HEAVY METALS IN TWO COMMONLY CONSUMED FISHES (*Clarias gariepinus and Tilapia zilli*) IN KANO CITY, NIGERIA

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Abstract
The study was a research on Clarias gariepinus and Tilapia zilli fish organs that were sampled randomly by buying directly from the fisher men around the ponds in Kano metropolis, Nigeria. The concentrations of eight heavy metals were investigated in the fish bones, gills, and muscle using atomic absorption Spectrophotometry. The metals: zinc, lead, nickel, cobalt, iron, manganese, copper and chromium were found to be significantly present in the samples. The result of this study showed that zinc ranged from 0.14± 0.03 - 0.27 ± 0.01 (µg/g) in Tilapia zilli gills sample having higher values than the Clarias gariepinus samples. Lead concentration in the samples were significant as it ranged from 0.27± 0.01 to 0.19± 0.02 (µg/g). The semi – essential metals; Chromium and Cobalt ranged between 0.16 ± 0.01 - 0.19 ± 0.03 and 0.32± 0.02 - 0.47± 0.01 (µg/g) respectively. The samples CF01BKN; Bone of Clarias gariepinus fish, TB06BKN; Bone of Tilapia zilli fish, at p < 0.05 were with highest concentration. Zn < Mn < Cu< Cr < Pb < Fe < Co < Ni. Consequently this result suggests that organisms like fishes could be used to monitor pollution levels in the ecosystem.

Keywords: Fish organs, heavy metals, pollution, *Clarias gariepinus and Tilapia zilli*.

Introduction
Heavy metals are ubiquitous as such are naturally found in the ecosystem, although some elements like copper, zinc, manganese, iron, nickel and manganese at low concentrations are reported to serve as an essential elements necessary for some enzymatic activities and some key biological processes in human and plant tissues, but these elements become very toxic above certain concentration limits. However, elements like lead, cobalt, Cadmium, mercury, and arsenic is also reported to have no known role that is essential to both plant and human body, so even at low concentrations these elements are toxic (Abel *and Papoutsouglou,* 1986; Al-Weher, 2008; Bryan, 1976; Larsson *et al.,* 1985).

Suzuki et al., (1988) in their study of binding of cadmium and copper in the may fly *Beatis thermicus* larvae reported that contamination of a river with heavy metals may have devastating effects on the ecological balance of aquatic life as the organisms becomes limited with the extent of contamination. Generally, most of the rivers are located in centres such that they are excessively contaminated with heavy metals released from domestic, industrial, mining and agricultural effluents (Le Land et al., 1978; Corbett, 1977; Mance, 1987; Langston, 1990). Researchers have shown that fish are able to accumulate and retain heavy metals from their environment and that the accumulation of the metals in tissues of fishes is dependent upon exposure, concentration, duration as well as other factors such as salinity, temperature, hardness and metabolism of the animals (IOSHI, 1999; Canli et al., 1998; Allen and Hansen, 1996). Once an aquatic organism accumulates heavy metals, they can be transferred through the upper classes of the food – chain including human beings. Human beings are known to obtain most of their heavy metals toxicity from the aquatic ecosystems through the consumption of aquatic animals as food particularly fishes (Mance, 1987; Langston, 1990; Lyman, 1995; Rand et al., 1995; Cubie, 1975). This study was carried out with the aim of investigating levels of heavy metals in two types of fishes; *Clarias* g*ariepinus and Tilapia zilli* collected from the sixteen (16) ponds available in Kano metropolitan cities in Nigeria.

Design of Hypothesis

Ho: There is no significant difference in the concentrations of heavy metals in the fishes in ponds during the seasons in Kano.

