

Assessment of heavy metals in water and organs (Gills and Muscles) of Clarias gariepinus from Wasai reservoir, Kano State Nigeria

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Abstract

This investigation was carried out to assess the levels of heavy metals in surface water and their bioaccumulation in the organs of the African catfish (Clarias gariepinus) obtained from Wasai Reservoir, Kano State of Nigeria. Surface water samples and fish (C. gariepinus) were collected using standard protocols for a period of ten months. Four different locations were mapped out as sampling stations. Heavy metals concentration in water, gills, and muscles of *Clarias gariepinus* were assessed. The experiment was arranged in a Completely Randomized Design with three replications. Data obtained were analysed using Analysis of Variance with Duncan's New Multiple Range Test used to separate significant means at 5% level. The result showed significant difference (P≤0.05) in the concentration of heavy metals at different locations with months. The result also showed that the levels of heavy metals were higher in location A due to high discharge from mechanic and agricultural activities in the area. More so, the level of heavy metals bioaccumulation in muscles was in the following sequence: $Cd > Pb > Cr$, while in the gills, the trend followed the sequence Pb $>$ Cd $>$ Cr. Thus, with the exception of Cr bioaccumulation in the gills, all the values of heavy metals studied were above tolerable limits.

Keywords: Bioaccumulation, Catfish, Heavy Metals, Wasai Reservoir

Introduction

The aquatic ecosystem all over the world is constantly being disturbed by rising levels of pollutants from anthropogenic discharges (Bamidele et al., 2022). A large amount of chemicals are being constantly discharged into aquatic environments, and these persist in biota, water and sediment (Schmeller et al., 2018). These pollutants alter the physicochemical attributes of the affected water body making it unsafe for human consumption and detrimental to aquatic biota (Oladeji, 2020). More so, the contamination of aquatic habitats with these pollutants poses a threat to public health via human consumption of fishery resources and other aquatic biotas (Meijide et al., 2018; Zhu et al., 2018). Although fish contributes immensely to human well-being as the major source of animal protein (Abolagba and Melle, 2008) characterized by low cholesterol content and the presence of vital amino acids (Kuton et al., 2021); it is easily contaminated by heavy metals (Alam *et al.*, 2023). Heavy metals are chemicals required in trace amounts but are considered toxic above certain limits in living organisms (Karahan, 2022). Malik et al. (2012) stressed that since fish are situated at the top of the aquatic food chain, they may accumulate heavy metals from water or sediment, thereby transferring them to humans through fish consumption leading to serious health problems.

Wasai Reservoir is one of the artificial reservoirs in Kano State, Northwestern Nigeria, where domestic and industrial effluents, mechanics and agricultural wastes from metropolitan Kano are discharged (Imam, 2012). The Reservoir receives heavy metal pollutants such as mercury, lead, aluminum, cadmium, zinc, nickel, chromium and cobalt, which have the potential to accumulate in fish (Adeboyejo et al., 2023; Bwala et al., 2023; Mendoza et al., 2023). Although trace metals are essential for normal physiological processes, high concentrations are toxic, affecting various organs and tissues in fish (Serezli et al., 2011).

Studies conducted in relation to the reservoir reported the presence of heavy metals in the surface water of Wasai Reservoir and its tributaries which were above the FEPA (2011) standard limit (Imam, 2012; Jamila and Sule, 2020). However, none of these studies focused on assessing the bioaccumulation of heavy metals in *Clarias* gariepinus. Therefore, this study is aimed at evaluating the concentration of heavy metals in surface water and their accumulation in the organs (gills and muscles) of *Clarias gariepinus* from Wasai reservoir.

Materials and Methods

Study area

The Wasai- Reservoir is situated on the Jakara River at a point about 2 km Southeast of Wasai village in Minjibir Local Government Area of Kano State (Amin, 1992). It is situated between latitudes 12°N and 13^oN and longitudes 8^oE and 9^oE. The reservoir was constructed in 1976 for recycling purposes. The dam has a maximum height of 9.33m, while the reservoir has a surface area of 1,250 hectares and a total storage capacity of 65.38 m3; this places the reservoir among the medium-sized man-made lakes in Kano State (Fig. 1).

Sampling stations

Four sampling stations were identified and designated for the purpose of this study based on the different anthropogenic activities carried out in the areas. Station A is characterized by domestic waste discharges, Station B by mechanic and domestic wastes, Station C by industrial wastes and Station D by agricultural waste discharges. Transect sampling across the basin was carried out, starting from the two tributaries, i.e. Jakara River, the confluence where the two rivers meet, the entry point where the water drains into the Wasai Reservoir, and the spillway of the reservoir. Samplings were conducted between 06:00 am and 07:00 am monthly. Water and fish samples were collected from the reservoir for a period of 10 months (September 2018 to June 2019).

