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### ASSESSMENT OF HEAVY METALS CONCENTRATION ON AFRICAN CATFISH (Clarias gariepinus) SAMPLES FROM FRESHWATER SOURCES IN ENUGU STATE DURING RAINY SEASON

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### ABSTRACT

The concentrations of heavy metals in the gills and muscles of *Clarias gariepinus* during the rainy season was investigated following standard procedures. Three fish samples of were gotten from freshwater in Nike Lake (Nike L.G.A), Ebenyi River (Isi-azu L.G.A) and Oji River (Oji River L.G.A). Heavy metals analyzed include lead, cadmium, copper, zinc, chromium and iron. In general, the heavy metal concentrations were higher in the gills than in the muscles of the fish species. Ebenyi River had higher concentrations of heavy metals (Pb  $0.48\pm0.002$ , Cd  $0.05\pm0.005$ , Fe  $0.59\pm0.006$ , Cu  $1.24\pm0.004$ , Cr  $0.35\pm0.010$ , Zn  $2.70\pm0.007$ ) than the other freshwater sources. The detection levels are in the following decreasing order; Ebenyi River > Nike Lake > Oji wonderful. All heavy metals are toxic to living organisms at excessive concentrations, and are able to induce toxicity even at lower levels of exposure.

**KEYWORDS:** Heavy Metals, Contamination, *Clarias gariepinus*, Nike Lake, Ebenyi River, Oji wonderful.

### **INTRODUCTION**

There are different types of pollution among which pollution caused by toxic level of heavy metal pollutants is called heavy metal pollution (Bose and Hemantaranjan, 2005). Heavy metals

are elements having a density greater than 5g/cm<sup>3</sup> in their elemental form (Bose and Hemantaranjan, 2005; Misra and Mani, 2009). Heavy metal pollution has received the attention of researchers all over the world, mainly due to their harmful effects on living beings (Misra and Mani, 2009).

Human biology is full of instances where heavy metal toxicity has led to mass deaths (Shrivastav, 2001). All heavy metals are toxic to living organisms at excessive concentrations, but some are essential for normal healthy growth and reproduction by plants at low but critical concentrations (Bose and Hemantaranjan, 2005). The heavy metals essential in trace elements to plants include Co, Cu, Fe, Mo and Zn and for animals are Cr, Ni and Sn. The heavy metals Cd, Hg and Pb have not been shown to be essential for either plants or animals (Misra and Mani, 2009).

Heavy metals are non-biodegradable and once they enter into an environment, they will stay there for a longtime (Voet *et al.*, 2008). Heavy metals are considered serious pollutants because of their toxicity, persistence and non-biodegradable conditions in the environment, thereby constituting a threat to human beings and other forms of biological life (Adeleken and Abegunde, 2011). Discharge of heavy metals into rivers or any other aquatic environment can change both aquatic species diversity and ecosystems due to their toxicity and accumulative behaviour (Al-Weher, 2008). Heavy metals dissolved in water also endanger the lives of the public who use it for drinking and also irrigation. When used for irrigation heavy metals have the danger of being incorporated in food chain and therefore ingested by the public (Wogu and Okaka, 2011).

Most communities in Enugu state situated close to rivers or streams depend on these water sources for a lot of domestic activities such as cooking, washing and drinking. The present study is necessary to investigate the heavy metal contamination of freshwater and the organisms inhabiting this freshwaters, in relation to acceptable limits of heavy metals in drinking water as specified by organizations concerned with standard guidelines.

### MATERIALS AND METHODS

Water sample and three fish samples of African catfish were collected from each of the three senatorial districts in Enugu state (Enugu North, East and West) during the rainy season (month of July and August). Samples for Nike L.G.A were collected from Nike Lake. Samples for Oji

River L.G.A were collected from Oji River, while samples for Isi-Uzu L.G.A were collected from Ebenyi River, all of which are in Enugu State.

