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Original Research

Studies on heavy metals in water, sediment and *Clarias gariepinus* of river Gongola, Gombe state

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ABSTRACT:

Evaluation of heavy metal contamination (Cu, Zn, Pb, and Cd) in water, sediments and in the muscles of *Clarias gariepinus* in river Gongola, Gombe state, was carried out between April and September 2019 in six sampling sites. The concentrations were determined using atomic absorption spectrophotometer. The data obtained was analyzed using one way analysis of variance and significant differences accepted at $P \leq 0.05$. Post hoc Duncan test was used to separate means. Mean heavy metal concentrations ($mg.kg^{-1}$) in the sediments were Cu (0.448-0.750) and Zn (0.019-0.025). Pb and Cd were below detectable limit. There was significant differences in metal concentrations for Cu ($P=0.002$), whereas Zn ($P=0.756$) showed no significant difference among the sites. Surface water from all the sites did not show significant difference in heavy metal contamination ($P>0.05$). The mean metal levels ($mg.kg^{-1}$) in *C. gariepinus* muscles, were Cu (0.388-0.759) and Zn (0.020-0.082), whereas Pb and Cd were below detectable limit. Copper exhibited significant difference between the sites ($P=0.00$) while for Zn there was no significant difference in the sites. Pearson matrix correlation analysis showed some significant correlations among the heavy metal levels in the water, sediments and different catfish muscles. The concentrations of all the metals in surface water, sediments and catfish muscles did not exceed the WHO recommended limit for drinking and consumption. Results from this study showed the need for an ecosystem approach towards sustainable management of rivers to curb aquatic pollution which is a risk to the entire ecosystem.

Keywords:

Heavy metals, Water, Sediments, Catfish, River Gongola.

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INTRODUCTION

Freshwater bodies play an important role in the livelihood of human populations. They are used as a source of domestic water supply, irrigation, fishery development, hydropower generation and flood control. Extra advantages of the reservoirs include attracting the tourists and developing new zones for improvement (Kitur, 2009). As per Dudgeon (2006) and Junk (2002), freshwater environments are more prone to human activities and consequently, they are probably going to be affected by catchment activities. This is on the grounds that both terrestrial and aquatic ecosystems are inter linked (UNEP, 2000). Aquatic ecosystem pollution in the recent decades have become a major problem (Yousafzai and Shakoori, 2008; Narayan and Vinodhini, 2008).

FAO (2003) noted that the contamination of water supplies from both natural and anthropogenic sources has impacted on the health and economic status of populations. Human activities results in pollutants such as heavy metals, pesticides and herbicides to enter the aquatic ecosystems. These anthropogenic activities continuously increase the amount of heavy metals in the environment, especially in aquatic ecosystems. Thus, heavy metal pollution is growing at an alarming rate and has become an important worldwide problem. The situation has become worse further due to the absence of proper environmental laws, populations, urbanization, industrialization and rural practices (Gupta *et al*., 2009).

.. In Nigeria, heavy metals have been ensnared as one of the important causes of liver and kidney ailments which ended up as the cause of high mortality. The intense neurological impacts of cadmium toxicity includes nausea, cramps, diarrhea, vomiting and chest pain, etc. Additionally, rheumatic arthritis, muscular pain and osteomalacia in the older people are proof of prolonged cadmium toxicity (Kobingi *et al*., 2009). Prolonged cadmium exposure leads to kidney and liver damage along with circulatory and nerve tissues (Osman and Kloas, 2010). Lead (Pb) toxicity can bring about a wide scope of negative impacts, especially in infants than adults. The mortality rate of Pb neurotoxicity is about 25% while about 40% of the survivors need to live with neurological consequences like mental retardation, optic atrophy and cerebral paralysis (Heath, 1991).

