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Heavy metal profile in smoked Atlantic cutlass fish (*Trichiurus lepturus, linnaeus 1758*) from some major markets in Benin metropolis, Nigeria

***Wangboje, O.M. and Okhuarobo, O. E.**

Department of aquaculture and fisheries management, University of Benin, P.M.B. 1154, Benin City, Nigeria

Corresponding author:** oiseoje.wangboje@uniben.edu* ***Telephone Number: *08023544500*

Abstract

The concentrations of heavy metals (Pb, Cd, Cu and Zn), in smoked Trichiurus lepturus (Trichiuridae) from some major Markets in Benin Metropolis, Nigeria, were determined employing Atomic Absorption Spectrophotometric technique, in order to ascertain their suitability for human consumption against the dearth of data regarding the metal content of such fish. The mean concentrations of metals in fish ranged from 0.118 mg/kg for Cd to 72.738 mg/kg for Zn. The mean concentration of Zn in fish ranged from 51.80 mg/kg at New Benin Market to 89.28 mg/kg at Ramat Market while the mean concentration of Cu ranged from 6.58 mg/kg at Oba Market to 9.29 mg/kg at Ramat Market. The mean concentration of Cd ranged from below detection limits at Oba and New Benin Markets to 0.31 mg/kg at Ramat Market while the mean the mean concentration of Pb ranged from 0.39 mg/kg at New Benin Market to 0.75 mg/kg at Uselu Market. There was no significant difference (P>0.05) in the mean concentrations of metals in fish between Markets. The toxicity quotient for heavy metals ranged from 0.271 for Cu to 2.425 for Zn. The mean concentrations of Zn, Cd and Pb in fish exceeded the Food and Agriculture Organization and Commission Regulation maximum limits for heavy metals in fish indicating that fish must be consumed with caution, to avert heavy metal poisoning.

Key words*: Heavy metals, Toxic quotient, Trichiurus lepturus, poisoning.*

Introduction

Heavy metals have been identified as hazardous environmental pollutants owing to their highly toxic properties (Anyanwu *et al.*, 2020; Yuguda *et al.*, 2020). These chemical elements have potential toxic effects on wildlife including fish especially when natural threshold levels are exceeded. For example, they are known to cause adverse histological alterations in recipient fish species (Cantanhede *et al.*, 2016) and also threaten the biodiversity of Piscean communities (Umar *et al.*, 2020).

Heavy metals are widely distributed in natural waters and are very essential in trace amounts for normal biological and physiological activities of aquatic organisms. Elevated levels of heavy metals in such water bodies are often related to a plethora of anthropogenic activities which can significantly alter the physical, chemical and biological properties of such aquatic media (Iyebor *et al.*, 2020; Lim *et al.*, 2020; Lubis *et al.*, 2020).

Fish is widely consumed in many parts of the world by man because of its high protein content, low saturated fat and omega 3 fatty acids, which are known to support good health (Boadi *et al.*, 2011). In addition, it is a good source of phosphorus, iron, selenium, taurine, iodine and a host of macronutrients (Spore, 2012). Because fishes are at the end of aquatic trophic level they have a higher tendency to accumulate heavy metals in their tissues via biomagnification (Wangboje *et al.*, 2019).

The knowledge about the potential accumulation of heavy metals in fish is very important for the health of unwary consumers.

Foods that lack chemical residues and are reasonably low in heavy metal content are generally preferred around the world for obvious health reasons (Spore, 2015). The effects of metals on man could be acute, chronic, local, systemic, reversible or irreversible (Herber *et al.,* 2001).

Benin City, the administrative capital of Edo State, Nigeria, has a large population and most people consume smoked fish as a partial or complete source of animal protein. Examples of fish species commonly consumed within the City include *Clarias gariepinus, Trichiurus lepturus, Gadus morhua,* and *Scomber scombrus* (Wangboje *et al.,* 2017).

According to the National Institute for Freshwater Fisheries Research (NIFFR), drying prolongs shelf-life by removing as much moisture as possible from fish flesh so that the resultant product is rendered unsuitable for microbial decay, insect infestation and other forms of deterioration prior to distribution and marketing (NIFFR, 1996). The contamination of fishery products by toxic elements has been recognized to be a potential health hazard to man who may eventually consume such products (Wangboje *et al.,* 2014).

From available literature, there is paucity of data regarding the heavy metal profile of *Trichiurus lepturus* in Benin Metropolis. Accordingly, the study was specifically geared towards determining the concentrations of Lead (Pb), Cadmium (Cd), Copper (Cu) and Zinc (Zn) in smoked *Trichiurus lepturus* (Atlantic cutlass fish; Trichiuridae, Linnaeus 1758) sold in some major Markets in Benin City, Edo State, Nigeria in order to ascertain its suitability for human consumption.

