British Journal of Multidisciplinary and Advanced Studies: 6(2),1-11, 2025
Agriculture
Print ISSN: 2517-276X
Online ISSN: 2517-2778
Website: https://bjmas.org/index.php/bjmas/index
Published by European Centre for Research Training and Development-UK

Species-Specific Bioaccumulation of Heavy Metals in *Oreochromis Niloticus*, *Synodontis Clarias* and *Clarias Gariepinus* from Kiri Reservoir, Nigeria

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doi: https://doi.org/10.37745/bjmas.2022.04245 Published March 06, 2025

Citation: Jibrin B., Jidauna S.B. and Kefas M. (2025) Species-Specific Bioaccumulation of Heavy Metals in Oreochromis Niloticus, Synodontis Clarias and Clarias Gariepinus from Kiri Reservoir, Nigeria, *British Journal of Multidisciplinary and Advanced Studies*: 6(2),1-11

Abstract: *Anthropogenic activities such as crop production in the watershed of Kiri Reservoir give rise to the use of fertilizers and pesticides to increase yield and enhance quality produce. However, these xenobiotics enter into the aquatic environment via runoff and are sources of heavy metals that cause harmful effects on nontarget organisms. Species-specific bioaccumulation of heavy metals in some commercial fish (Oreochromis niloticus, Synodontis clarias, and Clarias gariepinus) from Kiri Reservoir, Nigeria, were assessed on a temporal basis from August, 2023 through January 2024. An Atomic Absorption Spectrophotometer was used to identify and determine the bioaccumulation of six heavy metals; Cadmium, Nickel, Lead, Arsenic, Chromium, and Zinc in the fish species. Chromium recorded the highest mean bioaccumulation values in the order of 2.360 ± 0.016 µg/g, 2.060 ± 0.008 µg/g, and 2.043 ± 0.013 µg/g for C. gariepinus, S. clarias and O. niloticus respectively in October. Cadmium was the least with the following decreasing mean bioaccumulation of 0.080 ± 0.000µg/g in December, 0.038 ± 0.000 µg/g, 0.007 ± 0.000 µg/g in January for S. clarias, C. gariepinus and O. niloticus respectively. There were significant differences ($p < 0.05$) in the bioaccumulation of heavy metals among the three fish species and on a temporal basis. S. clarias recorded the highest level followed by C. gariepinus and then O. niloticus. This study concludes that the bioaccumulation of heavy metals in the fish species was influenced by the species type and local weather conditions beyond their chemical characterizations.*

Keywords: Bioaccumulation, **Fish,** Kiri, Heavy metals, Pollutant, Reservoir, Runoff, Season, Temporal, and Xenobiotic.

INTRODUCTION

The Kiri Reservoir was constructed 42 years ago as a water source for irrigating the 12,000-hectare plantation owned by the Savannah Sugar Company (Bobboi *et al*., 2021). As a result, dry-season farming (irrigation) in addition to wet-season farming was embarked upon by the people living around the water body. The Reservoir also provides water for drinking and other domestic purposes for the local inhabitants and a means of livelihood for the fisherfolks. However, the Reservoir is under threat from human activities ranging from the use of agrochemicals such as fertilizers, pesticides and other xenobiotic chemicals from domestic wastewater in its watershed which eventually find their ways into the water body. Additionally, when vegetations cover are removed for the purpose of crop cultivations, the influence is felt in adjacent aquatic ecosystems via the release of chemicals from the xenobiotics, soil erosion and the reduction of riparian cover (Akindele *et al*., 2020). These subsequently intensify runoff of suspended particulate matter into the Reservoir and consequently enhanced water pollution, thereby posing risks to nontarget organisms including fish in the aquatic ecosystems (Zira and Edward, 2021). Fertilizers and pesticides are applied for the purpose of enhancing crop yields and protecting its quality. However, these chemicals are good sources of heavy metals (Zira and Edward, 2021; Flomo and Chaki 2023; Guesmia *et al*., 2024). Heavy metals from the cropland can be introduced into a water body from stormwaters and subsequent runoffs. More so that the tropical rainfall is characterized by larger raindrop sizes compared to other climatic regions due to coalescence, leading to more intense precipitation (Ulbrich *et al.,* 2003). Yang *et al.* (2019) reported that the intense precipitation washes pollutants such as heavy metals into storm drains and eventually into rivers, pools, wetland, lakes among others. In addition to the natural occurring ones which may consequently increase the background concentrations to a concern level that can lead to adverse consequences in aquatic environment especially to resident aquatic biota.

