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Original Research Article

Contaminants Levels of African Cat Fish (*Clarias gariepinus*) Tissues: A Comparative Study of River Galma, River Kubanni and Fish Farms in Zaria, Nigeria

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Abstract

Bioaccumulation of heavy metals in tissues of marine organisms has been identified as an indirect measure of the abundance and availability of metals in the marine environment. Monitoring fish tissue contamination therefore serves an important function as an early warning indicator of sediment contamination or related water quality problems and enables appropriate action to be taken in order to protect public health and the environment. Trace elements contents of tissues of *Clarias gariepinus* from River Galma, River Kubanni and Fish farms in Zaria, Nigeria were investigated in the current work using Schimadzu atomic absorption spectrophotometer (model 6800, Japan) after wet digestion. Cadmium, Chromium and Nickel residues in the fish exhibited different patterns of distribution among the selected tissues and localities. It was evident from our study that, liver was the site of maximum accumulation for the elements followed by gills while muscle was the overall site of least metal accumulation. Cadmium and Chromium concentrations in fish tissues followed the order River Galma > River Kubanni > Fish Farms while Nickel followed the trend River Kubanni > River Galma > Fish Farms. The range of concentration was 0.02-16.33 mg/kg for Cadmium, 0.03-8.12 mg/kg for Chromium and 0.09- 13.90 for Nickel. These values were found to be higher than WHO/FAO maximum recommended limits in food fish. Consumption of Clarias gariepinus from the areas under study therefore poses serious toxicological risk. Implications of findings to public health are fully discussed.

Keywords: Clarias gariepinus, contamination, heavy metal, public health, toxicological risk

INTRODUCTION

Chemical substances that enter the water come from a myriad of sources. Until recently efforts towards the control of water pollutants have concentrated on point sources – easily identifiable sources such as effluent discharged pipes and other overflow devices. Non-point sources such as run-off from agricultural lands, roads, packing lots, mining sites and watersheds are increasingly being given more attention recently. The contamination of the waters, sediments and organisms of our rivers and other surface water bodies with a wide range of pollutants has become a matter of great concern world over especially in the last few decades. Water containing levels of pollutants so low that the water is deemed potable (fit to drink) can still be a source of problems due to biomagnifications, a phenomenon whereby chemical substances becomes increasingly more concentrated at successively higher trophic levels, which is a characteristic of substances that are fat soluble and difficult to be degraded to harmless substances (Suter, 1993). Metals are non-biodegradable and form part of environmental pollutants in which elevated levels forms threats to human health through food chain (Kusemiju et al., 2012). Heavy metals are natural components of the marine environment, but their levels have increased due to domestic, industrial, mining and agricultural activities (Bakan and Büyükgüngör, 2000; Altas and Büyükgüngör, 2007, Bat et al., 2012). The discharge of industrial wastes containing toxic heavy metals into water bodies may have significant effects on fish and other aquatic organisms, which may endanger public health. Marine organisms such as fish accumulate heavy metals to concentrations many times higher than present in water or sediment (Bat et al., 2012). When metals enter aquatic environment, a great portion settles and is absorbed by the bottom mud (Ada etal., 2012; Ayotunde, 2012), they could be recycled by chemical, physical and biological processes such that some quantity remains dissolved in the water column and some part absorbed by the inhabitants (Ada etal., 2012 and Kori-Siakpere and Ubogu, 2008). Fishes are at the apex of the marine food chain and can bioaccumulate some of these substances in their tissues (Ada etal., 2012; Olaifa *et al.,* 2004). Fish are therefore useful sentinel species bioindicators of metal pollution because they can help to understand the risk to aquatic ecosystem and to human (Peakall and Burger, 2003). Many biological factors of the fish such as age, lipid contents, mode of feeding and body size could play a role in the bioavailability of metals (Peakall and Burger, 2003). The use of wild and cultured fishes as biomonitors of metal pollution in the aquatic ecosystem is becoming popular throughout the world (Indrajith et al., 2008). Generally, the higher the metal concentration in the environment, the more the amount taken up and accumulated by fish. The quantity of metal accumulated has been reported to be directly related to the concentration to which the organisms are exposed and the period of exposure (Kusemiju et al., 2012, Kamaruzzaman *et al*., 2010). Metals are also preferentially accumulated by different organs of the body (Kusemiju et al., 2012, Rauf *et al*., 2009).

Clarias gariepinus is a very important source of animal protein in human diet. It forms a significant percentage of captured fish in River Galma and River Kubanni, Zaria, Nigeria, and is consumed in great quantities by the local dwellers. This study was aimed at Determining and comparing the concentration some metals namely, Cadmium (Cd), Chromium (Cr) and Nickel (Ni) in organs of *Clarias gariepinus* obtained from River Galma, River Kubanni and Fish farms in Zaria, with a view to having an insight into the pollution status of the rivers and ascertaining the suitability or otherwise, of the fish for human consumption by comparing concentrations obtained with FAO/WHO and Commission Regulation (EC) maximum recommended limits in food fish. The study also aimed at comparing the concentration of these heavy metals in *Clarias gariepinus* from River Galma, River Kubani and fish farms in Zaria. *Clarias gariepinus* is a bottom feeder, and ingestion of sediment will be reflected in the metal contents of their tissues (Udiba et al., 2013).

River Galma and River Kubanni serves as a major source of portable water and fish in Zaria. The Zaria dam is on River Galma and supply water to Zaria metropolis while the ABU dam is on River Kubanni and supply water to the Ahmadu Bello University community. Fishing is carried out daily on the two Rivers which also serve as a source of water for irrigation as the basins of the two rivers are booming crop farming areas. Most of the industries located in Zaria discharge their waste directly or indirectly into these rivers. Municipal and domestic wastes are also discharged directly or indirectly into the rivers (Nnaji et al., 2007, Udiba et al., 2013). Since there is no formal control of effluent discharge from industries and homes into the Rivers, it is important to monitor the levels of metals in fish from these rivers in comparison to what is obtained at privately owned fish farms. The concentration of Cadmium, Chromium and Nickel were measured in the head, gill, liver and muscle of fish in order to assess the potential risk associated with the consumption of fish from the study area.

