Journal of Chemical Health Risks

ORIGINAL ARTICLE

Determination of Heavy Metals Contamination on Smoked Fish Sold at Some Fish Markets in Borno State, Nigeria

Mathias Nzitiri Bwala[*1], Tijjani Sabiu Imam[2], Idris Umar Zungum[3]

[1]*National Environmental Standards and Regulations Enforcement Agency (NESREA), Borno State, Nigeria*

[2]*Department of Biological Sciences, Bayero University, Kano State, Nigeria*

[3]*Department of biological science, Federal University Gashua, PMB 1005, Yobe State, Nigeria*

ABSTRACT: Fish smoking is the oldest known traditional method of fish processing and preservation. Fish provide the protein needed for bodybuilding and repairs of tissues, and form part of a healthy balanced and nutritious diet. Heavy metal contamination on ingested food substances is an issue of a serious health concern due to their high level of toxicological effects on humans. Fish products may become contaminated during processing or as a result of the intake of heavy metals from a polluted aquatic environment. The study was aimed at assessing the level some Heavy Metal (Pd, Cr, Cd, Hg, and As) contamination of smoked fish sold at Maiduguri fish markets. Fish samples (Smoked and unsmoked) were obtained from 8 major fish markets in Borno State. The samples were oven-dried and grounded. The grounded samples were digested using concentrated nitric acid and hydrogen peroxide (2:1) v/v and analyzed for heavy metals using AAS both at the Chemistry Department, Yobe State University, Damaturu. The results obtained, reveals that Cr, As, and Hg concentrations were below the set national permissible limits as set by NAFDAC in all sampling stations in the study area while Pd concentration exceed the set permissible limit in sample station E and F (2.768 ± 0.251 and 2.602 ± 0.241 mg kg^{-1} respectively). Furthermore, Hazard index (HI) values of the heavy metals (Pd, Cd, Cr, As, and Hg) were all greater than 1, revealing an unacceptable level of non-carcinogenic adverse health effects. The study recommends a continuous assessment of the level of heavy metals in smoked fish from the study area.

INTRODUCTION

Fish represent forms part of a healthy and balanced nutritious diet and provide the needed protein for bodybuilding and repairs of tissues. Fish contains vital micronutrients such as iodine, zinc, iron calcium, for many households [1-3]. Fish smoking is the oldest known traditional method of fish processing and preservation [4]. It was estimated that about 61% of fish products consumed and available stock in the market in Nigeria is smoked fish [5].

Food commercial handling and processing could increase the level of heavy metal contaminants, [6] as processes such as smoking, drying, frying, roasting, etc reduces the moisture content thereby increasing the concentration of heavy metals. Processed food substances are also being preserved with chemicals that may contain trace amounts of heavy metals with bioaccumulation potential.

Smoked fish samples were reported to have higher concentrations of heavy metals than the fresh samples

[6]. Roasted snacks were reported to possess a high concentration of chromium and lead compared to the raw food item, surprisingly, roasted plantain was reported to have a lower concentration of lead (0.0048 μg g^{-1}) than the raw (0.0074 μg g^{-1}) [7].

Thermal treatments and processing of food at high temperature having direct contact with combustion gases, such methods as smoking, results in direct microbial destruction [6]. and also leads to the concentration of other nutrients which may include heavy metals due to a reduction in moisture content in such food [6, 8]. Although, fish may intake heavy metals from their polluted environment, processing and preservation methods like smoking and the use of chemicals to preserve and enhance longevity may have an effect on the level of heavy metals contamination and hence the need to assess the impact of such methods for effective health risk management.

The smoked fish from Borno State, Nigeria is one of the commonest fish products and is widely patronized by many families across Nigeria. The Borno State smoked fish products are also exported across to the region of Chad, Niger, and the Cameroun Republic [9]. An assessment conducted by Adah [5]. Revealed a low level of hygiene during processing, preservation, and packaging as only 16% were observed to practice a very high level of hygiene; this also possesses serious health risks and concerns.