Materials and Methods

Description of study area

Benin City (Fig. 1) is the administrative capital of Edo State, Nigeria. It is located approximately 40 kilometers north of the Benin River and is gridlocked between Latitude 6° 00' N and Longitude 5° 28' E. The scope of the research encompassed four (4) major Markets in three (3) Local Government Areas (LGAs). The Markets are; New Benin and Oba Markets in Oredo LGA, Ramat Market in Ikpoba-Okha LGA and Uselu Market in Egor LGA. The aforementioned Markets are major sale outlets for smoked *Trichiurus lepturus.* Samples of fish were purchased between September 2016 and February 2017 from the aforementioned Markets. New Benin Market is one of the largest and busiest Markets in the City. It is located within the Mission road and New Lagos road axis while Uselu Market, also known as Edaiken Market, is located along the Ugowo-Uselu road of the City. Oba Market, also known as Ekioba Market, is located at the Ring road section of the City while Ramat Market, also known as Oregbeni Market, is located at the Ikpoba Hill axis of the City. This Market opens to the public every four days and is typically characterized with heavy human and vehicular traffic.

Collection of fish samples

Smoked fish samples worth ₦250, were purchased from the aforementioned Markets, wrapped separately in foil paper and immediately taken to the laboratory. Total lengths (cm) of fish samples were measured using a translucent ruler and cotton thread while weights (g) of fish samples were recorded using a Mettler® PM 2000 top loading electronic scale (Table 1).

Preparation of fish samples

Fish samples were dried using a thermostatic drying oven (DHG®9202 Healthquip Medical, England) at a temperature of 70°C until a constant weight was attained. Each sample was milled separately for homogeneity using a porcelain mortar and pestle. The milled product was thereafter stored in labeled air tight plastic vials prior to digestion.

Digestion of fish samples

One gram of milled fish was carefully weighed into a 100 mi Erlenmeyer flask, after which 5 ml perchloric acid (70%) and 10 ml nitric acid (55%) were added (Van Loon, 1980). Digestion was done on a Binatone® Hotplate (Model ECP-207) at 200°C, for about four hours or until the solution became clear. Filtration was achieved using acid-resistant filter paper (0.45µm) and a vacuum pump. After filtration, the filtering system was rinsed with distilled water to remove all traces of metals. Samples were made up to 50 ml with distilled water (Nussey *et al.*, 2000). Blanks were prepared using the same volume of mixed acids (without samples) while all reagents used were of analytical grade (BDH, Poole, England) as part of the quality control assurance procedures.