MATERIALS AND METHODS

Study Location

Zaria is located at latitude 1103’N and longitude 7040’E, 128km South- East of Kano and 64km North-East of Kaduna City. River Galma is located at the southeastern part of Zaria and its source is the Jos Plateau. The Zaria dam is located on River Galma (Nnaji et al., 2007). Kubanni River originates in the precincts of the Ahmad Bello University (ABU) Main Campus, Zaria (Northern Nigeria), as a trench in an undulating agricultural land and is fed by a number of tributaries (Uzairu et al., 2009). Kubanni River drains the northwest zone of the city of Zaria and receives effluents mainly from domestic activity and runoff from intense cropping located in the adjoining land. The ABU dam is on the river (Uzairu et al., 2009).

Sample collection and preparation

Ten *Clarias gariepinus* each (mean weight 130±3g, Mean length 26.8±2.6cm) were obtained on site from fishermen at the two Rivers (River Galma, River kubanni) and five each from two fish farms in Sabon Gari area of Zaria, Nigeria. They were stored in a cooler packed with ice block in order to maintain the freshness and latter transported to the Environmental laboratory of the National Research Institute for Chemical Technology (NARICT), Zaria, Nigeria for dissection of the organs after

Table 1. Results of analysis of reference material (animal blood IAEA-A-13) compared to the certified reference value (mg/kg).

Element (mg/kg)	Pb	Ni	Cu	Fe	Zn
A Value	0.20	1.20	4.45	2389	14.2
R value	0.18	1.00	4.30	2400	13.0

***A Value** = Analyzed value **R Value** = Reference value.*

Table 2. Results of analysis of reference material (Lichen IAEA -336) compared to the certified reference value (mg/kg).

Element (mg/kg)	Pb	Cd	Cu	Mn	Zn
A Value	5.25	0.140	4.00	55.78	29.18
R value	4.2-5.5	0.1-2.34	3.1- 4.1	56-70	37-33.80

***A Value** = Analyzed value **R Value** = Reference value.*

being washed thoroughly. 5g (wet weight) of fish tissue was weighed and placed in a beaker, 10ml of freshly prepared concentrated nitric acid / hydrogen per oxide (1:1) was added and covered with a wash glass for initial reaction to subside. The beaker was placed on a water bath at a temperature not exceeding 80^{o}C for two hours to reduce the volume to 3-4ml. The digest was cold filtered into 50ml volumetric flask and made up to the mark with distilled deionized water.

Metal analysis

Metal analysis was carried out using flame atomic absorption spectrophotometer AA-6800 (Shimadzu, Japan) at National Research Institute for Chemical Technology (NARICT), Zaria-Nigeria. The calibration curves were prepared separately for each of the metals by running different concentrations of standard solutions. The instrument was set to zero by running the respective reagent blanks. Average values of three replicates were taken for each determination and were subjected to statistical analysis. The metals determined includes: Cadmium, Chromium, and Nickel.

Analytical Quality Assurance

The result of the analysis was validated by digesting and analyzing Standard Reference Materials, animal blood coded IAEA-A-13 and Lichens coded IAEA-336 following the same procedure. The analysed values and the certified reference values of the elements determined were compared to ascertain the reliability of the analytical method employed. Double distilled and deionized water was used throughout the experimentation. All the reagents used in this work were AnalaR grades from BDH Chemicals (UK).

Statistical Analysis

All statistical analyses were done by SPSS software 17.0 for windows.

Analysis of Variance Test

Data collected were subjected to statistical tests of significance using Analysis of Variance (ANOVA) with post hoc test analysis to assess significant variation in metal levels of *Clarias gariepinus* tissues across the three sources (River Galma, River Kubanni and fish farms). A P-value of 0.05 or less was considered statistically significant.

Pearson product moment Correlation Coefficient

Correlation coefficient was used to determine the association between the three metals (Cadmium, Chromium and Nickel) under consideration

RESULTS AND DISCUSSION

To evaluate the accuracy and precision of the analytical procedure employed, Standard reference materials of animal blood coded IAEA-A-13 and lichen coded IAEA-336 were analyzed in like manner to our samples. The analyzed values and the certified reference values of the elements determined were very close, suggesting the reliability of the method (Table 1 and 2).

The Mean concentration, standard deviation and range of Cadmium, Chromium and Nickel of tissues of *Clarias gariepinus* from River Galma, River Kubanni and fish farms in Zaria are presented in Table 3, Table 4 and Table 5 respectively. The distribution of Cadmium, Chromium and Nickel in the head, gills, liver and muscle

Table 3. Mean ± S.D, and Range of Cadmium, Chromium and Nickel in *Clarias garipenus* from River Galma, Zaria, Nigeria

Station	Element	Sample	Mean ± S.D	Range
River Galma	Cadmium	Head	0.18±0.15	0.02 – 0.31
		Gills	0.56±0.08	1.56 -1.72
		Liver	7.44±7.49	0.91 – 16.33
		Muscle	0.35 ± 0.04	0.32 – 0.39
		Average	2.40±4.60	0.02-16.33
	Chromium	Head	0.26±0.02	0.24 – 0.28
		Gills	0.56±0.18	0.38 – 0.75
		Liver	5.39±2.47	3.32 – 8.12
		Muscle	0.35±0.09	0.26 – 0.44
		Average	1.64±2.50	0.24-8.12
	Nickel	Head	2.91±1.50	1.70 – 4.59
		Gills	3.47±3.01	0.60 – 6.61
		Liver	5.08±4.40	2.01 – 10.12
		Muscle	1.80±0.88	0.99 – 2.75
		Average	3.31±2.70	0.60-10.12

Table 4. Mean ± S.D, and Range of Cadmium, Chromium and Nickel in *Clarias garipenus* from River Kubanni, Zaria, Nigeria

Station	Element	Sample	Mean ± S.D	Range
River Kubanni	Cadmium	Head	0.28±0.12	0.14 – 0.39
		Gills	0.82±0.24	0.55 – 1.03
		Liver	2.93±2.13	0.99 – 5.21
		Muscle	0.28±0.20	0.06 – 0.42
		Average	1.08±0.47	0.06-5.21
	Chromium	Head	0.63±0.57	0.06 – 1.21
		Gills	0.38±0.16	0.21 – 0.53
		Liver	1.56±1.00	0.95 – 2.71
		Muscle	0.48±0.06	0.42 – 0.54
		Average	0.76±0.70	0.06-2.71
	Nickel	Head	2.19±0.41	1.86 – 2.65
		Gills	4.16±1.99	2.64 – 6.41
		Liver	8.57±4.73	4.88 – 13.90
		Muscle	1.38±1,37	0.17 – 2.87
		Average	4.07±3.70	0.17-13.90

Table 5. Mean ± S.D, and Range of Cadmium, Chromium and Nickel in *Clarias garipenus* from Fish Farms in Zaria, Nigeria