The samples were thawed at room temperature, and then dissected for analysis using stainless steel scalpels. The gills and muscles on the dorsal surface of the fish were dried in an oven at 80°C for two days until they reached a constant weight. The samples were then removed from the oven and allowed to cool. Each dried sample was pulverized using a porcelain mortar and pestle. A half gram dry weight of the powdered form of muscle and gill compared in duplicate were digested using laboratory hot water bath. The samples were digested by adding 3 ml of nitric acid (65%) and 1ml hydrogen peroxide (35%)(Taghipoura and Aziz, 2010). The samples were then transferred to clean volumetric flasks, and diluted to 50ml with deionized water, and filtered using Whatman filter paper ( $0.45\mu$ m). All analysis was processed in triplicate. Heavy metals (Pb, Cd, Fe, Cu, Cr and Zn) were determined in this solution, using Atomic Absorption Spectrophotometry (AAS, Bulk Scientific). All the plastics and glassware were washed in nitric acid for 15 min and rinsed with deionized water before being used.

### **RESULTS AND DISCUSSION**

The results of the control and water analysis are summarized in table 1 and 2 respectively. Concentration of Pb, Cd, Fe, Cu, Cr and Zn in the gills and muscles of the catfish were summarized in tale 3. The concentrations of Heavy metals in the water and fish tissues were compared with the corresponding permissible limits established by the World Health Organization (2003). According to WHO (2003), the permissible limits for Pb, Cd, Fe, Cu, Cr and Zn are 0.01, 0.003, 2.00, 2.00, 0.05 and 3.00-5.00 mg/l respectively.

The control samples of three catfishes (grown in distill water) were run in the machine (AAS) for each element that was being analyzed. Their absorbances were read. The mean of each three replicates was calculated and hence the detection limits determined for each element. The experimental values were all in good agreement with the WHO recommended values.

Parameters	Control Exp (n	MAL (WHO 2002) mg/l		
	Catfish Gills Catfish Muscle		2003) mg/1	
Lead (Pb)	0.01±0.001	$0.00 \pm 0.000$	0.01	
Cadmium (Cd)	0.004±0.000	$0.00 \pm 0.000$	0.003	
Iron (Fe)	3.12±0.007	1.63±0.002	2.00	
Copper (Cu)	0.12±0.001	0.15±0.001	2.00	
Chromium (Cr)	$0.01 \pm 0.001$	$0.00 \pm 0.000$	0.02±0.001	
Zinc (Zn)	3.17±0.001	2.24±0.002	3.00 - 5.00	
Results are in mean±SE				

### Table 1 Control Experimental Value with the recommended WHO Value

# Table 2 Water Analysis of freshwater Samples from Nike Lake, Ebenyi River and Oji River during Rainy Season

Parameters	Nike Lake	Ebenyi River	Oji River	MAL (WHO 2003) mg/l
рН	7.12±0.010	6.21±0.009	7.18±0.015	6.50
Conductivity (µs/cm)	91±1.060	223±1.050	112±1.050	-
Total Solid (mg/l)	223±1.000	451±1.150	113±0.250	500
Total dissolved solid (mg/l)	327±1.250	570±1.060	302±1.000	-
Total suspended solid (mg/l)	186±1.150	306±1.000	104±0.250	-
Turbidity (mg/l)	8.26±0.024	34.16±0.010	6.48±0.010	5.00
Chloride (mg/l)	15.79±0.009	11.20±0.008	9.23±0.005	250
Sulphate (mg/l)	51.27±0.014	57.37±0.010	37.51±0.010	250
Nitrate (mg/l)	$1.28 \pm 0.005$	$1.81 \pm 0.007$	1.25±0.007	50
Phosphate (mg/l)	$0.14 \pm 0.002$	0.30±0.005	$0.09 \pm 0.005$	-
Dissolved Oxygen	7.51±0.009	5.33±0.004	8.53±0.010	-

(mg/l)				
Biochemical oxygen demand (mg/l)	0.40±0.002	0.83±0.003	0.38±0.002	-
Lead (Pb) (mg/l)	0.15±0.002	$0.48 \pm 0.002$	0.03±0.001	0.01
Cadmium (Cd) (mg/l)	$0.08 \pm 0.005$	$0.05 \pm 0.005$	$0.02 \pm 0.001$	0.003
Iron (Fe) (mg/l)	0.39±0.005	0.58±0.006	0.32±0.003	2.00
Copper (Cu) (mg/l)	$0.42 \pm 0.005$	1.24±0.004	1.12±0.005	2.00
Chromium(Cr) (mg/l)	$0.10 \pm 0.005$	0.35±0.010	$0.05 \pm 0.005$	0.05
Zinc (Zn) (mg/l)	1.27±0.003	2.70±0.007	2.10±0.005	3.00 - 5.00
Results are in mean±SE				