Heavy metals are among the most persistence, bioaccumulative and ubiquitous toxicants in aquatic ecosystems thus, their implication in both public and environmental health (Akindele *et al*., 2020). Fish inhabiting heavy metals polluted waters have a higher tendency to bioaccumulate significant amounts of toxicants because of their very close contact with the medium that carries the substances and also because fish have to extract dissolved oxygen from the medium by passing enormous volumes of water over gills and by ingestion through its foods. Thus, presenting potential health hazards to the fish and subsequently to the consumers over time (Orosum *et al.,* 2016). Fish being the most important component of aquatic environment can be used as a sentinel to assess the health of the aquatic eco-system. Heavy metals in fish have also been associated with its survival, reproduction, growth rates among others (Fianko et al., 2013; Adharsh *et al.,* 2022). The level of heavy metals bioaccumulation in fish is influenced by species type, sex, lipid content, feeding habits, season, water pH among others (Authman *et al*., 2015).

The most commercial and the most relished fish species of the Reservoir include; Nile tilapia (*Oreochromis niloticus*), Upside down catfish (*Synodontis clarias*) and African mud catfish (*Clarias gariepinus*) and which contribute close to 50% of fish landing (Zira and Edward, 2021). *O. niloticus* is predominantly herbivores and occasionally feeds on other zooplanktons and insects (FAO, 2012). *Synodontis clarias* primarily feeds as a bottom-dweller, consuming insect larvae, plants, and debris (Diouf *et al.,* 2020). *Clarias gariepinus* diet is made of both living and detritus; encompassing insects, plankton, snails, crabs, shrimp, other invertebrates, birds, reptiles, amphibians, small mammals, other fish, and eggs, along with plant material like fruits and seeds (Anoop *et al.,* 2009).

Bearing in mind the potential toxicity of heavy metals to fish and man as well as its' adverse effects on the environment, it is important to have an up-to date baseline data of the toxicants in some of the most common fish species in the Reservoir. Scanty information is available on the species-specific bioaccumulation of the toxicants. Zira and Edward (2021) studied bioaccumulation of heavy metals in some fishes of the Kiri Reservoir. Therefore, this work aims to assess the differences in the bioaccumulation of some heavy metals on monthly basis among three fish species (*Oreochromis niloticus*, *Synodontis clarias* and *Clarias gariepinus*) from Kiri Reservoir.

MATERIALS AND METHODS

Study Area

Kiri Reservoir is situated in Kiri village along the bank of River Gongola in Shelleng Local Government Area of Adamawa State, Nigeria. The Reservoir is at an elevation of 158 m above sea level, with geographical coordinates of latitude 9º 40' 47'' N and longitude 12º 0' 51.01'' E (Figure 1). The Reservoir was constructed in 1982 and has a capacity of 615 million m³. It has a length of 1.2 Km with an average depth of 8.48 m. The Reservoir serves as a source of water for the irrigation of the 12,000-hectare plantation owned by the Savannah Sugar Company (Gadiga and Garandi 2018). The rainfall in the area is a tropical continental type of single peak usually in August or September. The wet season ranges from April to October, with annual values of between 510 and 1040 mm, and the dry season lasts for about 6 months. Kiri area has a warm temperature with a mean minimum yearly value of 18ºC in December and a mean annual maximum of 38ºC in March. The high relative humidity ranges from 60 to 78% from May to October but has low values of 27 to 35% during the dry season (Zemba *et al*., 2016).