MATERIALS AND METHODS

The study area

The study was conducted in Borno State, Northeastern, Nigeria. The State is located between latitudes 10°N and 14°N and longitudes 11°31E and 14°41E, and has a total area of 61, 435km^2. The State is the second-largest state in terms of land mass in the Federation. It occupies a substantial part of the Chad Basin, and it's known for its fishing activities. Fishermen and traders preferred to smoke their fish products as a preservation techniques, and export the same to the remaining part of the country and other countries it shares borders with, the Republics of Niger to the North, Chad to the North-East, and Cameron to the East [9-11].Figure 1 shows the locations of the sampling stations in the study area.

Sampling stations

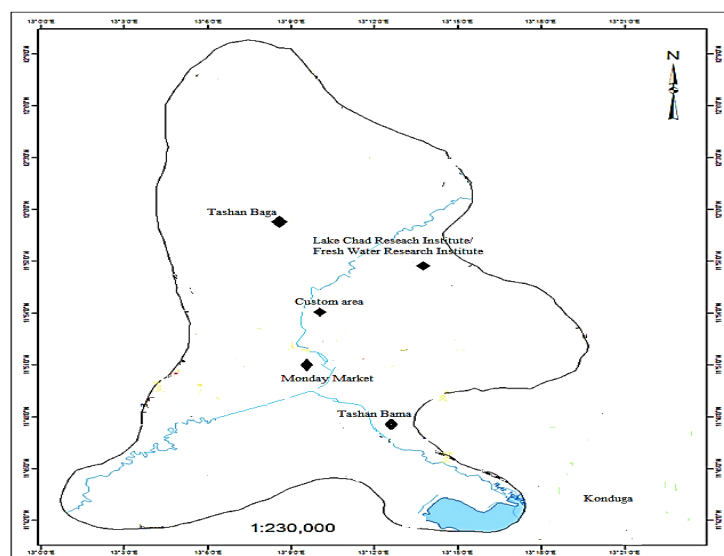Fish samples were collected from the following stations as shown in Table 1.

Figure 1. Map of Maiduguri and environs showing the sampling stations.
Sources: [12].

Table 1. Sampling stations.

S/ N	Station	Location	GPS Coordinate	Fish Sample Collected
1	A	Tashan Baga Fish Market, Maiduguri	11° 51' 58.02" N 13° 7' 11.14" E	✓ Smoked
2	B	Maiduguri Monday Market	11° 49' 54.02" N 13° 9' 16.72" E	✓ Smoked
3	C	Custom Market, Maiduguri	11° 51' 8.36" N 13° 10' 20.51" E	✓ Smoked
4	D	Tashan Bama, Maiduguri	11° 48' 39.53" N 13° 10' 53.02" E	✓ Smoked
5	E	Gomburu Market	11° 51' 1.37" N 13° 10' 30.69" E	✓ Smoked
6	F	Konduga village (Sabon Gari), Konduga LGA	11° 38' 46.24" N 13° 25' 00.35" E	✓ Smoked and unsmoked ✓ Smoked samples marked as **F1** ✓ Unsmoked samples marked as **F2**
7	G	Baga town	13° 07' 18.69" N 13° 51' 50.79" E	✓ Smoked and unsmoked ✓ Smoked samples marked as **G1** ✓ Unsmoked samples marked as **G2**
8	H	Bulunkutu Kasuwa	11° 50' 5.50" N 13° 5' 10.04" E	✓ Smoked

Fish sample collection

Unsmoked fish samples

Unsmoked fish samples were brought directly from the fishermen/fish processors (smokers) at two (2) different sampling stations (Baga town and Konduga).

Smoked Fish samples

Smoked fish samples were brought from traders in eight (8) different locations within the study area as follows: Maiduguri Monday Market, Gomburu Market, Tashan Baga, Tashan Bama, Custom Market, Bulunkutu Kasuwa, Baga town, and Konduga.

Sample processing

The smoked fish samples obtained from the sampling stations were oven-dried at 105^0C temperature for 10h, while the fresh fish samples were oven-dried for 144h (6 days). The samples will then be ground and kept in air tight containers before the extraction process [13].

