



Determination of Cobalt, Nickel and Cadmium Levels in Selected Fish Species from Komadugu River in Gashua, Yobe State Nigeria

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Abstract: Fish is a major source of protein for human consumption. Thus, accumulation of heavy metals in fish species is a serious environmental problem. In this study, Concentrations of cobalt (Co), nickel (Ni) and cadmium (Cd) in African characid (*Clarias gariepinus*) and African arowana (*Heterotis niloticus*) were determined by Atomic Absorption Spectrophotometry after microwave digestion of samples of the fish species. The mean concentration of Co for African characid (*Clarias gariepinus*) is 0.099 ± 0.00 mg/kg, which is below the 0.1mg/kg set by the World Health Organization (WHO) and Food and Agricultural Organization (FAO). However, the value obtained for African Arowana (*Heterotis niloticus*), 0.237 ± 0.00 mg/kg is above the WHO/FAO permissible limit. The Ni permissible limit of 0.3mg/kg for fish set by the European Commission is below the mean concentrations of Ni in this study for African Characid (*Clarias gariepinus*), 0.3475 ± 0.03 mg/kg and African Arowana (*Heterotis niloticus*), 0.420 ± 0.01 mg/kg. The permissible limit for Ni in fish set by the World Health Organization (WHO) is 0.5 -0.6mg/kg. The mean value of Cd for African characid (*Clarias gariepinus*) is 0.5775 ± 0.17 mg/kg, which is slightly greater than 0.2mg/kg set by the World Health Organization (WHO) and Food and Agricultural Organization (FAO).

Keyword: Fish; Heavy metals; Accumulation; Digestion; Permissible limit

1. Introduction

Fish is one of the most important food to be eaten for a healthy life because it has a high protein quality and nutritional value [1]. Likewise, it is suggested word wide that fish and seafood are consumed more to prevent cardiovascular diseases. Fish is especially recommended for infants, elderly, cardiac patients, those who had a brain hemorrhage, and those experiencing digestion problems because it has high mineral content and low energy level [2]. Consumption of fish and seafood is useful for nutrition and human health. It may cause toxic effects by transmission of heavy metal ions into the human body as a result of a pollutant that may be present in water and cause a risk to human health [3].

Heavy metals have significant harmful impacts on the public health, which may result in mutation in the genetic materials, influence the biochemical processes by impairment of synthesis and metabolism of carbohydrates, protein and lipids [4]. The hazards of heavy metals was represented in their ability of bioaccumulation within body tissues resulting in poisoning of fish as well as in water [5, 6].

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 longitude $12^{\circ}52'N$ and latitude $10^{\circ}58'E$ 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 [7]. 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 [8]. 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 [9].



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 48 hours at 120°C . 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 [10].

2.4 Atomic Absorption Spectrometric Analysis

The fish extracts were analyzed for cobalt (240.7nm), nickel (232.0nm) and cadmium (228.8nm) 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 [10].

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

Different fish species which may vary in size, gender and sexual maturity take up heavy metals (HMs) under different environmental factors; water chemistry, salinity, temperature and levels of contamination [11]. These HMs are transported to human because of their higher uptake mechanism in their tissues towards these elements; [12]. Water toxicity in aquatic environment is partly due to the presence of heavy metals. The level of toxicity depends on the type of metal, its biological role and the type of organisms that are exposed to it [13]. HMs enter the food chain from the primary producers and affect the whole chain most especially fishes, which are often the most vulnerable [12]. They are affected directly, particularly because they feed and live in the aquatic environment, where they are constantly exposed to pesticide and heavy metals. This decreases the food sources, eventually disrupting the food chain leading to lowering of aquatic habitat [12, 14]

3.2 Levels of Cobalt, Nickel and Cadmium in Fish Species

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

Table 1: Mean Concentrations of Co, Ni and Cd

Fish Specie	Co	Ni	Cd
African Characid	0.099±0.00	0.3475±0.03	0.5775±0.17
African Arowana	0.237±0.00	0.420±0.01	1.130±0.11
WHO	0.1	0.5 – 0.6	0.2
EC		0.3	
NAFDAC	0.1		2.0

