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Accumulation of Copper, Manganese and Iron in Selected Fish Species from Komadugu River in Gashua, Yobe State Nigeria

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Abstract: *Heavy metals are found in the aquatic environment as a result of contamination from industrial, agricultural, domestic wastes and their by-products. The increasing level of heavy metals in fish is alarming and has spurred scientists to make researches on the dangers caused by heavy metal accumulation and bioaccumulation of life cells. In this study, accumulation of copper (Cu), manganese (Mn) and iron (Fe) in African characid (Clarias gariepinus) and African arowana (Heterotis niloticus) was investigated by Atomic Absorption Spectrophotometry after microwave digestion of samples of the fish species. The mean value of Cr for African characid (Clarias gariepinus) in this study, 1.31±0.41 is greater than the recommended value of 0.05 –0.15mg/kg set by the World Health Organization (WHO) and Food and Agricultural Organization (FAO), but less than 12 – 13mg/kg set by Food and Drug Agency (FDA). The permissible limit for Cu in fish set by the World Health Organization (WHO) and the Food and Agricultural Organization is 30mg/kg. This is far above the results for African characid (Clarias gariepinus), 1.94±0.14 mg/kg and 2.648±0.38mg/kg for African arowana (Heterotis niloticus) in this study. The permissible limit for Mn in fish set by the World Health Organization (WHO) is 0.5 – 0.6 mg/kg.The result for African arowana (Heterotis niloticus) in this study, 0.597±0.06 mg/kg falls in this range. However, the result for African characid (Clarias gariepinus), 2.021±0.00 mg/kg is above the WHO permissible limit.The permissible limits for Fe in fish set by the World Health Organization (WHO) and Food and Agricultural Organization (FAO) are 1 – 3 and 100 mg/kg respectively. The results for African arowana (Heterotis niloticus), 1.013±0.08 mg/kg and African characid (Clarias gariepinus), 2.941±0.00 mg/kg and in this study, fall within the WHO range, but less than the FAO permissible limit.*

Keywords: *Domestic wastes; Aquatic environment; Bioaccumulation; Permissible limit; Digestion; Fish.*

1. Introduction

Fish is a basic and important food for human nutrition, providing protein, healthy fatty acid with low cholesterol level that is healthy for consumption and capable of reducing the risk of heart diseases and stroke as well as essential minerals and vitamins (Agbugui *et al.,* 2011). The role of Fisheries in the ecosystem serving as food along the food chain, hence their presence and importance cannot be overlooked as the heavy metal accrued in fish results to an impact in human health (Azaman *et al*., 2015; Agbugui *et al.,* 2019).

Heavy metals (HMs) are easily accumulated in fishes because they are readily taken up by body parts of fishes such as body surface, gills, digestive tract, liver and muscles. The highest point of HM levels of concentration in the organs of organisms are often the gills then the liver and then the muscle shows the lowest concentration levels. However, the muscles are the most source of heavy metal intake to the body since the muscles are the largest consumed parts of the body hence the ability to cause negative impact towards health (Mahmood and Alkhafaji 2016). Caution must be taken to assess the levels of heavy metals for consumption (Mensoor and Said 2018, Azaman *et al.,* 2015; WHO 2011). Freshwater fishes are more prone to HM pollution because of their higher ability to bioaccumulate thus are easily exposed and vulnerable (Authman *et al.,* 2013a; Authman *et al.,* 2013b).

Since fishes are an integral component of the human diet, they need to carefully screen to ensure that unnecessary high level of heavy metals are not being transferred to human population via consumption of fish (Rahman *et al.*,2012). . Therefore, it is important to observe the level of heavy metals in consumed fishes to get some ideas about the safety of fish protein supplied to the consumers and to understand its harmful effects on individuals, population or ecosystem. Moreover, for the existence and conservation of aquatic resources, it is essential to investigate the fish quality of the river.

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2. Materials and Methods

2.1 The Study Area

The Yobe River, also known as the Komadugu Yobe River is a river in West Africa that flows into Lake Chad through Nigeria and Niger. In Yobe State, it is located on longitud12º52´N and latitude 10º58´E in Gashua, Bade Local Government Area. Its tributaries include River Hadejia , River Jama'are , and the Komadugu Gana River. The river forms a small part of the international border between Niger and Nigeria with 150 km and flows a total of 320 km (KYBP, 2006). There are concerns about changes in the river flow, economy and ecology due to upstream dams, the largest at present being the Tiga Dam in Kano State, with plans for the Kafin Zaki dam in Bauchi State (NPC, (2006). The River Yobe provides a means of subsistence for hundreds of thousands of people who work in a variety of commercial and agricultural endeavours along its almost 200 km length in the state's northern region, which spans seven local government areas (LGAs) from Nguru to Yunusari. Notable towns near the river include Gashua, Geidam and Damasak in Nigeria, and Diffa in Niger (Wakawa *et al*, 2017).