Materials and Methods

Fish Digestion

Same day average fishes were caught, they were brought into the laboratory; cut with clean instrument. The tissues of three fishes of about the same size and the same species and from the same ponds were pooled off to make three sub-samples: The muscle (flesh), the gills and the bones. The sub-samples were dried at 120^oC to a constant weight in an oven. 0.50g of each weighed on a watch glass and transferred into a conical flask and digested in 80.0 cm^3 HNO_3 and 4.0 cm^3 $HClO_4$ at 130^oC using hot plate carefully and gradually until the entire sample dissolved. The sample was washed into 100cm^3 volumetric flask and the resulting solution was made up to the mark with distilled water and portions of these solutions were taken for the required metal determination using AAS (Canli *et al.,* 1998).

Result and Discussion

The result of the study showed that fish samples contain during dry season heavy metals ranging from *0.14± 0.03 to 0.27± 0.01 µg/g for Zinc which is on the average below allowable limit of 0.5* µg/g . While *0.23± 0.02 to* 0.59 ± 0.02 µg/g (Fe), which is clearly above minimum limit of 0.30 µg/g permissible limit. Lead concentration from the study ranged from 0.19 ± 0.02 to *0.27± 0.01* µg/g. levels of lead however small have been implicated to be toxic even as low as 0.02 µg/g. The nickel concentration ranged from 0.29 ± 0.02 to *0.71± 0.03* µg/g which is also above the permissible limit of 0.02 µg/g. While cobalt concentration ranged from 0.32 ± 0.02 to *0.47± 0.01*µg/g which is above 0.03µg/g permissible limit. While manganese concentration in the samples gave a range between 0.16 ±0.01 to 0.23 ±0.01 µg/g which clearly shows some sample are above the allowable limit of 0.2 µg/g. Copper concentration in the sample ranged from 0.16 ± 0.03 to 0.19 ± 0.01 µg/g which below permissible limit 1.0

µg/g. However, chromium concentration in the samples gave a range of 0.16 ±0.01 to 0.19 ±0.03 µg/g which is above allowable concentration of 0.05 µg/g (FAO, 1983; WHO, 1987).

Table 1: Mean concentration of fish samples from Kano (Dry season) in µg/g

Element	*Fish Organ in ppm*					
	Clarias gariepinus (Cat fish)			*Tilapia zilli (Tilapia fish)*		
	Muscle	*Gill*	*Bone*	*Muscle*	*Gill*	*Bone*
Zn	*0.18± 0.04*	*0.24± 0.01*	*0.21± 0.02*	*0.24± 0.03*	*0.27± 0.01*	*0.14± 0.03*
Pb	*0.22± 0.02*	*0.27± 0.01*	*0.23± 0.03*	*0.19± 0.02*	*0.25± 0.04*	*0.22± 0.01*
Ni	*0.36± 0.03*	*0.29± 0.02*	*0.43± 0.01*	*0.42± 0.04*	*0.57± 0.01*	*0.71± 0.03*
Co	*0.47± 0.01*	*0.44± 0.02*	*0.38± 0.01*	*0.35± 0.03*	*0.32± 0.02*	*0.35± 0.04*
Fe	*0.59± 0.02*	*0.28± 0.03*	*0.59± 0.01*	*0.56± 0.04*	*0.51± 0.05*	*0.23± 0.02*
Mn	*0.19± 0.03*	*0.18± 0.02*	*0.21± 0.04*	*0.23± 0.01*	*0.18± 0.03*	*0.16± 0.01*
Cu	*0.19± 0.01*	*0.17± 0.03*	*0.19± 0.02*	*0.16± 0.03*	*0.18± 0.01*	*0.16± 0.03*
Cr	*0.19± 0.03*	*0.18± 0.02*	*0.16± 0.04*	*0.18± 0.01*	*0.17± 0.03*	*0.16± 0.01*

