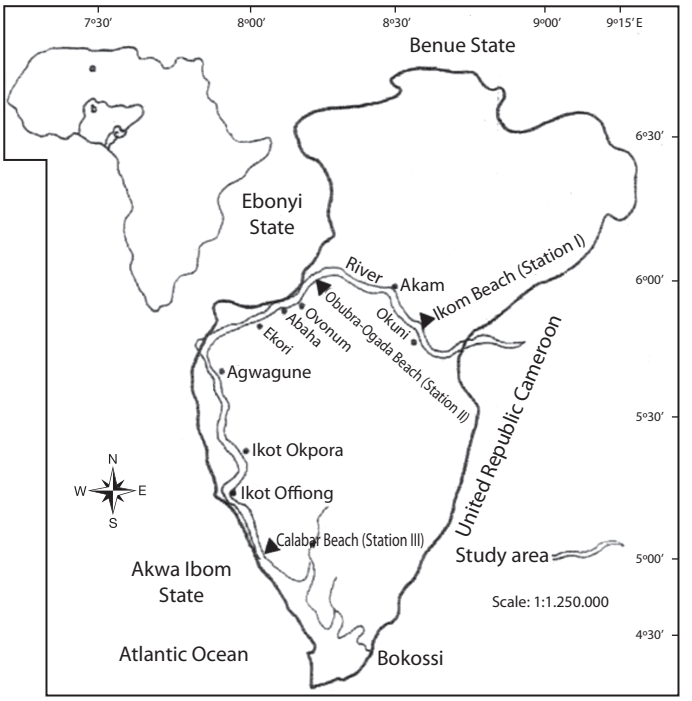

Fig. 1. Map of Cross River showing the study areas.

32.6±5.4ºC (dry season). For the purpose of this study three sampling sites were selected along the length of the river, with one site randomly selected in each of the following beaches; Ikom Beach (Station I), upriver, Obubra (Ogada) Beach, middle river (Station II); and Calabar Beach (Station III), downriver. Upriver was located 3km from the river source with rocky, gravel and sandy substratum. The shoreline is covered with savanna grassland and has wood and paper industries located close to the source. The middle river was 100km from river source with rocky substratum and shoreline sparsely shaded by forest and savanna grassland. Downriver station had a muddy substratum and opens up into the Cross River estuary, with shoreline thickly shaded with rainforest.

Sample collection: Three sample stations designated stations Ikom (Station I), Obubra (Station II), and Calabar (Station III) were selected randomly for the purpose of the study. Samples of the freshwater Silver Catfish (*Chryshchythys nigrogitatus*), sediment and water were collected from the sampling Stations, from June 2009-June 2010. Ten samples each of water, sediment and *C. nigrodigitatus*) were collected from each of the three sampling stations every three months. A water sample was collected at 30cm below the surface and bottom using one liter polythene bottles with screw caps. Sediment samples was collected using Eckman grab into plastic bags previously cleaned with detergent and treated with 10% nitric acid. Ten specimens of *Chryshchythys nigrodigitatus* (29.4-39.5cm SL, 310-510g) were caught from each sampling station using three inch beach seine nets, set gill nets, baited hooks various sizes, and traps set overnight prior to collection. The specimens were taken in polythene bags and stored in a deep freezer at -10°C in the laboratory prior to treatment and analysis where skin, gills and liver were evaluated (Obasohan *et al.* 2007).

Samples treatment and analysis: Sediment samples were oven dried to constant weight at 105ºC. The samples were grounded using mortar and pestle and sieved through 2mm mesh size to remove coarse materials. The fish samples were allowed to defrost and then dried to constant weight in an oven at 105ºC. Water samples were not subjected to any further treatment and were sent directly for analysis using a Buck Scientific 200A model, Atomic Absorption Spectrophotometer (AAS) and the values obtained expressed in micrograms per gram (µg/g). A quantity 0.2g each of sediment and fish samples was digested using 0.02M HNO_3 and HCl in the ratio 1:3 (aquaregia) in a fume cupboard at 80ºC. Heavy-metals (Cr, Co, Cu, Zn and Pb), Ca and Mg were detected by atomic absorption spectrometer (AAS) (GBC-902, Australia) (APHA 1995, APHA 1998).

