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Heavy metal profile in a smoked *Cynoglossus* Fish species from selected markets in Owo Town, South Western, Nigeria

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Abstract
The dearth of information on the levels of heavy metals in smoked fishes sold in various markets in Owo town, Ondo state, Nigeria, warranted this research against the backdrop of the popularity of smoked fish products amongst the populace. Specifically, the levels of Pb, Cd, Cu and Zn in smoked *Cynoglossus senegalensis* (Mean total length= 31.35 cm; Mean weight= 37.72 g) were quantified by Atomic Adsorption Spectrometric technique in order to ascertain their suitability for human consumption. The mean heavy metal concentrations in smoked *C. senegalensis,* ranged from 0.10 mg/kg (Cu) to 61.11 mg/kg (Zn) while the mean concentrations of metals in fish by market ranged from below detection limit for Cd at Iyere market to 66.77 mg/kg (Zn) at Oba market. The toxic/hazard quotient (TQ) values for Pb, Cd and Zn indicated a risk to the potential fish consuming public. Smoked *C. senegalensis* must thus be consumed with caution because of the risk associated with heavy metal poisoning especially from Pb, Cd and Zn over time.

Keywords: Heavy metals, *Cynoglossus senegalensis,* Toxic/hazard quotient

Introduction
Environmental pollution is generally defined as the contamination of water, soil, or the atmosphere by the discharge of substances that are harmful to living things (Obianime *et al.,* 2017) [20]. In this realm, heavy metals are typical pollutants in urban environments which are of immediate concern due to their persistence in the environment and toxicity to humans (Odewande and Abimbola, 2008; Adamu *et al.,* 2016; Alhassan *et al.,* 2016) [21, 1, 6]. Heavy metals enter the aquatic environment from both natural pathways and a variety of anthropogenic sources and they can have a negative impact on aquatic ecosystems, the food chain and human health (Arantes *et al.,* 2016) [9]. Anthropogenic input of heavy metals has been considered a threat to the integrity of the environment especially with regard to living aquatic resources such as fish species (Rajeshkumar and Xiaoyu, 2018) [22]. Heavy metals have been reported to change the genetic, physiological, biochemical and behavioral parameters of aquatic organisms including fish (Mahboob *et al*., 2016) [16]. Fish have been the most popular choice as test organisms for heavy metals because they are presumably the best understood organisms in the aquatic environment and are an important source of protein to man (Murtala *et al.,* 2012) [17]. Owo is a moderately populated urban area in Ondo state, south western Nigeria. The town is widely recognized for its agricultural production and fish markets. The fish markets display an array of smoked fish, common to most of these markets is smoked *Cynoglossus senegalensis.* The paucity of information on the levels of heavy metals in smoked fishes sold in various markets in this town warranted this study against the backdrop of the popularity of smoked fish products amongst the local populace. The study specifically quantified the levels of Pb, Cd, Cu and Zn in smoked *C. senegalensis* in order to ascertain their suitability for human consumption. Lead and Cd are non-essential chemical elements that are of no use in the human body and are therefore undesirable while Cu and Zn are essential elements needed by the body for a host of enzymatic and metabolic functions.

Materials and Methods
Description of study area
The study was conducted in Owo town, Owo local government area of Ondo state, Nigeria. Owo town is located within 7º 11' North and 5 º 35 ' East and has a population of 258, 230 people (Wikipedia, 2017) [25]. Four major markets; Oba market, Koko market, Iyere market and Jokes Motors market (Fig.1) were purposely selected for the study owing to the relative abundance of smoked *Cynoglossus senegalensis* in these markets. The Oba market is named after the Oba of Owo Palace. It is unique in the sense that, it is the only market in Owo town that is patronized for six days out of the seven days of the week. It is the largest market in Owo town. Koko market is another renowned market in the town. It is open every five days. It is the second largest market in Owo town. It is surrounded by the local government library, a micro finance bank and post office. Iyere market is patronized mainly by people that stay in the Iyere district. It opens every five days. It is surrounded by residential houses, a central mosque, restaurants and barbing salons. Jokes motors market is located along the Akure-Benin Express-way. It is the third largest after Oba and Koko market. It is surrounded by the deeper life camp ground and the Jokes motors from which it takes its name. It opens to the public every five days.