Heavy metal determination

Digestion

The powdered (grounded) sample was subjected to digestion using concentrated nitric acid and hydrogen peroxide (2:1) v/v according to [14]. Two grams (2g) of the grounded sample were weight into a digestion tube and then HNO_3 (65%) and H_2O_2 (30%) (2:1) were added and allowed for reaction. The content of the digestion tube was then mounted onto the digestion chamber for 2 – 3 hours and reduced to about 4 – 5mL. The digested sample was then allowed to cool and filtered and then topped up with deionized water and marked for the Heavy metal analysis.

Heavy analysis

The digested samples were subjected to heavy metals (lead, mercury, arsenic, cadmium, and chromium) analysis using Atomic Absorption Spectrophotometer (Buck Scientific Model 210 VGP) at Chemistry Department, Yobe State University.

Statistical analysis

Data obtained was tabulated using Microsoft Excel 2010 and a simple descriptive statistical tool was used.

Health risk assessment of heavy metal

To assess the potential health risks associated with long-term ingestion of vegetables contaminated with heavy metals, the Average Daily Dose (ADD) of heavy metals, Target Hazard Quotient (THQ), and Hazard Index (HI) were calculated

Average Daily Dose (ADD)

$$ADD = EF \times ED \times C_i \times InR \ / \ BW \times AT \text{ cited in [15-17].}$$

Where: C_i is the concentration of heavy metals (kg kg^{-1});

InR is the ratio of smoked fish intake of 0.5kg d^{-1}

EF is exposure frequency (365 d/a);

ED is exposure duration (70 years);

BW represents the average body weight (60 kg);

AT represents the average exposure time for non-carcinogenic effects (70 years);

Target Hazard Quotient (THQ)

Target hazard quotient is a ratio of the determined dose of a contaminant to the oral reference dose considered detrimental. If the ratio is greater than or equal to 1, an exposed population is at risk. The non-carcinogenic was computed as

$$\text{Hazard Quotient (HQ)} = ADD \ / \ RFD$$

Where ADD is the average daily dose

RfD is the daily reference dose of heavy metals (μg (kg·d)$^{-1}$),

Reference dose

The reference dose is the maximum amount of a chemical (in mg kg^{-1} body weight day^{-1}) that the human body can absorb without experiencing chronic health effects over a lifetime [17, 18]. The Reference dose of the analyzed heavy metals is presented in Table 2.

Table 2. Reference Dose of some Chemical Hazards.

Heavy Metals	R_fD (mg kg^{-1}day^{-1})	Reference
Arsenic (As)	3×10^{-4}	[18]
Lead (Pd)	1.4×10^{-4}	[18]
Mercury (Hg)	3.0×10^{-4}	[18]
Cadmium (Cd)	5×10^{-4}	[18]
Chromium (Cr)	3.5×10^{-3}	[18]

Hazard Index (HI)

Hazard Index was calculated using the formula below:

$$\mathbf{HI} = \sum THQ \text{ cited in [16]}$$

If the value of **HQ** or **HI** is **≤ 1.0**, there is no obvious health risk to individuals who patronizes the smoked fish; on the contrary, the non-carcinogenic risks are likely to occur when **THQ** or **HI** is **>1.0**, and the human health risk increases with the increase of THQ or HI [15-17].

RESULTS

Table 3 shows the level of heavy metals (Pb, Cd, Cr, As, and Hg) concentration in relation to the National Agency for Food and Drug Administration Control (NAFDAC) regulated standard on ingested food.

Table 3. Mean concentration of Heavy Metal (Pb, Cd, Cr, As, and Hg) with Standard Deviation on smoked fish sold at Maiduguri fish markets.