Water sampling

Samples were collected in 250 mL plastic bottles for chemical parameters analysis. The sampling was carried out midstream by dipping the sample plastic bottle to approximately $20 - 30$ cm below the water surface, projecting the mouth of the containers against the direction of flow direction. Water samples for heavy metals analysis were collected in 1L bottles, to which 2 drops of $HNO₃$ were added (APHA, 2005).

Fish sample collection

A total of two hundred *Clarias gariepinus* adults were procured from local fishermen around the reservoir. Fish samples obtained were immediately kept in pre-cleaned polythene bags, sealed, labelled and kept in ice boxes for transportation to the Biological Science Laboratory, Bayero University, Kano. The samples were dissected for gills and muscle, which were dried in an oven at 105°C for 24 hrs and thereafter ground to powder with mortar and pestle.

Figure 1: Map of the study area showing the sampling Stations (Source: GIS Lab Department of Geography Using Arc GIS 10.3 Software)

Preparation of water samples for heavy metals analysis Three samples of water from each sampling site were preserved using nitric acid ($HNO₃$) to ensure that metals do not adhere to the walls of the container. Sample aliquots for digestion were taken after vigorous shaking to ensure the suspension of solids that may have settled. Water samples were digested on a hot plate using hydrochloric acid (HCl) and $HNO₃$ in a volume-to-volume ratio (1:0.5%).

Preparation of fish organ samples

The fish were washed with distilled water; dissection was done using a sharp stainless-steel knife and the organs of interest- gills and muscles were isolated. The organs of investigation were transferred to an oven and dried at a temperature of 105°C following the method of Eneji et al. (2011). 10 g portion of the ground samples were carefully weighed using digital chemical balance, 10 ml of $HNO₃$ and 2 ml of $HClO₃$ were added and heated over a hot plate for one hour. After complete digestion, the residues were diluted with 0.2% v/v HNO³ to 20 mL (APHA, 2005).

Data analyses

Bioaccumulation factor (BAF) was calculated according to Evans and Engel (1994) formula:

$$
\mathsf{BAF} = M_{\mathsf{tissue}} \ (mg/L)
$$

M water(mg/L)

Where:

 M_{tissue} = Heavy metal concentration in the tissue of fish

 M_{water} = Heavy metal concentration in water

Data collected were subjected to analysis of variance (ANOVA) with Duncan's New Multiple Range Test used to separate significant means at 5% level to compare the levels of heavy metals at different stations. SAS (2012) Version 9.1 was used for the analyses.

Results

Heavy metals in surface water from Wasai Reservoir

The results for heavy metal concentrations in surface water of Wasai reservoir are shown in Table 1. The result showed a significant difference (P≤0.05) across the months in the level of heavy metals concentrations. Cr level was highest in May 2019 (1.17 mg/L) and lowest in September 2018 (0.28 mg/L). The concentration of Pb was highest in April 2019 with a value of 0.136 mg/L and lowest in March 2019 (0.016 mg/L). The concentration of Cr was 0.012 mg/L in November 2018 but rose to 0.106 mg/L by March 2019.

The result for the spatial and monthly concentrations of each heavy metal in surface water for all the stations is presented in Table 2. The

mean concentration (mg/L) of heavy metals in water ranged from 0.019 - 0.288 mg/L. Cr highest level of 0.41 \pm 0.01 mg/L was recorded in samples collected at station D in May 2019. Similarly, there was an increasing trend in Pb concentration from the months of September and October to June in all the sampling of the study stations along Wasai Reservoir. The concentrations of the heavy metals were significantly different (P≤0.05) across the stations, with station C having the highest mean concentration for Cr (0.24 mg/L), station A with the highest mean concentration for Pb (0.288 mg/L), and station B having the highest concentration of Cd (0.234 mg/L).

