



Heavy Metals Level in *Clarias gariepinus* (Catfish), *Oreochromis niloticus* (Tilapia) and *Chrysichthys nigroditatus* (Bagrid catfish) collected from Ogun River, Ogun State, Nigeria

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ABSTRACT: Aquatic organisms such as fish are prone to contamination by water pollutants such as heavy metals. This study aims at assessing the levels of heavy metals in the fillet tissues of 75 fish samples comprising *Clarias gariepinus* (Catfish), *Oreochromis niloticus* (Tilapia) and *Chrysichthys nigroditatus* (Bagrid catfish) from five (5) different fishing locations along the Ogun River, Ogun State. The fillet tissues of the fish samples were digested and analysed for Zn, Pb, Fe, Cr and Cd using a Perkin Elmer, AAnalyst – 200 Atomic Absorption Spectrometer. The concentration of Zn in *Clarias gariepinus*, *Oreochromis niloticus* and *Chrysichthys nigroditatus* were 5.37 ± 2.558 , 6.58 ± 2.35 and 5.11 ± 1.55 respectively; while the levels of Pb in the species were *Clarias gariepinus* (1.30 ± 3.099), *Oreochromis niloticus* (1.01 ± 0.95) and *Chrysichthys nigroditatus* (0.35 ± 0.59). Concentrations of Fe, Cr and Cd in the species were *Clarias gariepinus* (8.87 ± 3.547 , 0.08 ± 0.098 and 0.09 ± 0.100), *Oreochromis niloticus* (8.96 ± 2.21 , 0.12 ± 0.11 and 0.11 ± 0.11) and *Chrysichthys nigroditatus* (8.16 ± 3.88 , 0.11 ± 0.11 and 0.11 ± 0.11). The data revealed that most of these values were lower than FAO/WHO permissible except Pb and Cr. Some of the fish sampled may pose health hazards to the consumers. There is a need for constant monitoring of pollutants in Ogun River.

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The modern societies are faced with serious concerns about some global environmental challenges; developing countries in particular currently experience growing and complex pollution problems. The global environmental pollution, water pollution and waste management in particular, have attracted international public health attention. From the perspective of chemicals or hazardous substances, river water samples, sediments and some species of fish in Nigeria have been investigated (Unyimadu *et al.*, 2019; 2018a,b,c; 2017). As an indicator of general environmental pollution and as a route of human exposure, animals like cattle have been investigated (Nwude *et al.*, 2012; 2011a,b; 2010a,b,c). Fish is often used as a biomarker of quality of water bodies since the quality of the fish depends on the quality of the water (Fakankun *et al.*, 2012; Olusola and Festus, 2015; Obot *et al.*, 2016; Bawuro *et al.*, 2018). Organic and inorganic chemical species often constitute the main water pollutants and their levels are some of the measures to determine the water quality. Apart from the implications for human health (Kayode *et al.*, 2011), the presence and/or the levels of inorganic and organic substances in water bodies pose threats to the

health of aquatic organisms including fish (Jacquin *et al.*, 2020; Adewuyi *et al.*, 2010; Austin, 1999). Anthropogenic activities are major sources of heavy metals pollution of rivers (Babayemi *et al.*, 2016). Agricultural activities, runoffs from industrial areas, sewage effluents from industrial activities (Zhou *et al.*, 2020) and mining activities (Gabrielyan *et al.*, 2018) contribute to the levels of heavy metals in the water bodies. Furthermore, inappropriate waste management or disposal is the main source of heavy metals pollution (Babayemi *et al.*, 2017a). Ogun State has a larger number of industries in Nigeria and the discharge of wastewater from these industries may have an impact on the chemical characteristics of Ogun River, which is the main river in Ogun State, and hence on the quality of fish in this river. Apart from the fact that fish may be used as an indicator of chemical contaminants in rivers, its safety for consumption as being sourced from major rivers in Nigeria should be assessed. It is a widely consumed aquatic product sourced from major rivers in Nigeria (Unyimadu *et al.*, 2017; 2018a, b). Therefore, the consumption of fish of various species may be a significant contributor to the consumers' intake of

