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Heavy Metals Levels in Fish Samples from North Central Nigerian Rivers

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ABSTRACT

Most aquatic organisms are capable of accumulating heavy metals to concentrations much higher than those present in water and sediments in their environment. In this piece of work, the concentrations of heavy metals were determined in fish organs of Albula *vulpe* and Tilapia *zilli* obtained from rivers in six different states within the North-Central metropolitan area using Atomic Absorption Spectrometry. The results showed that the liver of Tilapia *zilli* has the highest level of heavy metals with the concentration of Mn as 435.1mg/kg and the gills have the lowest concentration of Cd as 0.3mg/kg. Also the liver of Albula *vulpe* have the highest concentration with Mn as 292.6mg/kg and the muscles have the lowest concentration with Pb as <LOD. The trend for heavy metal accumulation is Mn>Cr>Pb>Cd>Ni in Albula *vulpe* and Mn>Cr>Pb>Ni>Cd in all the organs of Tilapia *zilli*. This indicates that the fish samples could be used to monitor Mn and Cr pollution levels in the North-Central Rivers.

Keywords: *Albula Vulpe,* Heavy metal, North Central Nigeria, *Tilapia Zilli,* River

INTRODUCTION

The aquatic environment contains heavy metals that occur mainly as a result of pollution which arise principally from the discharge of untreated wastes from the industry, traffic, utility waste and some herbicides into the rivers. Heavy metals are dangerous for living organisms because of their perseverance, high toxicity and their tendency of accumulation in ecosystems (Zeljka *et al.,* 2011).

The study of the bioaccumulation of heavy metals in tissues of aquatic organisms has been used as an indirect tool to measure the abundance of metals in the aquatic environment (Kucuksezgin *et al.,* 2006; Babatunde *et al.,* 2012). This is due to the fact that heavy metals in organisms such as fish, increases with the increments of the metal levels in water, sediment and fish food organism (Arvind, 2002; Jonathan and Maina, 2009). The rate of bioaccumulation of heavy metals in aquatic organisms depends on the ability of the organisms to break down the metals and the concentration of such metal in that environment. Also it has to do with the concentration of the metal in the surrounding soil sediments as well as the feeding habits of the organism, age and lipid content in the tissues of the organism. They are finally transferred to other animals including humans through the food chain. Other multiple factors including season, physical and chemical properties of water can play a significant role in metal accumulation in different tissues of aquatic organisms (Hayat *et al;* Karthikeyan *et al,* 2007; Romeo *et al*, 1999). Aquatic animals (including fish) bioaccumulate trace metals in considerable amounts and stay over a long period (Zeljka *et al.,* 2011).

The high levels of heavy metals in fish is becoming worrisome, especially when viewed in perspective of public health, as man depend directly on fish as an important source of protein in-take. One of the important ways to control heavy metals pollution in fishes is to monitor some fish as bioaccumulators of metal pollutants in aquatic environment (Shirvani and Jamili, 2009).

Demirak *et al.,* 2006 investigated the concentrations of heavy metals in water, bottom sediment and tissues (muscle and gills) of *Leuciscus cephalus* from the Dipsiz stream in the Yatagan basin (southwestern Turkey), the site of a thermal power plant. They found that there was metal accumulation in the gills compared to the muscle. Concentrations of Cd, Pb, Zn and Cr in the gills were higher than that in the muscle; however, Cu levels were higher in muscle than that in gills. Karadede and Unlu, 2000 on the concentrations of some heavy metals in the water, sediment and fish species (*Acanthobrama marmid, Chalcalburnus mossulensis, Chondrostoma regium, Carasobarbus luteus, Capoetta trutta and Cyprinus carpio*) from the Ataturk Dam Lake, Turkey indicated general absence of serious pollution. Nigeria's crude oil is known to contain heavy metals in reasonable quantity. Bioaccumulation of heavy metals in fish (*Tilapia zilli and Claria gariepinus*) organs from river Benue has been investigated by Eneji *et* al (2011). Their results indicated that the gills of Tilapia. *zilli* contained the highest concentration (52.2%) of all detected heavy metals, followed by the intestines (26.3%). While the muscles tissues appeared to be the least preferred site for the bioaccumulation of metals as the lowest metal concentration (21.5%) were detected in the tissues. Many studies have implicated industrial or human activities as possible source of pollution of the water body and biota (Shirvani and Jamili, 2009; Demirak *et al.*, 2006; Karadede and Unlu, 2000; Eneji, 2010). This work aimed at determining the concentrations of Pb, Cd, Ni, Cr, Mn in the muscle, liver, and gill of *A. Vulpe* and *T. Zilli* collected from Rivers in North central Nigeria.

MATERIALS AND METHOD

Reagents

All chemicals and reagents used were of analytical grade. The reagents were manufactured by Sigma Aldrich and purchased from Kritz Nigeria Ltd High Level, Makurdi. Stock solutions of these reagents were prepared and kept in the refrigerator until the need arises.