Table 1: Concentrations of heavy metals in surface water of Wasai Reservoir (mg/L)

Month	cr	\sim \sim \sim Pb	Cd
Sept	0.28 ± 0.01 ^e	0.06 ± 0.01 ab	0.022 ± 0.01 c
0 _{ct}	0.80 ± 0.02 ^{ab}	0.076 ± 0.01 ^{ab}	0.026 ± 0.01 c
Nov	0.65 ± 0.02 c	0.077 ± 0.01 ^{ab}	0.012 ± 0.01 ^d
Dec	0.59 ± 0.02 d	0.026 ± 0.01 ^a	0.016 ± 0.01 ^d
Jan	0.65 ± 0.02 c	0.034 ± 0.01 ^b	0.027 ± 0.01 c
Feb	0.82 ± 0.04 ab	0.033 ± 0.01 ^b	0.028 ± 0.01 c
Mar	0.80 ± 0.04 ^{ab}	0.016 ± 0.01 c	0.106 ± 0.01 ^a
April	0.76 ± 0.01 ^b	0.136 ± 0.01 ^a	0.023 ± 0.01 c
May	$1.17 \pm 0.01a$	0.032 ± 0.01 ^b	0.032 ± 0.01 ^b
June	0.61 ± 0.01 c	0.024 ± 0.01 c	0.086 ± 0.01 ^{ab}
Mean	0.71	0.051	0.038

N.B: Value(s) with the same superscript(s) down a column are NOT significantly different (P**≥**0.05)

The highest value for Pb (0.055 \pm 0.005 mg/L) was found at station C in April 2019, while the highest levels of cadmium in the water samples (0.045 \pm 0.009 mg/L) were recorded in May 2019 at station B. There was significant difference (P≤0.05) across the months in the levels of heavy metals in the surface water of Wasai Reservoir (Table 2). Lead had the highest value of 0.288 mg/L in station A and the lowest (0.0029 mg/L) in station D.

Heavy metals in fish organs from Wasai Reservoir **Muscles**

The result for heavy metals accumulation in the muscles of C. gariepinus from Wasai Reservoir is presented in Table 3. The result showed that, the highest accumulation of Pb (0.07 mg/L) was recorded in January and March 2019. However, the highest value (0.22 mg/L) for Cd accumulation in the muscles was recorded in April and June 2019. The highest Cr bioaccumulation was recorded in September 2018.

The BAF values in the fish muscles were 0.78 for Pb, 0.79 for Cd and 0.17 for Cr. The trend for heavy metals bioaccumulation in the fish muscles showed that $Cd > Pb > Cr$.

N.B: Value(s) with the same superscripts across a row are not significantly different at P**≥**0.05

Table 3: Levels of heavy metals (mg/L) in the muscles of *Clarias garipienus* from Wasai Reservoir

Month	Pb	P- Value	Cd	P- Value	Cr	P- Value	FAO (2004)
Sept	0.02 ± 0.00	0.19	0.01 ± 0.00	0.23	0.32 ± 0.01	0.24	Pb 0.05
0ct	0.02 ± 0.00	0.54	0.01 ± 0.00	0.17	0.10 ± 0.01	0.76	Cd 0.1
Nov	0.06 ± 0.01	0.69	0.01 ± 0.00	0.16	0.03 ± 0.01	0.29	Cr 0.05
Dec	0.01 ± 0.00	0.07	0.01 ± 0.00	0.16	0.16 ± 0.12	0.98	
Jan	0.07 ± 0.01	0.44	0.01 ± 0.00	0.04	0.03 ± 0.01	0.47	
Feb	0.02 ± 0.00	0.80	0.02 ± 0.01	0.2	0.03 ± 0.00	0.05	
Mar	0.07 ± 0.01	0.70	0.13 ± 0.01	0.52	0.31 ± 0.02	0.53	
April	0.06 ± 0.01	0.92	0.02 ± 0.00	0.42	0.13 ± 0.01	0.77	
May	0.03 ± 0.00	0.72	0.02 ± 0.00	0.50	0.04 ± 0.01	0.64	
June	0.04 ± 0.01	0.43	0.02 ± 0.00	0.29	0.07 ± 0.01	0.44	
Mean	0.04		0.03		0.12		
BAF	0.78		0.79		0.17		
F	0.05		0.01		0.05		
P-Value	51.95		525.04		22.64		
	0.00		0.00		0.00		

N.B: Value(s) with the same superscripts across a row are not significantly different at P**≥**.05

Gills

The result for the accumulation of heavy metals in the gills of C. gariepinus is presented in Table 4. The highest values for Pb (0.12 mg/L), Cd (0.35 mg/L) and Cr (0.26 mg/L) were all recorded in March

2019. The BAF values in the gills of C . *gariepinus* were as follows: 0.18 for Pb, 0.17 for Cd and 0.01 for Cr. The pattern of bioaccumulation followed the trend: $Pb > Cd > Cr$ in the gills.