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some contaminants. Among other species, *Clarias gariepinus* (Catfish), *Oreochromis niloticus* (Tilapia) and *Chrysichthys nigroditatus* (Bagrid catfish) are very common in Ogun River (Iji and Adeogun, 2014); and also, some consumers have a preference for these (Unyimadu et al., 2018a,b). Investigating these fish species for the levels of heavy metals is therefore necessary. Common heavy metals assessed in previous studies to assess environmental pollution status in some parts of Nigeria include Pb, Cd, Cr, Fe and Zn (Azeez and Babayemi, 2020; Bawuro et al., 2018; Gabrielyan et al., 2018; Babayemi et al., 2017b). Though previous studies have carried out some assessments to determine the levels of heavy metals in fish, water or sediments from some surface waters in Nigeria (Ibrahim et al., 2018; Obot et al., 2016), and other locations along Ogun River: Opeji (Adeosun et al., 2015), Oke-Odan (Makanjuola and Makanjuola, 2018), Abeokuta (Olatunde et al., 2014; Ayanda et al., 2019) and Ketu (Adeniyi et al., 2008), spatial and seasonal changes in the physical and chemical properties of water, and consequently the health or

quality of fish, call for continual monitoring of every other location along this river for levels of heavy metals. Therefore, the objective of this research was to evaluate and report the levels of Zn, Pb, Fe, Cr and Cd in *Clarias gariepinus* (Catfish), *Oreochromis niloticus* (Tilapia) and *Chrysichthys nigroditatus* (Bagrid catfish) collected from Ogun River in Ogun State, Nigeria.

MATERIALS AND METHODS

Sample Collection: A total of 75 (5 samples of each) fish samples of three different fish species were purchased in May 2019 from five different fishing points along Ogun River. The coordinates of the sampling locations are shown in Table 1. All samples were packaged using an aluminium foil on ice, properly labeled and transported to the laboratory freezer for proper storage, awaiting analysis. The fish samples were: *Clarias gariepinus* (Catfish), *Oreochromis niloticus* (Tilapia) and *Chrysichthys nigroditatus* (Bagrid catfish).

Table 1: GPS locations and names of sampled sites

Oyan Dam	Oriyanrin	Adigbe Bridge	Apo Village	Odo-Eran Lafenwa
N6°39'38.5452''	N6°40'14.502''	N6°41'7.6164''	N6°41'5.4704''	N6°40'51.654''
E3°5'23.082''	E3°6'44.2224''	E3°10'12.9792''	E3°10'42.3588''	E3°12'1.53''

Sample Digestion: All glassware used was soaked in water and soap for two hours, rinsed with distilled water and then with a mixture consisting of 520 mL de-ionized water, 200 mL concentrated HCl and 80 mL H₂O₂. They were rinsed with de-ionized water and then oven-dried, away from dust and contamination. The bench was cleaned with soap and water and rinsed with acetone. Foil paper was spread on the bench. The frozen fish samples were placed on top and allowed to defrost. The fish samples were filleted, and the fillets were digested using the wet digestion method. The analytical procedure followed that of Muinde et al. (2013) with some modifications. Five grams (5g) of each of the individual fish samples were weighed using electronic weighing balance into a 50 mL Pyrex beaker for digestion using 10 mL mixture of concentrated HCl and HNO₃, in the ratio of 3:1 (Aqua regia) for 3h at 60°C using a hot plate inside the fume chamber.

After digestion, the content of the flask was filtered into a 50 mL standard flask and made up to the mark with deionized water and then transferred into the laboratory sample bottles and kept at room temperature until analysis. Sample blanks were prepared by taking 10 mL of the reagents mixture through the same procedure.

Analysis of heavy metals: Aliquots of the filtrates were analysed for Zn, Pb, Cr, Cd and Fe using Atomic Absorption Spectrophotometer (AAS) (model-Perkins Elmer AAnalyst-200). The calibration of the instrument was carried out using standard solutions. The standard analytical conditions are shown in Table 2. The data were analysed using SPSS.

Table 2: Standard Analytical Condition for Perkin Elmer, AAnalyst-200 AAS

Element	Wavelength (nm)	Lamp Current (mA)	Slit Width (nm)
Pb	217.0	5	1.0
Cd	228.8	3	0.5
Cr	359.3	6	0.2
Fe	248.3	7	0.2

RESULTS AND DISCUSSION

The detailed results are presented in Table 3. Generally, the concentrations of the heavy metals were Zn (2.34 – 8.85 mg/kg), Pb (ND – 4.18 mg/kg), Fe (5.76 – 11.60 mg/kg), Cr (0.03 – 0.28 mg/kg) and Cd (0.03 – 0.28 mg/kg).