Proper assessment of water bodies is a viable strategy for ensuring the safety of living beings from heavy metals. Notwithstanding, many water bodies in Nigeria have not been sufficiently evaluated for heavy metals pollution. Hence, this study assessed the concentration of heavy metals in water, sediments and catfish muscles from river Gongola; a recipient of sewage effluent, agricultural waste as well as other anthropogenic inputs and a provider of water as well as fish consumed by People of Gombe State of Nigeria.

MATERIALS AND METHODS

Study area

The examination site is river Gongola which is the principal tributary of the Benue river. It ascends in to many branches (comprising of the Lere and Maijuju streams) on the eastern slants of the Jos Plateau and cascades (with many) onto the fields of the Gongola basin, where it follows a northeasterly course. It then flows past Northern parts of Dukku local government, Nafada and takes an abrupt turn toward the southern parts of Gombe state.

River Gongola transverses Gombe state through Gombe North senatorial district at a latitude of 10.817° and longitude of 10.767°. Soils in this area are shallow to the deep loamy, sandy clay, loam and vertisols with cracking clays that have weathered from shales (Table 1).

Sampling

Six sampling sites were identified from river Gongola. The river were divided into three regions; the upper, middle and lower regions. The upper, middle and lower regions had two sites each (Kunde and Gombe

Abba, Lafiya and Hashidu, Wuro Tale and Jamari respectively). The six sampling sites were chosen to represent different sub basins that drain into the river in order to understand the influence of natural and human activities on the river. Sampling were carried out once a month for six months (April 2019 – September 2019) in all the sampling sites in the river.

Sampling of water, sediments and fish

Sampling of water was done based on the method of Ndimele and Kumolu-Johnson (2012). Water tests from each of the six sampling sites were collected at a depth of 0.3m into 500 mL plastic containers. The bottles were rinsed three times with the river water at the time of sampling. Samples were then collected by direct immersion of the sampling bottle into the river. Immediately after sample collection, 2 mL nitric acid (AR grade) was added to the water samples to reduce adsorption of metals onto the walls of the plastic bottles. Samples were transported in an ice-box to the laboratory and stored at 4^{o} C awaiting analysis.

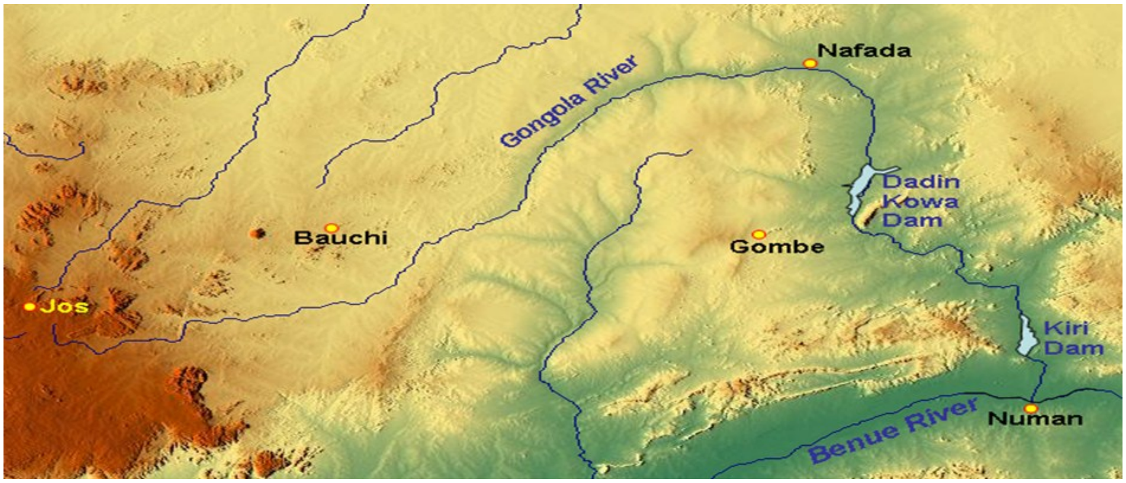
Sediment samples were collected from the bottom surface (1-2 cm thick) using method described by Omozokpia *et al* (2015). For each sampling site, three sediment samples were collected randomly, homogenized and kept in clean polyethylene bags samples were then stored in ice box for transportation to the laboratory. In the laboratory, the samples were kept in a freezer at -200^{o}C until they are processed for heavy metal analysis. *Clarias gariepinus* samples were collected with fishing net of mesh size three (3) inches by local fishermen from each sampling site. Fish samples collected were kept in a pre-cleaned polythene bags, that were sealed, labeled and kept with an ice blocks for transportation to the laboratory at ATBU Bauchi. The samples were then kept in a deeper freezer until muscle tissues were being extracted for analysis.

