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Heavy metals variations in organs of *Clarias gariepinus* and *Tilapia dageti* from landing sites at lower Benue River, Ibi, Taraba, Nigeria

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Abstract
This research studied heavy metal variations in organs of *Clarias gariepinus* and *Tilapia dageti* from landing sites by lower Benue River at Ibi, Taraba State, Nigeria. The results of heavy metal variations examined showed *C. gariepinus* recorded higher concentrations of the metals compare to *T. dageti.* Among the metals studied zinc (Zn) values were higher for both species while cadmium (Cd) values were lower. Ranking profile in organs was: liver >Gills > muscles with metal in order of Zn > Pb > Cu > Cd. Concentration of metals varied significantly (p<0.05) in organs for *T. dageti*. Zinc (Zn) recorded higher concentration (1.2000 mg/kg) while cadmium recorded lower values (0.0034 mg/kg). Also the correlation results during the study for the two species showed *C. gariepinus* have a strong association with the heavy metals compare to *T. dageti.* The Correlation association of heavy metals for cadmium (Cd) showed there was significant difference (p<0.05) for affinity for metal between the species. However, Lead (Pb) concentrations showed weak correlation between *C. gariepinus* and *T. dageti* during the study period. The correlation results also showed significant difference (p<0.05) in zinc (Zn) concentrations for *C. gariepinus* compare to *T. dageti*. Results of this study ascertained occurrence of heavy metals in lower river Benue and that variations in levels affect fish. All metals studied were within safe range for fish and fisheries product by the Food and Agricultural Organization (FAO)/World Health Organization (WHO) in the two species. However continuous monitoring and check on fish species for heavy metals load should be encourage and sustained. Heavy metals concentrations should also be investigated in other commercial species of the river to assess their safety for consumption and routine studies of the river water should also be sustained.

Keywords: Heavy metal, tissues, *C. gariepinus, T. dageti,* lower Benue river

Introduction
Water contamination, waste management issues and global environmental challenges have attracted international health attention [33]. Major factor controlling cultured and wild fishes in aquatic environment is water quality. Contamination of aquatic environment by inorganic and organic chemicals is a major threat to survival of aquatic organisms including fish [13]. Apart from implications on human health [35], intensities of inorganic and organic substances in water bodies may threaten health of aquatic organisms including fish [7].
Heavy metal are exclusive naturally occurring elements that persevere in the environment for long time and may not be eco-friendly [11]. Heavy metal are naturally found in the Earth's crust. They enter water bodies from diverse sources [12]. Major sources of heavy metal in the ecosystem could be natural or anthropogenic activities. The natural occurring metals are already existing in nature and became part of the environment by weathering, metal-bearing rocks and volcanic eruptions, while anthropogenic sources of heavy metal include various industries, mining, and agricultural practices [23]. Human activities are the major sources of heavy metals contaminating rivers [13], activities such as farming, surface runoffs from manufacturing areas, effluents from industrial [38] and mining activities [20] contribute to the levels of heavy metals in the water bodies. Another source of heavy metals is inappropriate waste management or disposal [12]. The discharge of wastes containing toxic heavy metals into water bodies may substantially affect fish and other aquatic organisms, endangering public health.

Mining, smelting operations, industry, irrigation, urban development, transportation, and fertilizers have released specific quantities of heavy metals poisoning land soil [16]. Heavy metals are grouped into essential and non-essential elements. The essentials include iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), cobalt (Co), nickel (Ni), molybdenum (Mo) and selenium (Se). They are called essential since they are necessary for fundamental metabolic activities in living organisms. Most serve as cofactors, functionally and structurally important for enzymes and enzyme-catalyzed biochemical reactions, true for many life forms [31]. However, presence of 'essential' metals above certain levels results in damaging biological effects. The non-essential heavy metals have no physical benefits to living systems and many are toxic at low concentrations. Examples include lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As) and tin (Sn) [31]. Fish accumulate heavy metals many times higher than water or sediment [14]. When it enters aquatic environment, great percentage settle down and are absorbed by bottom mud [1]. Heavy metals accumulates in fishes through body parts of fishes such as body surface, gills, digestive tract, liver and muscles. The highest point of heavy metals levels of concentration in organs are often the gills then liver and muscle showing the least concentration levels [26]. Effects of metals occur when excretory, metabolic, storage and decontamination mechanisms are no longer able to counter uptake [33]. Heavy metal and other contaminants tend to bio accumulate, have long persistence and bio-magnified in food chain, endanger aquatic species and can also cause extinction of some species or aquatic fauna [22].

