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https://dx.doi.org/10.4314/nvj.v44i2.5 **ORIGINAL ARTICLE**

DETECTION, DISTRIBUTION, AND HEALTH RISK ASSESSMENT OF HEAVY METALS IN WILD CATFISH SOLD IN MAIDUGURI METROPOLIS OF BORNO STATE, NORTHEASTERN NIGERIA.

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SUMMARY

Heavy metals (HMs) are naturally occurring elements with high atomic weights and a density at least five times greater than water. HMs can be released into the soil, water, and air through industrial, domestic, agricultural run-offs, medical and technological activities. Thirty wild fresh catfish were bought from two major fish markets in Maiduguri (Custom and Monday markets). Zinc (Zn) and Arsenic (As) were determined by Atomic Absorption spectrophotometer. Data obtained were analyzed using descriptive statistics and independent sample t-tests. The estimated daily intake (EDI) of the metals was calculated, and the target cancer risk (TCR), target hazard quotient (THQ), and hazard index (HI) was derived. The mean concentration (mg/Kg ± SD) of Zn in the liver (0.26 ± 0.32) was higher compared to that in muscle (0.22 ± 0.27), but this was not statistically different ($t(58) = 0.608$, $p = 0.545$). However, the mean concentration of As in the liver (0.27 ± 0.33) was lower compared to that in the muscle (0.28 ± 0.23), but this was not statistically different ($t(52) = -0.003$, $p = 0.997$). Although, no significant statistical difference, the mean concentration ranking of Zn based on the Fish market was Monday market > custom market, while that of As was custom market > Monday market. EDI values were within tolerable limits. TCR, THQ, and HI values obtained were below the threshold of 1. In conclusion, HMs (Zn and As) were detected in the liver and muscle of all fish samples tested at a lower rate compared to their Maximum Permissible Limits (MPLs) set by the World Health Organization (WHO). However, because of their non-degradable nature and tendency to bio-accumulate in fish tissues and organs, it can be concluded that long-term consumption poses a greater Public Health risk of HMs intoxications in the study area. Therefore, fish consumers should be enlightened more about the harmful effects of HM toxicity by relevant health authorities.

Keywords: Wild catfish, Heavy metals, Liver, Muscles, North-eastern Nigeria

INTRODUCTION

Heavy metals (HMs) are naturally occurring elements with high atomic weights and a density at least five times greater than water (Tchounwou et al., 2012). HMs are potentially toxic and can be classified as essential and non-essential metals. While essential metals include copper (Cu), zinc (Zn), and selenium (Se) (Camara, 2001) among non-essential ones are aluminum (Al), Arsenic (As), cadmium (Cd), lead (Pb), and mercury (Hg) (Tao *et al*., 2012; Wuana and Okieimen, 2011; Tao *et al*., 2012). HMs can be released into the soil, water, and/or air through industrial, domestic, agricultural run-off, medical and technological activities (Jarup, 2003). Their leading portals of entry into humans, fish, and general aquatic life are basically through ingestion, inhalation, or skin. (Ekpo *et al*., 2008; Tue *et al*., 2015). Humans are often exposed to these HMs when passed up to the food chain and ingested (Ekpo *et al*., 2008). Their effects are temporary and appear after many years (Asaolu, 2002). Fish from open waters are considered “wild animals” as they cannot control the composition of their growing environment (Clarkson, 1998). The pollution of the aquatic environment with HMs has become a global problem in recent years because they are indestructible, and most have toxic effects on organisms (Tchounwou *et al*., 2012). All HMs are potentially harmful in fish at some levels of exposure and absorption (Okocha and Adedeji, 2011). However, they may affect not only the productivity and reproductive capabilities of such fish but ultimately the health of man that depend on these fish as a significant source of protein (Fonge *et al.*, 2011) as they tend to bioaccumulate in their organs and tissues (Hala *et al*., 2017). Zinc may be toxic to aquatic organisms, but the degree of toxicity varies greatly and depends on the physicochemical quality of the water as well as the aquatic species being considered (Datar and Vashishtha, 1990). The health effects of ingesting high zinc levels include stomach cramps, nausea, and vomiting (Damodharan, 2013). Other clinical signs of Zn toxicity were diarrhea, bloody urine, liver failure, kidney failure, and anemia (Duruibe *et al*., 2007). The term arsenicosis designated human health effects of chronic arsenic toxicity, implying a chronic disease caused by prolonged exposure to Arsenic in humans (Mazumder, 2015). A chronic health condition arising from protracted ingestion of Arsenic above the MPL is usually manifested by characteristic skin lesions of melanosis (hyperpigmentation) and keratosis, occurring alone or in combination with or without the involvement of internal organs. Increased risk of skin cancer, urinary bladder cancer, lung cancer, and liver cancer associated with arsenicosis has been reported in several studies (Mazumder, 2015). Over the last twenty years, increased agricultural, industrial, and other anthropogenic activities along Lake Chad and other rivers in Maiduguri have increased HMs accumulation in the river. Consequently, HMs are considered the most essential contaminant in the aquatic environment because of their toxicity and accumulation by marine organisms. Therefore, high levels of HMs in fish could lead to public health hazards; if perchance enter the food chain (Hala *et al*., 2017). Although the contamination of natural water bodies continues to persist, the demand and consumption of fish as a cheap alternate source of essential animal protein continue to increase (Maulu *et al.,* 2020; Maulu *et al*., 2021). Previous studies, mainly in the Southern region of Nigeria, on HM contamination in fish sold for human consumption were reported by Benard *et al*. (2020) and Njoga *et al*. (2021). Specific to the North-Eastern region. However, there is paucity regarding the prevalence of HMs in wild fish captured and processed for human consumption. This paucity of relevant data may impede establishing and implementing of food safety regulations regarding HMs contamination in wild fish. Besides, routine fish inspection is only possible in some Nigerian fish markets. When screening is conducted, it appears not to be a standard that needs to be changed. To supplement existing information, this work investigated the presence, distribution, and health risk of As and Zn in wild catfish (liver and muscle) sold in Maiduguri Metropolis of Borno State, North-eastern Nigeria.