Fig 1: Map of study area showing locations of markets; Source: Google maps (2016)

Collection of smoked fish samples
Samples of smoked fish (Plate 1) were purchased from the aforesaid markets fortnightly at an average price of N450. Collection of samples spanned 6 months (i.e. September 2016 to February 2017). The samples were placed in new polythene bags and sealed with selotape® after which the bags were taken to the laboratory within 24 hours, for further studies.

Plate 1: A sample of smoked *Cynoglossus senegalensis*

Laboratory procedures
Smoke fish samples were weighed whole in grams using an ATOM A-110C® electronic compact scale while their total lengths were recorded using a stainless steel ruler. Fish samples were oven dried at a temperature of 50 º C for 12 hours in a Surgifield-Uniscope® (SM 9023 model) laboratory oven. Each dried sample was milled separately using a porcelain mortar and pestle and kept in foil paper prior to digestion. Digestion was carried out using the double acid method as described by Fish digests were analyzed for Pb, Cr, Cu and Cd by means of an Atomic Absorption Spectrophotometer (Unicam® 696 series) equipped with solar software using air acetylene flame. Concentrations of metals in fish were expressed in mg/kg. Blanks and duplicate analyses were performed for all analytes as part of the quality assurance procedures. All reagents used were of analytical grade (BDH, Poole, England).

Estimated average daily intake (EADI) of heavy metals by man

The EADI was obtained by multiplying the mean heavy metal content in fish (mg/kg) by the per capita fish consumption of an area (0.04kg/person/day in the Niger Delta) and dividing the product by the typical human adult body weight, estimated to be 70 kg (Ezemonye *et al.*, 2017) [12].

Calculation of theoretical maximum daily intake (TMDI) for heavy metals

The TMDI is used for making a first estimate of heavy metal residue intake. It is calculated by multiplying the established maximum limit by the estimated average daily regional consumption for each food item and then summing the products (WHO, 1997) [26].

$TMDI = \sum ML^{1} * F^{1}$

Where: ML = Maximum limit for a given food; F =Per capita consumption

Calculation of total toxicity of mixtures (TTM) index for heavy metals

Whether or not a mixture of metals in a particular medium exceeds the quality guideline value for that medium, can be determined by applying the TTM index (ANZECC/ARMCANZ, 2000)

$TTM = \Sigma (C^{1}/GV^{1})$

Where: C^{1} = Concentration of the ‘ith’ component of mixture

GV^{1}= Guideline value for the ‘ith’ component

TTM >1= The mixture has exceeded the Guideline value

Toxicity/hazard quotient (TQ) for heavy metals

The Toxicity/hazard 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) [18].

$$TQ = \frac{\text{Concentration of heavy metal in fish sample}}{\text{Health based criteria}}$$

Statistical protocol

Statistical software (GENSTAT® version 13.3 for Windows) was used for analyzing data. One-way analysis of variance (ANOVA) was used to test for significant differences between mean values of heavy metals at 5% level of probability while Duncan Multiple Range Test was used to separate significant means. Microsoft Excel (for Windows 2010), was used for all graphical presentations.

Results and Discussion

As shown in Table 1, the mean heavy metal concentrations in smoked *Cynoglossus senegalensis,* ranged from 0.10 mg/kg (Cu) to 61.11 mg/kg (Zn) while the mean concentrations of metals in fish by market ranged from below detection limit for Cd at Iyere market to 66.77 mg/kg for Zn at 7Oba market, with no significant difference (P>0.05) in the mean concentrations of metals in fish between markets (Table 2). The mean concentrations of metals in fish by months ranged from below detection limit for Cd in January to 72.10 mg/kg for Zn in October with a significant difference (P<0.05) in the mean concentrations of Zn and Cu in fish between months (Table 3). As shown in Fig. 2, the EADI ranged from 0.00006 mg/kg/day for Cd to 0.035 mg/kg/day for Zn while the calculated TMDI was 2414 mg/person/day (Fig. 3). The TQ values ranged from 0.24 for Cu to 2.04 for Zn, as shown in Fig. 5. The heavy metal quota in fish ranged from 0.14% (Cd) to 88.75% (Zn) as shown in Fig. 6 while the total heavy metal load in fish ranged from 63.57 mg/kg at Jokes motors market to 75.32 mg/kg at Oba market, as presented in Fig. 7. The heavy metal quota in fish by market ranged from 0% for Cd at Iyere market to 90.13% for Zn at Koko market (Fig.8).