Materials and Methods

Study Area

The study was conducted by Lower River Benue, ibi, between rimi and Kabawa axis located in Taraba south bordering Shandam town of Plateau state. It is found within Latitude 8º18'N and 9º 51'E about 350 meter below sea level. The axis of the river receives effluents discharge from Agricultural fields, Block molding cottage industries close by the river and huge dump sites just by the river. The river is also utilized for commercial activities such as fishing, domestic purposes and as a commercial transportation route. The inhabitant are majorly farmers, fishermen and traders.

Collection of Samples

Fish: Fish samples were obtained from landing sites at rimi and Kabawa using various fishing mesh size and nets. Sampling of fish was carried out monthly for six (6) months from September 2022 to February 2023. Fish obtained were identified using identification keys and monographs. The weight (g) and length (cm) was measured using a top loader (mettle balance) and recorded to the nearest 0.1g. Organs (gills, liver and muscles) were oven dried at 80 °C for 48 hours milled separately, placed in well labeled polyethylene bags and stored at -5 ºC before digestion and analysis.

Digestion of samples

Fish: Each fish part was digested using organic extraction method described by [30] Sreedivi *et al*. (1992). 1g of milled sampled were placed in 50ml Kjeldhal flask. 10ml of HNO_3 aqueous solution, 2 ml $HCLO_4$ aqueous acid solution and 2 ml Sulphoric aqueous solution (5:1:1) ratio, was added to the sample in the flask. Contents of the flask was treated with adequate heat under a hood. Digestion was terminated at the occurrence of white fumes. An aliquot of the digest was diluted with 10ml distilled water and further boiled for a few minutes and allowed to cool. This was then filtered into a 50ml volumetric flask and made up to mark. Black samples were prepared using same quantity of mixed acids.

Statistical analysis

Data was presented as means and standard deviation. Means were subjected to one way analysis of variance (ANOVA) via 9.0 statistical packages for the social sciences (SPSS) 2012 to ascertain significant differences at 5% level of probability. Significant means was subjected to Duncan Multiple Range Test (DMRT).

Results and Discussion

Variations of some heavy metal in organs of *C. gariepinus* and *T. dageti* from Lower Benue River, ibi local government area, Taraba state are presented in table 1 to 4. The samples were collected monthly for 6 months from September, 2022 to February, 2023.

Mean variation of heavy metals (mg/kg) in organs of *Clarias gariepinus*

Result on variation of some heavy metals in organs of *Clarias gariepinus* during period of study is shown in Table 1. The result showed that zinc recorded higher concentrations in all the tissues during the study compare to other metals. High concentrations was recorded in the liver, follow by the gills and the muscles with the concentration of 1.7167 mg/kg, 1.2250 mg/kg and 0.6584 mg/kg respectively. Copper (Cu) has the second highest value in the liver, followed by Lead (Pb) concentration in the muscles, gills, and liver in following ranking order muscles >gills > liver with values as follows 0.2573 mg/kg, 0.2470 mg/kg, and 0.1853 mg/kg respectively. Copper (Cu,) recorded higher concentration in the gills compare to the muscles. The lower concentrations recorded for *Clarias gariepinus* was observed in Cadmium (Cd). The values recorded in the organs were 0.0039 mg/kg, 0.0033 mg/kg, and 0.0031mg/kg. Though, no significant difference was observed in concentration of Cadmium (Cd) among organs studied (Table 1).