Heavy metal concentrations based on locations: Table 4 shows the heavy metals concentration in tissues of fish collected from five (5) different locations in Ogun River. Zn concentration was highest in tissues of fish collected from Odo-Eran Lafenwa and lowest at Oyan Dam with mean values of 7.77 mg/kg and 4.60 mg/kg

respectively; and with the overall mean of 5.69 mg/kg for the Ogun River. There is a significant difference ($P < 0.05$) in the levels of Zn in the fish samples obtained from the five different locations. The Pb concentration was highest in Oriyanrin and least in Odo-Eran Lafenwa with mean values of 1.67mg/kg and 0.57mg/kg respectively. Generally fishes collected from Ogun River have a Pb concentration of 0.88 mg/kg. No significant difference ($P > 0.05$) was observed in the levels of Pb in the samples from the five (5) different locations. The highest Fe concentration was obtained in fish samples from Oriyanrin (10.39mg/kg) and the least was obtained from fish fillet tissues from Oyan Dam (7.81 mg/kg)

with a mean of 8.66 mg/kg for all the five locations. There is no significant difference ($P > 0.05$) in the levels of Fe in the fish samples from all the locations. For Cr, samples of fish obtained from Apo Village had the highest Cr concentration while those obtained from Odo-Eran Lafenwa had the least, having a mean of 0.10 mg/kg for all the samples. There is a significant difference ($P < 0.05$) in the levels of Cr for all the locations. Cd concentration was highest in fish tissues obtained from Apo Village (0.17 mg/kg) and least in the one from Oriyanrin (0.07mg/kg), with a mean of 0.10 mg/kg. There is a significant difference ($P < 0.05$) in the concentrations of Cd in the samples.

Table 3: Mean values of heavy metals concentration (mg/kg) in fish from different locations along Ogun River

Fish species	Location	Zn	Pb	Fe	Cr	Cd
<i>Clarias gariepinus</i>	Oyan Dam	2.34±1.64	ND	5.76±3.71	0.21±0.14	0.21±0.14
	Oriyanrin	6.01±1.29	4.18±6.45	9.12±2.08	0.06±0.08	0.08±0.09
	Adigbe Bridge	4.34±1.39	0.45±0.53	7.57±0.60	0.05±0.04	0.07±0.06
	Apo Village	5.29±1.26	1.23±1.03	11.60±4.62	0.05±0.05	0.05±0.05
	Odo-Eran Lafenwa	8.85±1.71	0.83±0.51	10.28±3.10	0.03±0.20	0.03±0.02
<i>Oreochromis niloticus</i>	Oyan Dam	7.42±2.76	2.18±0.71	9.11±0.72	0.05±0.01	0.05±0.01
	Oriyanrin	3.99±0.69	0.13±0.49	10.86±2.29	0.05±0.05	0.03±0.05
	Adigbe Bridge	6.03±2.68	1.24±0.91	10.24±1.75	0.14±0.13	0.12±0.14
	Apo Village	6.85±1.21	1.10±0.69	5.94±1.35	0.28±0.04	0.28±0.04
	Odo-Eran Lafenwa	8.59±1.31	0.42±0.15	8.66±0.63	0.06±0.06	0.06±0.63
<i>Chrysichthys nigroditatus</i>	Oyan Dam	4.03±0.88	ND	8.54±1.69	0.04±0.06	0.04±0.06
	Oriyanrin	5.28±0.65	0.70±1.03	11.19±7.59	0.12±0.081	0.11±0.08
	Adigbe Bridge	3.82±1.41	0.53±0.57	7.04±1.37	0.12±0.09	0.12±0.09
	Apo Village	6.55±1.27	0.08±0.13	6.38±3.15	0.20±0.20	0.20±0.19
	Odo-Eran Lafenwa	5.88±1.62	0.46±0.17	7.67±0.59	0.06±0.01	0.06±0.01

Table 4: Mean Values of Heavy Metals Concentration (mg/kg) in fish based on the sample locations