The data obtained were collated and subjected to one-way analysis of variance. The (ANOVA) and Duncan's Multiple Range Test (DMRT) was used to assess whether heavy metal concentrations varied significantly between stations (Olaifa *et al.* 2004, APHA 1998).

RESULTS

The result of the accumulation of heavy metals in Catfish *Chrysichthys nigrodigitatus* is presented in table 2, the highest concentration of copper (0.279±0.022 µg/g) was observed in the gill at Ikom (Station I) ($p<0.05$). However, there was a non significant difference (0.034±0.017 and 0.031±0.024 µg/g) between liver and skin at Ikom (Station I) and Obubra (Station II), respectively. The minimum concentration of Copper (0.001±0.001µg/g) was found in the fish gills and skin from Calabar (Station III). The highest concentration of Iron (0.376±0.49µg/g) was observed in the liver at Ikom (Station I) ($p<0.05$). However, there was a significant difference (0.067±0.006 and 0.043±0.034µg/g) between gill and skin of fish from Obubra (Station II) and Calabar (Station III), respectively. The minimum concentration of Iron (0.043±0.039µg/g and 0.043±0.034µg/g) was found in the gills and skin at Calabar (Station III) (Table 1). The

TABLE 1
Working conditions for the analysis of trace elements by atomic absorption spectrophotometer

Metals µg/g	Wave length (nm)	Slit width (nm)	Lamp current (mA)	Gas	Support
Fe	248.4	0.1	5	Acetylene	Air
Cu	324.8	0.1	4	Acetylene	Air
Zn	213.9	0.1	5	Acetylene	Air
Cd	326.1	0.1	4	Acetylene	Air
Pb	283.3	0.1	5	Acetylene	Air
Co	241.7	0.1	7	Acetylene	Air
Cr	357.9	0.1	7	Acetylene	Air

highest concentration of Lead (0.008±0.008 µg/g) was observed in the liver at Ikom (Station I) ($p<0.05$), there was a significant difference (0.005±0.009 and 0.003±0.002 µg/g) between gill and skin at Obubra (Station II) and Calabar (Station III), respectively. The minimum concentration of Lead (0.001±0.001µg/g) was found in the liver at Obubra (Station II).

The highest concentration of Cadmium (0.011±0.007µg/g) was observed in the liver at Ikom (Station I) and Gill at Calabar (Station III) ($p<0.05$), there was a significant difference (0.004±0.004 and 0.003±0.005 µg/g) between gill and skin at Obubra (Station II) and Calabar (Station III), respectively. The minimum concentration of Cadmium (0.000±0.000µg/g) was found in the liver and skin at Obubra (Station II). The highest concentration of Zinc (0.009±0.001µg/g) was observed in the liver at Calabar (Station III) ($p<0.05$), there was a significant difference (0.004±0.004 and 0.003±0.002µg/g) between gill and skin at Ikom (Station I) and Obubra (Station II), respectively. The minimum concentration of Zinc (0.002±0.002µg/g and 0.002±0.002µg/g) was found in the gill and skin at Obubra (Station II). Chromium and Cobalt were not detected in all the stations during the experiment (Table 2).

The result of the accumulation of heavy metals in water is presented in table 2 and the mean concentrations for Cu, Fe, Pb, Cr, Co, Ca and Zn in surface and bottom water observed different concentrations among the studied stations, but higher concentration values were observed in bottom water samples in all stations, when compared to surface samples. Chromium and Cobalt observed the lowest values for both surface and bottom water, while Iron resulted with the highest concentration value (0.053±0.04µg/g and 0.044±0.05µg/g) in bottom water samples from Ikom Beach (Station I) and Obubra Ogada Beach (Station II), respectively. These Stations resulted also with the highest heavy metal concentration values for bottom water samples (0.0782µg/g and 0.0787µg/g) when compared to Calabar Station with 0.059µg/g. Copper concentrations were highest (0.037±0.03 µg/g) in Calabar Beach bottom samples. Besides, Copper and Iron were the most common heavy metals for both surface and bottom water, but also in sediment samples from the evaluated stations.