Values are the mean replicate analysis n = 6

Table 2: Mean concentration of fish samples from Kano (Rainy season) in µg/g

Element	*Fish Organ*					
	Clarias Gariepinus (Cat fish)			*Tilapia Zilli (Tilapia fish)*		
	Muscle	*Gill*	*Bone*	*Muscle*	*Gill*	*Bone*
Zn	*0.15± 0.09*	*0.18± 0.05*	*0.17± 0.01*	*0.22± 0.02*	*0.20± 0.03*	*0.21± 0.05*
Pb	*0.19± 0.09*	*0.25± 0.02*	*0.18± 0.01*	*0.12± 0.06*	*0.02± 0.04*	*0.18± 0.01*
Ni	*0.21± 0.01*	*0.17± 0.02*	*0.22± 0.03*	*0.27± 0.01*	*0.28± 0.01*	*0.25± 0.02*
Co	*0.28± 0.01*	*0.24± 0.01*	*0.29± 0.04*	*0.23± 0.03*	*0.20± 0.05*	*0.25± 0.03*
Fe	*0.49± 0.07*	*0.26± 0.06*	*0.38± 0.02*	*0.37± 0.04*	*0.36± 0.02*	*0.18± 0.04*
Mn	*0.08± 0.09*	*0.07± 0.06*	*0.13± 0.04*	*0.07± 0.03*	*0.10± 0.03*	*0.08± 0.06*
Cu	*0.13± 0.03*	*0.12± 0.09*	*0.13± 0.02*	*0.14± 0.02*	*0.15± 0.04*	*0.07± 0.03*
Cr	*0.05± 0.05*	*0.06± 0.07*	*0.07± 0.04*	*0.04± 0.09*	*0.05± 0.03*	*0.06± 0.04*

Values are the mean replicate analysis n = 6

The significant values of metal concentration observed during rainy season might be attributed to the fact that environmental pollution is highly prevalent in Kano during this period coupled with traffic hold up resulting into the atmospheric deposition of poisonous gasses which ultimately settle into these ponds. Zinc concentration ranges from *0.15± 0.09 to 0.22± 0.02 which is on the average below allowable limit of 0.5* µg/g. While *0.23± 0.02 to* 0.59 ± 0.02 µg/g (Fe), which is clearly above minimum limit of 0.30 µg/g permissible limit. Lead concentration from the study ranged from 0.19 ± 0.02 to *0.27± 0.01* µg/g. levels of lead however small have been implicated to be toxic even as low as 0.02 µg/g (FAO, 1983; WHO, 1987). The nickel concentration ranged from 0.29 ± 0.02 to *0.71± 0.03* µg/g which is also above the permissible limit of 0.02 µg/g .While cobalt concentration ranged from 0.32 ± 0.02 to *0.47± 0.01* µg/g which is above 0.03 µg/g permissible limit (FAO, 1983; WHO, 1987). While manganese concentration in the samples gave a range between 0.16 ±0.01 to 0.23 ±0.01 µg/g which is clearly shows some sample are above the allowable limit of 0.2 µg/g. Copper concentration in the sample ranged from 0.16 ± 0.03 to 0.19 ± 0.01 µg/g which below permissible limit 1.0 µg/g. However, chromium concentration in the samples gave a range of 0.16 ±0.01 to 0.19 ±0.03 µg/g which is above allowable concentration of 0.05 µg/g (FAO, 1983; WHO, 1987).

Generally fishes tend to bioaccumulate metals in their systems more during dry than the rainy seasons. The trend is similar in both seasons in both cities. The results of metal concentration in the fish samples investigated during dry season are higher than those of rainy season in the same fish organ. Possibly, the fishes might have been exposed to more available metal concentration in dry season than rainy season (Ayodele and Gaya, 2003 and Ayodele and Salami, 2007). The concentration of metals in the water and period of exposure might play vital role in the accumulation of the heavy metals in aquatic lives. Similar studies and results of high concentration of heavy metals are reported (Canli, *et al,* 1998; Ishaq, 2011; Mance, 1987; Woo et al., 1993; Ogbonda, 19992; Weis and Weis, 1989; FAO, 1983; WHO, 1987). Stake holders in fishing business have the general believe that there is continues decrease in fish population water bodies such that there might be period in the future when no fish would be found in water bodies if nothing is done to arrest the present trend as more heavy metals will be deposited with time.

