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Research Article

Assessment of Heavy Metals in Sediments, Water and *Clarias gariepinus* from Alau Dam, Borno State – Nigeria

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ABSTRACT

Alau Dam attracts commercial fishing and farming activities creating a booming market for individuals involved in the fish and vegetable businesses. The lake having flowed into several towns and villages coupled with the socio-economic activities along its bank received effluents with different concentrations of heavy metals. The study was aimed at assessing the levels of selected heavy metals (Pb, Cd, Cr, As and Hg) concentrations in the sediments, water and *Clarias gariepinus* from Alau Dam, Borno State, Nigeria. Samples were collected bi-weekly for 3 months and analyzed using standards methods. The result of the study indicates that heavy metal concentrations (Pb, Cd and Cr) in the sediments (2.120 ± 0.011, 1.004 ± 0.010 and 0.300 ± 0.010 mg/kg respectively) were all above USEPA permissible limits. The study further shows that exception of Cr (0.011 ± 0.007) all other analyzed metals were above NESREA limits. Additionally, the concentrations of Pb, Cd, Cr, As and Hg in the fish samples (1.020 ± 0.011, 0.940 ± 0.022, 0.001 ± 0.017, 0.010 ± 0.112 and 0.005 ± 0.033 mg/kg respectively) were within the NAFDAC limit. The Non-Cancer Risk (HQ were > 1 in all calculated samples) and Cancer Risks (>10^{-3} in all calculated samples) revealed high health risk from ingestion of the *C. gariepinus* from the study area. Furthermore, the BAF ratio shows Cd > Pb > Hg > As > Cr. The study recommends strict enforcement of NESREA regulations and a continuous monitoring of the levels of heavy metals concentration in the Dam.

Keywords: Non-Cancer Risk; Cancer Risk; Bioaccumulation Factor; Sediment; Fish; Water

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INTRODUCTION

Globally, the need to improve the standard of living and ensure food security has raised new environmental challenges, as the continuous strive for urbanization and industrialization without due regards to the principles of environmental protection and sustainability has continued to endanger the entire biosphere [Bennett *et al.,* 2003; Bwala, 2021a; Bwala *et al*., 2023]. These two-fold issues continue to mound pressures on ecosystems and their resources, particularly the aquatic ecosystems because most anthropogenic activities that release heavy metals worldwide end up flowing into the water bodies becoming toxic to the aquatic organisms [Sehar *et al*., 2014; Bwala, 2021b, 2021c] with the tendencies of reaching even terrestrial biota through the food web.

Heavy metals are unique natural elements deposited in the earth's crust which have been known and used for centuries by man; present in different concentrations in all ecosystems and are persistent in the environment [Ibrahim *et al*., 2006; Muhammad *et al*., 2022]. They are "metallic elements possessing a relatively high density compared to water" [Bwala, 2021b]. Based on the assumption that heaviness, severity and toxicity are linked and interrelated, metalloids such as mercury, arsenic, lead are considered heavy metals because they can be toxic even at low levels of exposure [Duffus, 2022]. Man can be exposed to these metals both from natural and anthropogenic sources. Regardless of the mode of exposure, heavy metals are all toxic in a sufficient quantity and/or concentration to man and other living organisms in the environment [NESREA, 2011].

The bioavailability of heavy metal to an organism is a factor of different physical conditions such as temperature, its state of matter, adsorption and sequestration and chemical conditions such as thermodynamic equilibrium, lipid solubility and octanol/water partition coefficients [Tchounwou *et al*., 2010; Bwala, 2021a]. Bio-physical conditions in the ecosystems such as trophic relationships, species features, geologic conditions and the ecological adaptation strategies of living organisms, also impacts on its bioavailability [Rizwi *et al*., 2005; Bwala, 2021b]. The impacts of heavy metals on the environment, particularly on the aquatic environment are major concern due to their ability to be toxic, bioaccumulate and bio-magnify in biological systems even at low levels of concentration [Opaluwa *et al*., 2012]. The bio-availability of heavy metals in ecosystems are not necessarily proportional to the total level of concentrations of these metals [Opaluwa *et al*., 2012], as anthropogenic activities may increase their concentration beyond the natural levels [Bennett *et al.,* 2003; Opaluwa *et al*., 2012; Bwala, 2021a]

