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Lead (Ld) and cadmium (Cd) concentration in catfish (*Clarias gariepenus)* of River Gashua, Bade Local Government Area, Yobe State

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ABSTRACT

The research work was designed to assess the concentrations of heavy metals (lead and cadmium) in water and fish (*Clarias gariepenus*) from three different sampling points: Gada, Usur and Katuzu. A total of 21 water samples (seven from each sampling points) and 60 fish samples (20 from each sampling points) were collected biweekly from March to April 2021. The samples were transported to the Research Laboratory of the Department of Chemistry, Yobe State University, Damaturu. Atomic absorption spectrophotometer methods were adopted for determination of heavy metals. The mean concentration of temperature (°C) recorded was highest in Usur (27.42±0.25), (25.75±0.11), and lowest in Katuzu (25.50±0.21) respectively recorded highest value in Usur(8.06±0.29), (7.49±0.18) and lowest in Gada (7.36±0.16) respectively, whereas, dissolved oxygen (mg/L) was highest in Gada (8.01±0.05), (7.45±0.21) and the least value was recorded in Usur (7.40±0.17) respectively. From the results obtained the mean concentration (mg/kg) of heavy metals in fish from Katuzu was higher (0.50±0.07) in lead and (0.55±0.07) in cadmium compared to Gada and Usur that recorded (0.18±0.06) (0.31±0.05) in lead and (0.24±0.10) (0.40±0.07) in cadmium respectively. All the heavy metals assessed in fish from this study were within WHO/FAO and NASREA permissible limits. There was no significant difference in concentrations among heavy metals in fish samples from the three different sampling points ($p<0.05$). The need for adoption and enforcement of appropriate monitoring and management strategies for the protection of the river and its biota was therefore recommended.

Keywords: Heavy metals; river Gashua; bioaccumulation

INTRODUCTION

Water, a vital element for the sustenance of life on earth, contains essential minerals crucial for both human and global aquatic ecosystems. Drinking water primarily originates from rivers, streams, and lakes, making the pollution of these natural reservoirs a pressing environmental concern. Inorganic compounds, originating from both natural and human-related sources, continually infiltrate aquatic ecosystems, posing significant threats due to their toxicity, prolonged persistence, and potential for bioaccumulation and biomagnification within the food chain (Karadede-akin and Unlu, 2007; Papagiannis *et al.*, 2004). Heavy

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metals, denoting metals or metalloids with elevated concentrations often harmful to organisms (Dufus, 2002), constitute natural components of aquatic environments whose levels have surged due to domestic, industrial, mining, and agricultural activities (Limba *et al*., 2018). The acidic nature of many industrial wastes adversely impacts aquatic organisms, resulting in various abnormalities such as reduced growth rates and subsequently diminishing the abundance and diversity of species in ecosystems (Ayotunde *et al.*, 2011). The accumulation of heavy metals in fish is contingent on factors like growth rate, metabolism, feeding habits, and ecological requirements specific to each fish species (Yilmal *et al*., 2005; 2010).

Common heavy metal contaminants, including Lead (Pb) and Cadmium (Cd), as well as non-essential and toxic metals like Iron (Fe), Copper (Cu), and Zinc (Zn), are distributed and discharged into aquatic environments through industrial sources such as mining and ore refining (Hala *et al.,* 2015). Cadmium and lead stand out as two of the most toxic contaminants within the food chain (Hala *et al.,* 2015). Cadmium (Cd) has detrimental effects on the lungs and is linked to the development of Itai-itai disease (Hala *et al*., 2015), while lead (Pb) adversely affects the blood, various organs, and the nervous system (Malhat, 2011). Bioaccumulation occurs when fish come into contact with heavy metals in their environment, potentially leading to the manifestation of Itai-itai disease (Chen *et al.*, 2007).

