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Trace Elements Accumulationin the Organs of Clarias Gariepinus Sold in Makurdi, Benue State Nigeria

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Abstract
The concentration of trace metals were determined in the organs of *Clariasgariepinus*sold withinMakurdi Metropolitan area using atomic absorption spectrophotometer for two seasons. The trend of the accumulation of heavy metals in the organ of the fish was gills> liver > kidney> bone> skin during the rainy season while during the dry season it was kidney > skin>liver>gills> bone of the fish. There was no significant difference in the examined trace elements in the different organs of the fish during dry season (P>0.05). All the same during the rainy season there was a significant difference in the bio accumulation of trace metals in the different organs of the fish (P<0.05). The trace elements in the water are transferred to the organs of the fish (*Clariasgariepinus)* which have an implication for public health due to the fact the fish is a rich source of protein for humans and is widely consumed within this area. There is clear evidence that the fish that is majorly obtained from River Benue within Makurdi is polluted with trace elements and this a severe consequence and implication for public health. This is because the fish is consumed by humansand the trace metals may accumulate into their organs and may result to illness due to the toxicity of the elements.
Keywords: Trace elements, Bio accumulation, *Clariasgariepinus*Makurdi

Introduction

Among different pollutants, heavy metals are the most toxic, persistent and abundant pollutants that can accumulate in aquatic habitats and their concentration increases through biomagnifications (Oyewale and Musa, 2006). Therefore organism like fish living in rivers, elevated heavy metals content may impart a significant impact on their health, reproduction and survival (Moore, *et al.*, 2009). Fish can respond to environmental changes and they can be used in pollution indicator study. Fish is a bio indicator organism because it is easy to be obtained in large quantity, has the potential to accumulate heavy metals and have a long life span as compared to other aquatic organisms (Anim-Gyampo*et al.,* 2013).

Heavy metals intake by fish in polluted aquatic environment depends on the ecological requirements, metabolism and other factors such as salinity water pollution level, food and sediments (Anim-Gyampo*et al.,* 2013). Fish has the ability to accumulate metals in its tissues through absorption and the metals gets to the humans through food web. This may cause acute and chronic effect to humans (Nord *et al.,* 2004). The accumulation of heavy metals in the aquatic environment has direct consequences to man and to the ecosystem (Krishna *et al.,* 2014). This impact is pronounced because of the non-degradability of the heavy metals that results to bioaccumulation and is transported along the successive food chain (Gesielski*et al.,* 2010). Studies have established that fish are good indicators of chemical pollution and have long been used to monitor heavy metal pollution in coastal and marine environments (Krishna *et al.,* 2014). Environmental pollution is a worldwide problem as heavy metals belong to the most important pollutants (Zeitoun and Mehana, 2014). The development of industries has resulted to increased emission of pollutants into ecosystem (Wang *et al.,* 2013). Environmental degradation therefore result to poisoning, diseases and even death for fish (Zeitoun and Melana, 2014). Therefore monitoring heavy metals accumulation in the commonly consumed fish in Makurdi*Clariasgaripinus* serves as an important function as an early warning indicator to take appropriate action to protect public health and the environment.

MATERIALS AND METHODS

Study Area

The study was carried out in Makurdi, the capital city of Benue State, and Nigeria. The city is located in central Nigeria where the second largest River, River Benue passes through. The town lies in the guinea savanna vegetative belt on the bank of the River Benue in Nigeria. Makurdi is situated at latitude $7^0$15’ -$7^0$45’ North and Longitude $8^0$15’ - $8^0$40’ East and 104 meters elevation above the sea level Figure 1). The river divides the town into North and south Banks and the town covers an area of about 16 kilometers square. The river constitutes the main source of water supply for the inhabitants of the town and for irrigation agriculture. Makurdi is fast becoming a metropolitan center with attendant health, social, housing and associated environmental problems. The rainfall seasons at Makurdi produces a river regime of peak flows from August to early October and low flow from December to April. The rainy season which last for seven months (April to October) has a mean annual rainfall ranging from 1200-2000mm. High temperature values averaging 28-33^{0}C are recorded in Makurdi throughout the year, most notable from March to April. Harmantan winds are accompanied with cooling effects mostly during the nights of December and January (Nyagba, 1995).