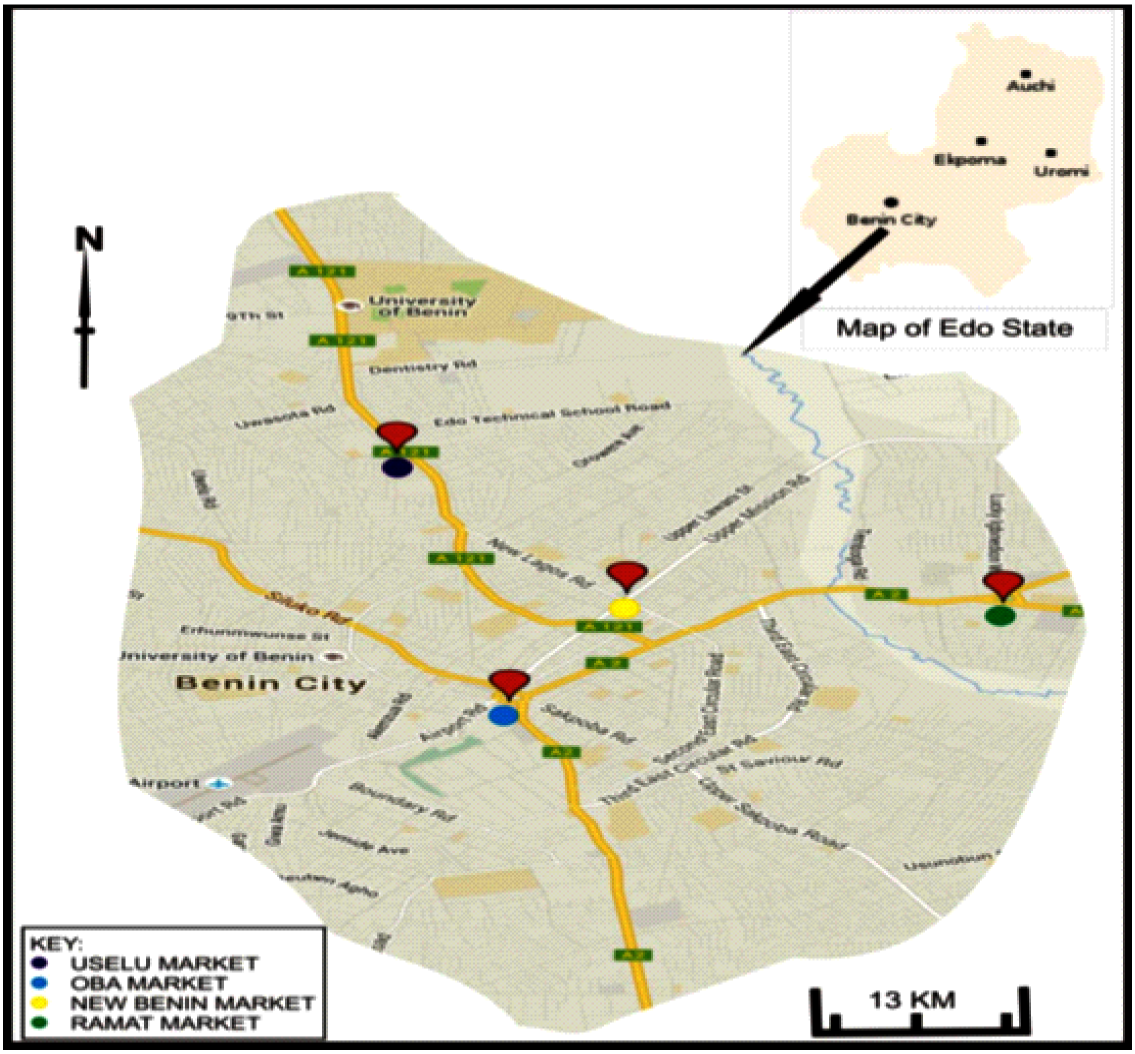

Fig. 1: Satellite road map of Benin City showing the surveyed Markets
Source: Google map (2016)

Table 1: Morphometric measurements for experimental Atlantic cutlass fish samples

Month/Year	No.	Total Length (TL, cm)	Weight (W, g)	Mean TL (cm)	Mean W (g)
September, 2016	4	21.60-31.00	25.64-45.20	26.05	32.61
October, 2016	4	27.70-31.00	50.48-85.02	29.55	61.91
November, 2016	4	25.30-30.00	35.00-48.84	27.70	40.25
December, 2016	4	25.20-26.30	26.54-35.55	25.50	31.14
January, 2017	4	21.00-29.10	39.18-64.63	26.40	50.96
February, 2017	4	25.00-28.60	35.86-69.76	26.53	50.78

Analysis for heavy metals

Fish digests were analyzed for Cu, Zn, Cd and Pb by means of an Atomic Absorption Spectrophotometer (PG® Instruments AA-500F Series, Leicestershire, United Kingdom) equipped with solar software using air acetylene flame as oxidant. All concentrations of heavy metals were expressed in mg/kg (Gross, 2017).

Estimation of daily intake (EDI) of heavy metals by man

The daily intake of metals (mg/person/day) was calculated in order to estimate the daily loading of metals into the body system of man by consumption of fish. The EDI of heavy metals takes into consideration the estimated consumption of fish by man and the heavy metal levels in such fish (Anyakora *et al.*, 2008; Wangboje *et al.*, 2014).

EDI=

$$40 \text{ g/person/day x HM (mg/kg)}/1000 g/kg$$

Where: 40g/person/day = Estimated consumption of fishery products in Niger Delta, Nigeria.

HM= Mean concentration of heavy metal in fish species.

Margin of exposure (MOE) for heavy metals

This is a ratio of the reference dose or health based criteria to the calculated or actual exposure. This ratio gives an indication of the metal of significant ecological concern (Purchase, 2000). The MOE was estimated using the following formula:

MOE=

$$Reference\ dose \Big/ Calculated\ or\ actual\ exposure$$

Theoretical maximum daily intake (TMDI)

This represents a relationship between the maximum limit for metal in fish and the per capita/food regional consumption. It serves as a theoretical indication of the expected maximum daily intake of heavy metal via fish and fishery products (World Health Organization, 1997; Wangboje and Innocent, 2020).

$$TMDI= \Sigma\ ML^1 * F^1$$

ML= Maximum limit for metal in fish; F= per capita/food regional consumption

Toxicity quotient (TQ) for heavy metals

Toxicity quotient (TQ) for chemical elements is a comparison of the measured concentration of site-related elements in ecological matrices with specific health-based criteria (Newstead *et al.*, 2002; Wangboje and Innocent, 2020).

$$TQ = Measured\ concentration\ of\ heavy\ metal\ in\ fish\ sample \Big/ Health\ based\ criteria$$

Statistical method

Data generated from the study were analyzed using GENSTAT® computer software (Version 12.1 for Windows). Analysis of variance (ANOVA) was used to test for significant differences (P<0.05) between mean values of metals while significant means were separated with the New Duncan Multiple Range Test®.