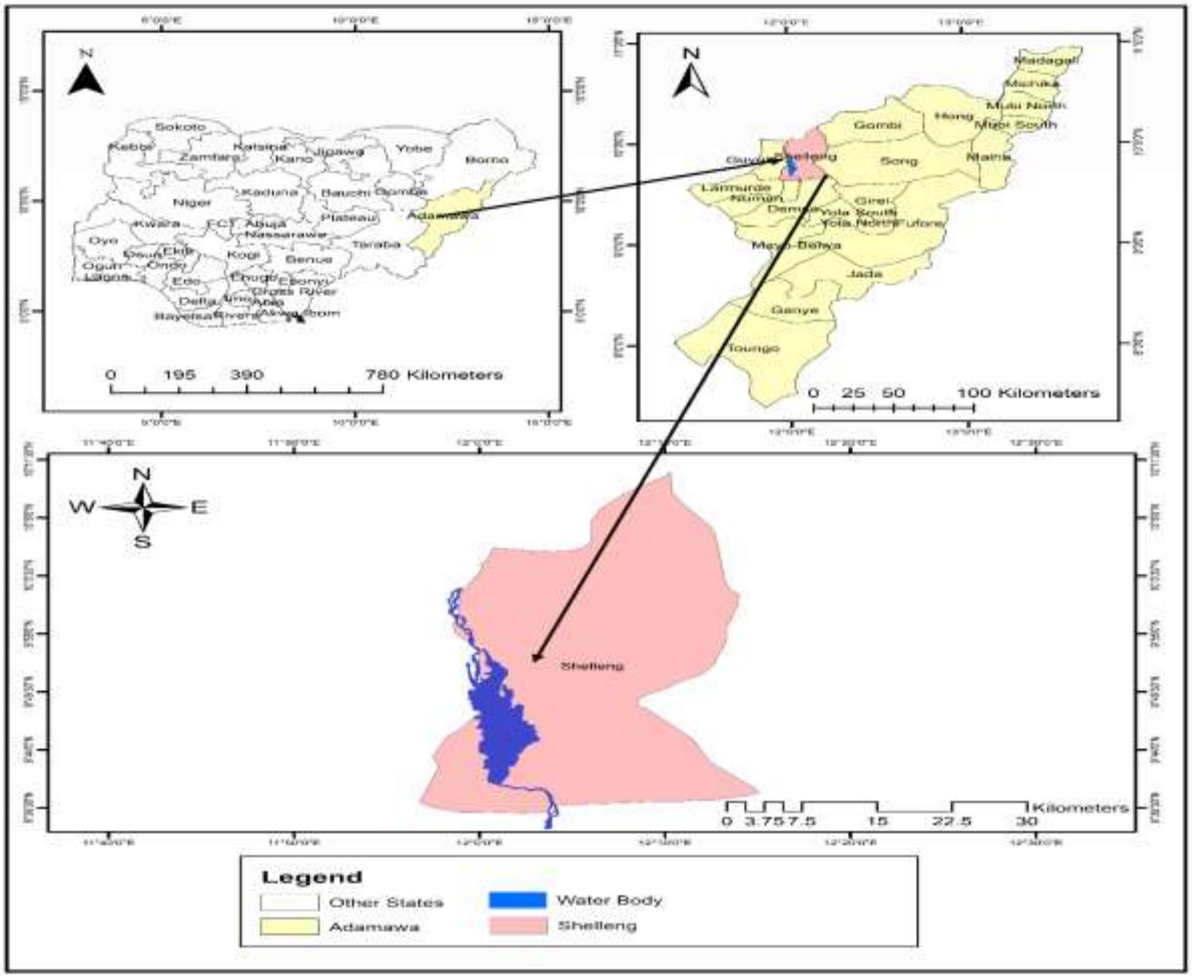

Figure 1: Map of Study Area (Kiri Reservoir)

Preparation for Digestion

The fish sample was washed with distilled water and dried for 24 hours to constant weight in an oven at 105°C. After drying the fish sample in the oven, the bone, head and scales (*O. niloticus*) of the dried fish sample were removed and the muscle was milled with a mortar and pestle. Then it was put in a dry labeled pre-cleaned crucible and stored until digestions (Adebayo 2017).

Digestion of Sample

Exactly 2 g of the grounded sample was mixed with 5 mL of HNO_3 and 2 mL of $HClO_4$ in triplicate and then heated on a hot plate for 30 minutes at 85°C. After the digestion, the residue was allowed to cool and filtered into a 50 mL volumetric flask. Distilled water was added to make up to the mark. The filtrate was transferred into a pre-cleaned sample bottle and stored under cool temperature until it was ready further Atomic Adsorption Spectrophotometer (AAS) analysis (Adebayo 2017).