Station	Element	Sample	Mean ± S.D	Range
Fish Farm	Cadmium	Head	0.63±0.08	0.56 – 0.72
		Gills	0.48±0.46	0.05 – 0.96
		Liver	1.10±0.50	0.69 – 1.65
		Muscle	0.33±0.18	0.15 – 0.50
		Average	0.63±0.42	0.05-1.65
	Chromium	Head	0.78±0.42	0.42 – 1.24
		Gills	0.40±0.06	0.35 – 0.46
		Liver	0.88±0.77	0.03 - 1.51
		Muscle	0.25±0.07	0.21 – 0.34
		Total	0.58±0.46	0.03-1.51
	Nickel	Head	1.70±1.39	0.09 – 2.58
		Gills	2.23±2.42	0.42 – 4.99
		Liver	1.33±1.08	0.43 – 2.53
		Muscle	1.11±1.82	0.58 – 4.12
		Average	1.84±1.54	0.09-4.99

of *Clarias gariepinus* across River Galma, River Kubni and fish farms in Zaria are shown in Figures 1, 2, 3 and 4 respectively. Percentage concentration of Cadmium, Chromium and Nickel of organs of *Clarias gariepinus*

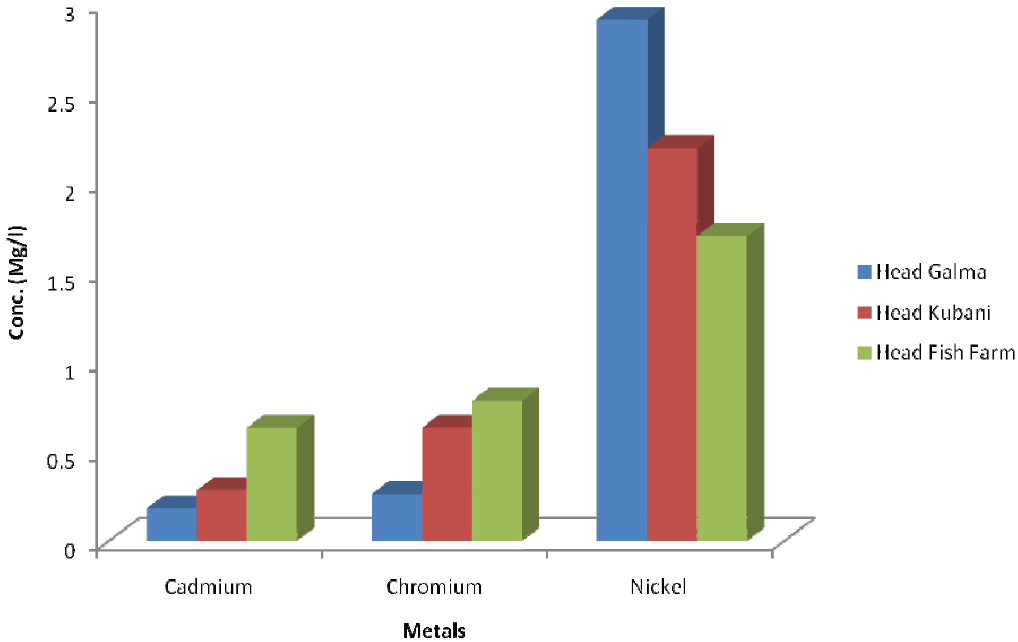

Figure 1. The dispersion of Cadmium, Chromium and Nickel in the head of *Clarias Gariepinus* across River Galma, River Kubanni and Fish farms in Zaria

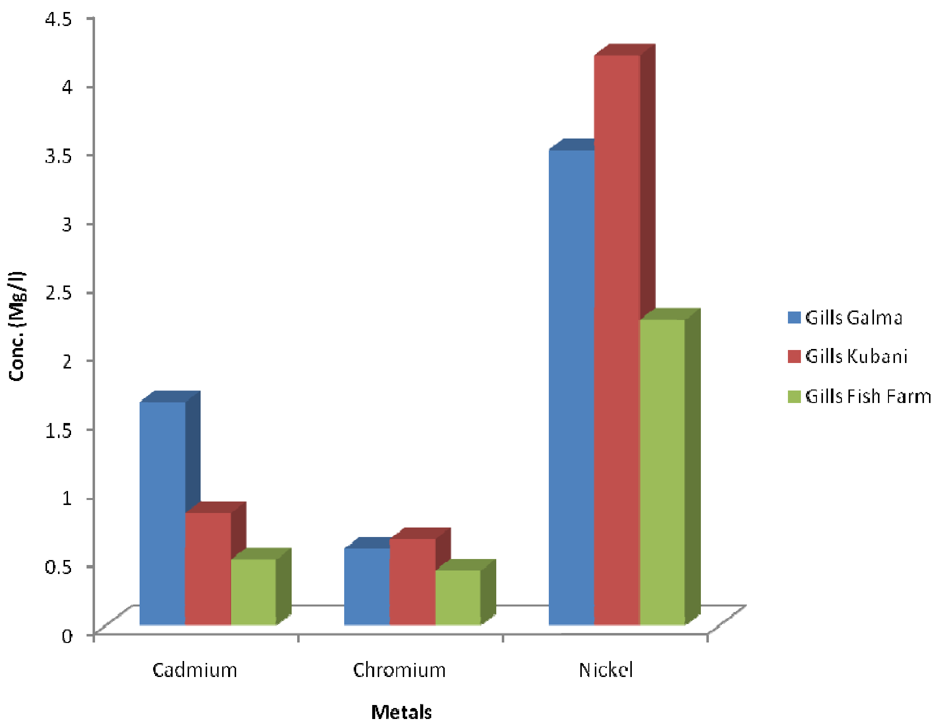

Figure 2. The dispersion of Cadmium, Chromium and Nickel in gills of *Clarias Gariepinus* across River Galma, River Kubanni and Fish farms in Zaria