Table 1: Heavy metals in organs of *Clarias gariepinus* during study period

	Concentrations			
Fish organs	**Cd**	**Pb**	**Zn**	**Cu**
Liver	0.0031±0.0005 a	0.1853±0.0387 b	1.7167±0.1160 a	0.3492±0.0525 a
Muscle	0.0033±0.0006 a	0.2573±0.0592 b	0.6584±0.0336 b	0.0429±0.00545 b
Gills Safe Limit [18].	0.0039±0.0006 a 0.05mg/kg	0.2470±0.0509 b 2.0mg/kg	1.2250±0.0789 c 1000mg/kg	0.0691±0.0323 b 2.0mg/kg

Data are presented as Mean ± S.E.M. Values with different letters are not significance different (p>0.05).

Mean concentrations of heavy metals (mg/kg) in organs of *Tilapia dageti*

The result of mean metal concentrations in organs of *Tilapia dageti* at Lower River Benue is presented in Table 2. Zinc (Zn) recorded higher concentration for all tissues studied with mean variation of 1.0834mg/kg, 0.9500mg/kg, and 0.6917mg/kg in the gills, liver, and muscles respectively. Also lead (Pb) recorded high values for liver (0.2419mg/kg) and gills (0.2162 mg/kg) respectively. Copper (Cu) recorded a higher value in the liver, followed by lead (Pd) while lower mean variations was recorded in the muscles. Lower mean value recorded for Copper (Cu) in the gills (0.0690 mglkg) and muscles (0.0377). While the lowest mean values (0.0037, 0.0033 and 0.0027) were recorded for cadmium (Cd) in the organs of *T. dageti* (Table 2).

Table 2: Mean concentrations of metal (mg/kg) in organs of *Tilapia dageti*

	Concentrations			
Fish organs	**Cd**	**Pb**	**Zn**	**Cu**
Liver	0.0037±0.0008 a	0.2419±0.0620 b	0.9500±0.0793 a	0.2056±0.0352 a
Muscle	0.0033±0.0005 a	0.1905±0.0257 b	0.6917±0.0434 b	0.0377±0.0072 b
Gills	0.0027±0.0004 a	0.2162±0.0629 b	1.0834±0.0747 a	0.0690±0.0098 b
Safe limit [18].	0.05mg/kg	2.0mg/kg	1000mg/kg	2.0mg/kg

Data are presented as Mean ± S.E.M. Data with the same letters are not significantly different ($p>0.05$)

Average mean comparison of metal variation between species

The results of Average mean comparison of heavy metals concentration between *Clarias gariepinus* and *Tilapia dageti* are presented in Table 3. Results showed that *C. gariepinus* recorded higher levels of the metals compared to *T. dageti* throughout the study period. The concentration ranking profile between the organs was Zn> Pb> Cu> > Cd. Zinc values were found to be higher for the two species, with average mean value (1.2000mg/kg) for *Clarias gariepinus* while for *T.* dageti (0.9084mg/kg). The result revealed there was significant difference ($p<0.05$) between heavy metal concentration for both fishes and in the organs considered throughout the study. However, there was no significant difference ($p>0.05$) for Lead (Pb) and Copper (Cu) between the two fish species but there was significant difference ($p<0.05$) for Zinc (Zn) and Cadmium (Cd) among species investigated.