Digestion of water, sediments and fish samples for metal analysis

Digestion of the water, sediments and fish samples was carried out in triplicates using concentrated nitric acid (analytical grade) according to the method described by Zhang (2007). A blank solution was also prepared. All the digested samples were filtered using Whatman 0.42 µm filter paper into a 50 mL volumetric flask and top up to the mark with distilled water. Heavy metal analysis was done using atomic absorption spectrometer at the ATBU Bauchi Public Health Research Laboratory, Nigeria.

Statistical data analysis

Data analysis was carried out using computerize



KEY ● - SAMPLING SITES < - RIVER GONGOLA

Figure 1. Google Map of river Gongola, Gombe state, Nigeria

Table 1. Sampling sites and their geographical coordinates of river Gongola, Gombe state

S. No	Sampling sites	Latitude ^{0}N	Longitude ^{0}E
1	Kunde	10.695054	10.497167
2	Gombe Abba	10.815250	10.583070
3	Hashidu	10.906380	10.665124
4	Lafiya	10.942264	10.698010
5	Wuro Tale	10.915633	10.671575
6	Jamari	11.072901	11.006636

Source: Google Map

statistical Programme (MINITAB 7.0). The data were subjected to one-way analysis of variance (ANOVA) and significant differences accepted at $P \leq 0.05$. Where significant differences are found, the mean values were separated using Duncan Post Hoc test. Correlation analysis was done to determine associations among various variables. Descriptive statistics for all collected data was also obtained using MINITAB software.

RESULTS

Heavy metal concentrations in surface water

The mean concentrations of Cu (mg/L) in surface water from all sampling sites did not vary (Table 4). The mean Cu concentrations recorded were 0.371±0.141mg/L (Kunde), 0.335±0.125 mg.L^{-1} (G/abba), 0.295±0.129 mg/L (Hashidu), 0.260±0.141mg/L (Lafiya), 0.315±0.156 mg/L (W/Tale) and 0.451±55.57mg/L (Jamari). One way ANOVA showed that there was no significant variation (P=0.470; df=101) in Cu concentrations levels between the different sampling sites. The concentration of Zn in the surface water recorded in this study did not exceed the recommended limit of 3 mg.L^{-1} for Zn levels in drinking water (WHO, 2008). While lead and cadmium were below detectable limit in the water samples collected from the studied area indicated in the Table 2 below.

Heavy metal concentrations in sediments

The mean Cu concentrations (mg.kg^{-1}) at the six sampling sites showed modest variations (Table 4). The mean Cu concentrations were Kunde (0.550±0.291 mg.kg^{-1}), G/Abba (0.678±0.231 mg.kg^{-1}), Hashidu (0.728±0.245 mg.kg^{-1}), Lafiya (0.750±0.259 mg kg^{-1}), W/Tale (0.686±0.211 mg.kg^{-1}) and Jamari (0.448±0.262 mg.kg^{-1}). One way ANOVA showed significant differences (P = 0.002; df = 107) between the sites (Table 4.2). Duncan Post Hoc test demonstrated that copper levels recorded at Lafiya was essentially not the same as Jamari and Kunde, however not significantly different in relation to the next three sites. Jamari does not show significant difference in Cu concentration levels with Kunde, but showed significant variation with G/Abba, Hashidu, Lafiya and W/Tale. There was no significant difference (P = 0.756; df = 80) in Zn levels between the different sites. However, the sediment samples of river Gongola showed that lead and cadmium were below detectable limit (Table 3).