Table 4: Levels of heavy metals (mg/L) in the gills of *Clarias garipienus* from Wasai Reservoir

Month	Pb	P- Value	Cd	P- Value	Cr	P- Value	FAO (2004)
Sept	0.06 ± 0.007	0.170	0.04 ± 0.005	0.238	0.12 ± 0.015	0.311	Pb 0.05
0 _{ct}	0.09 ± 0.011	0.810	0.04 ± 0.005	0.251	0.07 ± 0.051	0.974	Cd 0.1
Nov	0.07 ± 0.002	0.957	0.02 ± 0.004	0.494	0.19 ± 0.010	0.374	Cr 0.05
Dec	0.09 ± 0.009	0.670	0.02 ± 0.004	0.770	0.02 ± 0.001	0.650	
Jan	0.08 ± 0.006	0.536	0.03 ± 0.004	0.877	0.03 ± 0.01	0.374	
Feb	0.08 ± 001	0.119	0.03 ± 0.002	0.834	0.03 ± 0.011	0.132	
Mar	0.12 ± 0.010	1.000	0.35 ± 0.06	1.000	0.26 ± 0.01	1.000	
April	0.07 ± 0.005	0.238	0.04 ± 0.001	0.652	0.07 ± 0.01	0.830	
May	0.09 ± 0.009	0.599	0.04 ± 0.010	0.786	0.05 ± 0.005	0.561	
June	0.09 ± 0.005	0.255	0.035 ± 0.008	0.016	0.06 ± 0.006	0.541	
Mean	0.0092		0.00645		0.0093		
BAF	0.18		0.17		0.01		
F	13.519		88.094		54.368		
P-Value	0.000		0.000		0.000		

N.B: Value(s) with the same superscripts across a row are not significantly different at P**≥**0.05

Discussion

The presence of various concentrations of heavy metals in the surface water of Wasai Reservoir reported in this study is similar to the report of Farafara (2021), who reported wastes and high concentrations of heavy metals in the surface water of Geidem Reservoir in Yobe State. This finding unveils the likely adverse health effects posed by direct consumption of these heavy metal-polluted water by the public. The high concentrations are due to the high levels of municipal waste the reservoir receives from domestic and industrial effluents coupled with agricultural fields' runoffs.

Heavy metals are potent toxic substances due to their slow degradation rate and long half-life (Prajapati et al., 2012). Results from the present study revealed that fish exhibited wide range of variations in the heavy metals accumulation capacity in its various organs. Several studies have attributed the high heavy metal concentration to the feeding habit of C . gariepinus (Meador et al., 2005; Hao et al., 2013; Wu et al., 2023). The heavy metal levels in the surface water and their bioaccumulation in the tissues and organs of C. *gariepinus* differed significantly. This finding is in conformity with that of Abdulrahman et al. (2018), who reported that there is variation in the bioaccumulation capacity of heavy metals by different organs of fish. The accumulation of these heavy metals differs with season due to the fact that from March through May, the environmental temperature is so high that much of the water evaporates, leaving high concentrations of the metals. However, the differences observed with the sampling stations could be attributed to the type of anthropogenic activities carried out close to these stations. Similarly, some fish organs, such as gills, have more direct contact with the water than the muscles and, as such, accumulate higher levels of heavy metals. This variation probably depends on a number of factors, such as the age of the fish, migratory ability, differential exposure and health conditions, as stressed by Ekweozor et al. (2017).

Cadmium is one of the most toxic elements with reported carcinogenic effects in humans. High concentrations of Cd have been found to lead

to chronic kidney dysfunction (Yan et al., 2021). Cadmium can bioaccumulates at all levels of aquatic and terrestrial food chains (Moses, 2018). The concentrations of Cd in fish muscles and gills analysed in this study were above the 0.01 mg/kg maximum permissible level approved by WHO (2004). The high levels of Cd in the study area could be attributed to water contamination with heavy metals from agricultural and domestic run-offs.

Chromium acts as a regulator of glucose and cholesterol metabolism, but at higher concentrations, it has been found to be toxic (Shin et al., 2023). The values of Cr obtained in the present study agree with that of Ahmad *et al.* (2018) who reported a similar range of Cr values accumulation in *Tilapia zilli* gills caught from Kafinchiri Reservoir in Kano State. The Chromium level recorded in this study is lower than the 29.8 - 31.6 ppm reported in T. zilli and 28.1 - 32.2 ppm in C. gariepinus caught from River Benue by Ishaq et al. (2011). Cr might have come from paint sprays, car-wash detergents, lubricating oils and domestic chemicals used by the inhabitants along the reservoir tributaries (Yilmaz, 2009).