Acid Digestion:

One gram (1.0) g of sample was accurately weighed into a 250-mL beaker, 25 mL of 1M HNO_3, was added to each of the fish organ and covered with a watch glass, heated on a hot plate until all dissolved. The mixture was cooled for 5 minutes, and then 1mL aliquots of 98 % H_2O_2 was added slowly. Heating was continued on the mixture until the volume was reduced to approximately 5 mL. After cooling, the mixture was transferred to a 100-mL volumetric flask, and made up to the mark with Milli-Q water. Filtration was carried out to remove any organic plastic precipitate. Prepared standard solutions with different concentrations (0.2, 0.5, 1 & 2.5 ppm) of cadmium and chromium, manganese, nickel and lead were used to calibrate the spectrophotometer prior to analysis using distilled water as the control.

Instrumentation:

The measurements were performed using the Perkin Elmer® Analyst 400 atomic absorption spectrophotometer (PerkinElmer, Inc. Shelton, CT, USA) equipped with WinLab32™ for AA (Atomic Absorption) version software, which features all the tools needed to analyze samples, report and archive data and ensure regulatory compliance. PerkinElmer high efficiency double beam optical system and solid–state Deuterium background correction eliminates most interference. A PerkinElmer corrosion – resistant nebulizer, which can be used for solutions containing HF, was used for all the flame absorption measurements. A single slot air-acetylene 10cm burner head was used for all air acetylene experiments

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Sample collection

Twelve sampling stations (coded 1 – 12) were selected from the six states namely: Benue (1 and 2), Kogi (3 and 4), Kwara (5 and 6), Nassarawa (7 and 8), Niger (9 and 10) and Plateau (coded 11 and 12) of North Central Nigeria (see Figure **1**). Points likely to have the have the selected fish samples were randomly selected and a local fisherman caught the fishes using a trawl net at the river and the fishes were assessed for heavy metals content.