Figure 1: Catchment Area of the Komadugu River

2.2 Instruments, Apparatus and Reagents

All equipment and instruments used in this research were calibrated before conducting the experiments. All glassware used were thoroughly washed with detergents and tap water and then rinsed with deionized water. Suspected contaminants wares were cleaned with 10% concentrated Nitric acid (HNO_3) and metal surfaces rinsed with deionized water. The digestion tubes were soaked with 1% (w/v) potassium dichromate in 98% (v/v) H_2SO_4.

In preparation of reagents, chemicals of analytical grade purity and distilled water were used. All glassware and plastic containers were washed with detergents.

2.3 Digestion of the Fish Samples

The fish samples were weighed, decapitated, cut into smaller pieces using knife and then dried in an oven for 48hours at 120^0C. The dried samples were ground and milled with a mortar and pestle into fine powder. A microwave digester (Master 40 serial No: 40G106M) was used in digesting the fish samples in a digestion tube to which 0.1g of sample was added at a time, followed by 6mL of 65% HNO_3 and 2mL of 30% H_2O_2 and allowed to stand for a while. The digestion was carried out at 180°C, 1800W in a time of 30mins.The digestion was followed by cooling at room temperature in the microwave and the sample was diluted with de-ionized water. Potential presences of selected heavy metals in chemicals used in digestion were determined. Blanks were used simultaneously in each batch of the analysis to authenticate the analytical quality (SINEO, 2013).

2.4 Atomic Absorption Spectrometric Analysis

The fish extracts were analyzed for copper (324.8nm), manganese (279.5nm) and iron (248.3nm) using flame atomic absorption spectrophotometry. Blank determinations were made prior to sample analysis. Heavy metal concentrations in fish extracts were obtained in triplicates from calibration curves and expressed as mg/kg. Metals in chemicals used in digestion were determined. Blanks were used simultaneously in each batch of the analysis to authenticate the analytical quality (SINEO, 2013).

2.5 Statistical Analysis

The data were analyzed in triplets and expressed as mean and standard deviation. The mean of all treatments was subjected to a One-way analysis of variance (ANOVA) using IBM SPSS Statistics 23 software and mean differences were performed using the Tukey test. All graphs were plotted using Microsoft Excel 2013.

3. Results and Discussion

Pollution of natural freshwater by heavy metals is a worldwide problem (Abdullah *et al.,* 2007). The Nigeria aquatic ecosystem is a home to several species of shelled and fin fish. Generally, fish species found in different location in Nigeria water ways have been widely studied by several authors (Odo *et al.,* 2009; Abowei and Hart, 2008; Abowei and Ogamba, 2013; Abowei *et al.* 2007). The availability of fish species depends on the type of the water body and prevailing water quality parameters. For instance, shell fish such as bivalve and periwinkle are found in brackish water or estuarine and sea/marine water; while different fish species are found in surface water including fresh, brackish and marine ecosystem. The water quality parameters such as salinity, ions vary significantly on three kinds of water bodies.

In aquatic ecosystem, three major constituents exists. These include water, sediment and aquatic life (i.e. planktons, fisheries etc). According to Titilayo and Olufemi (2014), fisheries are often found at the top of the aquatic food chain and can accumulate higher concentration more than the sediment and water. In a study conducted by Ogamba *et al*. (2015), a higher concentration of lead and cadmium was observed in muscle and bone of *Citharinu*s *citharaus* and *Synodontis clarias* than in sediment and water were both fish species were obtained from. Fisheries typically bioaccumaulate metals in their body (tissue, liver, kidneys, bone, blood, and fin) through the metal laden contaminated water when ingested and absorbed.

3.2 Levels of Copper, Manganese and Iron in Fish Species

The results of the mean concentrations of Cu, Mn and Fe in African characid (*Clarias gariepinus*) and African arowana (*Heterotis niloticus*) are presented in Table 1.