Fish Sample Collection

The fish samples (*Clariasgariepinus*) were bought directly from the fishermen at the bank River Benue at Wadata marketfishing port. All the same the control fish samples were obtained at the special science secondary scholl fish farm Makurdi. The fish samples were coded from A-L . The *Clariasgariepinus* samples had mean weight 263 ± 4.6g and mean length 36.42 ± 1.25cm. The fish samples were still alive and stored in an ice parked box in order to maintain the freshness and then transported to the laboratory within one hour for the dissection of skin, bone, kidney, liver and gills. The organs of the fish dissected were oven dried separately for 24 hours to constant weight at 105°C.

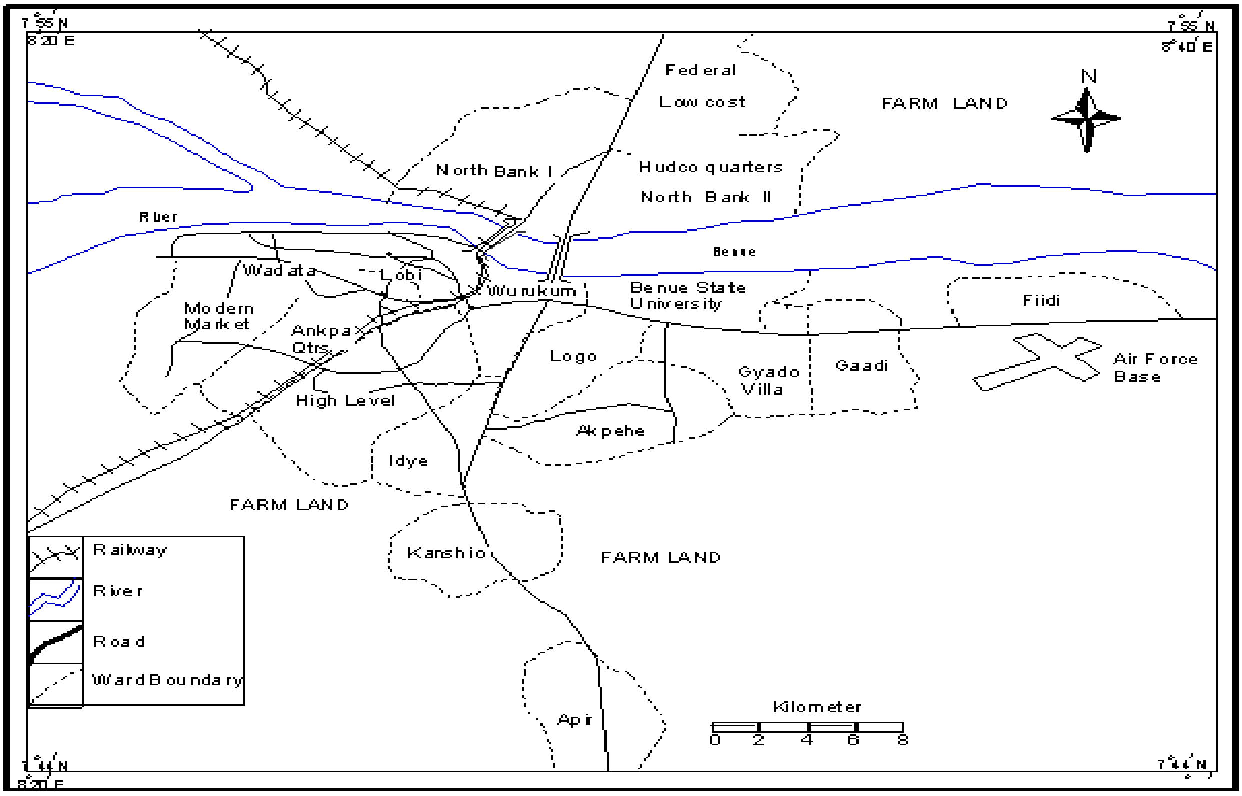

Fig 1: Map ofMakurdi Metropolis Showing its Different Settlements

Fish Sample Preparation

The skin, bone, liver, kidney and gills of the cat fish were pooled according to the tissues type and milled with a mortar and pestle. They were put separately in a dry and properly labeled plastic containers and stored in a desiccator pending digestion.

Digestion of the fish Samples

0.200g of dry powdered fish sample was weighed into a 50ml tube and 2.5ml of selenium/teratoxosurphate (VI) acid mixture was added to each tube and to 5 blanks used as standards. This mixture was placed in an aluminum block on a hot plate, heat at approximately 200°C until sample fumes. The tubes were then removed from the hot plates and allowed to cool for about 45 minutes. 1ml of 30% of hydrogen peroxide, H_2O_2 was carefully added to the samples and standards. After the reaction subsides, then additional 2ml H_2O_2 was added.

The tubes were taken back to the hot plates and a 15ml glass vial was placed on top of each tube and the tubes were heated up to 330°C. This was left on the hot plates for about two hours until the solutions become clear. These samples were allowed to cool and 0.2mL, 0.4mL. 0.6mL and 0.8mL of stock solutions of each of the heavy metals to be analyzed was added to the standard solutions. The sample and standards were then diluted to the 50ml mark. This procedure is constituent with Novozamsky*et al*. (1983).