Borno State, Northeastern, Nigeria being the most affected State by the Boko Haram insurgency in the federation has for more than a decade suffered humanitarian crisis with twenty-five out of its twenty-seven Local Government Areas (LGAs) heavily affected, displacing one-third of the total State's population [UNICEF, 2020]. Maiduguri, the State capital, became the major refuge city to the Internally Displaced Persons (IDPs) with multiple IDP camps scattered all over the city [Bwala, 2021c]. This rapid demographic change coupled with the induced change in economic activities and land-use resulted in direct and indirect ecological disturbances from anthropogenic activities releasing pollutants into the ecosystems. The release of pollutants from various activities taking place along Alau Dam like the use of pesticides, herbicides and other chemicals by famers and government agencies in controlling the weeds growing along the river bank and the vicinity of the Dam for agricultural and security purposes may result in water quality deterioration, polluting the freshwater body with heavy metals and this dynamism when not properly managed, may disrupt the lake's ecosystem, leading to bio-availability, bioaccumulation and biomagnification of these heavy metals [Syed, 2011; Akan *et al*., 2013a, 2013,b; Bwala, 2021c].

Alau Dam depends on the seasonal flow of river Ngadda [Babagana *et al.*, 2015]. River Ngadda is a freshwater body that receives effluents and runoffs from industrial, residentials and agricultural areas as it passes through different cities, towns, villages and forests before emptying into the Dam [Akan *et al*., 2013a, 2013b; Babagana *et al.*, 2015]. The Dam was primarily constructed for farming, domestic and industrial uses [Babagana *et al.*, 2015]. The study was aimed at assessing heavy metals in the sediments, water and a fish Specie (*Clarias gariepinus*) from Alau Dam, Borno State, Nigeria.

MATERIALS AND METHODS

Study Area

Lake Alau is located 20km away from Maiduguri the State capital of Borno State, Nigeria. Alau Dam is located at the present Alau community on latitude 11° 4`N and 12° 5`N and longitude 13° 05`E and 13° 20`E, Konduga Local Government Area, Borno State, Northeastern Nigeria [Akan *et al*., 2013b]. Alau community lies within the northern Sudan Savannah with distinct dry and wet (rainy) seasons. The community has an annual mean temperature of 29°C. The lake is a freshwater body which received water from river Yedzram and river Gombole which met at a confluent in Sambisa Forest and flows as river Ngadda into Alau DamDam. The Dam receives agricultural runoffs and domestic waste water [Akan *et al*., 2013a]. The lake is widely known for its commercial fishing activities with *Tillipia zillii* and *Clarias gariepinus* as the abundant species [Bwala, 2021b, 2021c].

Samples Collection

Water, sediments and fish (*C.* gariepinus) samples were collected bi-weekly for 3months from Alau Dam. Heavy metals (Pb, Cd, Cr, As and Hg) were analysed using Bulk Scientific Atomic Adsorption Spectrophotometry (AAS). Statistical analysis was done using Microsoft Excel 2010 statistical package.

Sediment Samples

Sediment samples were collected using procedure explained by Edward & Muhib [2020] bi-weekly for

3months using a soil scooping handheld equipment. The collected sediment samples kept in plain sterile polyethylene and transported in ice to the laboratory for further analysis.

Water Samples

Water samples were collected bi-weekly for 3months using 500 ml amber bottles. The collected samples were fixed with concentrated nitric acid in-situ using standard method as explained by APHA [2005]0; Usman *et al.* [2016]0; Gwana *et al*. [2017] and Edward & Muhib [2020]0 with slight modification and transported in ice to the laboratory for further analysis.