Table 1: Mean Concentrations (mg/kg) of Cu, Mn and Fe

Fish Specie	Cu	Mn	Fe
African Characid	1.94±0.14	2.021±0.00	2.941±0.00
African Arowana	2.648± 0.38	2.021 ± 0.00	1.013 ± 0.08
WHO	**30**	**05 – 0.6**	**1 - 3**
FAO			**100**
EC	**0.5**		
NAFDAC	**5**		

KEY

WHO: World Health Organization

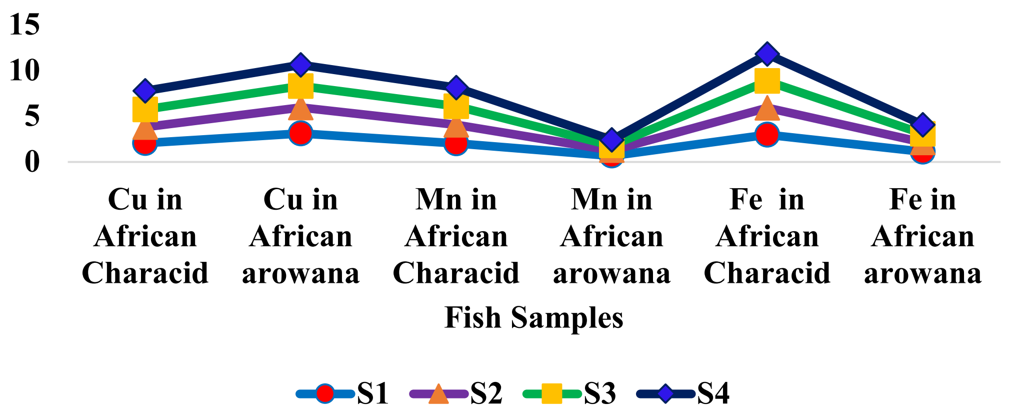
EC: European Commission

NAFDAC: National Agency for Food, Drug Administration and Control

FAO: Food and Agricultural Organization

The mean concentrations of copper, manganese and iron in African characid (*Clarias gariepinus*) and African arowana (*Heterotis niloticus*) fish species are shown in **Figure 1**

Figure 1: Concentrations of Copper, Manganese and Iron in African Characid (*Clarias gariepinus*) and African Arowana (*Heterotis niloticus*) Fish Species.



3.2.1 Copper

The permissible limit for Cu in fish set by the World Health Organization (WHO) and the Food and Agricultural Organization is 30mg/kg. This is far above the results for African characid

(*Clarias gariepinus*), 1.94±0.14 mg/kg and 2.648±0.38 mg/kg for African arowana (*Heterotis niloticus*) in this study. Values reported by El-Ishaq *et al.,* (2016); 0.58±0.35 - 0.61±0.49 mg/kg for African catfish (*clarias gariepinus)* and 0.52±0.01 - 0.74±0.09 mg/kg for tilapia fish (*Oreochromis niloticus*) are below the results in this study. The results of Elinge *et al.,* (2019), 0.27±0.03 - 0.28±0.09 mg/kg for *Synodontis schall* and 0.68±0.4 - 0.87±0.4 mg/kg for *Synodontis membranaceus* are also below the concentrations reported in this study. However, the result reported by Ojaniyi *et al.*, (2021), 2.161±0.03 mg/kg for cat fish (*Clarias garipinus*) and 2.197±0.007 mg/kg for African arowana (*Heterotis niloticus)* were higher than the result for African characid (*Clarias gariepinus*), but lower than the result for (*Clarias gariepinus*) African arowana (*Heterotis niloticus)* in this study. Jafiya *et al*., (2022) reported Cu concentrations of 1.63±2.31- 3.42±1.47 mg/kg in *Oreochromis niloticus,*1.87±1.65 - 2.52±4.67 mg/kg in *Clarias gariepinus* and 1.08±0.10 - 1.29±0.24 mg/kg in *Syndontis schall* which are below the 5.0 mg/kg limit set by the National Agency for Food and Drugs Administration and Control (NAFDAC), Nigeria and 0.05 mg/kg set by the European Commission (EC). In a separate work, Naseem *et al.,* (2015) reported that the lethal copper concentration for *Tilapia nilotica* was 47.56±1.18 mg/kg.

Copper (Cu) is an essential metal of enzymes and necessary for the haemoglobin synthesis. Impaired delivery of Cu can result in decreased cuproenzyme activity, the skeletal and vascular systems (Failla *et al.,* 2001) and also cause anaemia, neutropenia and osteoporosis. Impaired metabolism of Cu could cause two genetic diseases which are Mense disease and Wilson disease. Accumulation of Cu can expose to the Mense disease which is about a fatal disorder (Gu *et al.,*2002). Wilson disease also could occur due to Cu accumulates in the brain and eyes in the form of Kayaer-Fleischer ring (Attri *et al.,* 2006; Sarkar,1999). Excessive intake of Cu also could cause kidney damage and even death U.S. Dept. of Health and Human Services (2004).