Determination of Heavy Metals

Digested fish samples were poured into analyzer cups of the Atomic Absorption Spectrophotometer and

concentration of heavy metals (Cadmium, Chromium, lead, copper and Al) in each of the samples was determined using atomic absorption spectrophotometer (AAS). The values of the heavy metal concentrations in the tissues were calculated based on dry weight as this discounts the variability due to inner parts difference in the moisture content of the organisms using the formula , Heavy metals mg/kg = AAS reading (mg/L) x Volume diluted
Weight of sample digested

Statistical Analysis
Results obtained were subjected to mean, standard deviation and standard error of means. ANOVA was determined and $p < 0.05$ was considered to indicate statistical significance. Microsoft excel 2013 version was used in the plotting of the graphs.

RESULTS
The result presented in Tables1- 5 is the accumulation of heavy metals in the organs of the fish during the study period. The result presented in Figure 2 is the graphical form the accumulation of heavy metals in the organs of the fish during rainy season. The result depicts that the highest of concentration of Cr accumulated in the gills and the lowest concentration of Al in the bone of the fish. Similarly Figure 3 is the graphical representation of heavy metals in the organs of the fish during the dry season. The result indicate that the highest concentration of Cr was obtained in kidney and the lowest concentration of Al in bone, skin and kidney of the fish during the study period.

Table1: Trace Element Concentration (mg/Kg) in Liver of *Clariasgariepinus*

Sample code	Pb	Ni	Cu	Cr	Cd	Al
A	1	0.38	1.79	3.45	0.07	0.79
B	1.02	1.01	1.33	1.4	0.02	0.03
C	0.67	0.15	0.64	0.52	0.14	0.007
D	0.79	0.25	0.66	1.77	0.09	0.05
E	0.7	0.32	1.86	0.28	0.13	0.01
F	0.95	0.31	0.94	0.06	0.1	0.42
G	1.23	2.34	0.75	1.34	0.38	0.03
H	0.07	0.44	0.44	3.54	0.29	0.06
I	0.28	0.77	1.17	0.66	0.22	0.09
J	0.51	0.32	0.74	1.05	0.31	0.02
K	0.25	0.64	0.86	2.71	0.47	0.009
L	0.09	0.66	0.27	1.02	0.1	0.05
Mean	0.63	0.63	0.95	1.48	0.19	0.13
Std	0.39	0.59	0.49	1.17	0.14	0.24
Min	0.07	0.15	0.27	0.06	0.02	0.01
Max	1.23	2.34	1.86	3.54	0.47	0.79