Fish Samples

Samples of *C. gariepinus* were brought directly from fishermen at the landing site bi-weekly for 3months. The samples were identified using taxonomy key, marked and transported in ice to the laboratory for further analysis.

Digestion of Collected Samples

Sediment Samples Digestion

The sediment samples were digested using method explained by Edward & Muhib [2020]. The collected samples were weighted (1.5g) into a digestion tube and then topped up with of concentrated acids (65% HNO_3, 6 ml and 37% HCl, 3 ml) and 0.25 ml H_2O_2. The samples were then placed in a microwave digester for 30 min. The samples were allowed to cool and 5 ml of deionized water was added. The samples were further filtered using filter paper and marked for AAS analysis.

Water Samples Digestion

The water samples were digested using method explained by Edward & Muhib [2020] and Bwala [2021a, 2021b, 2021c]. The collected samples were weighted (1.5g) into a digestion tube and then topped up with of concentrated acids (65% HNO_3, 6 ml and 37% HCl, 3 ml) and 0.25 ml H_2O_2. The samples were then placed in a microwave digester for 30 min. The samples were allowed to cool and 5 ml of deionized water was added. The samples were further filtered using filter paper and marked for AAS analysis.

Fish Samples Digestion

The *C. gariepinus* fish samples were oven dried for 144 hours, grounded and kept in air tight containers prior in the laboratory as explained by Olabemiwo *et al*. [2011]. The sample digestion was done using concentrated nitric acid and hydrogen peroxide (2:1) v/v according to method explained by Musa *et al.* [2017]. Two grams of the grounded samples were weight into a digestion tube and then HNO_3 (65%) and H_2O_2 (30%) (2:1) was added and allow for reaction. The content of the digestion tube was then mounted unto the digestion chamber for 3 hours, reducing the content to 5mL. The digested sample was allowed to cool and filtered, then topped-up with deionized water. The filtered samples were then marked for the Heavy metal analysis.

Heavy Analysis

The level of heavy metals (lead, mercury, arsenic, cadmium and chromium) concentrations was determined in the digested samples (sediments, water and fish) using Atomic Absorption Spectrophotometer (Buck Scientific Model 210 VGP) at Chemistry Department, Yobe State University**.**

Health Risk Assessment

The Average Daily Dose (ADD) of heavy metals, Non-Cancer Hazard Index (HQ – Hazard Quotient) and Cancer Risk (CR) were calculated in order to determine the potential long term health risks associated with the ingestion of *C. gariepinus* contaminated with heavy metals from Alau Dam. The calculation was done using methods explained by Ametepey *et al*. [2018]; Nduka *et al.* [2019]; Edward & Muhib [2020]; Wang *et al.* [2021] and Bwala *et al.* [2023].

Average Daily Dose (ADD)

$$ADD = \frac{EF \times ED \times Ci \times InR}{BW \times AT}$$

where C_i is the concentration of heavy metals (kg/kg);

InR is the ratio of fish intake 0.5kg/d

EF is exposure frequency (365 d/a);

ED is exposure duration (70 years);

BW is the average of body weight (60 kg);

AT is the average exposure time for non-carcinogenic effects (70 years);

Non-Cancer Hazard Index (Hazard Quotient (HQ)

The non-carcinogenic risk associated with the ingestion of *C. gariepinus* contaminated with heavy metals from Alau Dam was determined using target hazard quotient values. Target hazard quotient is a ratio of the estimated dose of a contaminant to oral reference dose considered harmful and detrimental to human health. If the ratio is greater than or equal to 1, an exposed population is at risk. The non-carcinogenic health risk was computed as:

Hazard Quotient (HQ) = $\frac{ADD}{RfD}$

Where **ADD** is average daily dose

RfD is the daily reference dose of heavy metals (µg/(kg·d) as shown in **Table 1.**