KEY

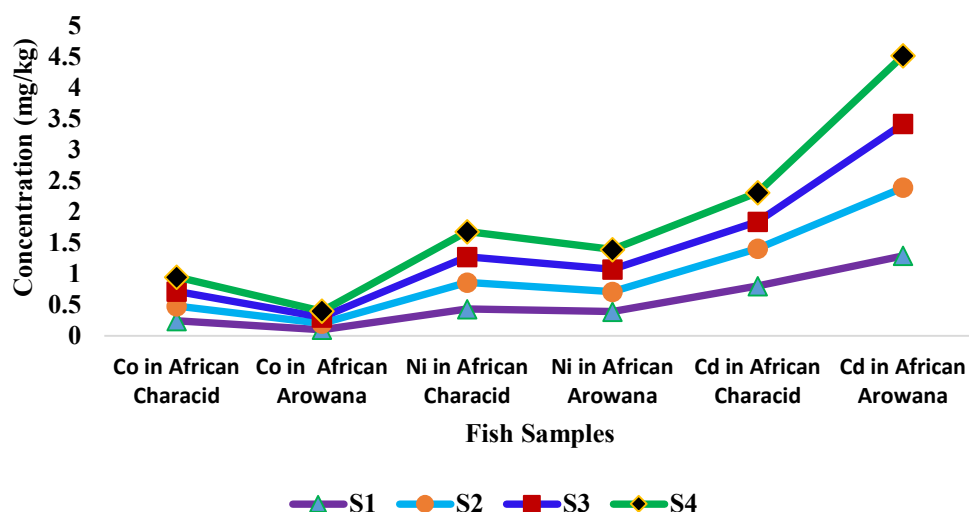
WHO: World Health Organization

EC: European Commission

NAFDAC: National Agency for Food, Drug Administration and Control

The mean concentrations of cobalt, nickel and cadmium in African characid (*Clarias gariepinus*) and African arowana (*Heterotis niloticus*) fish species are shown in **Figure 1**

Figure 4.1: Concentrations of Cobalt, Nickel and Cadmium in African Characid (*Clarias gariepinus*) and African Arowana (*Heterotis niloticus*) Fish Species



3.2.1 Cobalt

The mean concentration of Co for African characid (*Clarias gariepinus*) in this study is 0.099±0.00 mg/kg, which is below the 0.1mg/kg set by the World Health Organization (WHO) and NAFDAC (National Agency for Food, Drug Administration and Control). However, the value obtained for African Arowana (*Heterotis niloticus*), 0.237±0.00 mg/kg is above the WHO/NAFDAC permissible limit. Previous studies have revealed both lower and higher concentrations of cobalt in fish species. The mean values reported by [15] were 0.093±0.05, 0.243±0.17 and 0.150 ±0.32 mg/kg for cobalt in muscle, liver and skin in wild fish *Squalius cephalus* and *Barbus* tissues in Vardar River of North Macedonia. The levels of cobalt in

Tilapia guineensis and *Sarotherodon melanotheron* as reported by [16] were 3 and 4 mg/kg respectively. The lethal cobalt concentration for *Tilapia nilotica* was reported by [17] as 25.00 ± 0.00 mg/kg. A mean Co concentration of 1.33 ± 0.06 in muscle of *Channa Punctatus* was reported by [18].

Cobalt (Co) is an essential element to fish and other organisms. Its main role is as an intrinsic part of vitamin B₁₂ or cobalamin. Fish and all other animals are not capable of synthesizing this vitamin and are therefore dependent on bacterial production of this essential compound [19, 20]. The essentiality of Co makes it of importance in fish nutrition and aquaculture. The uptake, accumulation, and toxicity of stable Co in fish have received less attention, although the Co acute toxicity in freshwater fish is reasonably well documented. The Co uptake of in freshwater fish strongly depends on the speciation of Co and the calcium concentration in the water, but overall the effects of environmental conditions, including pH, remain poorly documented. The chronic toxicity of Co is also poorly documented, especially for the marine environment. Very little is known concerning the molecular mechanisms of Co uptake and toxicity in fish since no specific studies into this area have been conducted so far and possible mechanisms are inferred from mammalian studies [21].