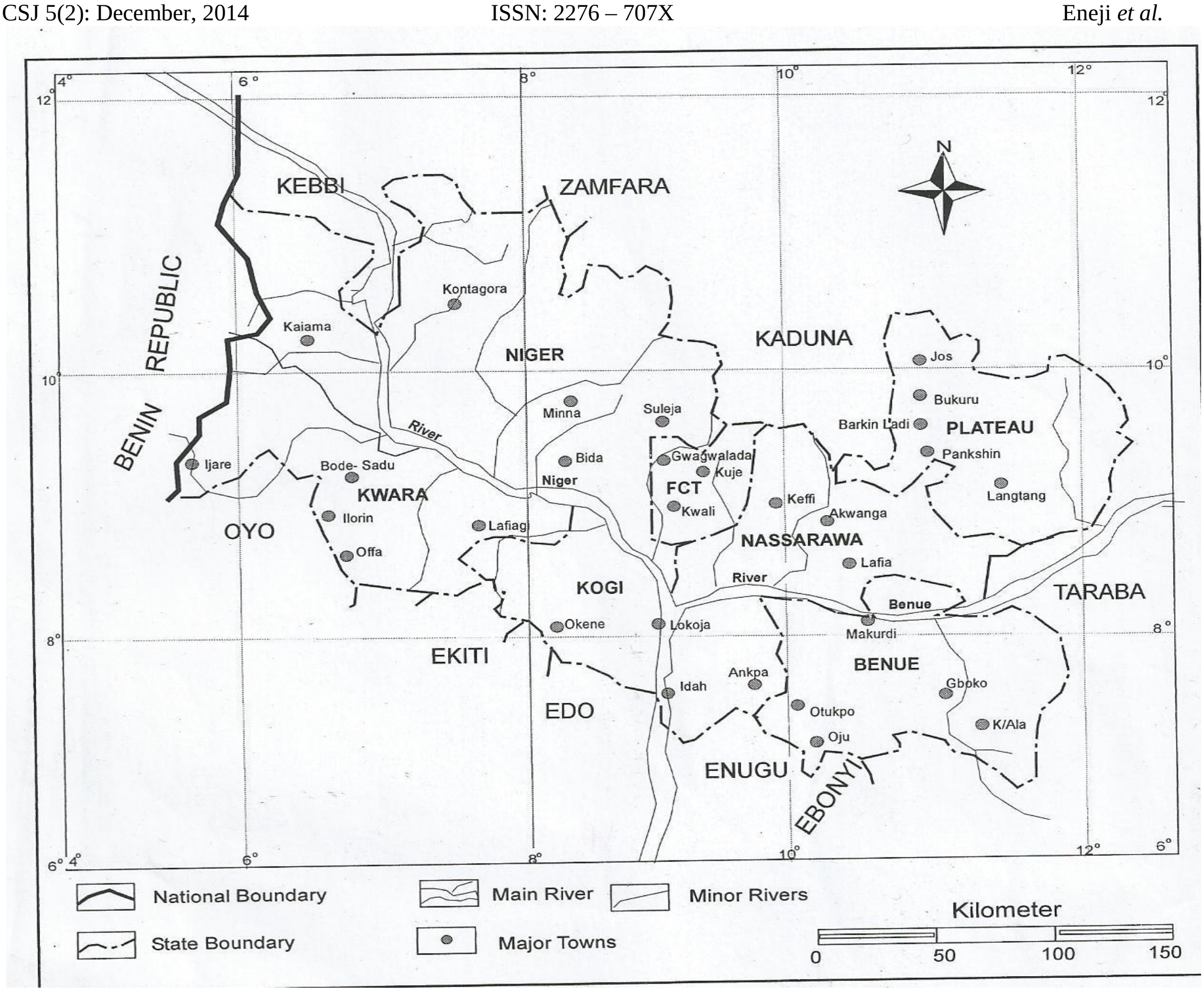

Figure 1: Map of North Central Nigeria Showing the Major and Minor Rivers

RESULTS AND DISCUSSION

Table 1: Elemental Concentrations (mg/kg) in Organs of *Albula vulpe*

Sample code	Gills					Liver					Muscle				
	Cd	Cr	Mn	Ni	Pb	Cd	Cr	Mn	Ni	Pb	Cd	Cr	Mn	Ni	Pb
1	1.7	6.2	25.4	2.1	9.0	3.4	21.1	1.4	13.8	2.5	10.1	4.1	20.2	0.8	10.4
2	10.2	13.1	39.3	0.9	15.6	3.7	21.3	84.1	8.9	15.1	11.1	7.4	5.1	3.7	10.4
3	16.7	5.6	32.6	0.8	20.4	16.7	1.6	1.5	1.2	14.8	0.2	7.2	25.8	2.2	5.9
4	2.0	6.6	10.0	1.2	1.8	26.9	4.3	121.3	2.1	2.3	2.5	6.2	20.8	0.3	5.3
5	14.1	6.2	31.9	0.7	1.4	1.9	20.2	45.2	1.1	9.2	0.2	11.3	8.2	8.0	<LOD
6	10.4	1.5	2.9	0.9	1.3	13.4	6.5	12.7	1.2	0.5	2.6	31.2	36.8	18.5	4.2
7	0.3	5.1	97.0	2.5	0.3	8.1	1.6	6.8	0.8	13.2	12.1	10.6	3.3	0.3	14.0
8	10.4	30.2	25.7	14.9	1.3	1.6	13.6	44.9	9.5	14.1	3.6	20.2	1.9	12.2	73.8
9	1.6	23.5	7.3	4.6	13.2	9.1	18.8	47.3	5.5	0.2	1.7	17.8	37.0	13.6	12.8
10	0.2	15.4	292.6	6.8	12.8	3.3	28.3	76.0	173.3	3.4	0.1	3.1	76.5	1.3	2.7
11	10.2	0.1	6.7	1.0	1.1	4.0	25.9	45.4	13.3	8.0	2.1	32.4	42.2	24.9	12.8
12	2.4	18.2	178.4	10.7	12.4	2.9	12.6	27.2	4.6	19.9	1.9	26.3	33.3	10.1	0.3

Table 2: Elemental Concentrations(mg/kg) in organs of *Tilapia zilli*

Sample code	Gills					Liver					Muscle				
	Cd	Cr	Mn	Ni	Pb	Cd	Cr	Mn	Ni	Pb	Cd	Cr	Mn	Ni	Pb
1	3.1	0.9	1.4	3.0	12.0	0.8	5.4	13.3	2.9	11.1	0.3	7.0	23.6	5.0	13.2
2	0.3	8.7	79.5	9.4	7.0	5.8	22.3	31.1	2.8	13.4	0.1	4.5	22.3	0.9	12.6
3	0.7	13.1	17.6	1.3	0.7	2.8	25.5	26.3	11.6	1.2	3.8	18.3	5.3	3.6	4.4
4	<LOD	31.8	94.4	6.6	4.1	15.1	9.3	11.9	2.2	14.2	8.7	4.9	27.7	0.5	0.4
5	10.8	40.2	70.4	12.6	0.7	18.2	4.6	31.4	1.7	13.2	1.6	4.8	3.0	12.2	4.2
6	13.0	20.2	8.2	2.1	12.1	1.6	26.7	27.6	14.0	6.9	11.6	2.4	30.8	0.9	4.4
7	2.6	9.7	171.5	10.6	14.4	0.2	7.8	435.1	4.5	12.0	0.5	5.2	40.3	10.8	1.1
8	2.1	7.7	165.3	1.6	6.4	0.7	16.6	220.4	0.8	3.4	0.8	26.4	12.8	0.9	12.6
9	1.5	17.1	12.8	1.3	15.2	0.5	6.9	24.6	0.7	25.4	0.6	6.9	28.4	1.2	7.8
10	1.4	12.5	23.6	6.5	2.1	1.6	15.2	14.4	0.7	0.9	7.8	4.2	38.2	3.7	0.5
11	4.7	21.6	80.0	5.7	9.8	3.4	24.0	35.6	15.7	11.2	0.9	16.0	9.2	0.8	0.9
12	0.6	24.8	40.0	8.4	13.1	2.5	16.9	40.4	9.7	2.7	0.3	6.0	36.0	1.5	0.5