Table 1. Reference Dose and Slope Factor of Some Selected Heavy Metals

Heavy Metals	**R_fD (mg/kg/day)**	**SF $[(mg/kg/day)]^{-1}$**
Arsenic (As)	3×10^{-4}	1.5E+0
Lead (Pd)	1.4×10^{-4}	8.5E-03
Mercury (Hg)	3.0×10^{-4}	
Cadmium (Cd)	5×10^{-4}	15
Chromium (Cr)	3.5×10^{-3}	5.0E-01

Cancer Risk (CR)

$$CR = ADD \times SF$$

Where **ADD** is average daily dose

SF - Slope Factor (1/mg/kg/day) as shown in **Table 1**

Bioaccumulation Factor (BAF)

The Bioaccumulation Factor (BAF) is determined as the ratio of heavy metals concentration in the *C. gariepinus* to the levels of the concentration in sediments. When the transfer factor is greater than 1.0, then bioaccumulation is said to have occurred in the fish species [Edward & Muhib, 2020].

$$BAF = \frac{Conc.\ of\ heavy\ metal\ in\ Fish}{Conc.\ of\ heavy\ metal\ in\ Sediment}$$

Data Analysis

Data obtained was tabulated using Microsoft Excel 2010 and simple descriptive statistical tool was employed.

RESULTS AND DISCUSSION

Heavy Metals Concentration in Sediments

The results the heavy metal concentrations in the sediments of Alau Dam in **Table 2** indicates that Pb, Cd and Cr (2.120 ± 0.011, 1.004 ± 0.010 and 0.300 ± 0.010 mg/kg respectively) were all above United State Environmental Protection Agency's permissible limits [USEPA, 1993]. This is consistent with the findings of Opaluwa *et al*. [2012]; Akan *et al.* [2013a] and Edward & Muhib [2020]. Heavy metals from residential, industrial and agricultural activities discharged into the lake maybe trapped by sediments this has biomagnification potential as it moves along the food chain [Muhammad *et al*. 2022; Bwala *et al.* 2023]. Heavy metals are generally environmental persistent, non-biodegradable, non-soluble and has bio-amplification potential. Their presences in the sediments of an aquatic ecosystem indicates their bio-availability [Muhammad *et al*., 2022].

Table 2. Concentration of Heavy Metals in Sediment Samples of Alau Dam

Heavy Metals	**Concentrations** (mg/kg)	**USEPA Limits** (mg/kg)
Lead (Pb)	2.120 ± 0.011	0.04
Cadmium (Cd)	1.004 ± 0.010	0.006
Chromium (Cr)	0.300 ± 0.010	0.1
Arsenic (As)	0.180 ± 0.020	-
Mercury (Hg)	0.081 ± 0.221	-

Values are mean ± SD of the sample fish analyzed

Heavy Metals Concentration in Water

Table 3 shows the results the heavy metal concentrations in water samples from Alau Dam. The results revealed that with the exception of Cr (0.011 ± 0.007 mg/kg), all other metals (Pb, Cd, As and Hg) (1.540 ± 0.100, 1.001 ± 0.002, 0.100 ± 0.111 and 0.015 ± 0.001 mg/kg respectively) were above the National Environmental Standards and Regulations Enforcement Agency's set permissible limits [NESREA, 2011]. This is consistent with the findings of 0Opaluwa *et al*. [2012]0; Akan *et al.* [2013a, 2013b]; Edward & Muhib [2020] and Bwala [2021a]. Fishes like other aquatic organisms are sensitive to heavy metal contamination and may accumulate same in their tissues [Muhammad *et al*., 2022]. In an ecosystem, there is constant exchange of elements between the trophic levels and their environment. This gives a pathway for the transfer of harmful and devastating metals such as Pb, Cr, Cd, As and Hg into the food chain, as organisms can easily ingest these metals from their polluted environment and transfer same to a higher organism in the trophic level [Syed, 2011].