3.2.2 Nickel

The Ni permissible limit of 0.3mg/kg for fish set by the European Commission is below the mean concentrations of Ni in this study for African Characid (*Clarias gariepinus*), 0.3475 ± 0.03 mg/kg and African Arowana (*Heterotis niloticus*), 0.420 ± 0.01 mg/kg. The permissible limit for Ni in fish set by the World Health Organization (WHO) is 0.5 - 0.6mg/kg. Previous studies have revealed both lower and higher concentrations of Ni in fish species. As reported by [16], the concentrations of Ni in *Tilapia guineensis* and *Sarotherodon melanotheron* were 10.2 and 8.7 mg/kg respectively. Nickel levels in fish species *Oreochromis niloticus*, *Clarias gariepinus* and *Syndontis schall* were 0.38 ± 0.20 - 4.19 ± 3.89 , 0.45 ± 0.07 - 2.65 ± 3.26 , and 0.41 ± 0.02 - 2.85 ± 0.47 mg/kg respectively [22]. In the determination of some heavy metals in three selected fish species from river Zamare, [23] reported the levels of Ni in *Synodontis schall* and *Synodontis membranaceus* as 1.27 ± 0.53 - 1.90 ± 0.39 and 1.44 ± 0.32 mg/kg respectively. The mean concentrations of Ni in cat fish (*Clarias gariepinus*), African Arowana (*Heterotis niloticus*) and African mottled eel (*Anguilla labiate*) as reported by [24] were 0.419 ± 0.009 , 0.514 ± 0.004 and 0.322 ± 0.006 mg/kg respectively. The average concentrations of Ni in *Capoeta capoeta* and *Cyprinus carpio* as reported by [25] were 2.8 ± 0.22 - 3.4 ± 0.31 and 3.0 ± 0.30 - 3.4 ± 0.2 mg/kg respectively. Normally, Ni is an essential metal and occurs at very low levels in the environment. However, a deficiency of Ni in humans has not been documented [26]. Nickel is known to be carcinogenic [27]. Moreover, fibrosis, tumours, lung inflammation and emphysema occur also caused by Ni [28]. Reports on the adverse effect of lethal and high concentrations of Nickel are reported by [29]. In the study, Fish growth was monitored in terms of wet weight and fork length increments, condition factor, feed intake and feed conversion efficiency (FCE). Fish species showed exploratory behavior such as loss of appetite to cause significant reduction in growth during exposure [29]. Nickel exposure is said to induce some histological changes in the fish structure of *Oreochromis niloticus*. These changes influenced hyperplasia, hypertrophy, shortening of secondary lamellae and fusion of adjacent lamella, significant rise

in the level of blood glucose, liver and pancreatic disorders causing hypercholesterolaemia, hyperproteinanaemia and hyperalbuminaemia [30, 31].

3.2.3 Cadmium

The mean values of Cd for African characid (*Clarias gariepinus*) in this study is 0.5775 ± 0.17 mg/kg, which is slightly greater than 0.2mg/kg set by the World Health Organization (WHO) and Food and Agricultural Organization (FAO). The National Agency for Food and Drug Administration and Control (NAFDAC) permissible limit of 2.0mg/kg is above the concentration of Cd, 1.130 ± 0.11 mg/kg for African Arowana (*Heterotis niloticus*) in this study. According to a report by [22], Cd concentrations in *Oreochromis niloticus*, *Clarias gariepinus* and *Syndontis schall* were 0.05 ± 0.01 - 0.06 ± 0.00 , 0.04 ± 0.01 - 0.05 ± 0.01 and 0.02 ± 0.004 - 0.031 ± 0.02 mg/kg respectively. The concentration of Cd in *O. niloticus*, 0.016 ± 0.003 mg/kg reported by [32] is lower than the concentrations of African characid (*Clarias gariepinus*) and African Arowana (*Heterotis niloticus*) in this study. Similarly [23] reported lower concentrations of Cd in *Synodontis schall*, 0.06 ± 0.03 - 0.12 ± 0.08 mg/kg and *Synodontis membranaceus*, 0.18 ± 0.15 mg/kg. Cadmium levels reported by [33] in *Clarias gariepinus*, 0.29 ± 0.08 - 1.52 ± 0.55 mg/kg, [34] in catfish, 0.063 ± 0.022 - 0.072 ± 0.021 mg/kg and tilapia, 0.126 ± 0.032 - 0.14 ± 0.017 mg/kg and [35] in fish tissues, 0.001 ± 0.003 - 0.004 ± 0.002 mg/kg are lower than results obtained in this study.

The use of cadmium for industrial uses such as manufacturing of batteries, electroplating, plastic stabilizers, pigments and fertilizers, agricultural chemicals, pesticides and sewage sludge in farm lands that often runoff into groundwater and surface water, might also contribute to the contamination of aquatic habitat hence fishes through bioaccumulation. The morphological and histological alterations in liver of fishes exposed to cadmium stating that higher doses of cadmium caused visible external lesions such as discoloration and necrosis on livers of *Cyprinus carpio*, *Carassius auratus* and *Corydoras paleatus* were reported by [36, 37]. Cadmium is primarily toxic to the kidney especially, to the proximal tubular cells; the main site of accumulation. Cd can also cause bone demineralization either through direct bone damage or indirectly as a result of renal dysfunction [38].

4. Conclusion

The mean concentrations of cobalt (Co), nickel (Ni) and cadmium (Cd) 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

Saminu Dagari: Conceptualization, design and supervision of the research work; Editing of the write-up

Usman Bala: Undertaking the research work, write-up and data analysis.

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