The concentration of Cr was generally high in the gills of fishes from the four sampling sites. This could be because of run-offs around the sampling areas where Chromium-rich fertilisers are applied during agricultural activities. A similar high concentration (1.313 mg/kg) of chromium was reported by Moses et al. (2018) in Abare River in Zamfara State. Similarly, Ibrahim et al. (2018) reported 0.77 mg/kg in gills of catfish sampled from Njuwa Lake in Adamawa State. The levels of Cr reported in this study were higher than that reported by Orosun et al. (2016) in *Clarias gariepinus* sampled from Kiru Dam and River Gongola in Adamawa State.

Lead is a non-essential element that constitutes body burden and a great threat to life if present in substantial quantity. It is toxic even at minimal concentrations and has no known function in biochemical processes (Moses et al., 2018). According to FAO (2007), the permissible level of Pb is 0.5 mg/kg dry weight. Like Cd, lead concentration in this study was lower than the recommended limit.

The values of Pb obtained by this study are in the range of those from the work of Faye-Ofori et al. (2015), who reported 0.039±0.009 mg/kg.

Heavy metals are considered potent toxic substances due to their slow degradation rate and long half-life (Prajapati et al., 2012). Fishes are often used as bioindicators of aquatic ecosystems for the estimation of heavy metals pollution and possible risk or humans through consumption (Agarwal et al., 2007). Bioaccumulation of heavy metals in fishes is directly from the water through the gills and indirectly from food (Barron, 1990). The bioaccumulation of Pb, Cd and Cr in the tissues of fish species reported in the present study agrees with that of Abalaka et al. (2020) who found high concentrations of zinc, cadmium, lead and iron in the tissues of Auchenoglanis occidentalis obtained from Tiga Dam, Kano State. The high concentration of lead in the muscles of C . gariepinus collected from Wasai Reservoir is of public health concern as the concentrations exceeded the recommended limit allowed by WHO (2004) in fish food. This finding is also in agreement with that of Doherty et al. (2010), who recorded high lead concentrations in fish tissue obtained from Lagos Lagoon. The values obtained for lead in this study contrast with those reported by Daka et al. (2008), who recorded low values (0.01 - 0.06 ppm) in fish species from Azuabie Creek in the Bonny Estuary, Nigeria.

Similarly, the bioaccumulation of Pb and Cd in the fish tissues reported agrees with the findings of Bawuro et al. (2018), who reported high bioaccumulation of Zn , Pb, Cd, and Cu in the tissues of Clarias anguillaris, Heterotis niloticus and Tilapia zilli from Lake Geriyo, Adamawa State, Nigeria. The variations in heavy metals bioaccumulation in the different species of fish from that study were attributed to their feeding habits and the presence or absence of scales that prevent their accumulation via the body surface. Some fish species, such as *Oreochromis niloticus*, showed bioaccumulation of Cd, Pb and Cr in the gills than in other tissues. Gills are pathways of metal ion exchange with water, as reported by Qadir and Malik (2011) because gills have a wide surface area that rapidly enhances metals' diffusion (Dhaneesh et al., 2012). Moore and Ramamorthy (1989) stressed that the heavy metals bioaccumulated in fish gills are mostly sourced from surface water and sediment. Similarly, previous studies by Kargin et al. (2000), Qadir and Malik (2011) and Musa (2021) reported high Cd accumulations in fish gills. The Cd, Cr and Pb concentrations reported in this study were above the WHO (2004) and FEPA (1998) prescribed limits for food fish. This corroborates the work of Nwani et al. (2009), who reported similar findings in freshwater fish species from the Anambra River in Southeastern Nigeria.

Conclusion

Heavy metals (Lead, Cadmium and Chromium) were recorded in the surface water of Wasai Reservoir. These heavy metals were found to bio-accumulate in high concentrations above tolerable limits in the gills of *Clarias gariepinus* (Pb = $0.02 - 0.12$ mg/kg, Cd = $0.02 - 0.35$ mg/kg, and $Cr = 0.02 - 0.26$ mg/kg). This means that the public is in danger if they consume fish gills caught within the reservoir. Thus, it is recommended that the gills of fish from this reservoir should be discarded. The BAF values (except for Cr in the gills) were above tolerable limits (Pb = 0.78; 0.18. Cd = 0.79; 0.17 and Cr = 0.17; 0.01 in muscles and gills respectively)

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