MATERIALS AND METHODS

Study area

This study was conducted in the Maiduguri metropolis of Borno state, North-eastern Nigeria. Borno State is located on latitude 11°50′N and 13°09′E of the equator. It occupies an area of 50,778 square kilometers. It remains center of trade, learning, culture, Durbar and home of tourism and history it bordered by the Republic of Niger to the north, the Cameroon Republic to the east, and the Tchad Republic to the northeast. The semi-arid zone is characterized by rather austere climate conditions with a dry season from November to early June, during which daily temperature varies between 30oC to 41oC, especially from March to June (Eresanya, 2018). The rainy season usually spanned from late June to October with low relative humidity and a short-wet season. The population of the State was estimated at 5,860,200 in 2016, with a population density of 83.0 inhabitants per km2. The inhabitants consist primarily of farmers, animal herders, fishermen, traders, and civil servants. Rivers, streams, and dams where wild fish are harvested are found across the State, some of which transverses the entire State and cut across neighboring countries, constituting the hydrologic network (Anonymous, 2023).

Study design and sample collection

A cross-sectional study was designed in which 30 wild fresh catfish were randomly sampled at different periods from different vendors in two Major markets (Custom Market and Monday Market) in Maiduguri Metropolis from June to August, 2021. The fish samples were dissected into liver and muscle specimens. The samples were then grouped based on purchase location (markets); 15 fish each from Custom Market and Monday Market in Maiduguri and its environs. The samples were collected based on availability. Information on fish markets was obtained through verbal interaction with the vendors, and sampling was by random. In order to avoid spoilage or external contamination, samples were placed in polyethylene bags with ice packs and immediately transported to the Analytical Laboratory, Department of Chemistry, Yobe State University, and were later stored in the refrigerator for preservation until processed.

Sample preparation, processing, and digestion.

At the laboratory, the process of analyzing samples collected was undertaken as described by the American Public Health Association 1020QC (2015). Briefly, the fish were thawed at room temperature after being washed with distilled water in the desiccators before dissection. The liver and muscles were cut and removed using a stainless-steel knife, the harvested parts were washed and placed in a labeled plastic container for their purchase area, and the separated parts were sun-dried for four days. The dried samples of fish were homogenized using a pestle and mortar. The digestion of fish samples was based on the microwave-assisted digestion (master 40) method. Briefly, 1g of constant-weight tissue/organ sample was placed in polytetrafluoroethylene (microwave test tube). Digestion reagents (mixture of 6ml of nitric acid at 65% concentration and 2ml of hydrogen-peroxide at 35% concentration as it reduces nitrous vapors and accelerates the digestion of organic matter by raising the temperature.) in a ratio of 3:1 was added and allowed to stay for a while. The tube was microwaved for 40 minutes at $180^{O}C$ and then allowed to cool at room temperature in the oven. The supernatant was harvested and diluted with 40ml-distilled water in a volumetric flask for both liver and muscle samples, filtered using filter paper (90mm Whatman filter paper No. 1). The metallic content of the digested samples, and the blanks were quantified using atomic absorption spectrophotometer (AAS_BUCK SCI. MODEL 210VGP, USA).

