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Heavy Metals Levels in Dried Fish Consumed in Benin and Warri Metropolis; Levels and Health Risk Assessment

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ABSTRACT: Heavy metals levels in dried *Clarias gariepinus* and *Channa obscura* from three major markets in Benin metropolis were investigated in this work. Samples were purchased, dried and digested by standard method and the metals levels were determined using Atomic Absorption Spectrophotometer (AAS). The mean levels of cadmium and lead (0.48±0.06 and 1.36±1.13 mg/kg) and (0.62±0.45 and 5.60±7.43 mg/kg) for *Clarias gariepinus* and *Channa obscura* were found to be higher than EU standard. Zinc, Cu, Cr, Fe and Mn had mean values of 2.2±0.85 and 3.18±3.36 mg/kg, 4.12±0.92 and 3.44±0.76 mg/kg, 0.11±0.02 and 0.26±0.3 mg/kg, 25.74±8.06 and 8.55±2.95 mg/kg, 1.8±0.56 and 0.6±0.21 mg/kg for *Clarias gariepinus* and *Channa obscura* respectively. The Estimated Daily Intake calculated were low and Target Hazard Quotient<1 with no risk of non-cancer toxic effect in both species. The levels of cadmium and lead in the dried fish suggest the need to constantly monitor these metals in our water bodies as well as our foods.

Key words: Heavy metals, fish, health risk

Introduction

Fish is a highly perishable food, and smoking has been a preferred cheap method of preservation. This method is carried out over smouldering wood, saw dust, or other sources of energy using traditional kilns constructed with locally sourced materials (Ako and Salihu, 2004). Fish is a valuable and cheap source of protein to man and dried cat fish has been a favoured delicacy option especially in Nigeria. But the rapid development of industrialization has resulted in heavy metal pollution in our water bodies, which is a significant environmental hazard for invertebrates, fish and humans (Uluturhan and Kucuksezgin 2007).

Heavy metals tend to accumulate in advanced organisms through bio-magnification along the food chain. Through this, they enter into human tissues, posing serious chronic toxicity. Chronic assimilation of heavy metals is known to cause cancer (Nabawi *et al.,* 1987) and can damage vital organs. Raikwar *et al.,* (2008) found that heavy metals such as Cd, Ni, As, Pb pose a number of hazards to humans. These metals are also potent carcinogenic and mutagenic elements. Heavy metal toxicity can result in damaged or reduced mental and central nervous system function, lower energy levels, and damage to blood composition, lungs, kidney, liver and other vital organs. Long term exposure may result in slowly progressing physical, muscular, and Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis (International Occupational Safety and Health Information Centre, IOSHIC 1999).

Heavy metal intakes by fish in polluted aquatic environment results in the accumulation of metals in tissues through absorption and humans are exposed through the food web. This causes acute and chronic effect

on humans (Fidan *et al.,* 2008). Risk assessment is the fastest method used to evaluate the impact of the hazards on human health (Zhang *et al.,* 2008) and estimated daily intake and target hazard quotient are indices that are often used (USEPA 1997). Thus as dried fish continue to occupy its important place as a delicacy in Nigeria dishes and technologies in harvesting, and processing remains crude, there is need to assess its probable contamination with heavy metals as well as the likely risk associated with its consumption which this study attempts to resolve.

Materials and Methods

***Study Area*:** The study was conducted in Benin City (6° 20' 5.95" N 5° 36' 13.486" E) in Edo State and Koko (6°0'3.68"N and 5°27'52.83"E) in Warri North Local Government Area of Delta State. The three markets where the samples were purchased are located in areas that receive products from riverine communities where oil exploration and other industrial activities are intense.

***Sample Collection and Preparation*:** The samples for this study; smoked *Clarias gariepinus* and *Channa obscura* were purchased from two different markets in Benin City; Ikpoba hill, and Ekenwan markets and a market from Delta state, Koko market. The samples were transported to the laboratory with a sterile polythene bag.In the laboratory, the samples were dried at 70°C for 1 hour and homogenized using a stainless steel micro hammer mill. The milled samples were stored in a glass vial for digestion and further analysis.

***Sample Digestion and analysis*:**Wet digestion of food was performed with nitric acid – perchloric acid – sulphuric acid (HNO_3–$HClO_4$–H_2SO_4). This procedure is for preparing samples for the determination heavy metals (Radojevic and Bashkin, 1999). About 0.2 g of the sample material was weighed. Then 10 ml of the nitric acid, 5 ml of perchloric acid and 10 ml of sulphuric acid was added, a small glass funnel was inserted to act as a reflux condenser and the mixture was heated for 15-30 min at 150 °C, when dense white fume was observed, the beaker was removed from the block, cooled to about 100 °C until a colourless solution was obtained. The solution was poured into a 100 ml flask and washed 5 times with water each time adding the washing to the flask. The solution was made to desired volume with water and the samples were read for heavy metals using AAS.

***Health Risk Assessment*:** Estimated Daily Intake **(**EDI): was calculated using the following equation, which is recommended by the US EPA (1997).

$$\mathrm{EDI} = \frac{\mathrm{C} \times \mathrm{IR} \times \mathrm{EF} \times \mathrm{ED}}{BW \times AT}$$

Where EDI is the average daily intake or dose through ingestion (mg/kg bw/day); C is the heavy metal concentration in the exposure medium (mg/L or mg/kg); IR is the ingestion rate (L/ day, or kg/day); EF is the exposure frequency (365 days/year); ED is the exposure duration (54 years, equivalent to the average lifespan); BW is the body weight (kg) and AT is the time period over which the dose is averaged (365 days/year × number of exposure years, assumed to be 54 years in this study).