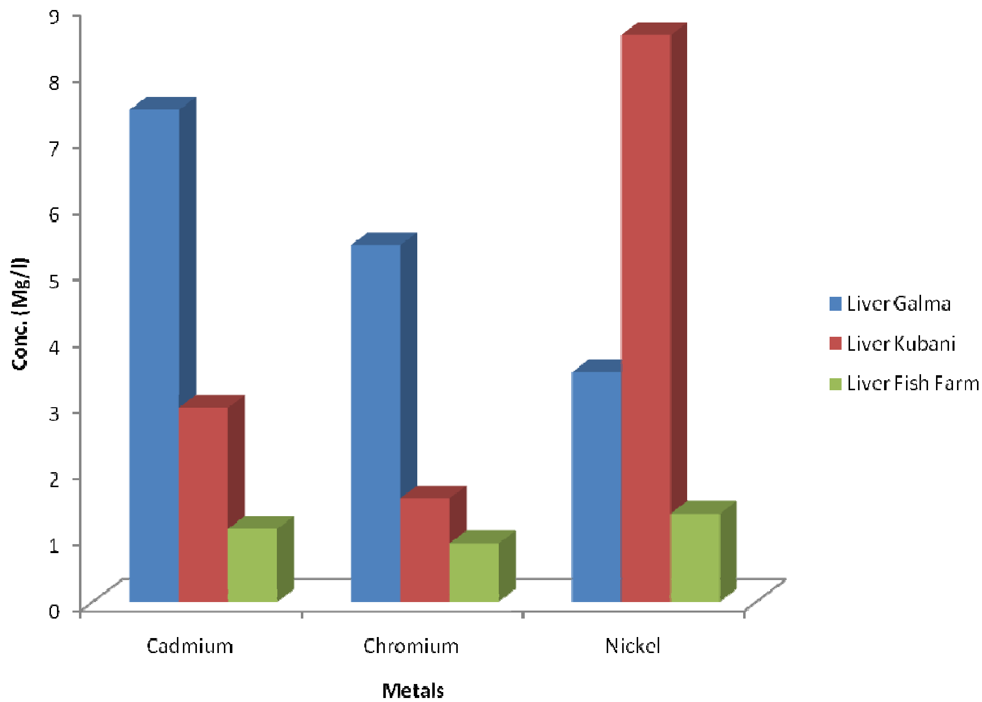

Figure 3. The dispersion of Cadmium, Chromium and Nickel in liver of *Clarias gariepinus* across River Galma, River Kubanni and Fish farms in Zaria

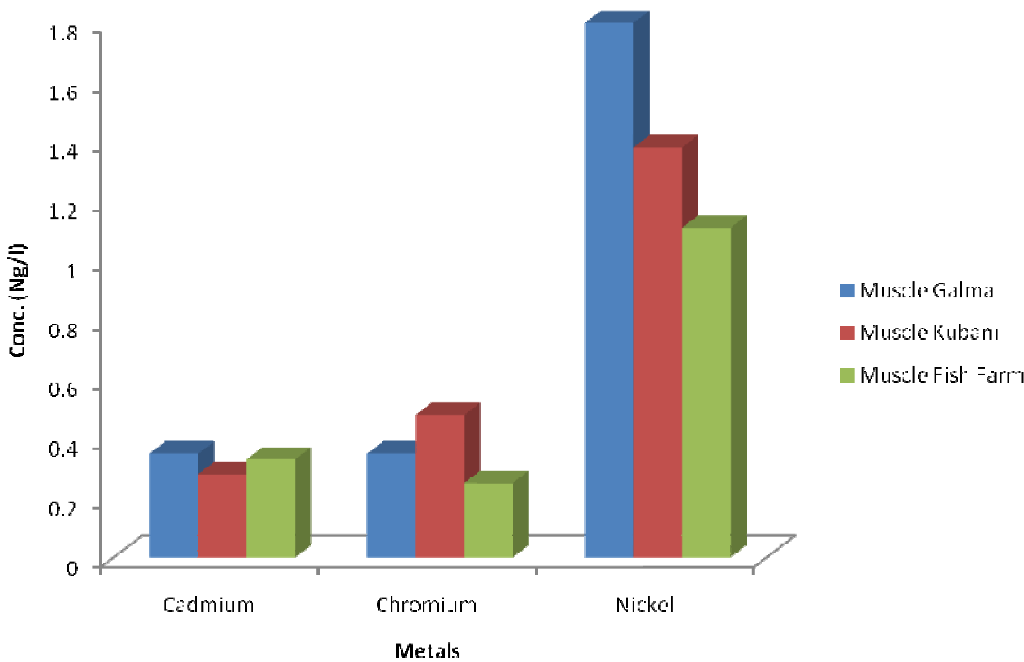

Figure 4. The dispersion of Cadmium, Chromium and Nickel in muscles of *Clarias Gariepinus* across River Galma, River Kubanni and fish Farms in Zaria

from River Galma, River Kubanni and fish farms in Zaria are shown in figures 5 – 12.

Average concentration of Cadmium in *Clarias gariepinus* tissues was found to be 2.40 mg/kg for River Galma, 1.08 mg/kg for River Kubanni and 0.64 mg/kg for Fish farms (Table 3, 4 and 5). The order of detection therefore was River Galma > River Kubanni > Fish farms. No statistically significant difference (ANOVA; P > 0.05)

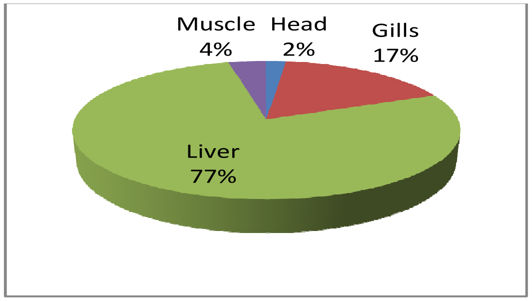

Figure 5: Percentage concentration of cadmium in organs of *Clarias gariepinus* from River Galma

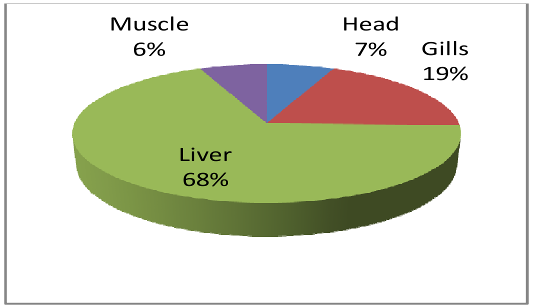

Figure 6: Percentage concentration of cadmium in organs of *Clarias gariepinus* from River Kubanni

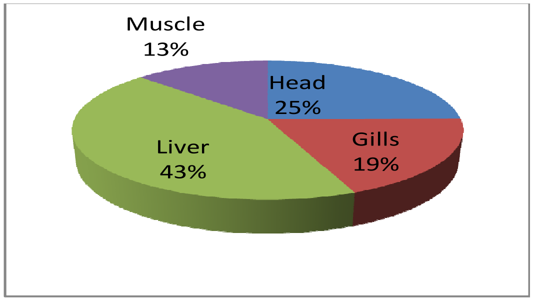

Figure 7. Percentage concentration of cadmium in organs of *Clarias gariepinus* from Fish farms in Zaria