Sampling Station/Heavy Metal	Lead (Pb) (mg kg^{-1})	Cadmium (Cd) (mg kg^{-1})	Chromium (Cr) (mg kg^{-1})	Arsenic (As) (mg kg^{-1})	Mercury (Hg) (µg Kg^{-1})
NAFDAC Standards	2.00	0.20	2.00	0.5	0.1
A	1.199 ± 0.025	0.266 ± 0.006	0.471 ± 0.043	BDL	BDL
B	1.220 ± 0.111	0.934 ± 0.027	0.311 ± 0.007	0.100 ± 0.002	0.052 ± 0.003
C	1.099 ± 0.023	0.337 ± 0.017	0.696 ± 0.029	0.077 ± 0.002	BDL
D	1.974 ± 0.183	1.006 ± 0.093	0.437 ± 0.014	0.139 ± 0.013	BDL
E	2.768 ± 0.251	0.698 ± 0.064	0.658 ± 0.061	BDL	BDL
F	2.602 ± 0.241	0.826 ± 0.077	1.144 ± 0.106	BDL	0.035 ± 0.004
F2	0.612 ± 0.013	0.194 ± 0.004	0.051 ± 0.005	BDL	BDL
G	0.606 ± 0.055	0.548 ± 0.012	0.121 ± 0.011	BDL	BDL
G2	BDL	0.160 ± 0.015	0.033 ± 0.000	BDL	BDL
H	0.815 ± 0.016	0.347 ± 0.040	0.026 ± 0.004	0.026 ± 0.002	0.042 ± 0.001

Values are mean ± SD of the sample fish analyzed. **BDL**: Below Detectable Limit

Health risk assessment of heavy metals

Table 4 shows the human health risk associated with the Average Daily Dose (ADD) was determined using the mean concentrations of Pd, Cd, Cr, As, and Hg in the smoked fish from Borno fish markets.

Table 5 indicates that HQ was greater than 1 suggesting an unacceptable level of non-carcinogenic adverse health risk in all the sampling stations where the heavy metals were detected except for sampling station H, in which Cr and As are less than 1 suggesting an acceptable level of non – carcinogenic adverse health risk of the heavy metals.

Table 4. Average Daily Dose (ADD) of the smoked fish from the study area.

Sampling Station/Heavy Metal	Lead (Pb) (mg kg^{-1} day^{-1})	Cadmium (Cd) (mg kg^{-1} day^{-1})	Chromium (Cr) (mg kg^{-1} day^{-1})	Arsenic (As) (mg kg^{-1} day^{-1})	Mercury (Hg) (mg kg^{-1} day^{-1})
A	0.022	0.003	0.005	0	0
B	0.030	0.010	0.003	0.001	0.0006
C	0.028	0.004	0.008	0.0008	0
D	0.007	0.011	0.005	0.0015	0
E	0.007	0.008	0.007	0	0
F	0	0.009	0.013	0	0.0004
F2	0.009	0.002	0.001	0	0
G	0	0.006	0.001	0	0
G2	0	0.002	0.0004	0	0
H	0	0.004	0.0003	0.0003	0.0005

Table 5. Non-carcinogenic risk (Hazard Quotient, HQ) and overall toxic risk (Hazard Index, HI) of Smoked fish in the Study Area.

Sampling Station/Heavy Metal	Lead (Pb)	Cadmium (Cd)	Chromium (Cr)	Arsenic (As)	Mercury (Hg)	HI
A	154.395	5.825	14.736	ND	ND	174.956
B	216.497	20.455	9.730	3.65	1.898	252.230
C	203.514	7.380	21.775	2.810	ND	235.479
D	47.867	22.031	13.672	5.074	ND	88.644
E	47.398	15.286	20.586	ND	ND	83.270
F	ND	18.089	35.791	ND	1.278	55.158
F2	63.745	4.249	1.596	ND	ND	69.589
G	ND	12.001	3.786	ND	ND	15.787
G2	ND	3.504	1.032	ND	ND	4.536
H	ND	7.599	0.813	0.949	1.533	10.895

ND: Not detected

DISCUSSION

Lead

The results obtained, indicates that the mean concentration of Pb ranges from 0.00 (Below the Detectable Limit) to 2.768 ± 0.251 mg kg^{-1} in Sample Stations E and G$_2$ respectively. The results when compared with NAFDAC [19] regulated standards indicates that all the sample stations except for station E and F (2.768 ± 0.251 and 2.602 ± 0.241 mg kg^{-1} respectively) are within the set permissible limit (2.00 mg kg^{-1}). This is consistent with the findings of Igwegbe *et al*, [6] who reported a similar trend in smoked fish. There is a need for caution in the consumption of smoked fish from Sample Station E and F (Gamboru Market, Maiduguri, and Sabon Gari, Konduga) as they are slightly above the set national permissible limits (2.00 mg kg^{-1})[19] .