Table 3: Heavy metals concentration (mg/kg) in fishes of Nigeria Rivers

Fish species	**Location**	**Cd**	**Cr**	**Mn**	**Ni**	**Pb**	
A. vulpe	North Central Nigeria	4.74	13.6	72.5	8.68	10.3	[This work]
T. zilli	North Central Nigeria	3.61	15.3	64.7	5.57	8.87	[This work]
C. gariepinus	River Benue	0.927	88.5	3.51	-	2.76	(Eneji, *et al.*, 2011)
S. membranaceus	Anambra River	-	-	94.07	-	61.32	(Obodo, 2004)
C. gariepinus	River Niger	0.183	-	0.292	-	-	(Oboh, 2007)
C. gariepinus	Niger Delta Area	0.030	-	2.390	-	0.480	(Kakulu and Osibanjo, 1988):
T. zilli	Anambra River	-	-	56.14	-	62.79	(Obodo 2004)
A. nurse	Oguta Lake	1.50	1.86	79.3	-	10.9	(Odoemena, 2 007)
S. nigritis	Oguta Lake	1.23	0.68	13.1	-	14.5	(Odoemena, 2007)

The total distance covered between the twelve sampling stations in the six states of central Nigeria was 434km. The longest distance was in Niger state which account for 120km between River Gudi, Shiroro and Kainji, while the least distance was in Benue state (about 7km distance from Wurukum to Wadata).

The mean concentration of heavy metals in gills, liver and muscle of A. *vulpe* fish species were shown in Figures 2, 3 and 4, respectively. From the results the maximum concentration of Cd in *A. vulpe* was found in the liver (26.9 mg/kg) at sample location (4) while the minimum concentration of Cd was found in the muscle (0.1 mg/kg). The general trend for Cd is Concentration in Liver >gills>muscle. The maximum concentration of Cr was reported in the muscle (32.4mg/kg) of *A. vulpe* at sample location (11). On the other hand, the maximum concentration of Cr was found in the gills at sample location, (11). The level of Cr (14.5 mg/kg) obtained in this work is within the literature values reported for Nigerian Rivers (Odoemena, 2005, Eneji *et al.,* 2011). Manganese showed maximum concentration in the gills (292.6 mg/kg) at sample location (10) while the minimum concentration was shown at sample location (8) (1.9 mg/kg). The mean level of Mn (68.6mg/kg) obtained in this work is within the literature values reported for fishes in Nigerian Rivers (Obodo, 2004, Odoemena, 2005). The maximum concentration of Ni was reported in the liver (173.3 mg/kg) of *A. Vulpe* at sample location (10), while the minimum concentration of 0.3 mg/kg were reported at sample location (4), (7). The mean level of Ni in the two fishes was 7.13mg/kg.

The maximum concentration of Pb (73.8 mg/kg) was found at sample location (8) in the muscle of *A. Vulpe* while the minimum concentration of <LOD was observed at location

code, (5). The mean level of Pb(9.53mg/kg) obtained in this work is within the literature values reported for fishes in Nigerian Rivers (Odoemena, 2005; Oboh and Edema, 2007; Eneji *et al.*, 2011).

The mean concentration of heavy metals in the organs of *T. zilli* fish species, that is gills , liver and muscles were represented in Figures 5 6, and 7, respectively. From the results the maximum concentration of Cd in *T. zilli* was found in the liver (18.2 mg/kg) at sample location (5) while the minimum concentration of Cd was found in the muscle (< LOD) at sample location (4). The concentrations of Cd reported for this work are higher than the FAO/WHO limit of 0.1mg/kg. The maximum concentration of Cr was reported in the gills (40.2 mg/kg) of *Cr was found* at sample location, (5) in the gills. On the other hand, the minimum concentration (0.9 mg/kg) for Cr was found in the gills at sample location (1). The concentrations of Cr reported for this work are higher than the FAO/WHO limit of 0.15mg/kg. Manganese showed maximum concentration in the liver () at sample location (7) while the minimum concentration was shown at location code 1(1.4mg/kg). The concentrations of Mn reported for this work exceed the FAO/WHO limit of 2.5mg/kg except the minimum concentration which is 0.4 mg/kg. The maximum concentration of Ni was reported in the liver (15.7mg/kg) of *T. zilli* at sample location (11) while the minimum concentration of 0.5mg/kg was reported at sample location (4). The concentrations of Ni reported for this work are higher than the FAO/WHO limit of 0.4mg/kg. The maximum concentration of Pb (25.4mg/kg) was found at location code (1) in the muscle of *T. zilli* while the minimum concentration of 0.4mg/kg was observed at location code, (4). The concentrations of Pb reported for this work are higher than the FAO/WHO limit of 0.5mg/kg except for the minimum concentration which is 0.4 mg/kg.