Table2: Trace Element Concentration (mg/Kg) in Kidney of *Clariasgariepinus*

Sample code	Pb	Ni	Cu	Cr	Cd	Al
A	0.69	0.28	0.5	3.03	0.15	0.57
B	1.21	0.95	0.44	0.04	0.003	0.05
C	0.78	0.14	0.49	0.55	0.09	0.07
D	1.27	0.3	0.43	0.92	0.05	0.02
E	0.73	0.2	0.23	1.06	0.09	0.03
F	0.83	0.52	0.68	0.67	0.15	0.02
G	0.97	2.07	0.51	1.64	0.08	0.01
H	0.24	1.93	0.15	1.66	0.14	0.07
I	0.33	1.26	0.6	0.05	0.29	0.02
J	0.66	1.12	0.08	0.62	0.005	0.03
K	0.61	0.83	0.83	0.38	0.43	0.007
L	0.76	1.65	0.25	3.28	0.11	0.04
Mean	0.76	0.94	0.43	1.16	0.13	0.08
Std	0.30	0.68	0.22	1.07	0.12	0.16
Min	0.24	0.14	0.08	0.04	0.00	0.01
Max	1.27	2.07	0.83	3.28	0.43	0.57

Table3: Trace Element Concentration (mg/Kg) in the Gills of *Clariasgariepinus*

Sample code	Pb	Ni	Cu	Cr	Cd	Al
A	0.67	0.56	0.21	4.89	0.12	0.09
B	1.2	0.31	0.35	1.09	0.03	0.03
C	0.91	0.23	0.29	0.33	0.09	0.02
D	1.1	1.33	0.34	1.76	0.009	0.02
E	0.64	0.16	0.36	0.15	0.13	0.03
F	1.24	1.54	0.3	4.08	0.07	0.01
G	0.97	2.33	1.75	2.2	0.04	0.42
H	0.55	1.36	0.09	0.59	0.28	0.01
I	0.35	0.24	0.79	0.27	0.06	0.42
J	1.09	1.71	0.39	0.62	0.009	0.03
K	0.69	0.52	0.82	0.55	0.39	0.02
L	0.48	1.55	0.93	4.12	0.1	0.01
Mean	0.82	0.98	0.55	1.72	0.11	0.09
Std	0.30	0.73	0.46	1.71	0.11	0.15
Min	0.35	0.16	0.09	0.15	0.01	0.01
Max	1.24	2.33	1.75	4.89	0.39	0.42

Table4: Trace Element Concentration (mg/Kg) in the skin ofClarias*gariepinus*

Sample code	Pb	Ni	Cu	Cr	Cd	Al
A	0.79	0.28	0.23	1.86	0.15	0.6
B	0.99	0.23	0.37	0.68	0.06	0.04
C	0.78	0.48	0.301	0.49	0.08	0.01
D	0.94	0.33	0.24	0.88	0.11	0.01
E	0.82	0.35	0.27	0.64	0.08	0.02
F	0.53	0.36	0.33	1.08	0.09	0.02
G	1.25	2.3	1.2	1.99	0.35	0.01
H	0.31	1.09	0.72	1.94	0.4	0.04
I	0.31	0.65	0.57	1.11	0.1	0.03
J	0.83	1.94	0.79	3.58	0.07	0.02
K	1.02	1.53	1.31	0.24	0.42	0.05
L	0.53	0.82	0.5	4.09	0.46	0.006
Mean	0.76	0.86	0.57	1.54	0.19	0.07
Std	0.29	0.70	0.37	1.21	0.16	0.17
Min	0.31	0.23	0.23	0.24	0.06	0.01
Max	1.25	2.30	1.31	4.09	0.46	0.60