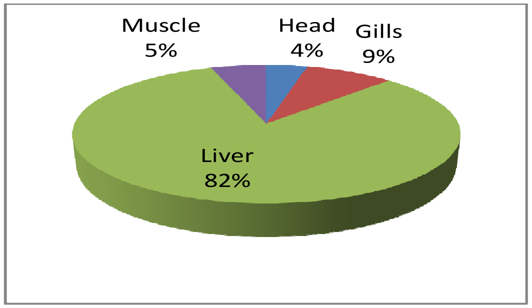

Figure 8. Percentage concentration of Chromium in organs of *Clarias gariepinus* from River Galma

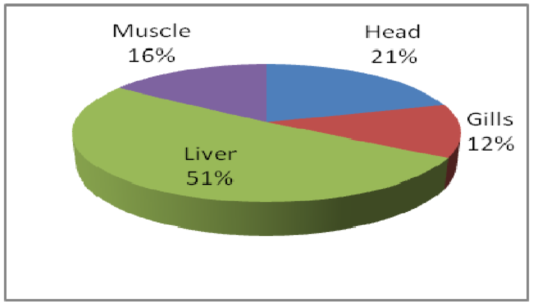

Figure 9. Percentage concentration of Chromium in organs of *Clarias gariepinus* from River Kubanni

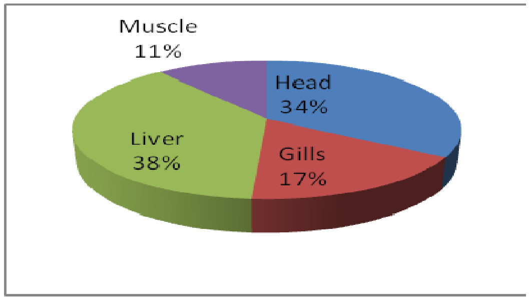

Figure 10. Percentage concentration of Chromium in organs of *Clarias gariepinus* from Fish farms in Zaria

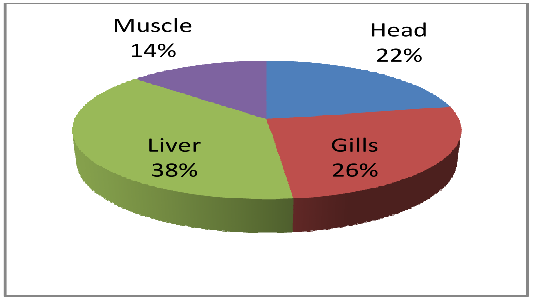

Figure 11. Percentage concentration of Nickel in organs of *Clarias gariepinus* from River Galma

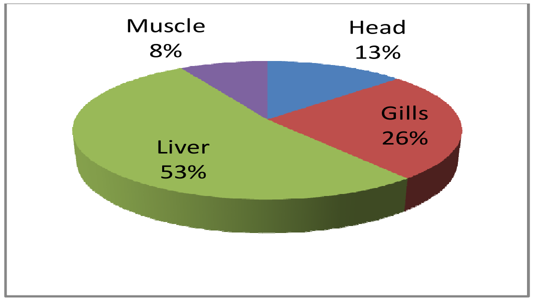

Figure 12. Percentage concentration of Nickel in organs of *Clarias gariepinus* from River Kubanni

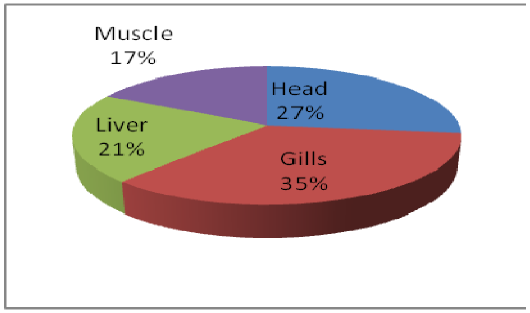

Figure 13. Percentage concentration of Nickel in organs of *Clarias gariepinus* from Fish farms

in cadmium concentration of *Clarias gariepinus* tissues (Head, gills, liver and muscles) was observed in each of the sampling stations (River Galma, River Kubanni and Fish farms). The detection of cadmium in the tissues followed the order liver > gills > muscle > head for River Galma, liver > gills > muscle = head for River Kubanni and liver > head > gills > muscle for Fish farms. The highest concentration of Cadmium was recorded in the liver in each of the sampling stations. The lowest concentration of Cadmium was recorded in head, muscle and gills in River Galma, River Kubanni and Fish farms respectively (Figure 1). Findings of this study shows that the percentage concentration of Cadmium in *Clarias gariepinus* tissue was Head 2%, Gills 17%, Liver 77% and Muscle 4% for River Galma, Head 7%, Gills 19%, Liver 68% and Muscle 6% for River Kubanni and Head 25%, Gills 19%, Liver 43% and Muscle 13% for Fish Farms (figures 5 - 7). Preferential accumulation of metals in the liver and gills has also been reported by Jantateemes *et al*., 1999; Raoud and Al-Dahshan, 2010). Muscles are known to show lower metal and concentrations than other organs (Falusi and Olanipekun, 2007). High accumulating ability of the liver is said to be the result of the activity of metallothioneins, the proteins that can bind to some metals, thus reducing their toxicity and allowing the liver to accumulate high concentrations (Udiba et al., 2013; Dahunsi et al., 2012; Wu et al., 2006). Due to the above reason, Liver has been recommended as the best environmental indicator of both the water pollution and chronic exposure to heavy metals (Dahunsi et al., 2012). The lower concentration of Cadmium in the gill than that of livers may possibly be due to lower binding affinity of Cadmium on the gill surface. Gills which are in direct contact with water accumulated some amount of heavy metals. The accumulation of such metals in the gills may be due to adsorption to the gill surfaces and dependent on the availability of proteins to which these metals may bind (Osman and Kloas, 2010). The low accumulation of metals in muscle may be due to lack of binding affinity of these metals with the proteins of muscle. This is particularly important because muscles contribute the greatest mass of the flesh that is consumed as food. The range of cadmium concentration reported in the muscles of *C. gariepinus* in this study was found to be in broad agreement with the studies by Osman and Kloas (2010) who reported a range of 0.20 - 0.78 mg/kg in the muscle of *C. gariepinus* from River Nile in Egypt. The range of cadmium concentration reported in liver and gills of *C. gariepinus* in this study is found to be above 0.57- 4.92mg/kg and 0.43- 0.90 reported by Osman and Kloas (2010) for liver and gills *C. gariepinus* from River Nile in Egypt. Eneji et al., (2011) reported lower cadmium concentration of 0.325mg/kg in gills of *C. gariepinus* from River Benue. Lower mean cadmium concentration of 0.927 mg/kg in *C. gariepinus tissues* was also reported (Eneji et al., 2011) and 0.190mg/kg by Ezemonye and Egbroge (1992) for Niger Delta Area.