The heavy metal concentrations in the muscle are important, because this the most commonly consumed part in fish species. The study showed that there is no remarkable difference in the of heavy metal concentration in the liver, gills or muscle despite the differences in the physiological role of each organ. Generally, *A. vulpe* contains more levels of heavy metals (Cd, Mn, Ni, Pb) compared to *T. zilli* except Cr. The results obtained in the two fish species were generally higher than previous results reported by various authors from different authors which signify bioaccumulation of the metals. Most of these metals concentrated more in the liver, followed by gills while the least concentration is in the muscles for the two fish species.

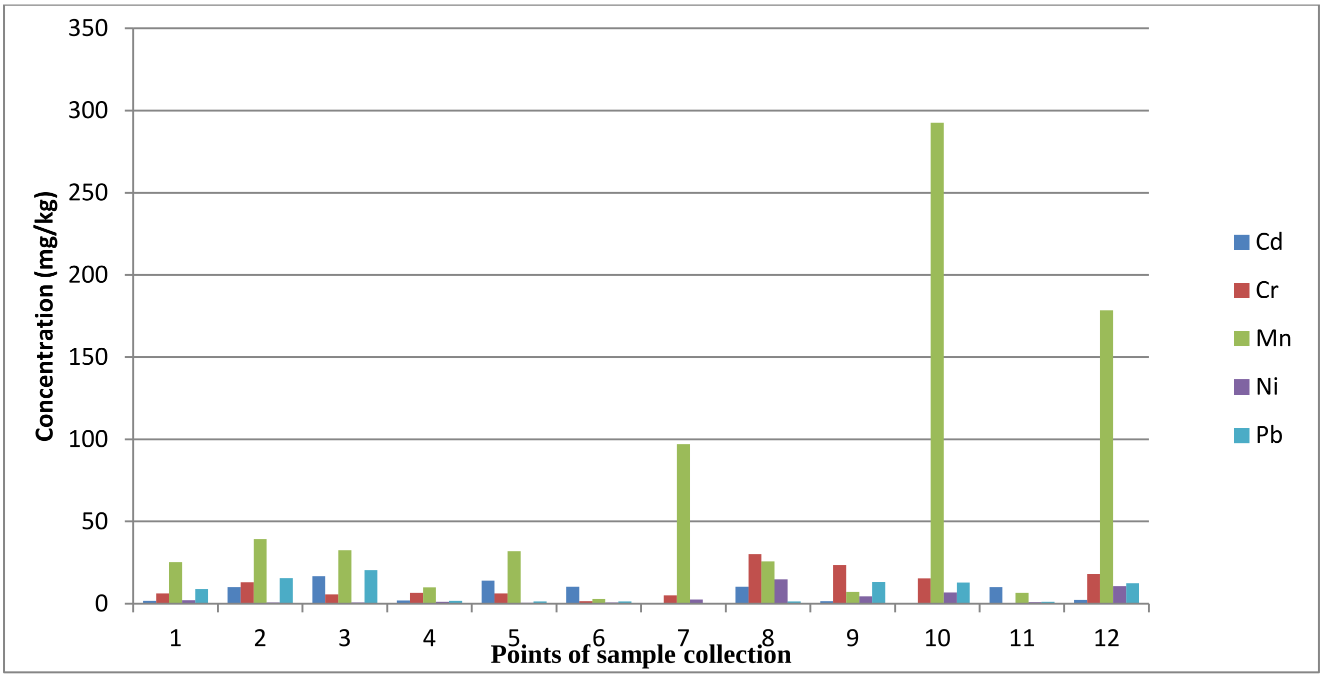

Figure 2: Concentration of Heavy Metals in the Gills of *Albula vulpe*

Key: 1 = Wadata, 2 = Wurukum, 3 = Ganaja, 4 = Lokoja, 5 = Jebba, 6 = Jebba Bridge, 7 = Yelwa, 8 = Gudi, 9 = Shiroro, 10 = Kainji, 11 = Kalong, 12 = Shendam Town.