Table 1: Summary statistics for heavy metals (mg/kg) in smoked *Cynoglossus senegalensis*

Metals	Mean	Minimum	Maximum
Pb	0.59	0.11	1.60
Cd	0.10	0.00	1.20
Zn	61.11	8.10	92.50
Cu	7.05	3.50	11.30

Table 2: Summary statistics for heavy metals (mg/kg) in smoked *Cynoglossus senegalensis* by market

Markets	Pb	Cd	Zn	Cu
Oba market	0.77^{a}	0.07^{a}	66.77^{a}	7.71^{a}
Koko market	0.51^{a}	0.12^{a}	65.32^{a}	6.24^{a}
Iyere market	0.46^{a}	0.00^{a}	57.17^{a}	6.76^{a}
Jokes motors Market	0.66^{a}	0.23^{a}	55.20^{a}	7.48^{a}

Means with similar superscripts are not significantly different (P>0.05).Vertical comparisons only.

Table 3: Mean heavy metal concentration in smoked *Cynoglossus senegalensis* by months

Months	Pb	Cd	Zn	Cu
September, 2016	0.65^{a}	0.30^{a}	53.95^{ab}	4.75^{a}
October, 2016	0.25^{a}	0.03^{a}	72.10^{b}	7.87^{b}
November, 2016	0.29^{a}	0.08^{a}	43.93^{a}	6.28^{ab}
December, 2016	0.84^{a}	0.10^{a}	70.03^{ab}	6.63^{ab}
January, 2017	0.76^{a}	0.00^{a}	59.68^{ab}	7.77^{b}
February, 2017	0.80^{a}	0.10^{a}	67.00^{ab}	8.96^{b}

Means with similar superscripts are not significantly different (P>0.05). Vertical comparisons only.