The African catfish (*Clariasgariepinus*) and Nile tilapia (*Oreochromisniloticus*) are widely distributed in freshwater ecosystems and are favored for their high palatability, low cholesterol content, and tender flesh (Ibrahim *et al.*, 2018). These fish species often serve as affordable sources of animal protein for households in both urban and rural areas (Bene and Heck, 2005). Numerous studies have investigated the pollution of fish by Pb and Cd in Egypt, particularly focusing on tilapia in the River Nile (Malhat, 2011). The maximum permissible limits for lead and cadmium in fish, as stipulated by the FAO (1983) and WHO (1985), are 0.5 ug/g and 0.05 ug/g, and 2.00 ug/g and 2.00 ug/g, respectively. This study aims to assess the concentrations of lead (Pb) and cadmium (Cd) in water samples and the catfish species *Clarias gariepinus* from the River Gashua in the Bade Local Government Area of Yobe State.

MATERIALS AND METHODS

Study Area

River Gashua is located in Gashua headquarters of Bade Local Government Area Yobe State in Northeastern part of Nigeria. Gashua is situated at latitude: 12º 52' 26.33"N and longitude: 11º02'26.05" E. The average elevation is 299 m; the population in 2006 was 125.000. The river Gashua is the sub-part of the River Kumadugu Yobe. People in the area are predominantly farmers with a lot of farming and fishing activities carried out throughout the year. Dumping of domestic and industrial waste in the river is a major practice of the inhabitants of the river.

Sample Collection

The sample collection process took place biweekly during the dry season, spanning from March to April 2021. A total of (21) water samples were collected in plastic bottle of 1liter capacity from 3 sampling points (separated 1 kilometer apart). Temperature, pH and Dissolved oxygen were determined *in-situ*, 60 catfish samples were procured from local fishermen at the landing site immediately after capture. Both the water and fish samples were carefully stored in an ice-chest container and transported to the Chemistry Research Laboratory at Yobe State University (YSU).

Collection of Water and Fish Sample

Water samples were collected from the river and the major tributaries that feed the river. Samples were collected from the three (3) different points at 1 kilometer apart. The samples were collected in three different containers, for water physico-chemical parameters and heavy metals concentration analysis. 60 ml polyethylene bottles were used to collect water samples for heavy metal determination. The samples were placed in an ice chest container and taken to the laboratory on the same day.

Fish sample catfish; *Clarias gariepinus* were purchased from local fishermen at landing site. Sampling was done biweekly and 14 fish samples each were collected, placed in an ice container and transported to the laboratory for further analysis.

Heavy Metals Analysis

All Glass wares were cleaned with 10% concentrated Nitric acid (HNO_3) in order to clear out any heavy metal on their surfaces and then rinsed with distilled-deionized water. The digestion tubes were soaked with 1% (w/v) potassium dichromate in 98% (v/v) H_2SO_4 and the volumetric flasks in 10% (v/v) HNO_3 for 24 hours followed by rinsing with deionized water and then dried in oven and kept in dust free place until analysis began. Prior to each use, the apparatus were soaked and rinsed in deionized water.

Equipment and Reagents

1. Analytical balance, 250-g capacity, resolution 0.0001g, OHAUS, PA214 pioneer USA
2. Glass ware: Borosilicate volumetric flasks (25, 50 ml, 100 ml & 1000 ml), Measuring cylinders,
3. Micropipettes (1-10 ml, 100-1000 ml)
4. Atomic absorption spectrophotometer (Buck scientific model 210VGP AAS, USA; equipped with hollow cathode lamps and air-acetylene flame)
5. Microwave digester (Master 40 serial No: 40G106M

Reagents and chemicals used for the laboratory works were all in analytical grade: Deionized water (chemically pure with conductivity 1.5 µs/cm and below was prepared in the laboratory) was used for dilution of sample and intermediate metal standard solutions prior to analysis and rinsing glassware and sample bottles.

Sample Pre-Treatment/Digestion (Fish samples)

The samples were allowed to dry using hot oven (Model 30GC lab oven) and then ground into fine powder by using a porcelain mortar and pestle.

200mg of each sample was weighed into thoroughly clean plastic container (microwave tube) and 6ml of 65% HNO_3 and 2ml of H_2O_2 (and 2 mL of HF for soil samples only) were added and allowed and to stand for a minute. The plastic container (microwave tube) was then covered and placed in to microwave digester (Master 40 serial No: 40G106M) and digested.

The digestion was carried out at a temperature of 75°C for 10 mins and then ramped at 10^0C per minute to 95^0C and held for 30 mins. The digestion was followed by a cooling to room temperature in the microwave.