Table5: Trace Element Concentration (mg/Kg) in the bone of *Clariasgariepinus*

Sample code	Pb	Ni	Cu	Cr	Cd	Al
A	0.84	0.35	0.3	3.03	0.15	0.05
B	0.53	0.33	0.35	0.7	0.13	0.03
C	1.2	0.43	0.27	1.49	0.02	0.01
D	0.82	0.28	0.29	0.08	0.11	0.006
E	0.63	0.49	0.28	0.59	0.14	0.01
F	2.41	0.34	0.25	0.07	0.06	0.02
G	1.56	2.63	0.74	2.74	0.69	0.03
H	0.76	1.97	0.43	1.52	0.06	0.03
I	0.61	0.16	1.23	2.79	0.42	0.05
J	0.77	1.61	0.78	4.25	0.09	0.004
K	1.26	2.05	0.22	0.15	0.04	0.09
L	1.09	0.38	0.14	3.56	0.12	0.01
Mean	1.04	0.92	0.44	1.74	0.16	0.03
Std	0.53	0.87	0.32	1.48	0.19	0.02
Min	0.53	0.16	0.14	0.07	0.02	0.00
Max	2.41	2.63	1.23	4.25	0.69	0.09

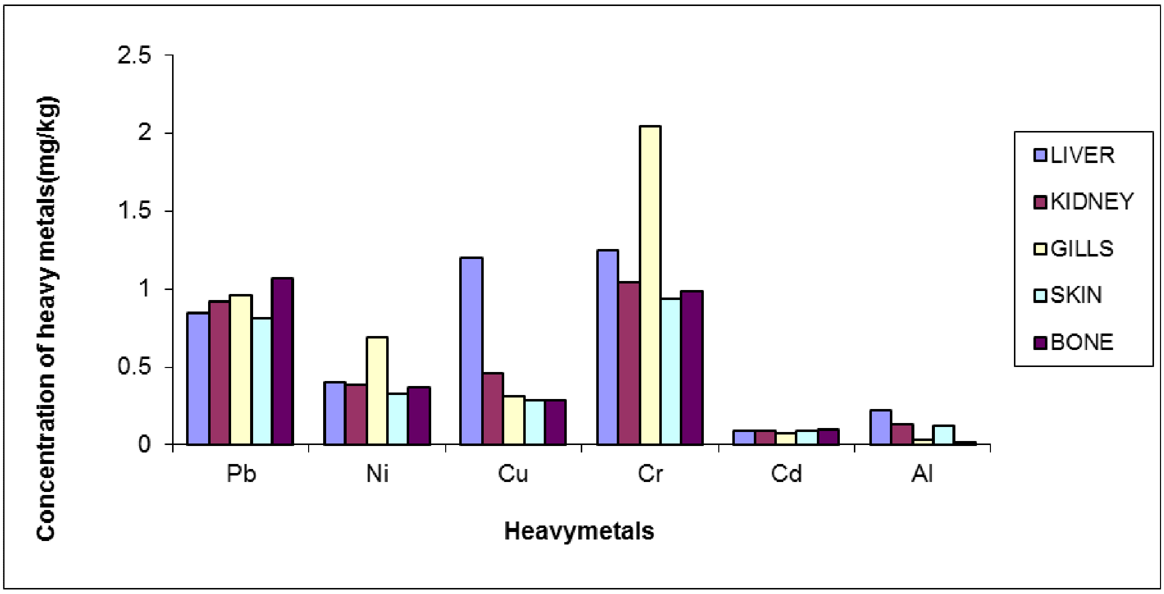

Fig 2: Mean concentration of Heavy metals accumulation in the organs of *Clarias gariepinus* in River Benue During Rainy season at Makurdi.