The results of the accumulation of heavy metals in sediments is presented in table 2, the mean concentrations of Cu, Fe, Pb, Cr, Co, Ca and Zn observed in different concentrations among the studied stations, but the highest value were observed at Calabar (Station III) and Ikom (Station I) ($p<0.05$). Copper and Cadmium observed the highest values at Calabar (Station III) and Ikom (Station I) (0.037±0.03µg/g and 0.099±0.004µg/g, respectively), while Cobalt and Cadmium observed the lowest (0.0001±0.00µg/g and 0.0000±0.000µg/g) at Obubra (Station II) and Calabar (Station III). Chromium was not detected in all the stations.

DISCUSSION

Knowledge of heavy metal concentrations in fish is important with respect to nature of management and human consumption of fish. Generally, heavy metal concentrations in the

TABLE 2
The heavy metal concentration of Cross River, Cross River State Nigeria, using different bioindicators

Bioindicators	Sampling Stations	Organs	Copper µg/g	Iron µg/g	Lead µg/g	Chromium µg/g	Cobalt µg/g	Cadmium µg/g	Zinc µg/g
Fish	Ikom Beah (Station I)	Gill	0.279±0.02	0.070±0.02	0.003±0.00	ND	ND	0.002±0.00	0.004±0.00
		Liver	0.037±0.02	0.376±0.49	0.008±0.00	ND	ND	0.011±0.01	0.006±0.00
		Skin	0.031±0.02	0.071±0.015	0.005±0.00	ND	ND	0.003±0.00	0.003±0.00
	Obubra Ogada Beach (Station II)	Gill	0.149±0.22	0.067±0.01	0.005±0.01	ND	ND	0.003±0.00	0.002±0.00
		Liver	0.034±0.02	0.058±0.04	0.001±0.01	ND	ND	0.000±0.00	0.005±0.00
		Skin	0.027±0.17	0.062±0.03	0.003±0.00	ND	ND	0.000±0.00	0.002±0.00
	Calabar Beach (Station III)	Gill	0.001±0.00	0.043±0.04	0.002±0.00	ND	ND	0.011±0.02	0.006±0.00
		Liver	0.014±0.02	0.055±0.04	0.004±0.00	ND	ND	0.003±0.00	0.009±0.00
		Skin	0.001±0.00	0.043±0.03	0.003±0.00	ND	ND	0.004±0.00	0.006±0.00
Water	Ikom Beach (Station I)	Surface Water	0.006±0.00	0.019±0.03	0.000±0.00	ND	ND	0.000±0.00	0.004±0.00
		Bottom Water	0.014±0.01	0.053±0.04	0.000±0.00	0.000±0.00	0.000±0.00	0.002±0.00	0.009±0.00
	Obubra Ogada Beach (Station II)	Surface Water	0.017±0.02	0.009±0.00	0.000±0.00	ND	ND	ND	0.000±0.00
		Bottom Water	0.033±0.03	0.044±0.05	0.000±0.00	0.000±0.00	0.000±0.00	ND	0.001±0.00
	Calabar Beach (Station III)	Surface Water	0.015±0.01	0.001±0.00	0.000±0.00	ND	ND	0.000±0.00	0.002±0.00
		Bottom Water	0.037±0.03	0.021±0.02	0.000±0.00	ND	0.000±0.00	0.000±0.00	0.001±0.00
Sediment	Ikom (Station I)		0.020±0.02	0.057±0.04	0.0002±0.00	ND	0.0001±0.00	0.0009±0.00	0.099±0.00
	Obubra Ogada (Station II)		0.036±0.03	0.019±0.01	0.0006±0.00	ND	0.0001±0.00	ND	0.0018±0.00
	Calabar Beach (Station III)		0.037±0.03	0.021±0.02	0.0002±0.00	ND	0.0002±0.00	0.0000 ±0.00	0.0013±0.00
WHO (WHO 1985) Specification			3	0.30	0.05	0.15	-	0.005	5.00
FEPA (FEPA 2003) Specification			<1.0	-	<1.0	-	-	<1.0	<1.0
USEPA (USEPA 1987) Specification			0.1	0.1	0.0058	0.05	-	0.008	0.0766