Heavy metal concentrations in *Clarias gariepinus* (catfish) muscles

Mean Cu levels recorded in *Clarias gariepinus* (Catfish) during the study were shown in Table 4. The levels ranged from 0.388±0.082 mg.kg^{-1} (Lafiya) to 0.759±0.413 mg.kg^{-1} (Jamari). The other mean Cu levels recorded were 0.460±0.143 mg.kg^{-1} (G/Abba), 0.566±0.255 mg.kg^{-1} (Kunde), 0.603±0.229 mg.kg^{-1} (W/Tale) and 0.529±0.146 mg.kg^{-1} (Hashidu). The results varied significantly (P=0.00; df=107) in Cu levels recorded at different sampling sites. The mean Zn concentration levels in catfish muscles varied (Table 4) with the highest levels observed at Lafiya (0.082±0.010 mg.kg^{-1}) and the lowest at G/Abba (0.019±0.012 mg.kg^{-1}). Jamari, W/Tale, Hashidu had mean Zn concentra-

Table 2. Mean ± standard deviation for heavy metal concentration in water recorded from April-September in river Gongola, Gombe state

Element /site	Kunde	G/abba	Hashidu	Lafiya	W/tale	Jamari	WHO standard limit
Cu (mgL^{-1})	0.371 ±0.141^{a}	0.335±0.125^{a}	0.295±0.129^{a}	0.260±0.141^{a}	0.315±0.156^{a}	0.451±55.57^{a}	1.00-2.00
Zn (mgL^{-1})	0.019±0.012^{a}	3.021±8.992^{a}	0.027±0.111^{a}	0.019±0.015^{a}	0.021±0.014^{a}	0.019±0.014^{a}	3.00
Pb (mgL^{-1})	BDL	BDL	BDL	BDL	BDL	BDL	0.01
Cd (mgL^{-1})	BDL	BDL	BDL	BDL	BDL	BDL	0.01

Mean in same row with different superscripts are significantly different at $P<0.05$ Levels.
BDL: Below detectable limit

tions of 0.020±0.010 $mg.kg^{-1}$, 0.022±0.009 $mg.kg^{-1}$ and 0.021±0.012 $mg.kg^{-1}$ respectively. Kunde recorded a mean Zn level of 0.024±0.015 $mg.kg^{-1}$. One way ANOVA revealed no significant difference (P=0.869; df=55) between the sampling sites. However, the Catfish muscles samples of river Gongola showed that lead and cadmium were below detectable limit (Table 4).

Relationships of heavy metal concentrations in the water, sediments and catfish muscles

Correlation analysis of heavy metals in the water, sediments and catfish muscles done by Pearson correlation coefficients to obtain associations between heavy metal variables in the surface water, sediments and catfish muscles were shown in Table 4. The concentration of Cu in surface water showed a positively significant correlation with Cu levels in sediments (r=0.166; P=0.010) but negatively significant with Cu in Catfish muscles (r=- 0.109; p=0.010). Also, Cu in the sediments showed a negative significant correlation with Cu in the catfish muscles (r =-0.490; P=0.010). The Zn levels in surface water had a significant positive correlations with Zn levels in the sediments (r=0.816; p=0.010) and a significant correlation with Zn levels in the catfish muscles.