Table 3: ANOVA comparison of mean of metal concentration in Kano fishes during dry season

	Sum of the squares	Degree of freedom (df)	Mean of the squares	F_{cal}	F_{crit}	Significant level
Between Groups	0.194	8	0.02424	21.974*	1.92	0.0001
Within Groups	0.09308	36	0.02586			
Total	0.287	44				

*- Significant at 0.05 level

Table 3 shows the ANOVA comparison of means of metal concentration in Kano fishes during dry season and from this study, there is significant difference in the means of the metal concentration in fishes during seasons. ($F\text{-}_{Cal}$ = 21.974 > $F\text{-}_{crit}$ = 1.92; df = 15, and 80; P<0.05). Therefore the null hypothesis; HO: There is no significant difference in the concentrations of heavy metals in the fishes during dry and rainy seasons in Kano is rejected. Hence there is significant difference in the concentration of the metals in Kano fishes during seasons. However there is need to find out where the difference lie, therefore the Duncan Post Hoc Test was used. There is significant difference in mean metal concentration between the Metals in Group B mean metal concentrations: C, D, E, and Group F as represented in the Appendix IV [A and B]. However, the set of metals in Group G: cobalt, iron, and nickel. There is significant difference between the metal in Group G and other metals in the samples in Groups A, B, C, D, E, and F. These metals in Group G are the most dominant in their respective samples.

The contaminations of high loads of heavy metals might be as a result of discharge into these ponds from domestic, industrial and agricultural effluents consequently creating devastating ecological imbalance by limiting the aquatic population. This might be attributed to the fact that environmental pollution is more prevalent during the dry season in Kano, coupled with traffic hold up resulting to the atmospheric deposition of poisonous gasses which ultimately settle into these ponds as reported (Ayodele and Gaya, 2003 and Ayodele and Salami, 2007). From the result of this study the fishes investigated are intuitively polluted therefore their continuous consumption may portend high risk inherent with complications in bioaccumulation over a period. Similar studies and results of high concentration of heavy metals have been reported (Canli, *et al,* 1998, Mance, 1987, Woo, Yoke and Wong, 1993, Ogbonda, 19992 and Weis and Weis, 1989). FAO, 1983 gave some limits as 0.03µg/g (Zn), 0.03 µg/g (Cu), 0.05 µg/g(Cr), 0.01 µg/g (Pb) and WHO, 1987 gave some limits as 1.0 µg/g (Zn), 0.03 µg/g (Cu), 0.01 µg/g (Pb).

Conclusion

Based on this study, it can be concluded that the samples of fish organs investigated were polluted, however, the bone of cat fish; bone of *Tilapia zilli* from Kano were implicated to be most polluted. This might be as a result of bioaccumulations of this metal from run-off, domestic waste, bioaccumulations of these metals over long period and other environmental factors. Therefore continues consumption of these fishes can result into health complications which ultimately could result in death. The sample CF01BKN; Bone of *Clarias gariepinus*, CFB03BKN; Bone of *Clarias gariepinus*, TB06BKN; Bone of *Tilapia zilli*, are the samples with highest concentration during dry season. Sample CF01BKN; Bone of *Clarias gariepinus* are the samples with highest concentrations during rainy season.

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APPENDICES

APPENDIX I : SPSS- ANOVA Analysis GUIDE CODES

1.	Zinc dry/rainy season Kano	2.	Lead dry/rainy season Kano
3.	Nickel ..	4.	Cobalt ..
5.	Iron ..	6.	Manganese ..
7.	Copper ..	8.	Chromium ..