Table 3: Average mean comparison of heavy metal variation between fish species studied (n=6)

	Concentrations (mg/kg)			
Heavy metal Species	**Cd**	**Pb**	**Zn**	**Cu**
CG	0.0034±0.0004a	0.2299±0.0288 a	1.2000±0.0868 b	0.1537±0.0309 a
TD	0.0032±0.0004 b	0.2162±0.0300 a	0.9084±0.0469 a	0.1041±0.0173 a

Key: CG= *Clarias gariepinus*, TD= *Tilapia dageti*

Data are presented as Mean ± S.E.M. Data with same letters are not significance difference ($p>0.05$)

Correlation of heavy metals in *Clarias gariepinus* (CG) and *Tilapia dageti* (TD)

The results of correlation of heavy metals in *Clarias gariepinus* and *Tilapia dageti* are presented in Table 5. The correlation comparison in the two species showed both positives and negative correlation. Cadmium (Cd) in *Clarias gariepinus* show positive correlation with cadmium (Cd) and zinc (Zn) in *Tilapia dageti* (0.112 mg/kg and 0.025 mg/kg respectively), but show negative correlation with lead (Pb) in *Tilapia dageti* (-0.128 mg/kg) and copper (Cu) in *Clarias gariepinus* (-0.183 mg/kg).While concentration of cadmium (Cd) in *Tilapia dageti* show negative correlation with concentration of lead (Pb) in *Clarias gariepinus* (-0.069 mg/kg), zinc (Zn) in *Tilapia dageti* (-0.110 mg/kg) and copper (Cu) in *Tilapia dageti* (-0.018 mg/kg). However copper (Cu) in *Clarias gariepinus* (0.727 mg/kg) showed strong correlation with *Tilapia dageti*, and Clarias *gariepinus* (-0.105 mg/kg) show weak correlation with lead (Pb) in *Tilapia dageti*. Only correlation of zinc (Zn) in *Clarias gariepinus* and zinc (Zn) in *Tilapia dageti* (0.465 mg/kg), zinc (Zn) and copper (Cu) *(*0.793 mg/kg), correlation of zinc (Zn) in *Clarias gariepinus*. Copper (Cu) concentration in *Tilapia dageti* (0.749mg/kg) and copper (Cu) in *Clarias gariepinus* and copper (Cu) in *Tilapia dageti* (0.727 mg/kg) showed Significant difference ($p<0.01$). It was also observed that negative correlation between lead (Pb) for *Clarias gariepinus* and lead (Pb) in *Tilapia dageti* (-0.105 mg/kg), lead (Pb) in *Clarias gariepinus* and zinc (Zn) for *Clarias gariepinus* (-0.136 mg/kg). Also the result showed negative correlation of lead (Pb) in *Clarias gariepinus* and copper (Cu) in *Clarias gariepinus* (-0.102 mg/kg) and copper (Cu) in *Tilapia dageti* (-0.103 mg/kg) thus there was no significant difference ($p>0.01$) in concentrations.

Table 4: Correlation between metals in *Clarias gariepinus* (CG) and *Tilapia dageti* (TD)

Heavy metals	CG (Cd)	TD (Cd)	CG (Pb)	TD (Pb)	CG (Zn)	TD (Zn)	CG (Cu)	TD (Cu)
CG (Cd)	1							
TD (Cd)	0.112	1						
CG (Pb)	0.062	-0.069	1					
TD (Pb)	-0.128	0.129	-0.105	1				
CG (Zn)	0.052	0.037	-0.136	0.113	1			
TD (Zn)	0.025	-0.110	0.057	0.061	0.465**	1		
CG (Cu)	-0.183	0.093	-0.102	0.136	0.793**	0.187	1	
TD (Cu)	0.006	-0.018	-0.103	0.109	0.749**	0.280	0.727**	1

**. Correlation is significant at the 0.01 level (2-tailed).

Heavy metals variations in organs of *Clarias gariepinus*

Mean metal variations in the organs of *C. gariepinus* studied at Lower River Benue showed zinc (Zn) has higher concentrations while cadmium (Cd) recorded lower values during the study period. This corroborates findings of [33] who reported higher concentrations of Zinc (Zn) in flesh of *C. gariepinus* and lower concentrations of cadmium (Cd) at River Galma and Kubanni in Zaria. Results obtained is similar to findings by [22] who reported higher concentrations of zinc