Health risk assessment

The potential health risks of HM consumption from wild fish were assessed based on the Estimated Daily Intake of metals (EDI), Target Hazard Quotient (THQ), Hazard Index (HI), and Target Cancer risk, according to standard protocols.

Estimated daily intake (EDI)

The EDI of heavy metals is the amount of a substance in food expressed on a body mass basis (usually in mg/kg body weight), which humans can ingest daily over a lifetime without appreciable health risk (Benard *et al*., 2020). The EDI of As and Zn through consumption of wild fish in the study area were determined using the formula: EDI = [C x QFC]/BW as described by the United States Environmental Protection Agency (USEPA) (2021), where C = mean concentration of As or Zn in the wild fish (mg/kg), BW = average body weight in kg (Children 0-17 years = 30 kg; Adult $\geq$ 18 years = 60 kg) and QFC is the estimated quantity of fish consumed daily (kg/person/day) = 0.0345 kg. The computed EDI values of As and Zn were then compared with their respective provisional tolerable daily intake (PTDI) of 0.003 mg/kg/day and 1.0 mg/kg/day set by the Food and Agriculture Organization of the United Nations and World Health Organization (FAO/WHO) (2011).

Target hazard quotient (THQ)

THQ is the non-carcinogenic health risk posed by the consumption of HMs (Njoga et al., 2021). The THQ of As and Zn through consumption of frozen fish in the study area was estimated as recommended by USEPA (2021); using the formula: THQ = [(Ef x Ed x QFC x C) / (RfD x BW x Et)] x 10-3. The Ef = exposure frequency in days (365), Ed = exposure duration (equivalent to an average life expectancy of Nigerian set at 55 years) (Benard et al., 2020), QFC = estimated quantity of fish consumed daily (kg/person/day) = 0.0345 kg, C = mean concentration of As or Zn in the fish (mg/kg), RfD = oral reference dose of 0.003 mg/kg/day for As and 0.3 mg/kg/day for Zn as was set by USEPA (2021), BW = average body weight in kg (Children 0-17 years = 30 kg; Adult ≥ 18 years = 60 kg) while Et (Ef x Ed) = exposure time (365 days x 55 years). The THQ has a benchmark of 1. Therefore, if the calculated THQ value is < 1, there is very little or no non-carcinogenic health risk, whereas a value ≥ 1 was considered a possibility that non-carcinogenic adverse health effects may ensue following fish consumption (Benard *et al*., 2020; Njoga *et al*., 2021).

Hazard index (HI)

The HI determines the potential risk to human health from the combined effect of pollutants, as fish may be contaminated with multiple HMs having similar adverse health effects. Therefore, it is appropriate to sum individual fish THQs of As and Zn detected in the study area using the formula: HI = THQAs + THQZn; HI, value < 1 depicts very little or no non-carcinogenic health risk, whereas value ≥ 1 foretells a possibility of adverse health effects (Njoga *et al*., 2021).

Target cancer risk (TCR)

The TCR was calculated to assess the potential carcinogenic risks associated with lifetime exposure to As and Zn using the formula: TCR = CSF x EDI as described by Naseri *et al*. (2021). Since Zn does not cause any carcinogenic effects, its CSF (cancer slope factor) has not yet been established (USEPA, 2021), so the TCR value for intake of only As was calculated with CSF set at 1.5 mg/kg/day by USEPA (2021). Therefore, if the calculated TCR > 1 = carcinogenic risk.

DATA ANALYSIS

The data generated from this study were computed with the IBM® SPSS Statistics version 20 (IBM, Armonk, NY: IBM Corp.) and analyzed using descriptive statistics (mean, standard deviation, range, minimum, and maximum). For comparing the mean concentration values, independent t-tests were performed to examine the effect of fish markets and organs of fish (liver and muscle tissues) on the levels of HMs (As and Zn) concentration. The assumption of homogeneity of variance of the dependent variables (As and Zn) concentration was tested using Levene’s Test of Equality of Variances. Values of $p \leq 0.05$ were considered statistically significant in the univariate analysis.