Results and Discussion

The summary statistics for heavy metals in fish showed that the mean concentration of metals ranged from 0.118 mg/kg for Cd to 72.738 mg/kg for Zn as presented in Table 2.

Table 2: Summary statistics for heavy metals (mg/kg) in experimental fish

Metals	Mean	Minimum	Maximum	SD(±)
Zn	72.738	15.92	147.80	34.55
Cu	8.134	2.40	25.40	6.04
Cd	0.118	0.00	0.85	0.22
Pb	0.605	0.15	1.40	0.36

As shown in Table 3, the mean concentration of Zn in fish ranged from 51.80 mg/kg at New Benin Market to 89.28 mg/kg at Ramat Market, while the mean concentration of Cu ranged from 6.58 mg/kg at Oba Market to 9.29 mg/kg at Ramat Market. The mean concentration of Cd ranged from 0.00 mg/kg at Oba and New Benin Market to 0.31 mg/kg at Ramat Market, while the mean concentration of Pb ranged from 0.39 mg/kg at New Benin Market to 0.75 mg/kg at Uselu Market. There was no significant difference (P>0.05) in the mean concentration of metals in fish between Markets.

Table 3: Mean heavy metal concentration (mg/kg) in Atlantic cutlass fish Marketed in Benin City, Nigeria

Market	Zn	Cu	Cd	Pb
Oba	63.90^{a}	6.58^{a}	0.00^{a}	0.73^{a}
Uselu	85.96^{a}	8.33^{a}	0.16^{ab}	0.75^{a}
New Benin	51.80^{a}	8.41^{a}	0.00^{a}	0.39^{a}
Ramat	89.28^{a}	9.29^{a}	0.31^{b}	0.54^{a}

Means with similar superscripts along the column are not significantly different (P>0.05).

The mean concentration of Zn in fish ranged from 36.20 mg/kg in February to 114.74 mg/kg in November, while the mean concentration of Cu in fish ranged from 3.56 mg/kg in November to 14.70 mg/kg in October. The mean concentration of Cd in fish ranged from 0.00 mg/kg in December to 0.23 mg/kg in February while the mean concentration of Pb in fish ranged from 0.26 mg/kg in December to 0.93 mg/kg in September. There were significant differences (P<0.05) in the mean concentration of the metals between months (Table 4).

Table 4: Mean heavy metal concentration (mg/kg) in Atlantic cutlass fish purchased in 2016-2017 in Benin City, Nigeria

Month/Year	Zn	Cu	Cd	Pb
September,2016	71.75^{ab}	13.73^{b}	0.21^{a}	0.93^{b}
October,2016	62.56^{ab}	14.70^{b}	0.12^{a}	0.51^{ab}
November,2016	114.74^{c}	3.56^{a}	0.05^{a}	0.51^{ab}
December,2016	59.03^{ab}	6.33^{a}	0.00^{a}	0.26^{a}
January, 2017	92.16^{bc}	6.12^{a}	0.10^{a}	0.89^{b}
February,2017	36.20^{a}	4.38^{a}	0.23^{a}	0.52^{ab}

Means with similar superscripts along the column are not significantly different (P>0.05).

The estimated daily intake (EDI) values for heavy metals in fish ranged from 0.005 mg/person/day for Cd to 2.910 mg/person/day for Zn (Fig. 3) while the margin of exposure (MOE) for heavy metals ranged from 0.412 for Zn to 3.688 for Cu (Fig. 4). The theoretical maximum daily intake (TMDI) value was 2414 mg/person/day (Table 5) while the toxic/hazard quotient (TQ) values for heavy metals ranged from 0.271 for Cu to 2.425 for Zn (Fig. 5). As shown in Figure 6, the dominant status of heavy metals in fish ranged from 0.14 % for Cd to 89.12% for Zn while the total heavy metal load in fish by Market ranged from 60.60 mg/kg at New Benin Market to 99.42 mg/kg at Ramat Market (Fig. 7).