tissue of freshwater fish vary considerably among different studies (Javed & Hayat 1998, Chattopadhyay *et al*. 2002, Papagiannis *et al*. 2004), possibly due to differences in metal concentrations and chemical characteristics of water from which fish were sampled, ecological needs, metabolism and feeding patterns of fish, and also the season in which studies were carried out. In the river, fish are often at the top of the food chain and have the tendency to concentrate heavy metals from water (Mansour & Sidky 2002). Therefore, bioaccumulation of metals in fish can be considered as an index of metal pollution in the aquatic bodies (Javed & Hayat 1998, Tawari-Fufeyin & Ekaye 2007, Karadede-Akin & Unlu 2007) that could be a useful tool to study the biological role of metals present at higher concentrations in fish (Dural *et al*. 2007, Anim *et al*. 2011).

In the present study, the result of the accumulation of heavy metals in Catfish *Chrysichthys nigrodigitatus* showed that the highest concentration of copper (0.297±0.022 µg/g) was observed in the gill at Ikom (Station I) ($p<0.05$). However, there was a non significant difference (0.034±0.017 and 0.031±0.024µg/g) between liver and skin at Obubra (Station II) and Calabar (Station III), respectively. The minimum concentration of Copper (0.001±0.001µg/g) was found in the gills at Calabar (Station III). Gills which are in direct contact with water accumulated some amount of copper. Bio-accumulation in fish has been reported by many researchers (Jernelov & Lann 1971, Goldwater 1971, Mathis & Cummings 1973, Chernof & Dooley 1979, Bull *et al*. 1981, Biney *et al.* 1991, Law & Singh 1991). The uptake of heavy metals in fish was found to occur through absorption across the gill surface or through the gut wall tract (Mathis & Cummings 1973). Diffusion facilitated transport or absorption in gills and surface mucus are the mechanisms of uptake from water (Oguzie 1996).

The concentrations of heavy metals in fish have been reported to depend upon the rate of uptake through the gut from food and the rate of excretion (Bull *et al*. 1981). The accumulation of copper in the gills may be due to adsorption to the gill surfaces and dependent on the availability of proteins to which the copper may bind. The low accumulation may be due to development of some defensive mechanism such as excessive mucous secretion and clogging of gills. The slow penetration of copper across the gills may be the reason for low toxicity of this metal to *Clarias batrachus*. Huges & Floss (1978) also found the low accumulation of zinc in gills of the rainbow trout.

The highest concentration of copper (0.65±0.11µg/g) was detected in the liver tissue of *O. niloticus*, while the lowest detected limit (0.01±0.01µg/g) was found in the bone tissue of *O. niloticus*. Liver concentrates higher levels of copper in all the six species of fishes than the other organs. Akan *et al*. (2009) recorded high level of copper from lake Chad in the liver tissues for all the fishes is due to the fact that, the liver is a target organ for the accumulation of this element. For the gills samples, it may be due to the fact that freshwater fish's gills might be expected to be the primary route for the uptake of water borne pollutants, Allen & Wilson (1991). WHO (1989) reported that copper toxicity in fish is taken up directly from the water via gills and stored in the liver, the present study showed the similar accumulation of copper in the gills and livers. Effects of high concentrations of copper in fish are not well (Woodward *et al.* 1994). Copper can combine with other contaminants such as ammonia, mercury, and zinc to produce an additive toxic effect on fish (Herbert *et al.* 1964, Rompala *et al*. 1984).

The higher levels of trace elements such as lead and chromium in liver relative to other tissues may be attributed to the affinity or strong coordination of metallothionein protein with these elements (Ikem *et al*. 2003). According to Allen-Gill & Martynov (1995), low levels of copper and zinc in fish muscles appear to be due to low levels of binding proteins in the muscles. Canli & Kalay (1998) determined the concentrations of cadmium and chromium in the gills, liver and muscles of *Cyprinus carpio*, *Barbus capito* and *Chondrostoma regium*

caught at five stations on the Seyhan river system. Liver and gill tissues showed higher metal concentrations than muscles tissue. Thus, heavy metals when discharged into the river enter the food chain and accumulate in the fish body as determined during this investigation. Similar work was carried out by Wegwu *et al*. (2006), they worked on the assessment of Heavy-Metal Profile of the New Calabar River and its impact on juvenile *Clarias gariepinus* and find out that the results indicate that trace metals (except for Zn), even at very low concentrations, negatively affect fish hatch and fry rearing, implying that aquatic milieus contaminated by trace metals are not suitable as nursery grounds for fish cultures.