Table 3. Concentration of Heavy Metals in Water Samples from Alau DamDam

Heavy Metals	**Concentrations** (mg/kg)	**NESREA Limits** (mg/kg)
Lead (Pb)	1.540 ± 0.100	0.01
Cadmium (Cd)	1.001 ± 0.002	0.005
Chromium (Cr)	0.011 ± 0.007	0.5
Arsenic (As)	0.100 ± 0.111	0.05
Mercury (Hg)	0.015 ± 0.001	0.001

Values are mean ± SD of the sample fish analyzed

Heavy metals Concentration in *Clarias gariepinus*

The results the heavy metal concentrations in *C. gariepinus* from Alau Dam in **Table 4** indicates that all measured metals (Pb, Cd, Cr, As and Hg) (1.020 ± 0.011, 0.940 ± 0.022, 0.001 ± 0.017, 0.010 ± 0.112 and 0.005 ± 0.033 mg/kg respectively) were within the national permissible limits as set by National Agency for Food and Drugs Administration Control [NAFDAC, 2019]. This agrees with the findings of Opaluwa *et al*. [2012]; Edward & Muhib [2020] and Bwala *et al.* [2023]0. Heavy metals are viewed as toxic and unsafe due to their risk, persistency, bio-accumulation and bio-magnification potentials. They are reported to cause severe diseases to both aquatic and terrestrial life [Syed, 2011; Muhammad *et al*., 2022].

Table 4. Concentration of Heavy Metals in *C. gariepinus* From Alau DamDam

Heavy Metals	**Concentrations** (mg/kg)	**NAFDAC Limits** (mg/kg)
Lead (Pb)	1.020 ± 0.011	2.0
Cadmium (Cd)	0.940 ± 0.022	0.2
Chromium (Cr)	0.001 ± 0.017	2.0
Arsenic (As)	0.010 ± 0.112	0.5
Mercury (Hg)	0.005 ± 0.033	0.1

Values are mean ± SD of the sample fish analyzed

Health Risk Assessment

The routes of exposure to heavy metals to target organisms are used to determine the health risk as it is a vital tool used in the determining the level of exposure. Notwithstanding the different method of human exposure to heavy metals, ingestion from contaminated food such as one of the methods could cause harm to the human health [Ametepey *et al*., 2018; Edward & Muhib, 2020].

The human health risk associated with the Average Daily Dose (ADD) was determined as presented in **Table 5**. This study agrees with the findings of Ametepey *et al*. [2018], who studied concentration of heavy metals on vegetables, and Nduka *et al.* [2019]; Wang *et al*. [2021] who studied the concentration of heavy metals on fish samples.

Table 5: Average Daily Dose (ADD), Non – Cancer Risk (HQ) and Cancer Risk (CR) of *C. gariepinus* Fish Samples from Alau Dam

Heavy Metals	**ADD**	**HQ**	**CR**
Lead (Pb)	3.1025	22160.71	0.0264
Cadmium (Cd)	2.8592	5718.333	42.8875
Chromium (Cr)	0.0030	8.6905	0.0015
Arsenic (As)	0.0304	101.3889	0.0456
Mercury (Hg)	0.0152	50.6944	-

Furthermore, the results in **Table 5** also revealed that Non-Cancer Risk (HQ) were greater than 1 in all the different metals analyzed (Pb, Cd, Cr, As and Hg), this suggests an unacceptable level of non-carcinogenic adverse health risk from the consumption of *C. gariepinus* from Alau DamDam.