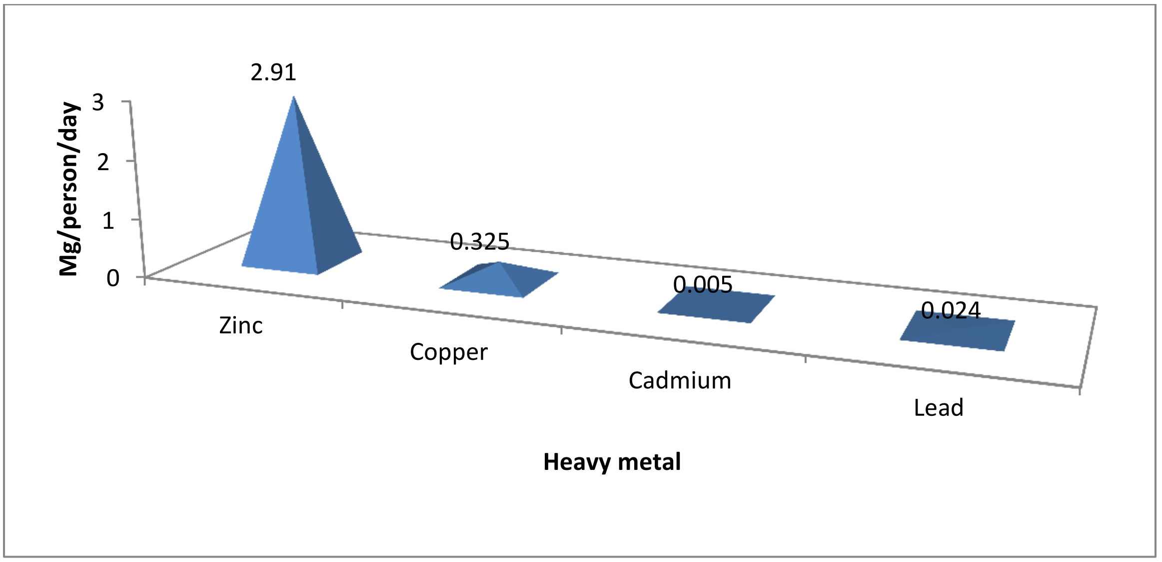

Fig. 3: Estimated daily intake (EDI) for heavy metals

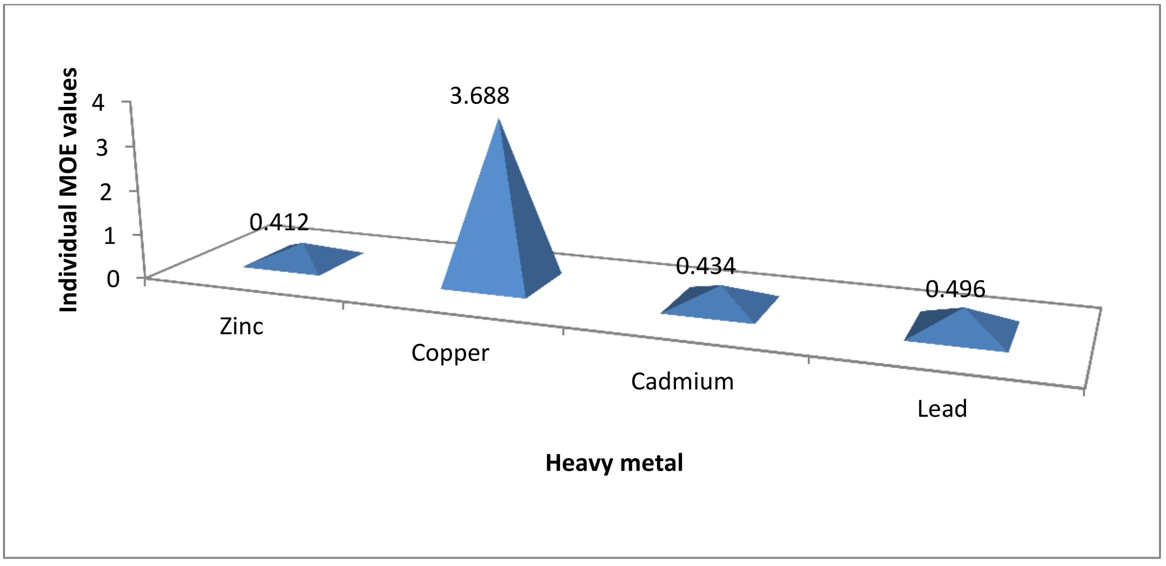

Fig.4: Margin of exposure (MOE) for heavy metals in experimental fish

Table 5: Theoretical maximum daily intake (TMDI) of heavy metals from Atlantic cutlass fish Marketed in Benin City Nigeria