APPENDIX II - FISH SAMPLES CODES OF IDENTIFICATIONS

CF01KN-*Clarias gariepinus* flesh from Kano, CF02KN— *Clarias gariepinus* Gills from Kano
CF03KN— *Clarias gariepinus* Bones from Kano, TF04KN--- *Tilapia zilli* flesh from Kano
TF05KN--- *Tilapia zilli* Gills from Kano, TF06KN--- *Tilapia zilli* Bones from Kano

APPENDIX III

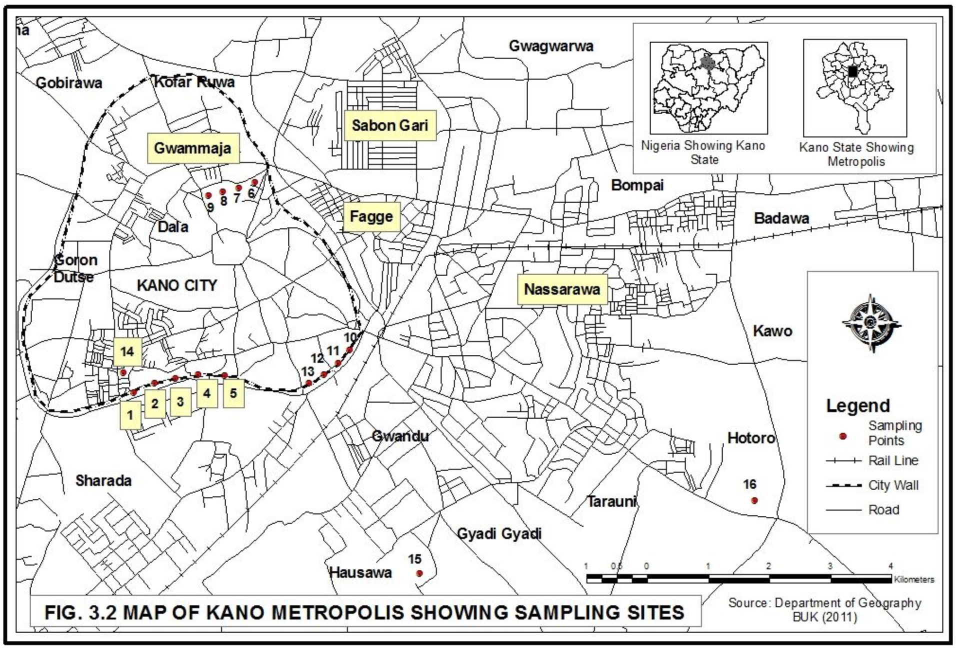

FIG. 3.2 MAP OF KANO METROPOLIS SHOWING SAMPLING SITES

APPENDIX IV [A] and [B]

	Sum of Squares	df	Mean Square	F-cal	Sig.	F-crit
Between Groups	1.417	15	9.445E-02	21.974	.000	1.92
Within Groups	.344	80	4.298E-03			
Total	1.761	95				

Metals	N	Subset for alpha = .05						
		Group A	Group B	Group C	Group D	Group E	Group F	Group G
16.00	6	6.333E-02						
10.00	6	9.000E-02	9.000E-02					
15.00	6	1.000E-01	1.000E-01	1.000E-01				
14.00	6	.1050	.1050	.1050	.1050			
11.00	6	.1283	.1283	.1283	.1283			
13.00	6	.1350	.1350	.1350	.1350	.1350		
9.00	6	.1450	.1450	.1450	.1450	.1450	.1450	
8.00	6		.1733	.1733	.1733	.1733	.1733	
7.00	6		.1750	.1750	.1750	.1750	.1750	
12.00	6			.1850	.1850	.1850	.1850	
6.00	6				.1917	.1917	.1917	
1.00	6					.2200	.2200	
2.00	6						.2300	
4.00	6							.3850
5.00	6							.4600
3.00	6							.4633
Sig.		.065	.057	.057	.052	.054	.054	.053

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 6.000.