DISSCUSION

Copper can get into aquatic ecosystems from diverse sources for example, from Cu compounds used in fungicides, algicides, insecticides, wood preservatives, electroplating and azo dye manufactures (Akan *et al*., 2010). The high Cu levels in Lafiya sampling site could be attributed to agricultural activities in the catchment especially the use of fertilizers, fungicides and insecticide. Therefore, during the rainy season Cu compounds added in fertilizers and animal feeds get into river Gongola through surface runoff. The mean levels of Cu in the study area were below the WHO standard values of 25 $mg.kg^{-1}$ for the survival of aquatic organisms (WHO, 2004) during the study period. Comparable mean Cu Concentration levels in the surface sediments have been observed in river Nile (0.024-0.054 $mg.kg^{-1}$) of Egypt (Osman and Kloas, 2010). Heavy metal contamination studies done in river Kaduna, Nigeria showed that the mean Cu concentration levels was 24.5 $mg.kg^{-1}$ at shiroro fishing settlement have been observed which is higher than that obtained at river Gongola Gombe state (Omozokpia *et al.,* 2015).

The alloys such as brass and bronze, batteries, fungicides and pigments were considered as the potential sources of Zn in the river sediments (Akan *et al*., 2010). Other sources of zinc carbonates could be the pesticides (Anglin-Brown *et al*.,1995) and sewage of textile industries (Smith, 1988). The raised Zn concentration recorded at Hashidu might be ascribed to Zn carbonates utilized as pesticides in the zone. The results obtained on mean Zn concentration levels in all the

Table 3. Mean ± standard deviation for heavy metal concentration in sediment samples recorded from April-September in river Gongola, Gombe state

Element /site	Kunde	G/abba	Hashidu	Lafiya	W/tale	Jamari	WHO Standard Limit
Cu ($mg.L^{-1}$)	0.550 ± 0.291^{ab}	0.678 ± 0.231^{bc}	0.728 ± 0.245^{bc}	0.750 ± 0.259^{c}	0.686 ± 0.211^{bc}	0.448 ± 0.262^{a}	18.70
Zn ($mg.L^{-1}$)	0.019 ± 0.009^{a}	0.021 ± 0.010^{a}	0.025 ± 0.007^{a}	0.020 ± 0.010^{a}	0.019 ± 0.011^{a}	0.021 ± 0.012^{a}	123.00
Pb ($mg.L^{-1}$)	BDL	BDL	BDL	BDL	BDL	BDL	30.20
Cd ($mg.L^{-1}$)	BDL	BDL	BDL	BDL	BDL	BDL	0.68

Mean in same row with different superscripts are significantly different at $P<0.05$ Levels.
BDL: Below Detectable Limit

sampling sites did not exceed the WHO recommended limit of 123 $mg.kg^{-1}$ (WHO, 2008). However, sediments have the capacity to accumulate more heavy metals with time and remobilize them back to water and the food chain (WHO, 2008). Compared to other studies, mean Zn levels in river Gongola Gombe state were lower than the results recorded for the Zn mean levels 0.213-0.444 $mg.kg^{-1}$ at river Gongola in Adamawa (Maitera *et al.,* 2011) and 84.33 $mg.kg^{-1}$ mean recorded in river Kaduna, Shiroro fishing settlement, Nigeria (Omozokpia *et al*., 2015).

The sources of Pb in the sediments include industrial wastes and from water pipes (Akan *et al*., 2010). Other likely sources of Pb are lead acid batteries, solder, alloys, cable sheathing, pigments, rust inhibitors, ammunition, glazes and plastic stabilizers (WHO, 2004). The consequences of excess lead in the human body range from low intelligent quotient in children and high blood pressure in adults (Ottaway, 1978). The Pb concentrations were Below Detection Limit (BDL) in the sediment samples obtained from river Gongola. Thus, indicating a little or no toxicity of the metal. These result were in conformity with the result recorded at river Kaduna, Shiroro fishing settlement (Omozokpia *et al*., 2015). However, it differed from the 0.287-0.474 mg/kg obtained at river Gongola, Adamawa catchement (Maitera *et al.,* 2011)

The Cd concentration was below detection limits in Gongola river. Thus, indicating a little or no toxicity of the metal. This finding differed from results for sediment samples reported in normal soil to contaminated soil which ranged between 0.02 and 184 mg/kg in various regions of Pakistan by Mwegoha WJS and Kihampa (2010). The values were below recommended maximum permissible limit (0.68 mg/kg) of Cd reported by WHO, (2004).