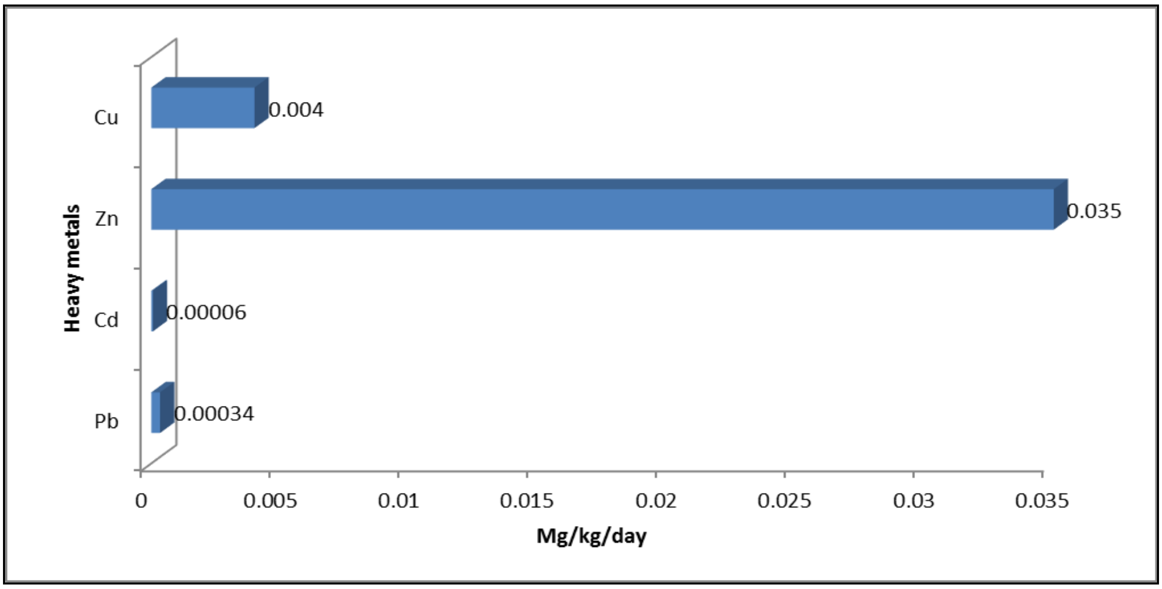

Fig 2: Estimated average daily intake (EADI) values for heavy metals

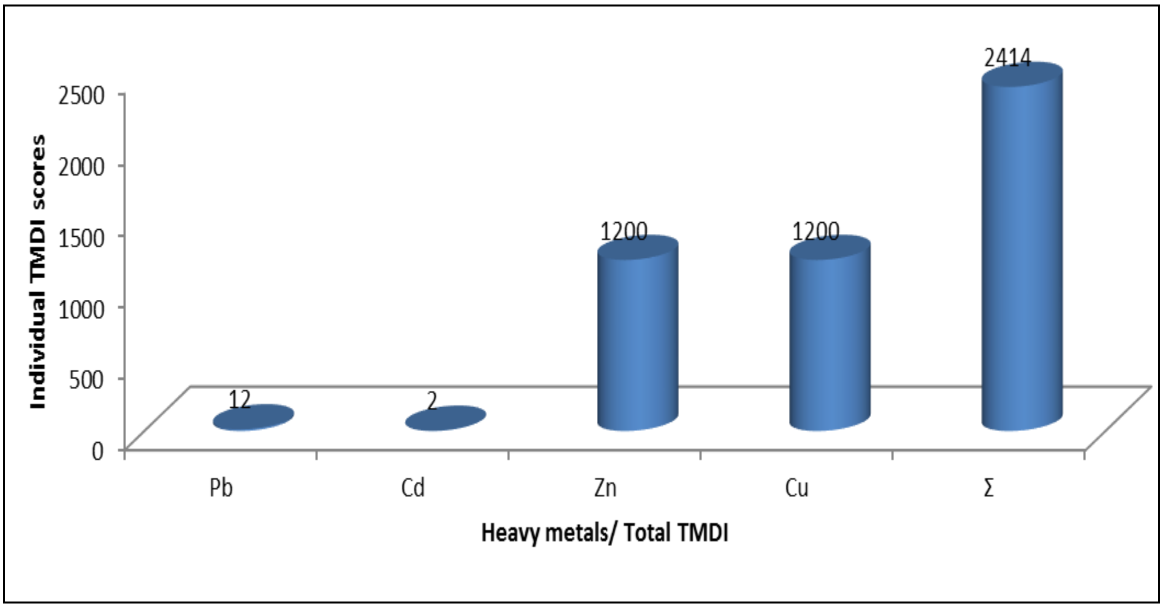

Fig 3: Theoretical maximum daily intake (TMDI) values for heavy metals

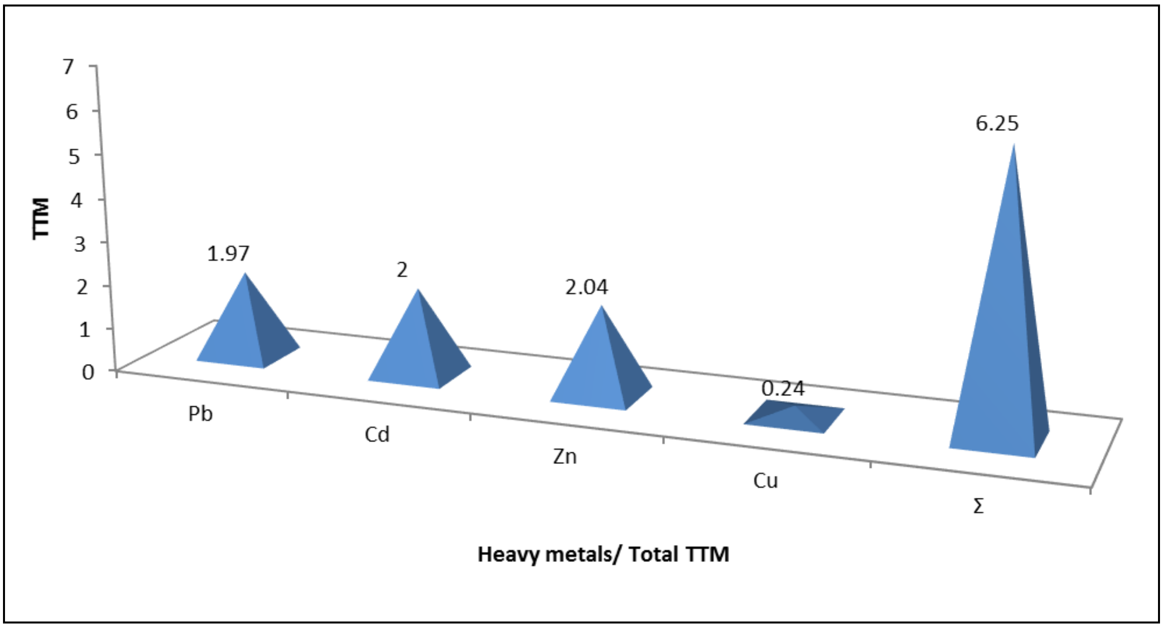

Fig 4: Total toxicity of mixtures (TTM) values for heavy metals

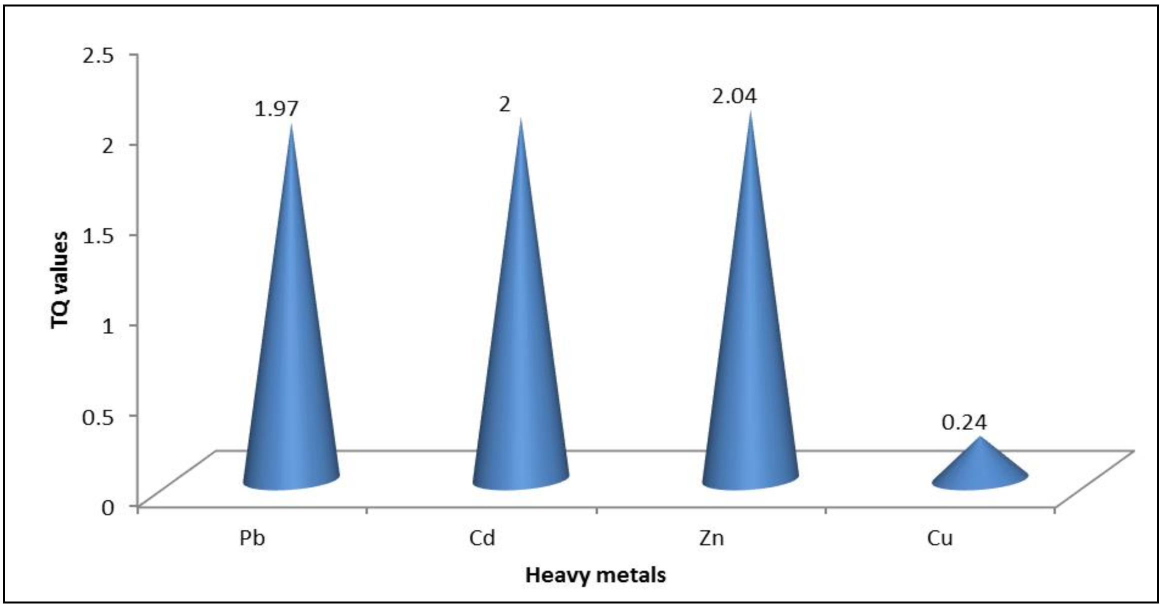

Fig 5: Toxic/hazard quotient (TQ) values for heavy metals

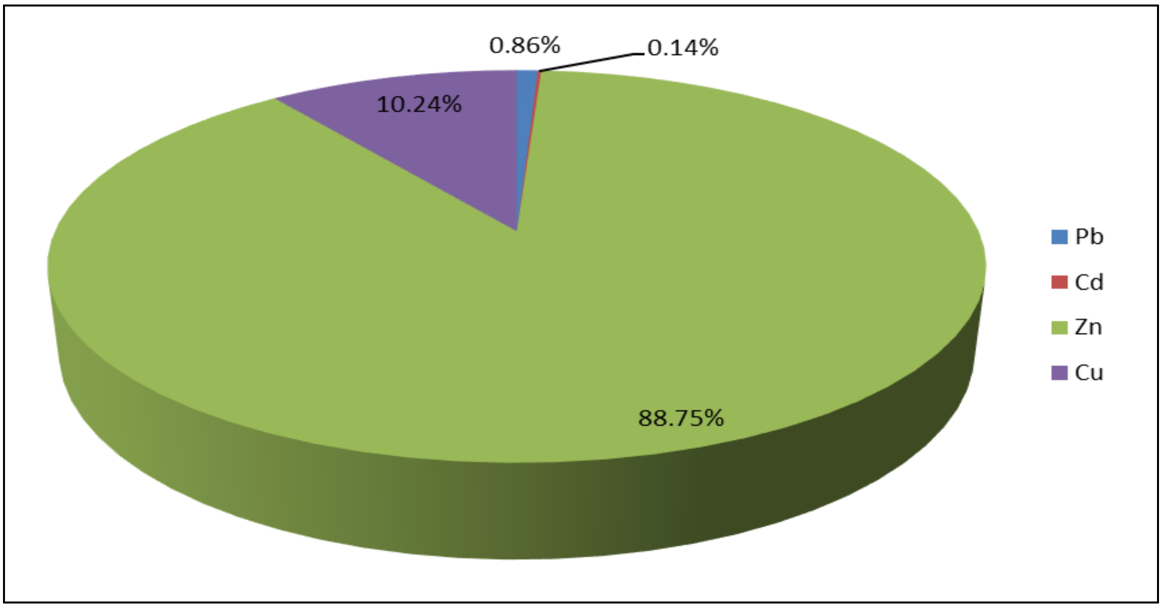

Fig 6: Heavy metal quota in smoked *Cynoglossus senegalensis*

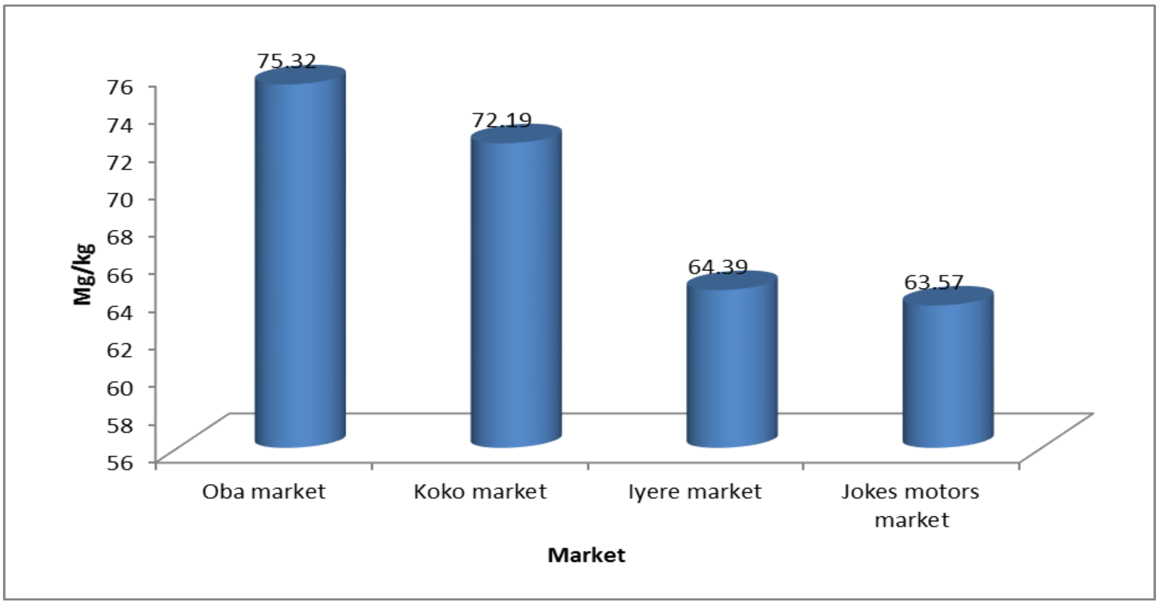

Fig 7: Total heavy metal load in smoked *Cynoglossus senegalensis* by market

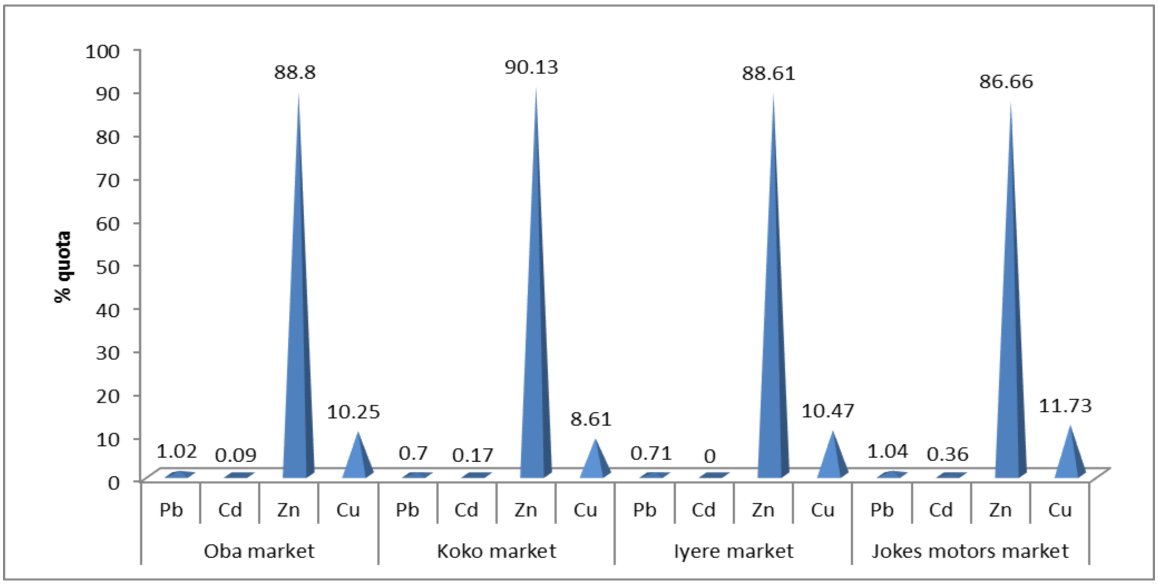

Fig 8: Heavy metal quota in smoked *Cynoglossus senegalensis* by market

Heavy metals are of concern due to their biodegradable nature and persistence in the natural environment (Agrahari *et al.*, 2017) [2]. Heavy metal intake by fish in polluted aquatic media depends on ecological requirements, metabolism and other factors such as salinity, water pollution level, food and sediment (Ashraf *et al.*, 2012) [10]. The heavy metal profile in smoked *Cynoglossus senegalensis* was Zn>Cu>Pb>Cd, with Zn clearly dominating the overall quota status, an indication that the fish species conceivably bioaccumulated more of Zn than the other metals from its host