Potential presences of metal/elements in chemicals used in digestion were determined. Blanks were used simultaneously in each batch of the analysis to authenticate the analytical quality. The digested samples were diluted with deionized water to a total volume of 100ml. (Perkin Elmer. 1997)

Sample Pre-Treatment (Water)

The samples were filtered through Whatman no 1 filter paper. One milliliter of HNO_3 was added to each 90 mL of sample (to make 1.0%). The presence of heavy metals in the samples was determined using AAS. Blanks were used simultaneously in each batch of the analysis to authenticate the analytical quality. (Perkin Elmer. 1997).

Determination of metal contents of each sample

Concentration of the metal ions present in the sample was determined by reading their absorbance using AAS (Buck scientific model 210GP) and comparing it on the respective standard calibration curve. Three replicate determinations were carried out on each sample. The metals were determined by absorption/concentration mode and the instrument readout was recorded for each solution manually. The same analytical procedure was employed for the determination of elements in digested blank solutions and for the spiked samples (Perkin Elmer. 1997).

Data Analyses

The data obtained were processed statistically and presented as mean ± standard error of mean. Statistical significance of comparison of data was analyzed using one way analysis of variance (ANOVA). Probability of less than 0.05 was considered statistically significant ($p< 0.05$).

RESULTS

Physico-chemical parameters from three different sampling points from river Gashua

Mean variation of physico-chemical parameters of water samples from river Gashua are presented in Table 1. The physicochemical parameters determined were Temperature (^{0}C), pH and dissolved oxygen (mg/l). Their levels were compared with national guideline limit (NGL) and NESREA. Table 1 indicated that water samples from Gada have the following range of physico-chemical parameter; 25.75±0.11, 7.36±0.16 and 8.01±0.05 of temperature, pH and dissolved oxygen respectively. The results from Usur recorded the following level of temperature (27.42±0.25), pH (8.06±0.29) and dissolved oxygen (7.40±0.17). Temperature (25.50±0.21), pH (7.49±0.18) and dissolved oxygen (7.45±0.21) were recorded from Katuzu. The level of temperature from Usur shows the higher concentration compared to Gada and Katuzu. So also, Usur had a higher level of pH than Gada and Katuzu. All physicochemical parameters were within standard permissible limits when compared with NGL and NESREA.

Table 1: Physico-chemical parameter from three different sampling points from river Gashua.

Parameters	Sampling points			FEFA (1991) Standard limit	NASREA (2011) Standard limit
	Gada Mean ± SE	Usur Mean ± SE	Katuzu Mean ± SE		
Temp (°C)	25.75±0.11[b]	27.42±0.25[a]	27.42±0.25[a]	<40	25
pH	7.36±0.16[b]	8.06±0.29[a]	7.49±0.18[ab]	6-9	6-8.5
Dissolved oxygen Mg/l	8.01±0.05[a]	7.40±0.17[b]	7.45±0.21[b]	nil	8-10

Mean ± SE followed by same superscript in same row show are not significantly different at P>0.05 level of significance.

Status of Heavy Metals in Water from Three Sampling Points at River Gashua

The level of heavy metals (lead and cadmium) in samples from three sampling points at river Gashua are presented in Table 2. All heavy metal had levels within the limit of SON, but some exceeded the limit from WHO and FEPA. The lead concentrations were 0.06±0.01, 0.07±0.05 and 0.03±0.07 of Gada, Usur and Katuzu respectively. Cadmium levels varied within sampling points as follows; Gada was 0.04Mg/l, Usur was lower with 0.03Mg/l and Katuzu recorded the highest level of cadmium (0.06Mg/l). From the Table 2 Gada (0.06±0.01) and Usur (0.07±0.05) has the higher concentration of lead compared to that of Katuzu (0.03±0.07) that has about half their concentrations.

Table 2: Status of heavy metals in water from three sampling points at river Gashua

Heavy metals	Sampling points			FEPA 2003	SON 2007	WHO 2003
	Gada Mean ± SE	Usur Mean ± SE	Katuzu Mean ± SE			
Lead (Mg/l)	0.06±0.01[a]	0.07±0.05[a]	0.03±0.07[a]	<1.0	0.01	0.05
Cadmium (Mg/l)	0.04±0.00[ab]	0.03±0.00[b]	0.06±0.00[a]	<1.0	0.03	0.01

Mean ± SE followed by same superscript in same row show are not significantly different at P>0.05 level of significance.