The highest concentration of iron (0.371±0.489µg/g) was observed in the liver at Ikom (Station I) ($p<0.05$). However, there was a significant difference (0.067±0.006 and 0.043±0.034µg/g) between gill and skin at Obubra (Station II) and Calabar (Station III), respectively. The minimum concentration of Iron (0.043±0.039 µg/g and 0.043±0.034 µgg-1) was found in the gills and skin at Calabar (Station III) (Table 1). Fish liver exhibited highest tendency to accumulate both the metals. The accumulation of both cadmium and chromium were the minimum in fish gills. Dural *et al*. (2007) and Ploetz *et al*. (2007) reported highest levels of cadmium, lead, copper, zinc and iron in the liver and gills of fish species viz. *Sparus aurata*, *Dicentrachus labrax*, *Mugil cephalus* and *Scomberomorus cavalla*. Yilmaz *et al*. (2007) reported that in *Leuciscus cephalus* and *Lepornis gibbosus*, cadmium, cobalt and copper accumulations in the liver and gills were maximum, while these accumulations were least in the fish muscle. Accumulation in the liver can be the result of detoxicating mechanisms and may originate from metal in the food (Karadede & Unlu 1998, Shoham-Frider *et al.* 2002). However, the liver is the preferred organ for metal accumulation as could be deduced from the present study.

The highest concentration of Lead (0.008±0.008µg/g) was observed in the liver at Ikom (Station I) ($p<0.05$), there was a significant difference (0.005±0.009 and 0.003±0.002µg/g) between gill and skin at Obubra (Station II) and Calabar (Station III), respectively. The minimum concentration of Lead (0.001±0.001µg/g) was found in the liver at Obubra (Station I). Lead accumulates significantly in the bone, liver, stomach, gills and kidney tissue of *T. zilli*, *C. anguillaris*, *Protoptenus*, *O. niloticus*, *E. niloticus* and *S. budgetti*. The highest levels of lead (0.32±0.12µg /g) were observed in the liver tissue of *T. zilli*, while the lowest limit (0.01±0.0.01Mg/g) was detected in the bones of *C. anguillaris* and *S. budgetti*. The concentrations of lead were higher in the following order liver>gills>stomach> kidney>bone. Similar findings were reported by Buhler *et al.* (1977).

Those highest concentrations were in gills, kidney and spleen in rainbow trout. (Oladimeji & Offem 1989), noticed in *O. niloticus*, that the gills consistently accumulated higher amount of lead as lead nitrate. Lead is highly toxic to aquatic organisms, especially fish (Rompala *et al.* 1984). The biological effects of sublethal concentrations of lead include delayed embryonic development, suppressed reproduction, and inhibition of growth, increased mucous formation, neurological problems, enzyme inhalation and kidney dysfunction (Rompala *et al*. 1984, Leland & Kuwabara 1985). The levels of lead in liver, gills, stomach, kidney and bone tissue of *T. zilli*, *C. anguillaris*, *Protoptenus*, *O. niloticus*, *E. niloticus* and *S. budgetti* were below the 0.5µg g-1 limits (Walsh *et al.* 1977).

The highest concentration of Cadmium (0.011±0.007µg/g) was observed in the liver at Ikom (Station I) ($p<0.05$), there was a significant difference (0.004±0.004 and 0.003±0.005µg/g) between gill and skin at Obubra (Station II) and Calabar (Station III), respectively. The minimum concentration of Cadmium (0.000±0.000µg/g) was found in the liver and skin at Obubra (Station II). Cadmium is a non essential trace metal that is potentially toxic to most fish and wildlife, particularly freshwater organisms (Robertson *et al.* 1991). The highest concentrations of (0.03±0.01-0.22±0.01µg/g) in liver tissues of the above

species were below the 0.5µg/g threshold considered harmful to fish and predators (Walsh *et al*. 1977). The cadmium-related contamination of the aquatic habitat has greatly increased in the last decades, resulting in an increase of cadmium deposits in tissues of aquatic organisms in all food chain systems (Giles 1988). It is important to note that cadmium is a highly toxic element for all mammals and fish. Cadmium levels have constantly been increasing, and consequently, the research on cadmium has become quite topical and urgent.