The results of the water analysis of the three freshwater sources showed the pH level of all the water samples were slightly above the WHO maximum allowable limit (6.50), making the water to be slightly alkaline. The total solid observed in all the water samples from the three freshwater sources were below the WHO maximum allowable limit (500). The turbidity of all the water samples were above the WHO maximum allowable limit (5.00) making the dissolved oxygen of the water samples relatively low. The heavy metal Pb and Cd analyzed were above WHO maximum allowable limit (0.01 and 0.003 respectively). While Fe, Cu, Cr and Zn concentrations observed in all the water samples were below WHO maximum allowable limit (2.00, 2.00, 0.05, and 3-5.00 mg/kg).

### Heavy Metals in Catfish Tissues from Freshwater Source in Enugu State during Rainy Season

The table 3 presents the mean concentrations of Pb, Cd, Fe, Cu, Cr and Zn in the gills and muscles of catfish from Nike Lake, Ebenyi River and Oji River analyzed using AAS.

Paramete r	Nike Lake		Ebenyi River		Oji Wonderful		MAL
	Gill (mg/kg)	Muscle (mg/kg)	Gill (mg/kg)	Muscle (mg/kg)	Gill (mg/kg)	Muscle (mg/kg)	2003) mg/l
Pb	0.06±0.002 a	0.04±0.004 a	0.03±0.002 <sup>a</sup>	0.01±0.002 ab	0.05±0.001 a	0.02±0.005 ab	0.01
Cd	0.04±0.008 a	0.01±0.000 1 <sup>ab</sup>	0.01±0.0005 ab	0.01±0.000 1 <sup>ab</sup>	0.01±0.000 1 <sup>ab</sup>	0.00±0.000 ab	0.003
Fe	1.23±0.007 ab	0.85±0.009 ab	1.88±0.012 <sup>a</sup> bc	1.24±0.006 ab	1.63±0.018 abc	1.08±0.013 abc	2.00
Cu	0.24±0.000 7 <sup>a</sup>	0.10±0.008 ab	0.19±0.010 <sup>a</sup> b	0.03±0.004	0.97±0.015 ba	0.43±0.010 ba	2.00
Cr	0.01±0.004 a	0.00±0.000 a	0.00±0.000 <sup>a</sup>	0.00±0.000 a	0.01±0.000 1 <sup>a</sup>	0.01±0.000 1 <sup>a</sup>	0.05
Zn	1.77±0.007 a	0.96±0.012	1.59±0.012 <sup>a</sup> bc	1.01±0.008 bc	1.22±0.008	0.77±0.010 abc	3.00- 5.00

## Table 3 Heavy Metals in the Gills and Muscles of African Catfish from the Nike Lake,Ebenyi River and Oji River during Rainy Season

Results are in mean±SE. Alphabets shows the differences in the mean. The same alphabets within a row are not significantly different at p<0.05

The mean concentration of Pb observed in the tissues of samples from all three freshwater sources are higher than WHO maximum allowed limit (0.01mg/kg) except for the concentration of Pb observed in the muscle of samples from Ebenyi River, which is similar to WHO maximum allowed limit. The gill sample from Nike Lake has the highest concentration of Pb (0.06mg/kg). ANOVA at 95% confidence level reveals that the mean concentration of Pb observed in the muscles of samples from Ebenyi and Oji River varies significantly to the mean concentration observed in the gills and muscles of the other samples. The concentration of Cd observed in the tissues of all the samples from the three freshwater sources were above the WHO maximum allowed limit (0.003mg/kg) except for the muscle samples from Oji River, which was below detection. The gill sample from Nike Lake which has the highest concentration of Cd

(0.04mg/kg) varies significantly to the concentration of Cd observed in the tissues of the other samples from the three freshwater sources.

The mean concentration of Fe observed in all the tissue samples from the three freshwater sources were below WHO maximum allowed limit (2.00mg/kg). The highest concentration of Fe was observed in the gill samples from Ebenyi River. ANOVA at 95% confidence level reveals that the mean concentration of Fe observed in the gills of samples from Ebenyi River and the gills and muscles of samples from Oji River varies significantly to the concentrations of Fe observed in the other tissue samples from Nike and Ebenyi River. Similar to Fe, Cu concentrations in all tissue samples from the three freshwater sources were below WHO maximum allowed limit (2.00mg/kg). The highest concentration of Cu (0.97mg/kg) was observed in the gills of samples from Oji River. No significant difference exists between the mean Cu concentration of Cu in the gills and muscles of samples from Oji River. Also, the mean concentration of Cu in the gills and muscles of samples from Oji River.