RESULTS

Detection and distribution of heavy metals in wild fish in Maiduguri Metropolis

The detection and distribution of HMs in the tissue of wild fish sold for human consumption in the Maiduguri metropolis of Borno State, Nigeria, is shown in Table 1.

TABLE I: Detection of heavy metals (mg/kg) in fish tissues in Maiduguri Metropolis.

HMs	WHO MPL	Organ	Range Conc.	Mean Conc. ± SD	*p-value*
Zn	100	Liver	0.923 – 0.005	0.26 ± 0.32	0.545
		Muscle	0.931 – 0.002	0.22 ± 0.27	
As	1	Liver	0.982 – 0.001	0.27 ± 0.33	
		Muscle	0.801 – 0.008	0.28 ± 0.23	0.997

WHO, World Health Organization; MPL, Maximum Permissible Limit Conc, Concentration; SD, Standard deviation

The values of Zn concentration in the liver ranged from 0.005 to 0.923 mg/kg and in muscle was from 0.002 to 0.931 mg/kg while that of As in the liver ranged from 0.001 to 0.982 mg/kg and 0.008 to 0.801 mg/kg in the muscle. The table also showed that the mean concentration (mg/kg ± SD) of Zn in the liver (0.26 ± 0.32) was higher compared to those in the muscle (0.22 ± 0.27), but this there was no statistically significant difference (t (58) = 0.608, p = 0.545). However, the mean concentration of As in the liver, (0.27 ± 0.33), was lower than in the muscle, (0.28 ± 0.23), but this difference was not statistically significant (t (52) = -0.003, p = 0.997).

The detection and distribution of HMs in wild fish sold for human consumption in the two Markets sampled in the Maiduguri metropolis of Borno State, Nigeria, is shown in Table 2.

TABLE II: Detection of heavy metals (mg/kg) in fish markets in Maiduguri Metropolis.

HMs	WHO MPL	Location	Range Conc.	Mean Conc. ± SD	*p-value*
Zn	100	Custom	0.002-0.931	0.22 ± 0.31	
		Monday	0.003-0.911	0.26 ± 0.29	0.633
As	1	Custom	0.001-0.902	0.34 ± 0.31	0.074
		Monday	0.008-0.982	0.21 ± 0.24	

The values of Zn concentration in tissues of fish obtained in the custom market ranged from 0.002 to 0.931 mg/kg and for those obtained in Monday market were between 0.003 and 0.911 mg/kg while that of As in the custom market ranged from 0.001 – 0.902 mg/kg and in Monday market was 0.008 – 0.974 mg/kg. The table also showed that the mean concentration of Zn in the custom market (0.22 ± 0.31) was lower compared to that in the Monday market (0.26 ± 0.29), but this was no statistically significant difference (t (0.05, 58) = -0.481, $p = 0.633$). However, the mean concentration of As in the custom market (0.34 ± 0.31), was higher than that in the Monday market (0.21 ± 0.24), but this difference was not statistically significant (t (55) = 1.819, $p = 0.074$).

Health risk assessment of Zn and As specific to children and adult consumers of wild fish in Maiduguri, Borno State, Nigeria

The Health Risk Assessment of Zn and As specific to the children and adult consumers of wild fish in Maiduguri were shown in Tables 3 and 4.

TABLE III: Estimated daily intake (EDI) and target cancer risk (TCR) specific to children and adult consumers of wild fish sold in Maiduguri Metropolis, Borno State, north-eastern Nigeria.

Metals	Organ	EDI		TCR	
		Children	Adult	Children	Adult
Zn	Liver	3.0E-04	1.5E-04	NA	NA
	Muscle	2.5E-04	1.3E-04	NA	NA
As	Liver	3.1E-04	1.6E-04	4.7E-04	2.3E-04
	Muscle	3.2E-04	1.6E-04	4.8E-04	2.4E-04

EDI, Estimated Daily Intake; TCR, Target Cancer risk. NA, Not applicable

TABLE IV: Target hazard quotient (THQ) and hazard index (HI) specific to children and adult consumers of wild fish sold in Maiduguri metropolis, Borno State, North-eastern Nigeria.