Determination of heavy metals

A black model 200A flame AAS (Perkin Elmer 2000) was used in the heavy metal analysis of the samples. The major underlined principle of AAS is that the ground state atoms are capable of absorbing radiant energy of their own specific resonance wavelength when passed through a solution containing the atoms in question, then part of the light will be absorbed. The extent of absorption is proportional to the number of ground state atoms present in the flame (Adebayo 2017). Six (6) different Heavy metals (Lead, Arsenic, Cadmium, Nickel, Chromium, and Zinc) were determined from the samples collected.

Quality *a*ssurance and *q*uality *c*ontrol

To ensure quality data, blanks and replicates were included in the analysis. One laboratory blank was performed for each of five (5) samples. Concentration of target HMs in the blanks were <5% of the minimum levels in the samples. A blank sample was also used to test the AAS instrument's data reporting accuracy. Calibration curves for HMs was prepared and the correlation coefficient of the calibration curves were more than 0.9. All analyses were done in triplicates and the mean concentration was calculated based on the number of sample ($n = 3$). All reagents were of analytical grades.

Data Analysis

Two ways analysis of variance (ANOVA) at 5% probability level was used to determine the temporal difference of heavy metals concentrations among the 3 fish species. Fisher's LSD was used as post-hoc test to separate the means if significant differences exist.

RESULTS

Oreochromis niloticus, *Synodontis clarias* and *Clarias gariepinus* were analyzed for Cd, Ni, Pb, As, Cr and Zn and the bioaccumulations of each heavy metals in each fish species were presented in Table 1. On the whole, Cr presented the highest value of 2.360 µg/g followed by Zn (0.790 µg/g), then Ni (0.214 µg/g), then Pb (0.167 µg/g), then As (0.085 µg/g) and finally Cd (0.080 µg/g). *O. niloticus* recorded the least mean values in all the heavy metals except Pb (0.167 ± 0.013 µg/g) which was highest in November. *S. clarias* had the highest mean bioaccumulations of Cd (0.080 ± 0.000 µg/g), Ni (0.214 ± 0.000 µg/g) and As (0.087 ± 0.001 µg/g) in December and January respectively. While *C. gariepinus* had the highest mean bioaccumulation of Cr (2.360 ± 0.016 µg/g) and Zn (0.790 ± 0.008 µg/g) in the months of October and August. There were significant differences ($p < 0.05$) in the bioaccumulations of heavy metals among the fish species and among the months.

TABLE 1: Monthly Variation of some Heavy Metal Bioaccumulations (µg/g) in *Oreochromis niloticus*, *Synodontis clarias* and *Clarias gariepinus* of Kiri Reservoir from august, 2023 – January, 2024.