Statistical analysis also showed significant (ANOVA, $p < 0.05$) differences the concentration of cadmium in head and gills of *Clarias gariepinus*. The mean concentration of cadmium in the head was found to be significantly higher for *Clarias gariepinus* from Fish farms than *Clarias gariepinus* from River Galma and River Kubanni. The order of detection was Fish farm > River Kubanni > River Galma (Figure 1). The difference in concentration of cadmium in the head of *Clarias gariepinus* from River Galma and River Kubanni was not statistically significant ($P > 0.05$). Cadmium concentration in the gills of *Clarias gariepinus* from River Kubanni was found to be significantly higher than that from River Galma. The trend was River Kubanni > River Galma > Fish farms (Figure 2). The difference in cadmium concentration of the liver and muscles across the sampling stations was not statistically significant at 95% confidence level. The order of detection was River Galma > River Kubanni > Fish farms for liver (figure 3) and River Galma > Fish farms > River Kubanni for muscles (figure 4).

The European Community threshold value of Cadmium concentration in food fish is 0.05mg/kg wet weight (EC, 1998; EU, 2002). Uptake of 3–330mg/day is toxic and 1.5–9 mg/day is lethal to humans (Zhang et al., 2007). The average Cadmium concentration recorded in *Clarias gariepinus* tissues in this study was found to be several folds above the acceptable limits. Consumption of *Clarias gariepinus* from the three sampling stations therefore poses serious risk of cadmium intoxication. Cadmium is highly toxic non-essential heavy metal and it does not have a role in biological processes in living organisms. Thus even in low concentration, Cadmium could be harmful to fishes. Cadmium injures kidneys causing impairment of kidney function, poor reproductive capacity, hypertension, tumours and hepatic dysfunction (Zhang et al., 2007). The elevated Cadmium concentration in fish from River Galma and River Kubanni may be attributed to industrial discharges and runoff of agricultural agrochemicals into the rivers. This was expected due to the fact that the water of both rivers receives high concentrations of organic and inorganic pollutants from industrial, domestic as well as runoff agrochemicals from the rich agricultural basin. On the other hand, feed stuff and water used in the fish farms may be responsible for the elevated levels of Cadmium in *Clarias gariepinus* from Fish farms.

The highest mean of total Chromium concentrations (1.64±2.50 mg/kg) was measured in *Clarias gariepinus* from River Galma (Table 3) while the lowest mean of total Chromium concentration (0.58±0.46mg/kg) was measured in *Clarias gariepinus* from Fish Farms (Table 5). Chromium contents of *Clarias gariepinus* from the three sampling locations followed the trend: River Galma > River Kubanni > Fish Farms. No statistical significant difference was observed in Chromium levels cross the locations (ANOVA, $p > 0.05$). A statistically signify-cant difference in Chromium concentration was observed between liver and other fish tissues (ANOVA, $P < 0.05$), with chromium concentration of the liver being significantly higher than the concentration in head, gills and muscles. Similar findings have also been recorded (Osman and Kloas 2010). Chromium content of *Clarias gariepinus* tissues followed the trend; liver > gills > muscle > head, for River Galma, liver > head > muscles > gills for River Kubanni, and liver > head > gills > muscle for Fish Farms (figures 8, 9, 10).

The highest concentration of Chromium was recorded in the liver in each of the sampling stations (table 3, 4 and 5). The lowest concentration was recorded in the head for River Galma, gills for River Kubanni and muscle for fish farms. Statistically significant difference in chromium concentration in *Clarias gariepinus* liver was observed across the three sampling locations at 95% confidence level. Chromium concentration in liver followed the order: River Galma > River Kubanni > Fish Farms (Figure 3). The tissue with the second highest Chromium concentration was the gills for River Galma, head for River Kubanni and muscle for Fish farms (figure 8, 9, 10). Chromium concentration in gills followed the order; River Galma > Fish Farms > River Kubanni (Figure 2). No statistically significant (ANOVA, $p > 0.05$) difference in chromium concentration was observed in the gills across the sampling locations. Chromium concentration of the head followed the order; Fish Farms >River Kubanni > River Galma (Figure 1). Statistical analysis also revealed no significant (ANOVA, $p > 0.5$) difference in Chromium concentration of head of *Clarias gariepinus* across the sampling stations. Chromium concentration in fish muscle on the other hand followed the order; River Kubanni > River Galma > Fish farms (Figure 4). The concentration of Chromium in the muscles of *Clarias gariepinus* from River Kubanni was found to be significantly higher than Fish farms. The difference in Chromium concentration of *Clarias gariepinus* Muscles between River Galma and River Kubanni, and between River Galma and Fish farms were not statistically significant (ANOVA, $p > 0.05$). The percentage concentration of Chromium in *Clarias gariepinus* organs was Head 4%, Gills 9%, Liver 82% and Muscle 5% for River Galma, Haed 21%, Gills 12%, Liver 51% and Muscle 16% for River Kubanni and Head 34%, Gills 17%, Liver 38% and Muscle 11% for Fish Farms (figures 8 - 10). The toxicity of Chromium is dependent on its chemical speciation. The associated health effects are influenced by the chemical form of the element to which organisms are exposed (Avenant-Oldewage and Marx, 2000). There are four states in which the Chromium ion is found: Cr^{2+}, Cr^{3+}, Cr^{5+} and Cr^{6+}. It is in the hexavalent form where Chromium is allowed to cross biological membranes of aquatic organisms (Avenant-Oldewage and Marx, 2000). Hexavalent Chromium behaves toxicologically in a manner quite different from most heavy metals. Because hexavalent Chromium can readily penetrate gill membranes by passive diffusion and concentrate at higher levels in various organs and tissues, it can manifest its toxic action internally as well as on the gill surface (Avenant-Oldewage and Marx, 2000). Chromium is particularly dangerous as it is a accumulative poison and bioaccumulate along the food change, sometimes as much as 4 000 times above the level of the surrounding environment. The findings of this study indicates that the average concentrations of Chromium measured in *Clarias gariepinus* from Rivier Galma (1.64mg/kg) was higher than the FAO/WHO recommended limits of 0.15-1.00ppm in fish foods (Murtala et al., 2012). Average concentrations of Chromium measured in *Clarias gariepinus* from River Kubanni (0.76mg/kg) and Fish Farms (0.58mg/kg) were below the FAO/WHO limit. Consuming *Clarias gariepinus* from River Galma Zaria thus pose significant toxicological risk with respect to Chromium intoxication. The results in this investigation were lower than 28.1 – 32.2ppm in *C. gariepinus* for River Benue reported by Eneji *et al.,* 2011. Raphael et al., 2011 reported lower values of 0.04 mg/kg, 0.i4 mg/kg, and 0.04 mg/kg for gills, liver and muscles of cat fish from Okumeshi river in Delta State, Nigeria. Mean Nickel concentration ranging from 4.22±1.77-8.46 mg/kg, 3.74-4.29 mg/kg and 2.37-5.47mg/kg was recorded for gills, liver and muscles of *Clarias gariepinus* from different site across River Nile, Egypt (Osman and Kloas 2010). The accumulation of Cr in gill tissue is usually associated with structural damage to the gill epithelium as well as impaired respiratory and osmoregulatory function in fish (Burton et al., 1972).