The highest concentration of Zinc (0.009±0.001µg/g) was observed in the liver at Calabar (Station III) ($p<0.05$), there was a significant difference (0.004±0.004 and 0.003±0.002µg/g) between gill and skin at Ikom (Station I) and Obubra (Station II), respectively. The minimum concentration of Zinc (0.002±0.002µg/g and 0.002±0.002µg/g) was found in the gill and skin at Obubra (Station II). Zinc was detected in all the fish samples, and the highest concentration was observed in the liver tissues followed by the gills, stomach and kidney. Fish can accumulate zinc from both the surrounding water and from their diet (Eisher 1993). Although zinc is an essential element, at high concentrations, it can be toxic to fish, cause mortality, growth retardation, and reproductive impairment (Sorenson 1991). Zinc is capable of interacting with other elements and producing antagonistic, additive, or synergistic effects (Eisher 1993). Zinc does not appear to present a contaminant hazard to fish in Cross River. Chromium and Cobalt were not detected in all the fish organs studied and for all the stations during the experiment. Chromium is an essential trace element in humans and some laboratory animals (Lee & Schultz 1994), but in excess, it could have lethal and sublethal effects on fish and wildlife (Robertson *et al*. 1991).

Prasathp & Khanth (2008) reported the impact of Tsunami on the Heavy Metal accumulation in water, sediments and fish at Poompuhar Coast, Southeast Coast of India and stated the highest recorded value among heavy metals was Mn which varied from 489.5µg/g to-506.9µg/g and the lowest recorded value among heavy metals was Pb which varied from 0.04µg/g to 0.07µg/g. Except Mn all the other metals (Zn, Cu, Fe, Co, Pb, Cd and Ni) recorded higher concentrations after the tsunami. This variation in metal concentrations is due to the presence of major sources of metal pollution, intensive human activity and discharge of municipal waste and industrial effluents. Also, the variation in the metal concentration is due to the impact of tsunami that caused large scale seawater inundation and the receding tidal waves carried into the sea, debris, anthropogenic wastes, adjacent terrestrial parts including plastic materials and domestic disposals from the near lands14. In sediments, the accumulation of heavy metals was found in the order of Mn>Fe>Cu>Zn>Pb>Co>Cd>Ni. Zn and Cu recorded higher values whereas Fe and Mn recorded lower values after tsunami. Highest recorded value among heavy metals was Mn which varied from 771.6µg/g to 851.1µg/g (Prasathp & Khanth 2008).

In sediment, metal levels differed significantly ($p<0.05$) and were highest at Station I, except Cu which level was highest at Stations II, III. The highest metal levels in sediment at Station I, is similar to the situation in water and could also be due to the nearness of Station I to the drainage discharge point from WEMCO Company. Sediment metal levels recorded in this study were low, when compared to the levels for unpolluted inland water sediment (GESAMP 1982). Sediments were considered an important indicator for environmental pollution; they act as permanent or temporary traps for material spread into the environment (DeGregori *et al*. 1996). Sediments have frequently been analyzed to identify sources of trace metal in the aquatic environment because of the high accumulation rates exhibited (Forstner *et al*. 1981). Sediment analysis allows contaminants that are adsorbed by particulate matter, which escape detection by water analysis, to be identified. The non-residual fraction of the sediment is considered to be mobile and therefore, is likely to become available to aquatic organisms (Waldichuk

1985). Concentrations of heavy metals in sediment usually exceed the levels of the overlying water by 3 to 5 orders of magnitude. With such concentrations Oguzie (1996), quoted in Defew *et al*. (2004) showed that the bioavailability of even a minute fraction of the total sediment metal assumes considerable importance. This is especially true to burrowing and filter feeding organisms.