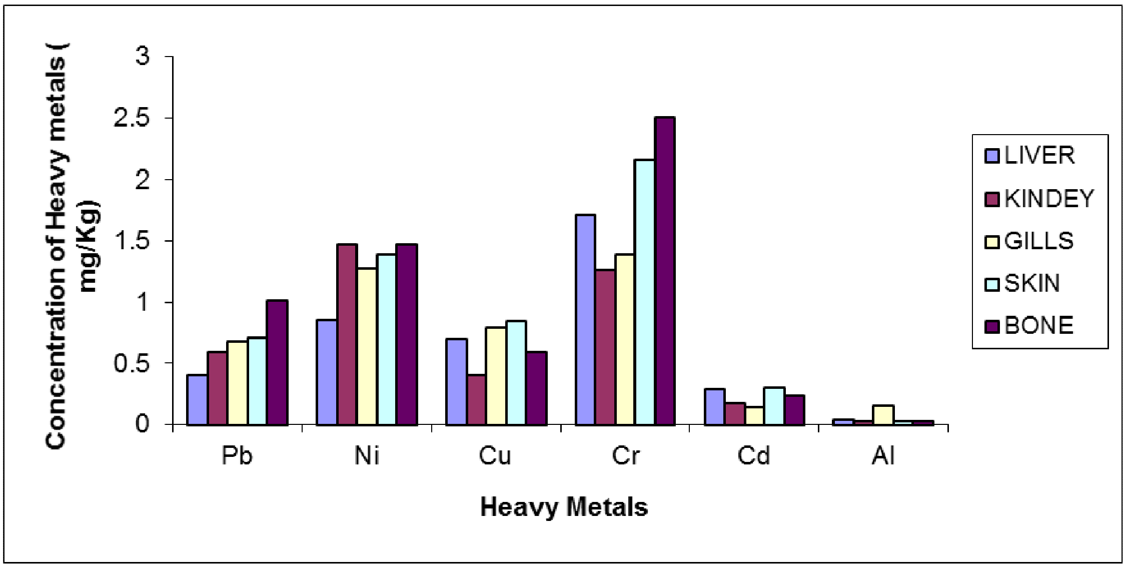

Fig 3: Mean concentration of Heavy metals accumulation in the organs of *Clarias gariepinus* in River Benue During Dry season at Makurdi.

DISCUSSION

Heavy metals have the ability to bio accumulate in the organs of the fish. In the course of this study heavy metals were accumulated in the liver, kidney, gills, skin and bone of *Clariasgaripinus* (African catfish). The heavy metals that are found in the water are transferred into the body organs of the fish where they become bio-accumulated. This result is consistent with the findings of Anim-Gyampo*et al*. (2013) who reported that heavy metal concentrations in water samples are usually less than what is obtained in the organs of the aquatic organisms. During the course of this study, Cr was the highest metal accumulated in the liver cells of the catfish while Cd was the lowest. However, the trend of heavy metal accumulation in the liver cells of the fish, was in the order Cr > Ni > Cu >Pb> Al > Cd. This is attributed to the chemical nature of the metals ionic strength and the pH of the liver cells that facilitate the metal accumulation (Eneji, *et al.*, 2011). In acidic state, enough hydrogen ion takes many of the negatively charged surfaces and little space is made available to bind heavy metals. The soluble form of heavy metals is thought to be more harmful because it is more easily transported and more readily available to aquatic organisms (Eneji*et al.*, 2011). The result of this study differs significantly from the result of an earlier study in North Central Nigeria that reported Ni as the highest accumulated metal in the liver cells of the fish and Pb with the lowest (Eneji*et al.*, 2014). However, the result of this study was consistent with the earlier work in River Benue where *Clariasgaripinus* bio accumulated Cr has the highest metals (Eneji*et al*., 2011).

Similarly in the kidney of the *Clariasgaripinus* Cr was still the highest accumulated metals and Cd the lowest during the study period. This could be that the liver and kidney may have different physiological processes but similar pH, in their cellular composition. All the same the trend of heavy metal accumulation in the kidney cells of the fish was in the order Cr > Ni >Pb> Cu > Al > Cd which is similar to the liver cells. This may be that the same content of the liver are transported directly to the kidney for excretion physiologically.