The lowest average concentration of Nickel (1.84mg/kg) was measured in *Clarias gariepinus* from Fish Farms (Table 5) while the highest average concentration (4.07 mg/kg) was measured in *Clarias gariepinus* from River Kubanni (table 4). The trend of Nickel in *Clarias gariepinus* from the three sampling locations was River Kubanni > River Galma > Fish Farms. Statistical analysis revealed that the difference in total Nickel concentrations between River Galma and River Kubanni, between River Galma and Fish Farm, and between River Kubanni and Fish Farm were not statistically significant (ANOVA, $p > 0.05$). There was no statistically significant difference in Nickel levels between the tissues (head, gills, liver and muscle) of *Clarias gariepinus* at 95% confidence level. The trend of Nickel in organs of *Clarias gariepinus* from River Galma and River Kubanni was liver > gills > head > muscle, while that of fish farms was gills > liver > head > muscle. The highest concentration of Nickel in the tissues of *Clarias gariepinus* from River Galma and River Kubanni was recorded in the liver (Table 3 and 4) while that of Fish farms was recorded in the gills (Table 5). The lowest concentrations were recorded in muscle in each station. Nickel concentration in liver followed the order: River Kubanni > River Galma > Fish farms (Figure 3). There was no statistically significant difference in liver Nickel concentration across the three stations (ANOVA < 0.05).

In this study gills recorded the second highest concentration in fish tissues. Nickel concentration in gills also followed the order River Galma > River Kubanni > Fish Farms (Figure 2). The difference in Nickel concentration across the three stations was not statistically significant at 95% confidence level. Nickel concentration in fish head followed the order River Galma > River Kubanni > Fish Farms (figure 1). There was no statistically significant difference in Nickel levels of the head across River Galma, River Kubanni and Fish Farms (ANOVA, p > 0.5). It was observed that Nickel concentration in muscle followed the order River Galma > River Kubanni > Fish Farms (figure 4). There was no statistically significant difference in Nickel levels in muscles across the three sampling locations (ANOVA, p > 0.05). Findings of this study shows that the percentage concentration of Nickel in *Clarias gariepinus* tissues was Head 22%, Gills 26%, Liver 38% and Muscle 14 % for River Galma, Head 13%, Gills 26%, Liver 21% and Muscle 8% for River Kubanni and Head 27%, Gills 35%, Liver 21% and Muscle 17% for Fish Farms (figures 11 - 13).

Raphael et al., 2011 reported 0.05 mg/kg, 0.09 mg/kg, and 0.13 mg/kg for gills, liver and muscles of cat fish from Okumeshi River in Delta State, Nigeria. These values were actually lower than the findings of this study. Kumar etal., 2011 reported a mean value of 4.03±0.55 mg/kg for selected aquaculture ponds in East Kolkat Wetlands. WHO, (1985) and FOA, 1983 limits for Nickel in food fish is 0.5 – 0.60 mg/kg. Nickel level recorded in this work was above the allowable limit. Consumption of *Clarias gariepinus* from the three sampling locations therefore poses serious risk with respect to nickel intoxication. Acute over exposure to Nickel is not known to cause any health problems, but chronic exposure can cause decreased body weight, heart and liver damage, thyroid disease, cancer and skin irritation. Other toxic effects of Nickel observed following chronic exposure include chronic bronchitis, emphysema, reduced vital capacity and asthma. Nickel can accumulate in aquatic life, but its presence is not magnified along food chains. (Environment Agency, 2009).

CONCLUSION

To constantly monitor our environment especially that which contain our food organisms is absolutely important. In this study, Cadmium, Chromium and Nickel levels were investigated in *Clarias gariepinus* from River Galma, River Kubanni and Fish farms in zaria, Nigeria. The investigation shows that the concentration of the three metals exceeded WHO/FAO allowable limits in food fish. The order of detection of Cadmium and Chromium in *Clarias gariepinus* was River Galma > River Kubanni > Fish Farms. Nickel concentration followed the order River Kubanni > River Galma > Fish Farms. Liver and gill tissues showed higher metal concentrations than muscle tissue. The higher level of trace elements in liver relative to other tissues was attributed to the affinity or strong coordination of metallothionein protein with these elements. Consumption of *Clarias gariepinus* from the three sampling stations therefore poses significant health risk with respect to Cadmium, Chromium and Nickel intoxication. The high concentrations of metals recorded in the study may suggest sediment or surface water contamination.

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REFERENCES

Ada FB, Ekpenyong E, Bayim BP (2012). Heavy metal concentration in some fishes (*Chrysichthys nigrodigitatus, Clarias gariepinus and Oreochromis niloticus*) in the Great Kwa River, Cross River State, Nigeria. Global Advanced Research J. Environ. Sci. Toxicol. (ISSN: 2315-5140) Vol. 1(7) pp. 183-189,

Altas L, Büyükgüngör H (2007). Heavy Metal Pollution in the Black Sea Shore and Offshore of Turkey. *Environmental Geology*, 52(3): 469-476.

Avenant-Oldewage A, Marx HM (2000). Bioaccumulation of chromium, copper and iron in the organs and tissues of Clarias gariepinus in the Olifants River, Kruger National Park. *Water SA* 26 (4) 569 – 582.