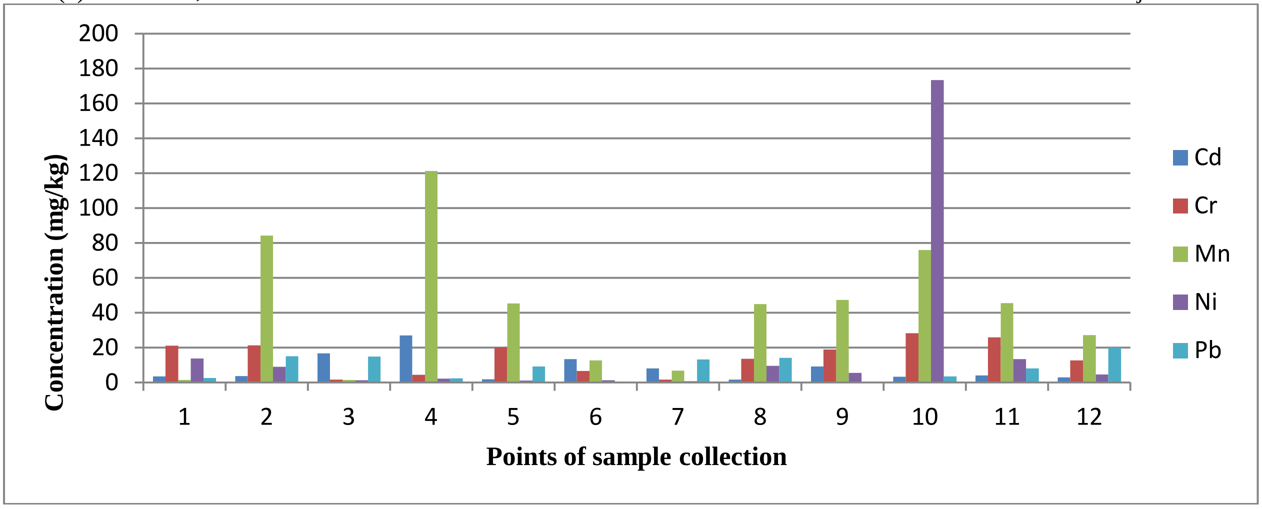

Figure 3: Concentration of Heavy Metals in the Liver of *A. vulpe*

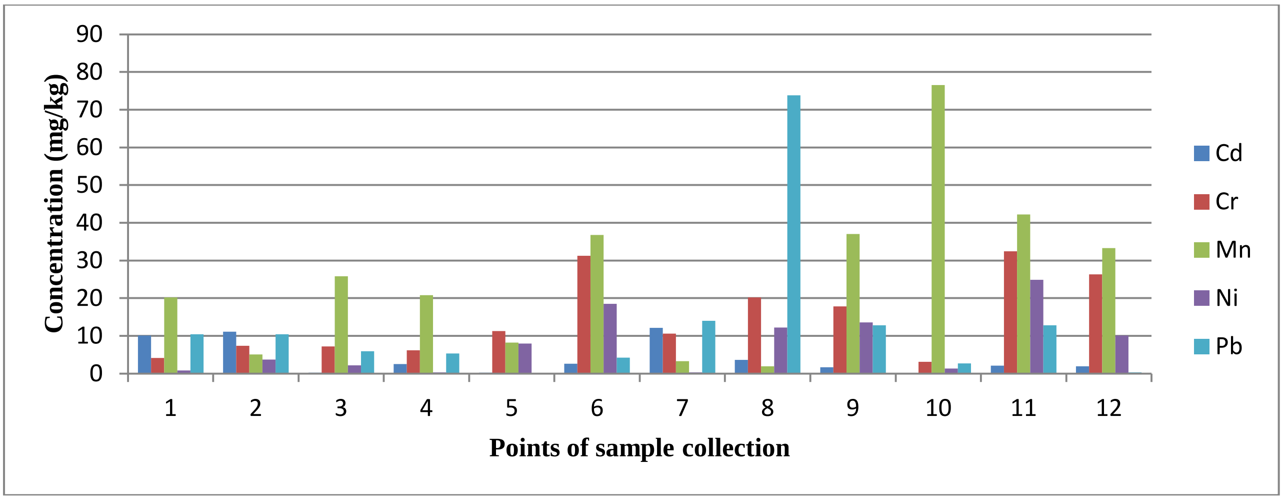

Figure 4: Concentration of Heavy Metals in the Muscle of *A. vulpe*

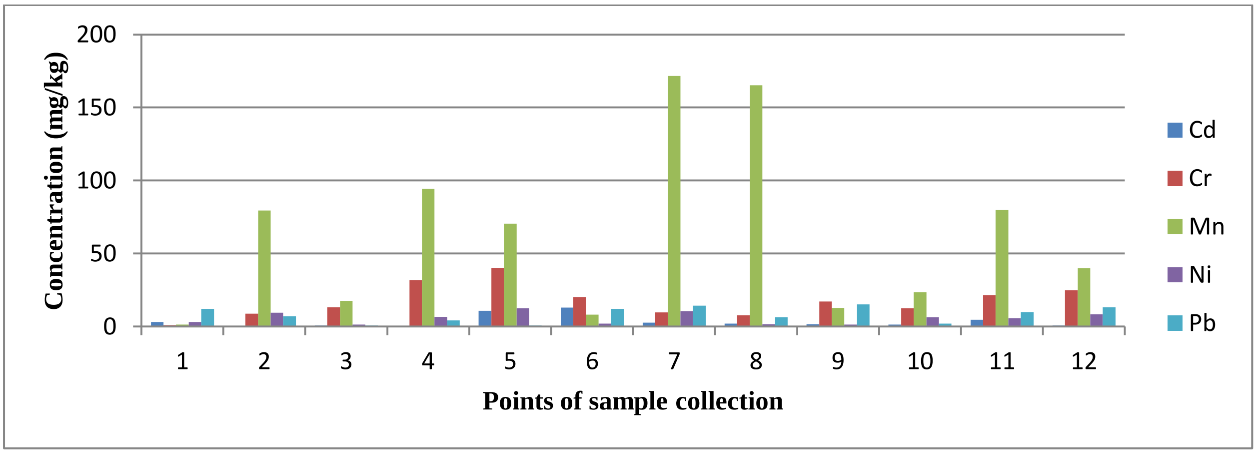

Figure 5: Concentration of heavy metals in the gills of *T. zilli*

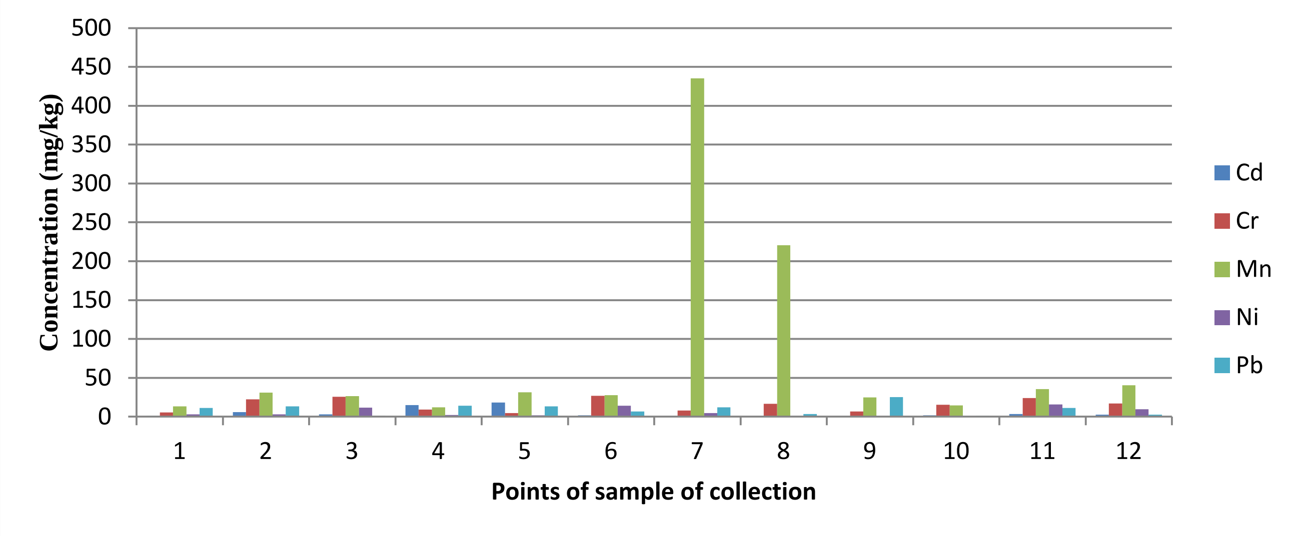

Figure 6: Concentration(mg/kg) of Heavy Metals in the Liver of *T. zilli*

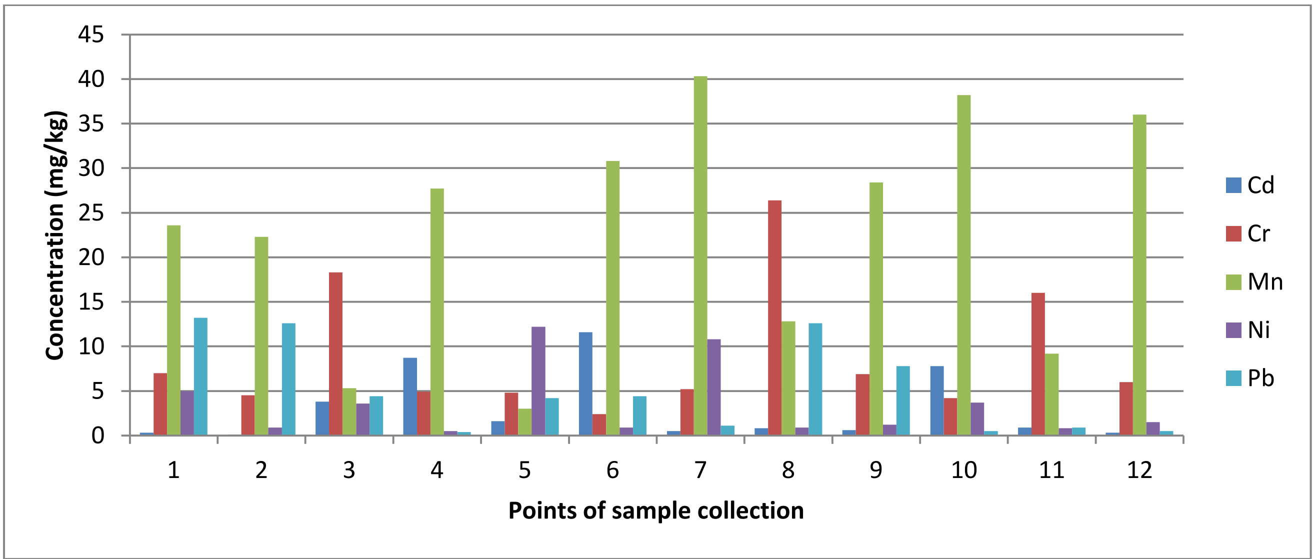

Figure 7: Concentration of Heavy Metals in the Muscles of *T. zilli*

CONCLUSION AND RECOMMENDATION

The significant levels of pollutants in the rivers and fish species studied, calls for concern and urgent measures. This should serve as a wake-up call for the introduction of decent environmental management techniques necessary for the support and maintenance of healthy aquatic life. As the practice of dumping waste into water bodies indiscriminately into water bodies should be discouraged in all ramifications. Environmental education should be brought to the front burner enlighten the populace on best global practices on freshwater protection from activities deleterious to aquatic organisms. It is also recommended that follow up research be conducted on fish reared in captivity to determine whether their controlled environment may cause a reduction in bioaccumulation of heavy metals and hence inform a preference for them.

REFERENCES

Arvind, K., (2002): Ecology of polluted waters, A.P.H Publishing Corporation. 5, Ansari Road, Darya Ganj-New Delhi- 11002, pp 290.