Organ	THQ				HI	
	Zn		As			
	Children	Adult	Children	Adult	Children	Adult
Liver	9.97E-07	4.98E-07	1.04E-04	5.18E-05	1.04E-04	5.22E-05
Muscle	8.43E-07	4.22E-07	1.07E-04	5.37E-05	1.08E-04	5.41E-05

THQ, Target Hazard Quotient; HI, hazard Index

The computed EDI for Zn in children and adult populations ranged between 1.3E-04 and 3.0E-04; EDI values of As in both children and adult populations ranged between 1.6E-04 and 3.2E-04 (Table 3). The calculated EDI values were generally higher in children than adults and lower than the WHO-recommended PTDI. The TCR for As in children and adult populations ranged between 2.3E-04 and 4.8E-04, lower than the TCR > 1 = carcinogenic risk (Table 3). The THQ of all the HMs and organs for children and adult populations ranged between 4.22E-07 and 1.07E-04 (Table 4). HI, the value for each of the two metals was less than unity for both children and adult populations (Table 4).

DISCUSSION

The HMs concentrations were detected in all wild fish liver and muscle tissues sold for human consumption sampled in this study; this, in our opinion, might have a lot to do with the pollution status of the environment where the fish have been harvested. The contamination of the environment with HMs can emanate from indiscriminate disposal of industrial effluents, household refuse, or excessive agricultural use of agrochemicals (Perera *et al*., 2016; Yedjou *et al*., 2016; Njoga *et al*., 2021). Therefore, runs from these environments usually contaminate water bodies (rivers, streams, and dams) where these wild fishes are usually captured. The accumulated HMs in the aquatic environment enter the fish; bio-accumulating in their tissues enhances the possibility of poisoning. Humans who consume such contaminated fish are at greater risk of HM poisoning and will suffer its deleterious health effects. In the present study, Zn concentration in the liver was higher than in the muscle. However, the concentration was within the MPL (100mg/kg) recommended by WHO (WHO, 1989). In addition, Zn is an essential element for normal homeostasis; only exposure to high doses has a toxic effect. However, the As concentration in the liver was lower than that in the muscle, although the concentration was within the WHO MPL (1.0mg/kg). The finding in this study was lower than the average total arsenic concentration in fish muscle tissue of 2.30 ± 1.72 mg/g dry weight reported by Tanamal *et al*. (2021). Sirot *et al*. (2009) also reported concentrations of inorganic Arsenic from 0.013 to 0.024 mg/kg, significantly lower than those recorded in the present study. However, the mean concentration of Arsenic obtained in this study was lower than the very low (<0.006 mg/kg) reported by Julshamn *et al*. (2012). According to Julshamn *et al*. (2012), the significant differences in the concentrations of total Arsenic between the different species and among individuals within a given fish species may be due to many factors, among which are the variability of Arsenic in the prey available for the fish in the aquatic and water environment. Few studies reported that As is naturally found in groundwater in numerous countries and is very toxic in its inorganic form (Mazumder, 2015). Long-term exposure to food contaminated with As can also lead to cancer, skin lesions, cardiovascular disease, and diabetes (Mazumder, 2015). Although no significant statistical difference was observed, the mean concentration of Zn in the custom market was lower than that in the Monday market. However, the mean concentration of As in the Custom market Maiduguri was higher than in the Monday market Maiduguri respectively. The mean concentration of Zn was higher in fish obtained in Monday Market Maiduguri than in those obtained in Custom Market Maiduguri, while that of As was higher in fish obtained in Custom Market compared to those obtained in Monday Market. Although the differences are insignificant in either case, the differences in fish sources could have been the factor as fish are being brought into the two markets from several sources, including Lake Chad, Lake Alau, and River Ngadda. The health risk assessment of this work revealed that the EDI for Zn and As values obtained were very low compared to PTDI set by the FAO/WHO. Similarly, TCR for As was lower than the carcinogenic risk (>1) values set by USEPA. The THQ and HI values recorded less than one. Thus, the consumption of wild fish in the Maiduguri Metropolis carries very little or no non-carcinogenic risk. Despite this, screening tests against toxic HMs in Nigerian fish markets should be instituted to ascertain the toxicological safety of fish intended for human consumption. In contrast to our findings, other researchers reported values above the threshold of 1 (Benard *et al*., 2020).

CONCLUSION

In conclusion, heavy metals (Zn and As) are detected in the samples of wild fish (liver and muscle) tested at a lower rate than their MPLs set by WHO. However, because of their non-degradable nature and tendency to bio-accumulate in fish tissues and organs, it can be concluded that long-term consumption poses a greater Public Health risk of heavy metals intoxications in the Maiduguri Metropolis. Therefore, fish that are being imported to Maiduguri metropolis should be observed for the heavy metals from time to time and consumers should be enlightened about the harmful effects of these heavy metals toxicity.

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