Heavy metal concentrations in surface water

The mean Cu levels obtained in this study were lower compared to 0.92 $mg.L^{-1}$ observed in surface waters of Dadinkowa Dam, Gombe state, Nigeria (Maigari *et al*., 2016) and higher than 0.23 $mg.L^{-1}$ obtained at river Kaduna, Shiroro fishing settlement (Omozokpia *et al*., 2015). Anyhow, they were within the same range of 0.005 – 0.01mg. L^{-1} of mean Cu levels recorded in five Rift Valley lakes in Kenya (Ochieng *et al*., 2007). Studies by Ochieng *et al*., (2008) discovered higher mean Cu levels of 0.012 – 0.043 $mg.L^{-1}$ in surface water of Lake Kanyaboli, Kenya. The mean Cu levels observed in River Gongola didn't surpass the WHO limits of 1.00 $mg.L^{-1}$ of Cu levels in drinking water (WHO, 2004).

Zn is brought into water bodies through man-mediated pathways, for example, during processing in the steel industries or coal-fired power stations and burning of waste materials (Damodharan, 2013). Differ-

Table 4. Mean ± standard deviation for heavy metal concentration in catfish muscles recorded from April-september in river Gongola, Gombe state

Element /site	Kunde	G/abba	Hashidu	Lafiya	W/tale	Jamari	Who Standard Limit
Cu (mgL^{-1})	0.566±0.255^{b}	0.460±0.143^{ab}	0.529±0.146^{ab}	0.388±0.082^{bc}	0.603±0.229^{bc}	0.759±0.413^{c}	3.00
Zn (mgL^{-1})	0.024±0.015 ^{a}	0.019±0.012^{a}	0.021±0.012^{a}	0.082±0.010^{a}	0.022±0.009^{a}	0.020±0.010^{a}	60.00
Pb (mgL^{-1})	BDL	BDL	BDL	BDL	BDL	BDL	0.30
Cd (mgL^{-1})	BDL	BDL	BDL	BDL	BDL	BDL	0.03

ent sources of Zn into water bodies encomprises of metropolitan and municipal runoff (Damodharan, 2013). Zn is a basic supplement for body development and growth; anyway drinking water containing elevated levels of zinc can prompt stomach issues, sickness and vomiting .

The Zn levels in surface water recorded in this investigation didn't surpass the recommended limit of 3 mg. L^{-1} in drinking water (WHO, 2008). Levels acquired from the current examination were lower than 3.19 mg/L revealed for water tests from Uke Stream, Nasarawa State, Nigeria by Opaluwa *et al*. (2012). The values from the current examination were within the recommended limits for drinking water (3.0 mg/L) as suggested by WHO (2008).

The levels of lead in all the water sample as given in Table 4 were Below Detection Limits (BDL), demonstrating least contamination of Pb in the studies by Opaluwa *et al*. (2012) and Mwegoha and Kihampa, (2010) in Uke Stream Nasarawa State, Red Sea at Jeddah Islamic Port Coast and Dares Salaam City, Tanzania revealed estimations of 0.04 mg/L, 1.20 mg/L and 0.08 mg/L respectively. This demonstrated that the pb levels were at times controlled by anthropogenic sources or by ecological variables. Acceptable limit of Pb in drinking water is 0.01 mg/L as suggested by WHO (2008).