Bakan G, Büyükgüngör H (2000). The Black Sea. *Marine Pollution Bulletin,* 41(1-6): 24-43.

Bat L, Sezgin M, Üstün F, Şahin F (2012). Heavy Metal Concentrations in Ten Species of Fishes Caught in Sinop Coastal Waters of the Black Sea, Turkey. *Turkish J. Fisheries and Aqua. Sci. 12, 371-376.*

Burton DT, Jones AH, Cairns J (1972). Acute zinc toxicity to rainbow trout (*Salmo gairdneri*): Confirmation of the hypothesis that death is related to tissue hypoxia. *J. Fish. Res. Bd. Can.* 29 1463-1456.

Dahunsi SO, Oranusi SU, Ishola RO (2012). Differential bioaccumulation of heavy metals in selected biomarkers of *Clarias gariepinus* (Burchell, 1822) exposed to chemical additives effluent, J. Res. Environ. Sci. Toxicol. Vol. 1(5) pp. 100-106

EC Directive. 02/221EEC (1998). European commission for standardization. European standard, maximum levels for heavy metal concentration in marine fish.

Eneji IS, Rufus S, PA Annune (2011). Bioaccumulation of Heavy Metals in Fish (*Tilapia Zilli* and *Clarias Gariepinus)* Organs from River Benue, North– Central Nigeria. Pak. J. Anal. Environ. Chem. Vol. 12, No. 1 and 2 (2011) 25-31

Environment Agency (2009). *Contaminants in soil: updated collation of toxicological data and intake values for humans. Nickel*. Science Report SC050021/SRTOX8. Bristol: Environment Agency).

EU, (2002). The Commission of the European Communities, Commission regulation (EC) No 221/2002 amending regulation (EC) No 466/2001 setting maximum levels for certain contaminants in food stuff in order to protect public health. Official Journal of the European Communities 7.2.2002, L37/5L37/6

Ezemonye LIN, Egbroge ABM (1992) National Seminar on petroleum: Petroleum Training Institute, Warri. Technical papers, 3, 91.

FAO (1983). Compilation of Legal Limits for hazardous substances in fish and fishery products. FAO Fishery circular no. 464. pp5-100.

Indrajith H, Pathiratne KAS, Pathiratne A (2008). Heavy Metl Leevels in two Food Fish Species from Negombo Estuary, Sri Lanka: Relationship with the Body Size. *Sri Lanka J. Aqua. Sci.* 13, 63-81.

Kamaruzzaman BY, Akbar B, Jalal KCA, Shahbudin S (2010). Accumilation of metals in the gills of Tilapia fingerlings (*Oreochromis niloticus*) from invitro toxicology study. *J. Fish. Aquat. Sci.* 5(6):503-509.

Kori-Siakpere D, Ubogu E (2008). Sub lethal haematological Effects of Zinc on the fresh water fish, *Heteroclarias sp. (Osteichthyes: Claridae). Afri. J. Biotechnol. 7(12): 2068 – 2073*

Kusemiju V, Amoruwa P, Aderinola JO (2012). Accumulation of lead in the tissues of freshwater catfish *Clarias gariepinus* exposed to static nominal concentrations of lead nitrate. Agric. Biol. J. North Ame. 3(12): 510-515

Murtala BA, WO Abdul, AA Akinyemi (2012). Bioaccumulation Of Heavy Metals In Fish (Hydrocynus Forskahlii, Hyperopisus Bebe Occidentalis And Clarias Gariepinus) Organs In Downstream Ogun Coastal Water, Nigeria, Transnational J. Sci. Technol. June edition vol. 2, No.5

Nnaji JC, Uzairu A, Harrison GFS, Balarabe ML (2007). Evaluation of Cadmium, Chromium, Copper, Lead And Zinc Concentrations in the Fish Head/Viscera of Oreochromis Niloticus and Synodontis Schall of River Galma, Zaria, Nigeria, *Ejeafche, 6 (10),* 2420-2426

Olaifa FE, AK Olaifa, AA Adelaja, AG Owolabi (2004). Heavy Metal contamination of *Clarias gariepinus* from a lake and fish farm in Ibadan, Nigeria. Afr. J. Biomed. Res. 7: 145-14

Osman AGM, Kloas W (2010). Water Quality and Heavy Metal Monitoring in Water, Sediments, and Tissues of the African Catfish *Clarias gariepinus* (Burchell, 1822) from the River Nile, Egypt. J. Environ. Protection, 2010, 1, 389-400.

Peakall D, Burger J (2003). Methodology for Assessing Exposure to Metals: Speciation Bioaavailbility of Metals and Ecological Host Factors. *Ecotoxicology and Environmental Safty*, 56,110-121

Raphael EC, AC Ogbuinyi, EO Frank (2011). Metal distribution in Fish Tissues, Bottom Sediments and water from Okumeshi River, in Delta State, Nigeria. Environ. Res J. 5(1), 6-12

Rauf A, Javed M, Ubaidullah M (2009). Heavy metal levels in three major carps *(Catla catla, Labeo rohita* and *Cirrhina mrigala*) from the river ravi, Pakistan. *Pak. Vet. J.* 29:24-26.

Suter GW (1993). *Ecological Risk Assessment*, Lewis Publishers, Boca Raton, 538 p.

Udiba UU, Odey MO, Gauje B, Ezike NN, Aribido OS, Otori M, Umar S, Ashade N (2013b). Toxicity Potential of African Cat Fish (*Clarias gariepinus*) Tissues: A Comparative Study of River Galma, River Kubanni and Fish Farms in Zaria, Nigeria, *Eur. J. Zool. Res.2(6), 210-221*

Uzairu A, GFS Harrison, ML Balarabe, JC Nnaji (2009). Concentration Levels of Trace Metals in Fish and Sediment from Kubanni River, Northern Nigeria, Bull. Chem. Soc. Ethiop. 23(1), 9-17

W.H.O. (World Health Organization) (1985). Guidelines for Drinking Water Quality (ii): Health Criteria and Supporting Information. Vol. 1, Recommendations. WHO, Geneva. 130pp.

Wu SM, Jong KJ, Lee YJ (2006). Relationship among methallothionein, cadmium accumulation, and cadmium tolerance in three species of fish. B. Environ. Cont. Tox., 76: 595-600.

Zhang Z, Li He, Jin Li, Zhen-bin Wu (2007). Analysis of Heavy Metals of Muscle and Intestine Tissue in Fish – in Banan Section of Chongqing from Three Gorges Reservoir, China. *Polish J. of Environ. Stud. Vol. 16, No. 6 949-958*