Babatunde, A.M., Waidi, O.A and Adeolu, A.A. (2012): Bioaccumulation of Heavy Metals in Fish (*Hydrocynus Forskahlii, Hyperopisus Bebe Occidentalis* and *Clarias Gariepinus*) Organs in Downstream Ogun Coastal Water, Nigeria. *Transnational Journal of Sci. and Tech.*, 2 (5): 119-133.

Demirak, A., F. Yilmaz, A.L. Tuna, Ozdemir, (2006): Heavy metals in water, sediment and tissues of Leuciscus cephalus from a stream in southwestern Turkey Chemosphere, 63(9): 1451-1458.

Eneji, I.S (2010): Spatial and temporal variation in the heavy metals loading of River Benue in Makurdi metropolitan area, Ph. D. Thesis, Department of Chemistry University of Agriculture Makurdi, Nigeria.

Eneji, I.S, Sha'Ato R. and Annune P.A. (2011): Bioaccumulation of Heavy Metals in Fish (Tillapia *zilli* and Clarias *gariepinus*) Organs from River Benue, North Central. Pakistan Journal of Analytical/ Envt Chem.12. (1&2): 25-31.

FAO (1983). Compilation of legal limits for hazardous substances in fish and fishery products, FAO fishery circular No. 464, pp. 5–100.

Hayat, S., Javed, M. and Razzaq, S. (2007): "Growth Performance of Metal Stressed Major Carps viz. *Catla Catla, Labeo Rohita and Cirrhina Mrigala* Reared under Semi-Intensive Culture System," *Pakistan Veterinary Journal*, 27, (1) 8-12.

Jonathan, B.Y and Maina H.M. (2009): Accumulation of some Heavy Metals in *Clarias anguillaris* and *Heterotis niloticus* from Lake Geriyo, Yola, Nigeria.*Nature and Science.*40-43