Level of Heavy Metals in Fish (*Clarias gariepenus*) from Three Sampling Points at River Gashua

The levels of lead and cadmium concentration in fish samples from three different sampling locations of river Gashua. Lead varied within sampling points; Gada was 0.18Mg/Kg, Usur (0.31Mg/Kg) was lower and Katuzu (0.50Mg/Kg) recorded the highest level of lead. All lead levels fall within the standard limit of WHO and FAO, but all exceeded the permissible limit of NAFDAC and only Gada falls nearer to that of NAFDAC standard. The levels of cadmium were (0.24±0.10), (0.40±0.07) of Usur Gada and (0.55±0.07) of Katuzu. From Table 3, Katuzu recorded the highest level of cadmium followed by Usur and Gada. All sample concentrations are within the standard limit of NAFDAC and WHO but exceed the permissible limit of FAO. Some samples exceeded the standard permissible limit of FAO; therefore, necessary measures have to be taken to control freshwater ecosystem.

Table 3: Status of heavy metals in fish from three sampling points at river Gashua

Heavy metals	Sampling points			NAFDAC 2016	FAO 1983	WHO 2003
	Gada Mean±SE	Usur Mean±SE	Katuzu Mean±SE			
Lead (Mg/Kg)	0.18±0.06[b]	0.31±0.05[ab]	0.50±0.07[a]	0.1	0.50	2.00
Cadmium (Mg/Kg)	0.24±0.10[c]	0.40±0.07[b]	0.55±0.07[a]	2.00	0.05	2.00

Mean ± SE followed by same superscript in same row show are not significantly different at P>0.05 level of significance.

DISCUSSION

Status of water samples from river Gashua were within the standard limits as compared with FEFA and NESREA. Temperature recorded from sampling location did not vary greatly and all were within the normal range for fish survival. As suggested by Boyd (1999) that an optimum growth temperature ranges from 26 - 28^{o}C for fishes in tropical and subtropical waters. Temperature has a large impact on the biological activity of aquatic organisms. It affects metabolic activities, growth, feeding, reproduction, distribution and migratory behaviors of aquatic organisms (Suski *et al*., 2006).

The level of pH from river Gashua; (7.36±0.16) (8.06±0.29) and (7.49±0.18) of Gada, Usur and Katuzu respectively are suitable for the productivity of aquatic organisms as reported by (NASREA, 2011) 6-8.5. pH value obtained in this study agrees with those documented by (Ibrahim *et al.*, 2018) as values most suitable for maximum productivity of aquatic organisms. It is also in accordance with the result obtained by Okachukwu (2012) that pH 5.5–8.0 is the most suitable range for freshwater fishes.

From the present study, the level of dissolved oxygen at all three different sampling points of River Gashua are within the normal range for fish survival as compared to the NESREA (2011) for permissible limits of (8-10 mg/L). Survival of aquatic organisms, especially fishes depend upon the level of DO. DO provides a source of oxygen needed for the oxidation of organic matter; when the concentration is high, very low or lacking, it causes the water body to become dead or devoid of aquatic life (Chukwu, 2008).

According to DFID (1999), dissolved oxygen is an important factor for water quality control and the effect of waste discharged into a river is largely determined by the oxygen balance of the system as its presence is essential to sustenance of aquatic life within the system. Roberts (1978) also observed that discharges of sewage reduce water quality depending on the degree of dilution achieved, the degree of treatment of the original material, its composition and the response in the water body.

From the present study, the results indicate no significant difference in lead concentrations among the three sampling points. However, a significant difference was observed in cadmium concentrations, with Katuzu exhibiting the highest levels compared to Gada and Usur. This discrepancy could be attributed to waste disposal and agricultural activities in the area.

Svobodova *et al*. (1993) reported that numerous water bodies in Nigeria face pollution from heavy metals due to increased industrial and agricultural activities. Heavy metals of particular concern for human and aquatic organism health include aluminum, arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel, and zinc.