Fish absorb metals through ingestion of water or contaminated food. Heavy metals have been shown to undergo bioaccumulation in the tissue of aquatic organisms. On consumption of fish and other aquatic organisms these metals become transferred to man. However, it is not yet known whether the fishes in the River have been severely affected by heavy metals, based on the results obtained from this study. Although the results do not explicitly indicate a manifestation of toxic effects, the possibility that deleterious effects could manifest after a long period of consumption of fish caught in Cross River with trace metal contamination cannot be ruled out. The concentrations of the heavy metals were observed to be higher in the upstream 2 which may be a result of improper dumping of refuse and sitting of wood processing (WEMCO) company near the sampling station 2 at Ikom.

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RESUMEN

Cross River funciona como una fuente importante de agua potable, transporte, actividades agrícolas y pesqueras en el Estado Cross River, Nigeria. Dado que no existe un control formal de los efluentes vertidos en el río, es importante monitorear los niveles de metales contaminantes en el mismo, por lo tanto la evaluación de su idoneidad para el uso doméstico y agrícola. Para la determinación de lo anterior, tres estaciones de muestreo designadas como Ikom (Estación I), Obubra Ogada (Estación II) y Calabar (Estación III) fueron seleccionadas al azar para el estudio. Se tomaron diez muestras de "Bagre de agua dulce de plata" (*Chryshchythys nigrogitatus*) de 29.4-39.5cm LE (longitud estándar) y 310-510g de peso, sedimentos y agua fueron recolectadas en cada estación de muestreo de junio 2009 a junio 2010. Los perfiles de metales pesados de Zn, Cu, Fe, Co, Pb, Cd y Cr, en agua, sedimentos y músculos de peces fueron analizados por espectrofotometría de absorción atómica (AAS). En los peces, la concentración de metales pesados que se determinó fue Cu>Fe>Zn>Cu>Pb>Cd>Co, para los peces se determinó una mayor concentración media de cobre (0.297±0.022g/g), cadmio (0.011±0.007µg/g), hierro (0.371±0.489µg/g) y plomo (0.008±0.008µg/g). En el agua, el orden se determinó como sigue: Fe>Pb>Zn>Cu>Cr>Cd>Co, con una mayor concentración promedio de hierro (0.009±0.00µg/g), cobre (0.015±0.01g/g), plomo (0.0002±0.00µg/g), cadmio (0.0006±0.001µg/g) y zinc (0.0036±0.003µg/g), se observaron en la superficie del agua, respectivamente. La mayor concentración promedio de cobre (0.037±0.03µg/g), hierro (0.053±0.04µg/g), plomo (0.0002±0.00µg/g), cobalto (0.0002±0.00µg/g), cadmio (0.0006±0.001g/g) y zinc (0.009±0.0015µg/g) se observó en el agua del fondo. En los sedimentos, el orden de concentración fue: Zn>Fe>Cu>Pb>Co>Cd, la mayor concentración media fue de 0.057±0.04µg/g, 0.043±0.03µg/g, 0.0006±0.00µg/g, 0.0002±0.00µg/g, 0.0009±0.00µg/g y 0.099±0.00404µg/g para hierro, cobre, plomo, cobalto, cadmio y zinc, respectivamente, no se detectó cromo. La mayoría de los metales pesados por debajo de los niveles máximos permisibles establecidos por la OMS, FEPA y USEPA, con excepción de zinc cuya concentración media fue de 0.099±0.00404µg/g estuvo por encima del límite recomendado de 0.0766µg/g de EPA en el sedimento de la Estación I (Ikom). Esto implica que la capacidad de asimilación de residuos del río es alta, un fenómeno que podría atribuirse a la dilución, la sedimentación y el intercambio continuo de agua. Lo cual es una indicación de que efluentes vertidos en el Cross River por zonas urbanas e industriales tienen un efecto significativo en el equilibrio ecológico del río. Así, las especies de peces del Río Cross son seguras para el consumo humano.

Palabras clave: río Cross, límite máximo, peces, agua, sedimentos, metales pesados.

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