Kakulu, S.E. and Osibanjo, O. (1988): Trace Heavy Metal Pollution Studies in Sediments of the Niger Delta Area of Nigeria.*Journal of Chem. Soc.of Nigeria* 13: 22-26.

Karadede, H., E. Unlu, (2000). Concentrations of some heavy metals in water, sediment and fish species from the Ataturk Dam Lake (Euphrates), Turkey, Chemosphere, 41(9): 1371-1376. 24.

Karthikeyan, S., Palaniappan, P.L.R.M. and Sabhanayakan, S. (2007): Influence of pH and water hardness upon Nickel accumulation in edible fish *Cirrhinus mrigala. J. Environ. Biol.*,**28**,484-492.

Kucuksezgin, F.A., Kontas, O., Altay, E. and Uluturhan, D. E. (2006):Assessment of marine pollution in Izmir Bay; Nutrient heavy metal and total hydrocarbon concentrations: *Environ. Int.*, 32: 41-51.

Oboh, I,P and Edema, C.U. (2007): Levels of Heavy Metals in Water and Fishes from River Niger. *Journal of Chemical Society of Nigeria*. 32(2): 29-34.

Odoemena, S.A. (2005): Bioaccumulation of Trace Elements in Fish from Oguta Lake in Nigeria. *Journal of Chem Soc. Nigeria* 30(1) 18-20.

Romeo, M., Siau, Z., Sidoumou, Y. and Gnassia, M. B. (1999): "Heavy Metal Distribution in Different Fish Species from the Mauritania Coast," *Science of the Total Environment*, 232 (3), 169-175.

Shirvani, E. and Jamili, S. (2009): Assessing Cd, Pb Accumulation in the Tissues of *Chalcalburus chacoides.Research J. Environ. Science, 3 (5):522-529.*

Zeljka, M., Marko, I., Visnja, O., Srebrenka, N. and Ivana, T.G. (2011): Heavy Metal Concentrations in Predator Fish. *Journal of Animal and Veterinary Advance,* 10 (9): 1214-1218