Metals/Months		***O. niloticus***	***S. clarias***	***C. gariepinus***
Cadmium	**Range**	**Mean ± SD**	**Mean ± SD**	**Mean ± SD**
August	BDL – 0.002	0.002 ± 0.001^{a}	BDL^{b}	0.001 ± 0.000^{b}
September	0.001 – 0.004	0.004 ± 0.001^{a}	0.001 ± 0.000^{b}	0.001 ± 0.000^{b}
October	0.002 – 0.004	0.002 ± 0.001^{a}	0.004 ± 0.001^{b}	0.002 ± 0.001^{a}
November	0.001 – 0.003	0.003 ± 0.001^{a}	0.001 ± 0.000^{b}	0.001 ± 0.000^{b}
December	0.004 – 0.080	0.004 ± 0.000^{a}	0.080 ± 0.000^{b}	0.012 ± 0.000^{c}
January	0.007 – 0.055	0.007 ± 0.000^{a}	0.055 ± 0.000^{b}	0.038 ± 0.000^{c}
Nickel				
August	BDL – 0.002	0.002 ± 0.000^{a}	BDL^{b}	0.001 ± 0.000^{a}
September	BDL – 0.008	0.008 ± 0.000^{a}	0.001 ± 0.000^{a}	BDL^{a}
October	0.060 – 0.180	0.060 ± 0.001^{a}	0.180 ± 0.008^{b}	0.180 ± 0.008^{b}
November	0.063 – 0.153	0.153 ± 0.017^{a}	0.070 ± 0.008^{b}	0.063 ± 0.009^{b}
December	0.035 – 0.067	0.048 ± 0.000^{a}	0.067 ± 0.000^{b}	0.035 ± 0.000^{a}
January	0.076 – 0.214	0.076 ± 0.001^{a}	0.214 ± 0.000^{b}	0.135 ± 0.002^{c}
Lead				
August	0.001 – 0.006	0.005 ± 0.000^{a}	0.006 ± 0.001^{a}	0.001 ± 0.000^{a}
September	0.004 – 0.007	0.004 ± 0.001^{a}	0.006 ± 0.001^{a}	0.007 ± 0.001^{a}
October	0.030 – 0.120	0.120 ± 0.001^{a}	0.030 ± 0.000^{b}	0.057 ± 0.013^{c}
November	0.057 – 0.167	0.167 ± 0.013^{a}	0.123 ± 0.009^{a}	0.057 ± 0.013^{b}
December	0.001 – 0.045	0.001 ± 0.000^{a}	0.045 ± 0.001^{b}	0.022 ± 0.000^{c}
January	0.006 – 0.036	0.006 ± 0.000^{a}	0.036 ± 0.000^{b}	0.028 ± 0.000^{b}
Arsenic				
August	0.004 – 0.007	0.004 ± 0.001^{a}	0.006 ± 0.001^{a}	0.007 ± 0.001^{a}
September	0.003 – 0.009	0.008 ± 0.001^{a}	0.009 ± 0.001^{a}	0.003 ± 0.000^{b}
October	0.002 – 0.007	0.007 ± 0.001^{a}	0.002 ± 0.001^{a}	0.002 ± 0.001^{a}
November	0.001 – 0.004	0.002 ± 0.001^{a}	0.004 ± 0.001^{a}	0.001 ± 0.000^{a}
December	0.009 – 0.063	0.009 ± 0.001^{a}	0.063 ± 0.001^{b}	0.039 ± 0.000^{b}
January	0.018 – 0.087	0.018 ± 0.000^{a}	0.087 ± 0.001^{b}	0.055 ± 0.000^{b}
Chromium				
August	0.140 – 0.610	0.140 ± 0.008^{a}	0.563 ± 0.005^{b}	0.610 ± 0.008^{c}
September	0.100 – 0.370	0.100 ± 0.000^{a}	0.180 ± 0.008^{b}	0.370 ± 0.008^{c}
October	2.043 – 2.360	2.060 ± 0.008^{a}	2.043 ± 0.013^{a}	2.360 ± 0.016^{c}
November	1.453 – 1.863	1.453 ± 0.009^{a}	1.863 ± 0.009^{b}	1.780 ± 0.008^{c}
December	0.057 – 0.153	0.086 ± 0.000^{a}	0.153 ± 0.001^{b}	0.057 ± 0.000^{c}
January	0.073 – 0.125	0.077 ± 0.000^{a}	0.125 ± 0.001^{b}	0.073 ± 0.000^{a}
Zinc				
August	0.400 – 0.790	0.540 ± 0.008^{a}	0.400 ± 0.008^{b}	0.790 ± 0.008^{a}
September	0.113 – 0.483	0.430 ± 0.008^{a}	0.113 ± 0.013^{b}	0.483 ± 0.005^{a}
October	0.113 – 0.160	0.160 ± 0.008^{a}	0.113 ± 0.005^{b}	0.127 ± 0.009^{ab}
November	0.043 – 0.667	0.043 ± 0.013^{a}	0.123 ± 0.005^{b}	0.667 ± 0.009^{a}
December	0.025 – 0.094	0.025 ± 0.001^{a}	0.058 ± 0.001^{b}	0.094 ± 0.001^{a}
January	0.058 – 0.085	0.058 ± 0.001^{a}	0.085 ± 0.005^{b}	0.063 ± 0.001^{bc}

Mean with different superscript letters across the rows are significantly different ($p < 0.005$),
BDL means 'Below Detection Limit'