Location	Zn	Pb	Fe	Cr	Cd
Oyan Dam	4.60±2.82	0.64±1.24	7.81±2.68	0.10±0.16	0.10±0.12
Oriyanrin	5.09±1.22	1.67±3.96	10.39±4.49	0.08±0.07	0.07±0.08
Adigbe Bridge	4.73±2.03	0.74±0.74	8.28±1.90	0.10±0.10	0.10±0.96
Apo Village	6.23±1.35	0.81±0.85	7.97±4.07	0.17±0.15	0.17±0.15
Odo-Eran Lafenwa	7.77±2.00	0.57±0.35	8.87±2.05	0.05±0.04	0.09±0.04
Mean	5.69±2.26	0.88±1.92	8.66±3.27	0.10±0.11	0.10±0.11

Heavy metals concentrations (mg/kg) based on fish species: Based on fish species (Table 5), all the metals (except Pb) were generally highest in *Oreochromis niloticus*; that is, this species accumulated more heavy metals than the others.

Table 5: Mean concentrations (mg/kg) of heavy metals based on the species of fish from Ogun River

Heavy Metals	<i>Clarias gariepinus</i>	<i>Oreochromis niloticus</i>	<i>Chrysichthys nigroditatus</i>
Zn	5.37±2.558	6.58±2.35	5.11±1.55
Pb	1.30±3.099	1.01±0.95	0.35±0.59
Fe	8.87±3.547	8.96±2.21	8.16±3.88
Cr	0.08±0.098	0.12±0.11	0.11±0.11
Cd	0.09±0.100	0.11±0.11	0.11±0.11

However, except in the levels of Zn, there is no significant difference ($P > 0.05$) in the levels of the metals in the different fish species. The hierarchy of the metal concentrations detected in the fish samples was $Fe > Zn > Pb > Cr > Cd$. Fe and Zn accounted for over 90% of all the metals studied. A similar observation was reported by Koleleni and Haji (2014), Bat *et al.* (2017) and Salam *et al.* (2019). The levels of concentration of these metals were comparable to those reported for the fillet of these fish species by Fakankun *et al.* (2012). For Ikorodu lagoon in Lagos, they reported 0.735-1.585 mg/kg, Zn; ND-0.392 mg/kg, Pb; 19.572-125.217 mg/kg, Fe; and ND-0.947 mg/kg, Cd. The observed slightly higher levels in this

study may mean that Ogun River is more polluted than Ikorodu lagoon. It is expected that Ogun River would have more point sources of pollution than Ikorodu lagoon, as there would have been a wider dispersion of pollutants in the latter. Further compared with other studies, the mean values obtained for Pb and Fe concentration were slightly higher than those reported by Usero *et al.* (2003), Karadede *et al.* (2004), Andreji *et al.* (2005) and Ayeloja *et al.*, (2014) but lower than that reported by Mbeh *et al.* (2019). The concentration of Cd was comparable with that reported by Ayeloja *et al.*, (2014) but slightly higher than that reported by Morhit *et al.*, (2013). The levels of Zn were similar to the results obtained by Usero *et al.*, (2003) (they studied *Anguilla anguilla* and *Solea vulgaris*) for the South Atlantic coast of Spain, higher than the values reported by Ayeloja *et al.* (2014) and slightly lower than the values reported by Mbeh *et al.* (2019). The European Commission Regulation (EC, 2006) indicates maximum levels of 0.30 mg/kg for Pb and 0.05 mg/kg wet wt. for Cd; and FAO (2003) maximum levels are 0.02 and 0.05. The levels in this study generally exceeded these values, indicating that the consumption of fish from the studied locations at the time of the study may pose potential health risks to the consumers. It also suggests the need for constant monitoring of Ogun River for pollution. Some heavy metals at certain doses are essential elements for human development. Zn and Fe are essential elements. Zn is involved in the nucleic acid synthesis, the immune system, and neurotransmission (MacDonald, 2000). However, at higher concentrations, it can be toxic to fish (Li *et al.*, 2019), and can be a modifier of the carcinogenic response (Bostanci *et al.*, 2016). In humans, acute Zn poisoning may result in nausea, vomiting, diarrhea and fever (Agnew and Slesinger, 2020). Fe is a very common component of effluents of many industries, and such effluents are often discharged into the rivers. The toxicity of Fe to aquatic organisms may depend on the oxidation state. For example, Fe²⁺ is reported to be more toxic to fish than Fe³⁺ (Rostern, 2017). As an essential element, Cr is required in the human body for the metabolism of carbohydrates (National Institutes of Health, 2020). However, hexavalent Cr (Cr⁶⁺) has powerful oxidative potential and ability to cross cell membranes (Nigam *et al.*, 2014) and is therefore considered to be toxic. Toxic heavy metals can be carcinogenic and mutagenic. And their toxicological mode of action can be the inhibition of some enzymatic systems involved in cellular energy production (Jan, 2015). Other toxic metals include Cd and Pb. Lead is categorised as a priority hazardous substance. It affects the central and peripheral nervous systems, causes brain damage, cardiovascular disease, adverse effects on the developmental stages of the foetus (WHO, 2019;