aquatic medium. In the same realm, the opposite scenario may have been the case for Cd. Bioaccumulation measurements refer to studies or methods monitoring the uptake and retention of pollutants like metals or biocides in tissues of organisms such as fish (Nussey, 2000) [19]. The bioaccumulation of heavy metals in living organisms and biomagnifications describes the processes and pathways of pollutants from one trophic level to another (Akan *et al.*, 2012) [3]. In bioaccumulation process the tissues of a living organism can absorb toxic metals if their availability is very high in the environment or food (Aldogachi *et al.*, 2016) [5]. It has been reported that elements can be introduced by smoke in addition to those absorbed through ingestion of contaminated food or through the gills from the surrounding water and concentrations could reach toxic levels (Ako and Salihu, 2004) [4]. It was observed that there were no significant differences (P>0.05) in the concentrations of heavy metals in fish between markets, probably because the smoked fish product may have been sourced from the same processors or distributors. There were however significant differences (P<0.05) in the concentrations of Zn and Cu in fish between between months, probably as a result of seasonal variation in the levels of these metals in the aquatic media of fish. Wangboje and Oghenesode (2016) [24], ascertained the levels of some heavy metals in smoke-dried Bonga fish (*Ethmalosa fimbriata)* sold in fish markets in Warri, Niger Delta, Nigeria and reported much higher values for Pb (2.62 mg/kg), Cd(0.19 mg/kg), Zn(87.90 mg/kg) and Cu(18.89 mg/kg) than was observed in this study. The seemingly higher values obtained in the former study may be attributed to the peculiarities of the host environment. For example, crude oil exploration activities take place in Warri compared to Owo which is totally void of such activities. It was observed that the EADI for heavy metals via potential consumption of fish was the least for Cd and highest for Zn. This is not surprising against the backdrop that Zn had the highest mean concentration and invariably the highest quota off all the metals in fish. The reverse scenario was the case for Cd. In effect, it would therefore mean that potential consumers of this smoked fish species would be exposed more to Zn and least exposed to Cd. According to Herber *et al.*, (2001) [15], the level of exposure could be acute or chronic depending on the duration such exposure. Heavy metals become toxic when they are not metabolized by the body and accumulate in soft tissues (Aldogachi *et al.