(Zn) in the intestine and gills of *Synodontis courteti and Mormyrus macrophthalmus* in previous study in Taraba state. The zinc (Zn) concentration was high in liver compare to gills and muscles. Zinc (Zn) has been reported to support nucleic acid production, the immune system, and neuro transmission, at greater concentrations it can be lethal to fish and maybe a modifier of cancer-causing response [25, 15]. In humans, severe, zinc (Zn) poisoning can result in vomiting, diarrhea and fever [8]. Copper (Cu) recorded the next higher concentrations of heavy metals during the study period. Copper (Cu) values for this study were high for liver compare to gills and muscle. This corroborates findings of [32] who reported higher concentration of copper (Cu) in liver of *Sarotherodon galilaeus* and opined that higher concentrations could be due to the detoxifying role of the liver. Lead (Pb) values for this study were higher in the muscles compare to the gills and liver. [10] in their work on accumulation of heavy metal in fishes from River Vinkilag, Adamawa made similar findings that high levels of lead in organs may result from bioavailability of lead (Pb) in the river from leaded gasoline, effluents from industries and geological sources. Throughout the study period, cadmium (Cd) recorded lower metal concentrations in the following ranking gill >muscle >liver. [29], however reported higher cadmium (Cd) concentration in liver and gill of *C. gariepinus*, river Nile in Egypt. Cadmium (Cd) had been described as a noxious non-essential metal which doesn't have any better role in biological processes in organisms [37]. But even low concentrations of Cadmium could harm fish and may injures organs like kidneys causing injury impairing kidney function, poor reproduction capability, hypertension, tumors besides liver malfunction [37]. The low concentration of Cadmium in *C. gariepinus* for this study may be attributed to lesser contact with discharges from heavy industries, higher contamination from runoff due to agrochemicals in the rivers [33]. This may be expected since the river receives high concentrations of organic and inorganic contaminations from household waste as well as runoff agrochemicals from the rich pastoral basin [33].

Concentrations of heavy metals in tissues of *Tilapia dageti*

Results of concentrations of heavy metals in *T. dageti* during the study showed that Zinc (Zn) recorded higher metals concentrations in the gills compare to those of C. gariepinus which was higher in the liver compare to the gills. Cadmium (Cd) has the least concentration in all the organs examined. This does not corroborate with findings of [3] who reported higher Cadmium (Cd) levels in their work at River Ogbere, Ibadan. Lower mean concentration of cadmium in gill compared to livers results from binding affinity of cadmium on gill surface which is in direct contact with water and adsorption occur at the gill surfaces, depending on availability of proteins which the metals will bind [29]. Muscles recorded the lowest metals concentrations compare to all other organs examined during the study period which may occur due to lack of binding affinity of metals to muscles, and it makeup greater mass of flesh consumed as food [33, 6]. Metals accumulation in the organs ranking Zn>Pd>Cu>Cd. Similar concentration ranking profile was reported by [14]. Copper (Cu) concentrations for this study were higher in the liver compare to other organs examined. This corroborate with findings of [32] who reported higher mean Cu concentration of liver in *C. gariepinus* with the least in skin as follows: skin<fins<gills<muscle<bone. Similar higher concentrations of Copper (Cu) was recorded in the liver of *Sarotherodon galilaeus* by [32]. There is no significance difference for cadmium (Cd) and lead (Pb) in the organs examined during the study period. This corroborate findings of [28] who reported that there was no variation in the Lead (Pb) levels in the muscles of *C. gariepinus*, *Oreochromis niloticus* and *Chrysichthys nigrodigitatus* at Ogun River. However significance difference in this study revealed zinc (Zn) and copper (Cu) showed variation corroborating findings of [2] at Kado fish market, Abuja, Nigeria, who investigated some metals in the muscles and intestine of *C. gariepinus* during wet and dry season period, reported that levels of copper (Cu) and zinc (Zn) showed variation with season.