DISCUSSION

African catfishes (*S. clarias* and *C. gariepinus*) are known for their relatively high fat content when compared to *O. niloticus* (Ugoala *et al.,* 2008; Adebayo *et al.* 2013) and this could be one of the reasons for the elevated bioaccumulation of most of the heavy metals: Cd, Ni, As and Cr, Zn in *S. clarias* and *C. gariepinus* respectively. The lipid content of fish species is a major factor that determines the levels of lipophilic contaminants in their body tissues. Fish species with higher lipid content in their body tissues are efficient in accumulating and retaining lipophilic contaminants (Davis *et al*., 2002; Erdogrul *et al*., 2005). The highest values of Cd, Ni, As, recorded in *S. clarias* as compared to Cr and Zn in *C. gariepinus* could be attributed to the fact that the former is a bottom feeder while the latter feeds in the benthic food materials but only at night. It exclusively feeds at the water surface during the day (Anoop *et al.,* 2009). Elevated bioaccumulation of heavy metals occurs when benthic fishes feed on benthic invertebrates that ingest particulate matter (Milam and Onyia, 2007). Benthic invertebrates are found to be an important link in the transfer of heavy metals to higher trophic levels because of their close association with sediments and their ability to accumulate heavy metals (Li *et al*., 2020). *O. niloticus* is predominantly herbivores due to its preference for plant food hence, the least bioaccumulation of heavy metals observed in the fish species. However, Javid and Usmani (2011) stated that bioaccumulation of heavy metals in different species is the function of their respective membrane permeability and enzyme system, which is species specific. Furthermore, some factors like season, environment, and size among others can influence feed preference and thus variation of heavy metals bioaccumulation in fish species (Tesfahun and Temesgen 2018).

Lipid reserve is metabolized during physiological stress such as starvation and the contaminants (heavy metals) level of the retained lipid is enlarged Gbeddy *et al.* (2015). This may be a plausible reason for the observed increased bioaccumulation of heavy metals during the dry season (November, 2023 through January, 2024) in all the fish species. This finding agrees with study of Igwegbe *et al*. (2014) from catfish of Doron Baga of Borno State, Nigeria who reported higher heavy metals during dry season when compared with the wet season. Dilution effects in the months of August to October during the peak of the wet season may be implicative in the decreased of heavy metals bioaccumulation in all the fish species.

The observed high bioaccumulation of Chromium (Cr) and Zinc (Zn) in all the fish species recorded during the wet season is because the season favors abundance plants growth in the watershed of the Reservoir and plants are known to be one of the good sources of Cr (Aziz *et al*., 2023) which subsequently enter the aquatic system as part of the runoff during rainfall events. Again, fertilizers and pesticides are good sources of Zn in aquatic environments (Guesmia *et al*., 2024) and large quantities of fertilizers and pesticides are applied on crops to enhance production and to kill pest and disease during wet season than the dry season because the high humidity of the wet season favors the growth of pests and diseases. However, heavy metals once in water partition into organic phases (USEPA, 2005) therefore, the enhanced bioaccumulation of Cr and Zn than the other heavy metals detected in this study can be ascribed to their octanol-water partition coefficients (log Kow) of 3.9 and 3.1 for Cr and Zn respectively. The log Kow for other heavy metals are lower than that of Cr and Zn except Pb with 4.2 (USEPA, 2005).

The Food and Agriculture Organization/World Health Organization (FAO/WHO) (2011) have set maximum allowable limits of 0.1 µg/g, 0.05 µg/g, 0.3 µg/g, 1.0 µg/g, 12 µg/g, and 50 µg/g for Cd, Ni, Pb. As, Cr and Zn respectively. All the heavy metals in the fish species under study were below the statutory permissible limits except Ni which was above 0.05 µg/g. The value of Ni reported in this study was lower than 0.69 µg/g reported by Sivaperumal *et al.* (2006) in fish species obtained from Indian freshwaters, but greater than 0.03 µg/g documented by Akoto *et al.* (2014) in some fish species of Fosu lagoon (Ghana). Elevated levels of Ni in aquatic systems can adversely affect fish by impairing growth, reproduction, and metabolism (Brinkman *et al.,* 2008). Consumption of these contaminated fish can lead to respiratory issues, skin allergies, nausea, headache, and potential carcinogenicity in humans (ATSDR, 2005; WHO, 2011).

CONCLUSION

The bioaccumulation of some heavy metals among the 3 most common fish species of Kiri Reservoir has been determined. The study revealed that *S. clarias* accumulated more heavy metals than *C. gariepinus* and then *O. niloticus*. The levels of bioaccumulation of heavy metals in the 3 fish species were also influenced by the seasonal (monthly) variations in weather conditions (rainfall and temperature among others) beyond their chemical properties. Further studies should be conducted to determine the influence of size and sex of the fish species on the bioaccumulation of heavy metals.

Acknowledgment

The authors thank the Management of Kiri Reservoir, Nigeria for permitting us to carry out this study. I gratefully acknowledge funding from Tertiary Education Trust Fund (TETFund), Nigeria.

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