Additionally, the results further revealed Cancer Risk to be a major concern as all the calculated values are $>10^{-3}$. This negates the findings of Ametepey *et al*. [2018]; Edward & Muhib [2020] and Wang *et al.* [2021]. This can have more adverse effect on children, elderly, pregnant women and individuals underlaying health issues [Bwala *et al*., 2023]. The potential human health risks of heavy metals accumulation through consumption of *C. gariepinus* from Alau DamDam is a factor of ADD of the contaminated fish, the bio-availability of the metals to the fish and bio-accumulation of the metals in the fish. Though *C. gariepinus* from Alau DamDam intake is just a proportion of food consumed in the study area, supplementary or complementary food that may also be contaminated include vegetables grown in the area, intake of the water as it's a major source of water to Maiduguri and its environs [Babagana *et al.*, 2015] and other foods, air and skin exposure routes.

Bioaccumulation Factor (BAF)

The results of the Bioaccumulation Factor (BAF) of the heavy metals (Pb, Cd, Cr, As and Hg) from *C. gariepinus* in **Table 6** reveals that the transfer factor were all less than 1 suggesting that there was minimal or no bioaccumulation that took place in *C. gariepinus* in the study area. The study further indicates the order of bioaccumulation of the heavy metals as Cd > Pb > Hg > As > Cr. This negates the findings of Edward & Muhib [2020] who reported Cr to as having a greater bioaccumulation in Escravo River.

Table 6: Bioaccumulation Factor (BAF) in *C. gariepinus* from Alau Dam

Heavy Metals	BAF
Lead (Pb)	0.4811
Cadmium (Cd)	0.9363
Chromium (Cr)	0.0033
Arsenic (As)	0.0556
Mercury (Hg)	0.0617

CONCLUSION

The levels of heavy metals (Pb, Cd and Cr) were all above the USEPA limits in the sediments. Additionally, the study revealed that in the water samples analyzed, the level of concentrations of heavy metals (Pb, Cd, As and Hg) exceeded the national limits set by NESREA with exception of Cr. Furthermore, all measured metals (Pb, Cd, Cr, As and Hg) were revealed to be within NAFDAC permissible limits.

In conclusion, the health risk associated with the ingestion of *C. gariepinus* from the study area revealed that the Non-Cancer Risk (HQ) were greater than 1 in all analyzed metals analyzed (Pb, Cd, Cr, As and Hg), this suggests an unacceptable level of non-carcinogenic adverse health risk from the consumption of *C. gariepinus* from Alau Dam. Additionally, the study further indicates that the Cancer Risk associated with the ingestion of *C. gariepinus* from the study area to be a major concern as all the calculated values are $>10^{-3}$.

The study further indicates the order of bioaccumulation of the heavy metals as Cd > Pb > Hg > As > Cr and suggests that there was minimal or no bioaccumulation in the *C. gariepinus* from the study area.

Heavy metals are highly toxic to biological systems which necessitate diligent and constant monitoring in order to assess the levels of concentration aimed at protecting public health and the health of the entire ecosystem. The aquatic ecosystem receives effluents from industrials, domestic, agricultural and commercials areas which continuous to pollutes the ecosystem with different types and concentrations of heavy metals. This study assessed the levels of heavy metals (Pb, Cd, Cr, As and Hg) in the sediments, water and *C. gariepinus* of Alau Dam. The Non-Cancer and Cancer Risks revealed high health risk from ingestion of the fish species from the study area.

The study recommends the strict enforcement of the National Environmental Standards and Regulations Enforcement Agency's (NESREA's) regulations and guidelines. Continuous monitoring and evaluation of the irrigation and other anthropogenic activities capable of polluting the aquatic ecosystem with heavy metals. Also, continuous monitoring of the levels of heavy metal concentrations in the sediments, water and other bio-systems is important. The Non-Cancer Risk (HQ) and the Cancer Risk assessments revealed high health risk from the ingestion of *C. gariepinus* from the area, this therefore calls for strict monitoring and continuous evaluation aimed at protecting public health.

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Conflict of Interest

No conflict of interest.

Data Availability

The data that support the findings of this study are available on request.

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