Comparison of heavy metals between *Clarias gariepinus* and *Tilapia dageti*

In this studies, *C. gariepinus* recorded higher metal concentrations compare to *T. dageti*. This may be due to their feeding habit, and their habitat [22]. Both *T. dageti* and *C. gariepinus* accumulate more Zinc (Zn) compare to cadmium (Cd). This does not corroborate with the findings of [9] who reported higher concentrations of cadmium (Cd) in the gills of *Cyprinus carpio.* However, this study reported lower concentrations of cadmium (Cd) in *T. dageti* and *C. gariepinus* compare to other metals investigated. This could be as a result of habitat change, size of fish, extent and time of metal exposure, water interaction, environmental needs, feeding pattern and food breakdown which may affect degree of accumulation of toxicants among fishes [5]. Species that spend longer time at bottom of rivers to feed are likely to accumulate more metals than those that feed at the surface [4]. Taking leads (Pb) as an example, the key issues for its concentration and bioavailability in the aquatic environment are species, sampling sites, pH, alkalinity and the degree of its absorption into the sediments in aquatic ecosystem [36, 20]. However all the metals reported in this studies were within safe limit established by [18] for fish and fish product. This does not corroborate with that of [2] who in their findings investigated concentration of heavy metals in *Clarias gariepinus* and *Synodontis* sp. obtained from Kado fish market Abuja, Nigeria.

Correlation between heavy metal in *Clarias gariepinus* and *Tilapia dageti*

Results between Organs of *Clarias gariepinus* and *Tilapia dageti* at lower river Benue, showed both positive and negatives correlation recorded in this studies. Value of Lead (Pb) (-0.105) in *Clarias gariepinus* (CG) showed Weak correlation compare with Lead (Pb) value (-0.105, -0.136, -0.102, and -0.103) in *T. dageti***,** Zinc (Zn) in *Clarias gariepinus*, Copper (Cu) in *C. gariepinus* and in *T. dageti* respectively, and also displayed no significant difference (p<0.01). This corroborate findings of [25] who in their findings at Moulouya River Morocco reported weak correlation between Zinc (Zn) and Lead (Pb), in the muscle of *C. gariepinus*, *T. zilli*, *O. mossambicus* indicating variation in their organs, and ability to accumulate heavy metals. Significant difference and Strong correlation was recorded between Zinc (Zn) in *Clarias gariepinus* and Zinc (Zn) in *T. dageti* (0.465), Copper (Cu) in *C. gariepinus* and copper (Cu) in *T, dageti* (0.727) respectively. This indicate both fish accumulate copper (Cu) and zinc (Zn) in their organs. This does not corroborate with findings of [24] who in their investigation at Dar es Salaam, Tanzania in the organs (gill, fin, and muscle) of *C. gariepinus* and *Tilapia zilli* showed strong correlation between metal in organs of the fishes. However this does not corroborate with the findings of [25] at Moulouya River Morocco who in their investigation reported weak association between zinc (Zn) and lead (Pb) in the species examined.

Conclusion

The results from this study showed zinc (Zn) concentrations were higher compare to other metals in the two fish tissues studied. *Clarias gariepinus* tissues reported higher accumulation of heavy metals compare to *Tilapia dageti*. Also cadmium (Cd) levels were generally lower during the study. However, gills of *Tilapia dageti* recorded higher mean metal concentrations compare to the other organs. This may be due to the gills been the first sites of receipt of nutrient and other food items by the fish.

Recommendations

In other to avoid serious hazard to the aquatic life and human in future. Routine monitoring of fishery product at Rimi and Kabawa landing sites by lower river Benue should be sustained for public health reasons and to prevent extinction of valuable species. Also assessment of other species of commercial value will be very important.

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