The concentrations of heavy metals usually peak during the dry season and decrease in the rainy season, which is attributed to the "dilution effect" (Malik *et al*., 2008). Many studies indicate that lead concentrations often surpass the permissible limits set by FAO and WHO. Pb levels exceeded the recommended values by FAO/WHO (1983/2003), while Cd and Ni remained within the recommended values except for Cd in the liver (Begum *et al*., 2013). Obasohan *et al*. (2008) assessed heavy metal concentrations in Ikpoba River, Benin City, revealing lead levels surpassing WHO (2003) recommendations for drinking water. However, Ozturk *et al*. (2008) found lower concentrations of Cadmium, Chromium, Copper, Iron, Nickel, and Lead in Avsar Dam Lake, Turkey, compared to the values obtained in the present study.

Higher temperatures are reported to promote cadmium accumulation, especially in the kidneys and liver (Yang *et al*., 1996). Environmental pollution, with heavy metals being a significant component, poses a universal problem due to their toxicity, accumulation, and bio-magnification in aquatic organisms (Shovon *et al*., 2017).

There exists a relationship between fish and water pollutants, with heavy metals, as part of water pollutants, influencing the prevalence and intensity of fish infections and infestations caused by bacteria, fungi, and parasites. Pollutants in water bodies can either directly affect fish or impact their associated defense mechanisms (Nda *et al*., 2018).

Results from the study revealed that heavy metal concentrations in the fish were higher than those in the surrounding waters from which the fishes were collected. This may be attributing to the bioaccumulation of heavy metals over time through the fish's diet or the lipophilic nature of heavy metals, causing them to accumulate in fatty tissues.

All lead concentrations fell within the standard limits set by WHO (2003) and FAO (1983) but exceeded the permissible limit of NAFDAC (2016), with only Gada approaching the NAFDAC standard. Katuzu exhibited the highest cadmium level, followed by Usur and Gada. While all sample concentrations adhered to the standards of NAFDAC (2016) and WHO (2003), they exceeded the permissible limit of FAO (1983). Given this variation within the standards, it is imperative to implement measures to control the freshwater ecosystem.

This aligns with the findings of Yielmaz (2003) and Benjamin (2003) in Mombasa, Kenya, who studied the levels of Cadmium and Lead in water, sediments, and selected fish species. Pb and Cd concentrations were generally low in the water column, with occasionally elevated levels in sediments and some fish species, especially during the rainy season. Most fish species analyzed adhered to acceptable limits set by FAO (1983) standards.

Lead (Pb) accumulation in fish tissues exceeded standard limits FAO (1983). Since human exposure to Pb is primarily through food, these fishes pose a potential threat to consumers. Lead, being toxic, can damage the brain, central nervous system, kidneys, liver, and reproductive system when exceeding tolerable limits in humans (Okachukwu, 2012). Although Cadmium concentrations were lower compared to other heavy metals, previous studies (Olaifa *et al.*, 2004) attribute this to the low tendency of cadmium towards available active sites. Accumulation of heavy metals in fish tissues depends on the bioavailability in water and sediments, as well as dietary intake.

Clarias gariepinus, being an omnivorous scavenger and predator associated with the bottom, especially in muddy environments, may contribute to heavy metal accumulation due to intake of silt with their food (Okachukwu, 2012). Ekpo *et al*. (2008) found similar results in Benin City, Nigeria, where Lead, Cadmium, and Mercury levels in fishes surpassed those in surrounding waters, aligning with the current findings of greater heavy metal concentrations in fish muscle than the surrounding water. (Okachukwu, 2012). Suggested that the potential bioaccumulation or chemical reactions occurring in fish bodies due to rapid increases in water temperature.

The consequences of heavy metal pollution in aquatic environments, particularly through the consumption of fish and water, pose potential hazards to human health. Therefore, continuous monitoring of heavy metal levels in aquatic environments, including water, sediment, and biota, is crucial. Monitoring heavy metal concentrations in commercial fishes is essential to assess the potential risks associated with fish consumption (Okachukwu, 2012).

CONCLUSION

It can be concluded from the research findings that the mean concentration of heavy metals (lead and cadmium) of both water and fish were within the permissible limit of NAFDAC, FAO, WHO and NASREA. However, the fish within river Gashua are said to be wholesome for human consumption, and there is need for caution as they have the potential to bio-accumulate some of these heavy metals in food chain over time.

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