Cadmium concentrations in water samples were below detection limit (Figure 2 and 3). Thus, indicating a little or no toxicity of the metal of cadmium in river Gongola. This could be as a result of low activities increasing the levels of the metal in the river particularly vehicles and motorcycle that may wash from upstream that flows to downstream that can led to the release of Cd based contaminants into the water. Thus, the concentration of Cd in river Gongola was within the maximum permissible limit of 0.003 mg/L (Yahaya *et al*., 2012). The concentrations of Cd in the river however, were within the permissible limit for irrigation water of 0.01 mg/L

Heavy metal concentrations in catfish

The uptake of heavy metals by fish occurs from water, food and sediment. Heavy metal concentrations in the tissue of fresh water fish varies due to differences in the metal concentrations and chemical characteristics of water from which fishes were sampled, their ecological needs; metabolism and feeding habits (Yilmaz, 2009). In this study, the mean Cu levels recorded at river Gongola varied with sites. The variations in Cu levels could be attributed to differences in the anthropogenic activities, the use of agrochemicals in the sites (Table 5).

Therefore, the source of Zn in the study area could be attributed to use of inorganic fertilizers within River Gongola. Also, Zn could be from sewage sludge from the towns distributed within the catchment such as Kunde, Gombe Abba, Hashidu, Lafiya, Wuro Tale and

Table 5. Pearson correlation coefficient of Cu and Zn concentration in water, sediment and catfish muscles

S. No		CU in water	Cu in catfish muscles	Zn in sediment	Zn in catfish muscles
1	Cu in water	1	-0.109	-	-
2	Cu sediment	-	-4.90**	-	-
3	Zn in water	-	-	0.816**	0.162
4	Zn in sediment	-	-	1	0.615**

NB: ** significantly different correlation coefficient value at P<0.05 level

Jamari to mention a few. The mean Zn concentration levels recorded in the catfish muscles showed modest variations in all the sampling. Zn concentration levels recorded was slightly higher in African catfish recorded in river Nile, Egypt (Osman and Kloas, 2010; (Benzer *et al*., 2013) which ranged between 33.24-224.59 mg/kg from Mogan Lake (Turkey). The levels of Zn in the present study were lower than the permissible limit of 60.00 mg/kg recommended by FAO (WHO, 1999).

It was observed that Pb is below detectable limits for fish samples from all the sampling sites of river Gongola indicating the absence or the minimum level of the metal. This study confronted well with that reported by Shabanda and Itodo, (2012) of BDL and 0.015 mg/kg respectively. Other study by Oyakhilome *et al*. (2013) however, were greater than the present study and ranged between 0.15 to 0.19 mg/kg and 0.07 to 2.39 mg/kg in Owena multi-purpose dam, Ondo state, Southern Nigeria and Mediterranean Sea (Libyan coastline), respectively. Therefore, the concentration of Pb from the present study falls within (WHO, 2008) permissible limit of 0.30 mg/kg for fish and edible foods.

Concentrations for Cd in catfish samples as shown in Table 4, indicated that cadmium concentration was below detectable limits. Ozturk *et al*. (2009) obtained a concentration ranging from 0.17±0.01 to 0.79±0.33 mg/kg from Avsdar dam lake in Turkey which is higher than catfish samples collected from river Gongola. Also, Ackacha *et al*. (2010) reported Cd concentrations ranging from 0.33 to 2.68 mg/k. However, the concentration of Cd from the present study were within (WHO, 2008) permissible limit of 0.03 mg/kg for fish and edible foods.

The correlation between heavy metals is influenced by physical and chemical processes occurring in an aquatic environment. The noted significant correlations among the variables may be a reflection of a common source of occurrence and an indication of similar biogeochemical pathways for subsequent accumulation in the muscle tissues of the fish species (Kumar *et al*., 2011).

CONCLUSION

The heavy metals studied (Cu, Zn, Pb and Cd) had lower levels than WHO recommended limit for drinking water. Therefore, it was concluded that the surface water in river Gongola is fit for human consumption. The heavy metal concentrations in the sediments and *Clarias gariepinus* muscles were below WHO set limits respectively for survival of aquatic organisms.

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