In the gills of the fish the Cr was the highest bio accumulated metal while Cd was still the least. However, there was a slight change ion the trend of the accumulation of the metals that follows: Cr > Ni > Cu >Pb> Al > Cd. This findings is consistent with an earlier study in River Benue that showed Cu was more accumulated in the gills than Pb (Eneji*et al*., 2011). However the findings of this study differs significantly from the result of an earlier study where Cu was the highest metal accumulated in the gills of the fish (Akan *et al*., 2012).

In the skin of the fish, the situation not was different, where Cr was still the most accumulated metal while Cd was the least. The trend of metal accumulation here was Cr > Ni >Pb> Cu > Al > Cd. This result differs significantly with the result of an earlier study that reported Cu and not Cr has the most accumulated metal in the skin of the fish (Akan *et al*., 2012). A slightly different situation was observed in the bone of the catfish. The most bio accumulated metals was Cr while the least was Al. The trend of the accumulation of the heavy metals was Cr > Ni >Pb> Cu > Cd > Al. This finding was not consistent with the result of an earlier study that reported Cu as the most accumulated metal in the bones of the fish. (Akan *et al*., 2012). Among the different organs of the fish there was no difference in the trend of metals accumulated in the tissue of the fish between and across the season (ANOVA, $p > 0.05$). This may be attributed to the fact that the bio accumulation is a time event that occurred over time.

Among the different metals (Pb, Ni, Cu, Cr, Cd and Al) examined in the organs of the fish, there was no significant different in all the organs of the catfish at Makurdi River Benue (ANOVA $p > 0.05$) during the dry season. However, during the rainy season a different situation was noticed, all the metals were not significant in the organs with the exception of Cu that significantly differs in the organs of the catfish (ANOVA, $p < 0.05$). This may be attributed to the fact that during the rainy season, the food is more abundant and the feeding habitat of the fish also change which contain more copper.During the rainy season the trend of accumulation of heavy metals in the organ of the fish was gills > liver > kidney > bone > skin. The highest accumulation of metal in the gills may be attributed to the water level and abundant food resources that followed this season. However, during the dry season the trend was kidney > skin > liver > gills > bone of the fish.

Generally in this study different metals accumulate at different concentration in various organs of the fish. This observation is consistent with the report of an earlier study in River Benue at Makurdi on *Clariasgariepinus* (Eneji*et al*., 2011). The different in the levels of bio accumulation in different organs of the fish may be linked to the different physiological function of each organ of the fish. Other plausible reasons may be the behaviour of the fish and feeding habits of the fish that may be significant in the bioaccumulation differences of the heavy metals in the organ of the fish (Eneji*et al*., 2011). The result of this study that reported Cr as the most accumulated heavy metals among the metals examined in the organs of the fish is consistent with the findings of an earlier study that reported Cr as the most accumulated metal among the other metals examined (Akan, *et al*., 2012). Similarly the findings of this study that Cd is the lowest metal accumulated in the organs of the fish is consistent with the findings of (Bashir, *et al*., 2013). The low accumulation of Cd in most organs of the catfish is attributed to the findings that the solubility of Cd is influence by large degree of acidity (Ros and Slooff, 1987).The general increase in mean concentration of heavy metals in the entire samples could be attributed to more bioaccumulation due to metal concentration from reduced water volume during dry season.

Conclusion

The bioaccumulation of the metals in the different physiological organs/tissue of the *Clariasgariepinus* sold in Makurdi is evident of environmental pollution with the metals of River Benue where these fish majorly obtained. This situation has a negative consequence on the public health of the residents of Makurdi and its environs that consume these fish as the most prevalent rich source of protein. The health implication of these metals on the fish and humans ranged from carcinogenic to fatal effects and total destruction of some body organs and physiological malfunction. However, the high level of bioaccumulation of Cr in all the organs of the fish is a clear indication as a good bio indicator and bio maker for the monitoring of pollution in the aquatic ecosystem.

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