Mason *et al.*, 2014). *Oreochromis niloticus* has the highest concentration of all the heavy metals analysed. The metal concentrations in the samples were ranked in the following sequence: *Oreochromis niloticus* > *Clarias gariepinus* > *Chrysichthys nigroditatus*. Data from the previous literature showed that metal concentrations in fish fillets varied widely depending on the location and species (Fakankun *et al.*, 2012) and the extent of contamination of the water body. The accumulation of heavy metals depends on the degree at which a particular species scavenges matters from the sediment and water (Koleleni and Haji, 2014, Ahmed *et al.*, 2019). Ecological needs, feeding habit and food metabolism may also influence the degree of accumulation of toxicants and variations among species (Yilmaz, 2003). The species that spend a longer time at the bottom of rivers and feed there are likely to concentrate metals than those that stay and feed at the surface (Tuzen, 2003). Taking Pb as an example, the key factors for its concentration and bioavailability in the aquatic environment are species, sampling sites, pH, alkalinity and hardness and the degree of its absorption into the sediments or the organic matter content of the water (Mountouris *et al.*, 2002; Gheorghe *et al.*, 2017; Yahya *et al.*, 2018). The points of release of effluents and wastewater and illegal dumping of wastes into water bodies are also key factors. Previous studies have documented both the natural and anthropogenic sources of heavy metals in the aquatic environment (Ahmed *et al.*, 2019; Hossain *et al.*, 2018; Babayemi *et al.*, 2016; Varol and Sen, 2012; Bing *et al.*, 2011). Specifically, the sources of Pb in the aquatic ecosystem may include effluents from industries (Rashed 2001). The anthropogenic sources of Pb include leaded gasoline, battery manufacturing, base metal mining, and its presence in water may result from industrial discharges and municipal wastewater (Babayemi *et al.*, 2016). Indiscriminate use of phosphate fertilizer and the release of effluents from industries are the likely sources of Cd; while textile industries may be the sources of Cr (Ahmed *et al.*, 2019). The sources of Cr in the aquatic environment include the release of effluents from industries such as metal finishing, pharmaceutical industries, dyeing and printing industries, leather tanneries and textiles (Babayemi *et al.*, 2016; Gabrielyan *et al.*, 2018; Zhou *et al.*, 2020). Therefore, controlling or monitoring the potential sources of heavy metals in the aquatic ecosystem could solve the problem of contamination of aquatic foods. Compared to the developed countries, there may be greater exposure to toxic metals in developing countries; and this may be as a result of inappropriate waste management or disposal (Babayemi *et al.*, 2017) or widespread pollution (Babayemi *et al.*, 2016). Ogun State has a larger percentage of industries in Nigeria.

Heavy industrial activities may result in the release of toxic substances that may contaminate water, air and soil. Furthermore, Ogun River passes through several towns and villages before linking the lagoon in Lagos. Such water bodies are sources of water for direct drinking, cooking and other activities like irrigation and fishing in some rural areas (Babayemi, 2016), and can therefore constitute a human route of exposure.

Conclusion: The presence and levels of Zn, Pb, Cr, Cd and Fe in fish from five different fishing locations along Ogun River were determined. Most of the results were lower than the FAO/WHO permissible limits except Pb and Cr which were higher. Some of the fish samples may pose health hazards to the consumers. There is the need for constant monitoring of pollutants in Ogun River.

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