*, 2016) [5]. The total heavy metal load in fish by market revealed that the least and highest values were recorded for Jokes motors market and Oba market respectively. The immediate implication of this finding is that potential consumers of smoked fish would be conceivably subjected to a greater metal burden should they decide to purchase fish from Oba market compared to Jokes motors market. The TMDI for heavy metals in this study was 2414 mg/person/day, with Zn and Cu contributing more to this value by having higher individual TMDI scores than Pb and Cd. This is attributed to the fact that Zn and Cu had higher guideline values or maximum allowable limits in fish than Pb and Cd. For example, the Food and Agriculture Organization of the United Nations (FAO) has published limits of 30 mg/kg for Zn and Cu in fish (FAO, 1983) [13] while Codex Alimentarius (2015) [11] has established limits of 0.30 mg/kg and 0.05 mg/kg for Pb and Cd in fish respectively. A TTM value of 6.25 was recorded in this study which clearly surpassed unity, indicating that the guideline values for heavy metals were surpassed (ANZECC/ARMCANZ, 2000). This assertion is buttressed by the fact that the mean concentrations of Pb, Cd and Zn in fish were all above the aforementioned limits for heavy metals in fish. The TQ values for Pb, Cd and Zn were all above unity, indicating a risk to the fish consuming public, the only exception being Cu. Apart from natural/lithogenic sources, Pb can come from batteries, alloys, solders, fossil fuels, plastics and pesticides while Cd can come from batteries, fossil fuels, fertilizers, plastics, alloys and paints. Zinc can be sourced from batteries, landfills, pesticides, alloys, dyes, fossil fuels, electroplating and metallurgical processes (Wangboje and Ekundayo, 2013) [23]. It becomes logical to categorically state that smoked *Cynoglossus* *senegalensis* must therefore be consumed with caution because of the risk associated with heavy metal poisoning especially from Pb, Cd and Zn. The adverse health effects of the aforementioned heavy metals have been well articulated (Food Safety Authority of Ireland, 2009; Jayaprabha *et al.*, 2014) [14, 7].

Conclusion

The study successfully ascertained and quantified the levels of Pb, Cd, Zn and Cu in smoked *Cynoglossus senegalensis* purchased from selected markets in Owo town, Ondo state, Nigeria. The applied ecological risk indices revealed that there is a glaring potential for heavy metal poisoning especially with regard to Pb, Cd and Zn. It is therefore imperative that smoked *C. senegalensis* be consumed with caution by people who patronize the aforesaid markets for the product in Owo town, in order to avert deleterious health effects in the long run.

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