The mean concentration of Cr observed in the tissue samples for all three freshwater sources were below WHO maximum allowed limit (0.05mg/kg). Cr was not detected in the gills and muscles of samples from Ebenyi River. There are no significant differences in the mean concentration of Cr observed in all samples from the three freshwater sources. The levels of Zn observed in the tissue samples from all three freshwater sources were below WHO maximum allowed limit (3.00-5.00mg/kg). The gills of samples from Nike Lake have the highest mean concentration of Zn (1.77mg/kg), while the least mean concentration of Zn was observed in the tissues of samples from Ebenyi River (1.01mg/kg). There were significant differences in the concentrations of Zn observed in the tissues of the samples from the three freshwater sources. Gill samples from Ebenyi River and muscle samples from Oji River vary significantly to samples from the three freshwater sources.

### DISCUSSION

The present study observed the presence of heavy metals (Pb, Cd, Fe, Cu, Cr, and Zn) in the tissues (gills and muscles) of *Clarias gariepinus* from three freshwater sources in Enugu state. There are some minerals which are useful for human and animal health in small doses beyond which, these are toxic. Zinc (Zn), Copper (Cu), Iron (Fe), etc. fall into this category (Rashmi and Pratima, 2013). The result from the water analysis showed a slightly alkaline pH value above WHO maximum allowable limit (6.50). The turbidity is high while the dissolved oxygen

the lethal effects on the aquatic organisms.

observed in all the water samples was relatively low. In view of this, the concentrations of heavy metals observed in the present study were low. This is in line with Siong *et al.*, (2016) that the mobility and availability of heavy metal in aquatic environments are primarily controlled by water quality parameters including pH, dissolved oxygen and organic matter content. Nwamba *et al.*, (2017) opined that, environmental factors such as pH, turbidity, dissolved oxygen, temperature and conductivity influence the rate of reaction of the pollutants entering the water or

The concentrations of Pb and Cd observed in the fish tissue samples in the present study were above WHO maximum allowable limit (0.01 and 0.003 mg/kg respectively). Lead (Pb) may slow cognitive development, impair intellectual performance in children and is implicated for causing increase in blood pressure and cardiovascular diseases (Georgescu *et al.*, 2011). The mean concentrations of Cd in the fishes from the three water source were quite low but slightly above the maximum allowed WHO limit (0.003mg/kg). Low level of Cd (0.0072 mg/l) was also reported in the water from Niger Delta region of Nigeria by Wogu and Okaka (2011). The exposure of Cd and especially chronic exposure can cause renal dysfunction, calcium metabolism disorders and also increased incidence of some forms of cancer (Selinus and Alloway, 2005).

The concentrations of Fe, Cu and Cr for all the samples were below WHO maximum allowable limit (2.00, 2.00, and 0.05 mg/kg respectively). The levels of Zn observed in the tissues of all the samples were within the range of WHO maximum allowable limit (3-5.00mg/kg). All these heavy metals observed, showed higher concentrations in the gills of the fish samples than the muscles. This may be because the gills of fishes are directly in contact with the contaminated medium (these metals are first absorbed through the gills) and also have the thinnest epithelium when compared to other organs (Akpanyung *et al.*, 2014).

### CONCLUSION

The present study revealed considerable amount of heavy metals in the fish tissues and water samples from the three freshwater sources; Nike Lake, Ebenyi River and Oji River. The levels of Pb and Cd observed were above WHO maximum allowable limit. Fe, Cu, Cr and Zn were below WHO maximum allowable limits. In most cases, Ebenyi River showed higher levels of heavy metals than the other freshwater sources. Nike Lake likewise showed higher levels of heavy metals than Oji River which showed the least levels of heavy metals in the entire freshwater sources.

### RECOMMENDATION

Further study should be done to include more heavy metals to determine their contamination. This is because of their anthropogenic origin and lack of recommended dumpsite within the areas of study. Also, researches needs to be carried out to ascertain the blood level concentration of these heavy metals among the communities.

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