3.2.2 Manganese

The permissible limit for Mn in fish set by the World Health Organization (WHO) is 0.5 – 0.6 mg/kg.The result for African arowana (*Heterotis niloticus*) in this study, 0.597±0.06 mg/kg falls in this range. However, the result for African characid (*Clarias gariepinus*), 2.021±0.00 mg/kg is above the WHO permissible limit.

A number of workers reported Mn concentrations lower than the results of this study. Elinge *et al.,* (2019) reported the concentration of Mn in *Synodontis schall* and *Synodontis membranaceus* as 0.39±0.25 - 0.83±0.49 and 0.07±0.05 - 0.36±0.18 mg/kg respectively. Also, Baharoma and Ishaka (2015) reported the concentration of Mn in *B. Schwanenfeldii, H. macrolepidota,* and *M. Marginatus,* as 0.014±0.003, 0.018±0.005 and 0.028±0.007 mg/kg respectively. The concentration of Mn in gill (0.13 mg/kg), liver (0.43mg/kg) muscle (1.89mg/kg) and bone (0.45 mg/kg) of cat fish were reported by (Izah and Angaye, 2016).

Manganese (Mn) is an element of low toxicity that has considerable biological significance due its ability to prevent heart attack, stroke and cardiac arrest. Deficiency of Mn gave congenital malformations in offspring, poor growth performance and low efficiency of the reproductive system (Goldhaber, 2003). However, it's become dangerous and toxic at high concentrations and usually may lead to the neurologic and psychological disorder (Saha and Zaman 2013; Perl and Olanow 2007).

3.2.3 Iron

The permissible limits for Fe in fish set by the World Health Organization (WHO) and Food and Agricultural Organization (FAO) are 1 – 3 and 100 mg/kg respectively. The results for African arowana (*Heterotis niloticus*), 1.013±0.08 mg/kg and African characid (*Clarias gariepinus*), 2.941±0.00 mg/kg and in this study, fall within the WHO range, but less than the FAO permissible limit.

The values for tilapia fish (*Oreochromis niloticus*), gills (2.74±1.54), tissue (1.17±0.73) and muscles (0.46±0.046) mg/kg and African catfish (*clarias gariepinus)*, gills (3.58±1.69), tissue (2.34±1.9) and muscles (2.03±1.2) mg/kg reported by El-Ishaq *et al.* (2016) were higher than the results for African arowana (*Heterotis niloticus*) in this study. In comparison, only the concentration of Fe in gills (3.58±1.69) of African catfish (*clarias gariepinus)* is greater than the concentration of Fe in African characid (*Clarias gariepinus*) in this study.Elinge *et al.,* (2019) reported that concentrations of Fe in gills(1.17±0.43) and muscle (0.65±0.46)mg/kg of *Synodontis Synodontis membranaceus*, were lower than the result for African characid (*Clarias gariepinus*), but higher than the result for African arowana (*Heterotis niloticus)* in this study. However, the result reported by Ojaniyi *et al.*,(2021), 1.755±0.028 mg/kg for cat fish (*Clarias garipinus*), 1.234±0.006 mg/kg for African Arowana (*Heterotis niloticus)* and 1.927±0.022 mg/kg for African mottled eel *(Anguilla labiate*) were higher than the result for African arowana (*Heterotis niloticus),*but lower than the result for African characid (*Clarias gariepinus*) in this study. Izah and Angaye (2016) reported the following values; 9.01-19.11 mg/kg for catfish (*Clarias gariepinus),* tissue (0.98- 8.88) mg/kg for *Clarias anguillari* , gills (64.25) , muscle (29.73), liver (90.3), kidney (88.01) and tissue (67.43) mg/kg for *Ilisha Africana*.

Iron (Fe) is a mineral essential for every living cell and necessary for the synthesis of myoglobin, haemoglobin and certain enzymes. Deficiency of Fe results in weakness, susceptibility and inability to concentrate (Akoto *et al.*, 2014; Anderson and Fitzgerald 2010). Erdman *et al.,*(2012) studied that one of the most common nutrient deficiencies in the world is Fe deficiency in anaemia such as malaria. Anaemia disease gives poor performance in circulatory transport and also reduces oxygen supply to muscle, less efficiency due to the decreasing of myoglobin content and impairing endurance capacity.

4. Conclusion

The mean concentrations of copper (Cu), manganese (Mn) and iron (Fe) in African characid (*Clarias gariepinus*) and African arowana (*Heterotis niloticus*) determined in this study were within the limits set by the World Health Organization (WHO), Food and Agricultural Organization (FAO) and National Agency for Food, Drug Administration and Control (NAFDAC).

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Authors' Contributions

Dagari M.S.: Conceptualization, design and supervision of the research work; Editing of the write-up
Bala U.M.: Undertaking the research work, write-up and data analysis.

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