Metal	ML (mg/kg)	F(mg/person/day)	Individual (mg/kg/day)	TMDI
Zinc	30*	40	1200	
Copper	30*	40	1200	
Cadmium	0.05**	40	2	
Lead	0.30**	40	12	
			Σ=2414	

*FAO limit (1983)
**Commission Regulation limit (2010) and Codex Alimentarius limit (2015)

Where: ML= Maximum limit for metal in fish; F= per capita/food regional consumption

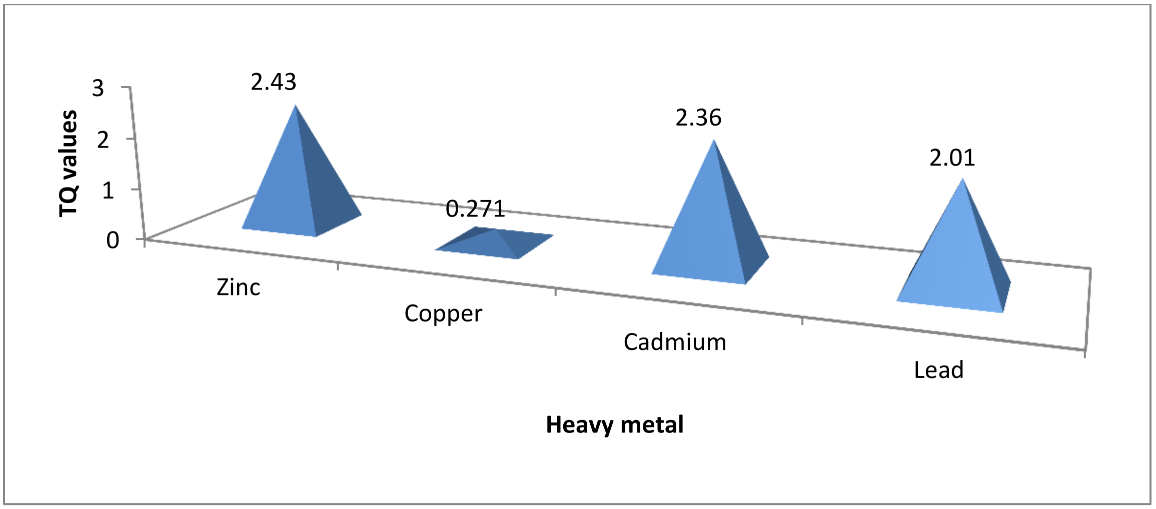

Fig. 5: Toxicity/hazard quotient (TQ) for heavy metals

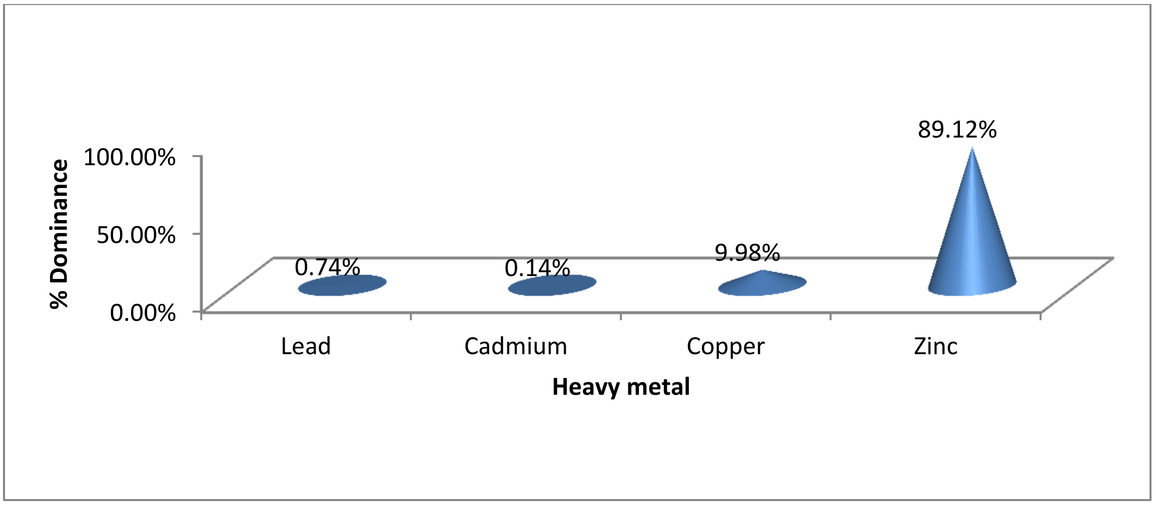

Fig. 6: Dominant status of heavy metals in smoked *Trichiurus lepturus*

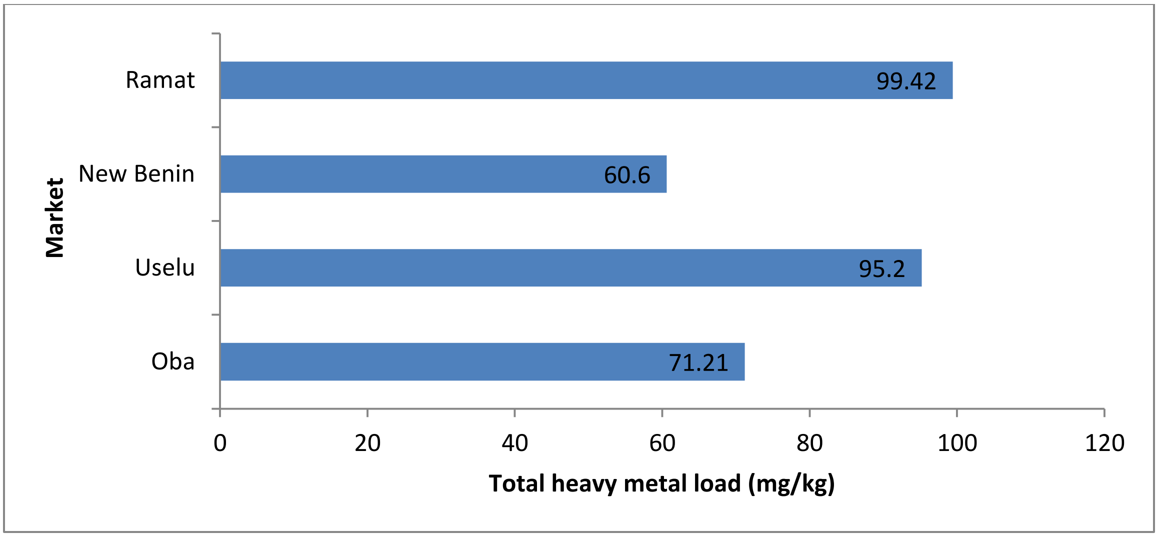

Fig. 7: Total heavy metal load in Atlantic cutlass fish purchased at selected Markets in Benin City, Nigeria

Table 6: Comparison of heavy metal content (mg/kg) in smoked *Trichiurus lepturus* to some other studies

Heavy metal	Smoked *Trichiurus lepturus* (This study)	Smoked *Clarias gariepinus* (Ako and Salihu, 2004)	Frozen *Clupia trachurus* (Igwemmar *et al.*, 2013)	Fresh *Mugil cephalus* (Wangboje *et al.*, 2016)
Zn	72.738	62.00	2.03	22.44
Cu	8.134	5.20	0.23	14.26
Cd	0.1189	ND	ND	ND
Pb	0.605	0.56	ND	0.04

ND= Not detected

In this study, it was observed that the heavy metal profile in smoked Atlantic cutlass fish *T. lepturus*, was in the order Zn>Cu>Pb>Cd. The heavy metal load that can be found in fish is closely related to the dynamics of bioavailability and bioaccumulation, in this case Zn was conceivably more bioavailable to the experimental fish in its aquatic medium hence resulting in a possible higher bioaccumulation of the metal. The reverse scenario may be reported in the case of Cd. Bioaccumulation has been described by Hamilton *et al.*, (2003) as a relationship between the concentration of a chemical in an organism's tissues to the concentration in the surrounding water. The description assumes all residues of the chemicals in the organism originate from the water, although the residue may originate from the diet or bottom sediment as well as the water itself. According to Nussey *et al.*, (2000) and Ahiakwo *et al.*, (2019) bioaccumulation of metals will take place if the rate of uptake by an organism exceeds the rate of elimination. Furthermore, hyperaccumulation of heavy metals in recipient organisms has been reported (Corso and De La Torre, 2020; Mesjasz-Przybytowicz and Przybytowicz, 2020). Cantanhede *et al.*, (2016), observed that heavy metals have a potential for bioaccumulation in fish tissues.