***Target Hazard Quotient (THQ)*:** The human health risk posed by contaminant exposure are usually characterized by the target hazard quotient (THQ) (USEPA 1997), the ratio of the average estimated daily intake (EDI) resulting from exposure compared to the reference dose (RfD) for an individual pathway and chemical. The THQ based on non-cancer toxic risk was determined by;

$$\mathrm{THQ} = \frac{EDI}{RfD}$$

If the value of THQ is less than 1, the risk of non-carcinogenic toxic effects is assumed to be low. When it exceeds 1, there may be concerns for potential health risks associated with overexposure.

Results

The results for heavy metals, Estimated Daily Intake (EDI) and Target Hazard Quotient (THQ) for *Clarias gariepinus* and *Channa obscura* are presented in Tables 1 and 2 below.

Table 1: Summarized data on heavy metal concentrations in the two fish species

	Clarias gariepinus				*Channa obscura*						
parameters (mg/kg)	mean	SD	Min	Max	mean	SD	Min	Max	P-Value	Standard	Reference
Cu	4.12	0.92	3.35	5.14	3.44	0.76	2.68	4.2	P>0.05	NA	
Cd	0.48	0.06	0.42	0.53	0.62	0.45	0.11	0.95	P>0.05	0.1µg/g	EU 2008
Zn	2.2	0.85	1.5	3.15	3.18	3.36	0.5	6.95	P>0.05	NA	
Pb	1.36	1.13	0.05	2.02	5.6	7.43	0.79	14.15	P>0.05	0.30mg/kg	EU 2008
Cr	0.11	0.02	0.09	0.13	0.26	0.3	0.08	0.6	P>0.05	NA	
Fe	25.74	8.06	17.37	33.46	8.55	2.95	5.15	10.29	P<0.05	15µg/g	Tuzen&Sylak 2007b
Mn	1.8	0.56	1.22	2.34	0.6	0.21	0.36	0.73	P<0.05	NA	

P<0.05 – Significant difference
P>0.05 – No significant difference
NA – Not Available, ND – Not detected.
Mean values reported in mg/kg

Table 2: Health risk assessment of heavy metals in sampled fish species

Fish Sp	*Claria gariepinus*							*Channa obscura*						
	Cu	**Cd**	**Zn**	**Pb**	**Cr**	**Fe**	**Mn**	**Cu**	**Cd**	**Zn**	**Pb**	**Cr**	**Fe**	**Mn**
EDI	0.0025	0.0003	0.0014	0.0008	0.0001	0.0158	0.0011	0.0021	0.0004	0.0020	0.0034	0.0002	0.0053	0.0004
THQ	0.0633	0.2949	0.0045	0.2321	0.0000	0.0226	0.0079	0.0528	0.3809	0.0065	0.9556	0.0001	0.0075	0.0026

EDI values are reported in – mg/kg bw/day

Discussion

From the study, Cu had a mean value of 4.12±0.92 mg/kg in *Clarias gariepinus* which was higher than 3.44 mg/kg in *C. obscura* and also higher than 0.0205 µg/g reported by Amirah *et al.,* (2013). The EDI in both were quite low and the THQ <1 but Cd in both species of fish was found to be higher than EU standards of 0.1 µg/g. Cd had a mean of 0.48±0.06 and 0.62±0.45 mg/kg for *Clarias gariepinus* and *C. obscura* respectively, besides these values were higher than 0.0004 µg/g reported by Amirah *et al.* (2013).

Zinc was found to be higher in *C. obscura* with a mean of 3.18±3.36 mg/kg as against 2.2±0.85 mg/kg in *Clarias* sp, whereas Pb in *Clarias* sp with mean concentration of 1.36±1.13 mg/kg was found to be far lower than 5.6±7.43 reported in *C. obscura*. These levels were found to be extremely higher than 0.30 mg/kg set by EU (2008) hence there is a potential risk of Pb poisoning or toxicity when these species are consumed. Lead (Pb) toxicity results in decrease of haemoglobin production, disorder in the working of kidney, reproductive system joints and cardiovascular systems and causes long lasting injury to the central and peripheral nervous systems (Nolan, 2003). Cr level was quite low in this study with a mean concentration of 0.11±0.02 mg/kg and 0.26±0.30 mg/kg in *Claria gariepinus* and *C. obscura* respectively. Iron (Fe) recorded the highest value in this study with a mean of 25.74±8.06 mg/kg in *C. gariepinus* and 8.55±2.95 mg/kg for *C. obscura*. These values were found to be significant across the sampled species (P<0.05). Mn also showed a level of significance across the species (P<0.05) with a mean value of 1.8±0.56 mg/kg and 0.60±0.21 mg/kg in *C. gariepinus* and *C. obscura* respectively. Mercury (Hg) was not detected throughout the study. Mn, Zn, Cr, in this study were found to be below the findings of Eletta *et al.,* (2003) who investigated the heavy metal concentrations in two fish

species reported a mean values that ranged from 0.56 – 2.69, 5.62 – 15.11, 0.09 – 0.35 ppm respectively while their Fe and Pb concentrations of 3.79 – 18.16 and 0.78 – 1.57 ppm were below the findings of this study.
The EDI for this study were quite low and also below JECFA set standard for metals in fish. But the THQ were all below 1 suggesting no potential risk of non-carcinogenic toxic effect except the THQ for Pb in *C. obscura* whose value is approximately 1.

In conclusion, the results from this study suggest that the fish sampled were not totally free from heavy metal contamination. Hence, consumption of various delicacies prepared with dried fish may lead to bioaccumulation of these metals in tissues, thus posing health risk. There is therefore the need to constantly monitor these metals in our water bodies as well as our foods.

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