The ecological habit of *T. lepturus* may also contribute to its heavy metal load as it is a known active piscivore and a bentho-pelagic species, living in coastal waters and estuaries. Such habitats have been reported to be important repositories for heavy metal contamination (Nasser, 2013; Zhao and Marriot, 2013). Market-wise, it was observed that the mean concentrations of Zn, Cu and Cd were at a peak in fish at Ramat Market while the mean concentrations of Pb in fish were at a peak at Uselu Market. The seemingly higher concentrations of metals in fish at Ramat Market may be attributed to exhaust fumes from vehicles as the Market is located within a zone of particularly heavy vehicular traffic. Furthermore, the area plays host to several motor parks which may further compound the problem of emissions. This assertion is based on the fact that fossil fuels contain heavy metals especially Ni, Pb. Cd, Cu and Zn, which are spewed into the atmosphere upon combustion (Calamari and Naeve, 1994; Wangboje *et al.*, 2018). The higher concentrations of metals in fish at Ramat Market may also be attributed to variations in handling and processing methods as smoked fish could come from different sources. Distribution and transportation may further contribute to the additional heavy metal burden. There was a significant difference (P<0.05) in the mean concentrations of Cd in fish between Markets, suggesting that the metal could have been introduced from various sources and points. The total heavy metal load in Atlantic cutlass fish obtained from the Markets followed the order: Ramat Market>Uselu Market>Oba Market>New Benin Market. This observation implied that the smoked *T. lepturus* bought from New Benin Market was comparatively safer for human consumption than those obtained from other Markets owing to a lower heavy metal burden. Monthly-wise, there were significant differences (P<0.05) in the mean concentrations of Zn, Cu and Pb in fish. This observation could be adduced to seasonal variations, as the study cut across both wet and dry months. Etim *et al.*, (2013), reported that seasonal variation may directly influence the dynamics of physiochemical parameters in the environment. The EDI values calculated in this study revealed that Zn and Cd had the highest and lowest values respectively. Wangboje *et al.*, (2016), worked on heavy metals in fish species sold in Lagos Markets and similarly reported highest and lowest EDI values for Zn and Cd respectively, although their values of 0.63 (Zn) and 0.0 (Cd), were lower than what was obtained in this study. It would thus appear that potential consumers of smoked *T. lepturus* in Benin metropolis will get more of Zn and less of Cd in their fish diets. The MOE values revealed that Cu had the highest value (3.688), suggesting that the metal has potential for risk in the future and should thus be closely monitored. This finding is not surprising against the backdrop that the metal ranked second to Zn in terms of highest mean concentration in *T. lepturus.* Wangboje *et al.*, (2016), reported a higher MOE value of 3.75 for Cu and similarly concluded that the metal should be closely monitored because of potential risk to fish consumers. The TMDI for heavy metals in fish was 2414 mg/person/day. Wangboje *et al.*, (2016), in their study on fish from Markets in Lagos metropolis, reported a slightly lower TMDI value of 2404 mg/person/day. It was observed that the mean concentrations of Zn, Cd and Pb in fish in this study exceeded the Food and Agriculture Organization of the United Nations (FAO, 1983), Commission Regulation (2010) and Codex Alimentarius (2015) maximum limits for heavy metals in fish, indicating a potential health risk to consumers. This observation was further buttressed by the calculated TQ values for these same metals which exceeded unity. It has been reported that transition metals like Zn, Cd and Pb are potential human carcinogens (United States Environmental Protection Agency, 2006). Furthermore, when found above recommended limits in the human body, Zn is known to cause serious gastrointestinal disturbances (South African Water Quality Guideline, 1996) while Pb causes a decrease of at least 3 intelligence quotient (IQ) points in children and an increase in systolic blood pressure of approximately 3 mmHg in adults (Codex Alimentarius, 2015). Cadmium according to the Environmental Protection Agency (EPA, 2001), is associated with bone damage, chronic kidney disease and hypertension in man. It is clear from the study that smoked *T. lepturus* from the aforementioned Markets, must be consumed with caution in order to avoid heavy metal poisoning over time especially with regard to Zn, Cd and Pb. The mean concentrations of heavy metals in smoked *T. lepturus* were slightly higher than the values reported in earlier studies (Table 6).

Conclusion and Recommendations

The study revealed that the heavy metals of critical ecological concern in smoked *T. lepturus*, were Zn, Cd and Pb, as their respective mean concentrations exceeded International standard maximum limits for heavy metals in fish. Borne out of findings from this study, it becomes necessary for relevant agencies such as the Ministries of Environment and Health to advise the consuming public to eat such fish with caution in order to avert adverse health problems related to heavy metal poisoning. It is suggested that heavy metals not covered in the present study be included in future studies in order to expand the profile of such metals in Atlantic cutlass fish (*T. lepturus*) and other commonly consumed smoked fish species.

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