Ingestion of processed (smoked) fish contaminated with Pb can affect the central nervous system. It is particularly dangerous to babies and children. Pb exposure from contaminated food can result in stunt growth and development often with the following symptoms stomach upset, loss of appetite, headaches, sleeping problems, anemia, kidney dysfunction, hearing problems, memory loss, severe abdominal pain, and stumbling when walking [20].

Cadmium

From the results of this study, the mean concentration of Cd ranges from $0.160 \pm 0.015 - 1.006 \pm 0.093$ mg kg^{-1} in stations G2 and D respectively. Again, it is noteworthy that the unsmoked fish samples (station F2 and G2) recorded a lesser mean concentration of Cd (0.194 ± 0.004 and 0.160 ± 0.015 mg kg^{-1} respectively) and were the only stations below the national threshold (0.02 mg kg^{-1}) as set by NAFDAC[19] .This implies that either smoking or the use of additives (preservatives) on the smoked fish may have attributed to the increase in the concentration of Cd on the smoked fish. Igwegbe *et al.,* [6]. Suggested that smoking may increase the level of concentration of heavy metals in the smoked fish. The results of Cd concentration in this study were higher than those obtained from other studies [6, 21]. The results of this study call for concern as Cd has no known beneficial function in the human system. Cd is transported in the blood and is reported to accumulate in the liver and kidney. It poses a great toxic effect on the human kidney, the respiratory and skeleton systems. It also has carcinogenic effects on humans making it to be classified as a human carcinogen [22].

Chromium

The mean Cr concentration ranges from $0.026 \pm 0.004 - 1.144 \pm 0.106$ mg kg^{-1} in sample stations H and F respectively. All the stations measured were below the permissible national limits (2.00 mg kg^{-1}) as set by NAFDAC[19]. This is consistent with the findings of [10]. The Cr concentration was also detected in the

control samples (unsmoked fish) (0.051 ± 0.005 − 0.033 ± 0.000 mg kg^{-1} in station F2 and G2 respectively) which negate the findings of Ismail and Saleh, [8]. The concentration of Cr in the smoked fish samples except for station H (0.026 ± 0.004 mg kg^{-1}) doubles that of the control (unsmoked) samples, this agrees with the findings [6, 21].

Cr from ingested contaminated food can bind to proteins to form complexes that are transported to the kidneys where it damages the kidneys [20].Other health effects include; Diarrhoea, Vomiting, Stomach upset, Fractures in bone, Mutagenicity and carcinogenicity effects, Fertility and teratogenicity, and damaging to the nervous and immune systems [23].

Arsenic

As concentration were detected in stations B, C, D and H (0.100 ± 0.002, 0.077 ± 0.002, 0.139 ± 0.013 and 0.026 ± 0.002 mg kg^{-1} respectively) and were below the national permissible limits (0.50 mg kg^{-1}) as set by NAFDAC [19]. It is noteworthy that As were not detected in the control (unsmoked) samples, this implies that the processing and handling (storage, preservation, etc.) may have contaminated the smoked fish [6, 21].

As ingestion from contaminated is food associated with blood in the urine, hair loss, stomach upset, convulsions, vomiting, diarrhoea, and it's also reported to affect the skin, liver, lungs, and kidneys which may lead to a coma or even death [20].

Mercury

Hg concentrations were detected in station B, F and H (0.052 ± 0.003, 0.035 ± 0.004 and 0.042 ± 0.001 μg Kg^{-1} respectively). All the detected Hg concentration was within the permissible standards (0.1 μg Kg^{-1}) as set by NAFDAC[19]. Hg also was not detected in the control (unsmoked) samples; this implies that the processing and handling may have contaminated the smoked fish[6, 21] .

Ingestion of food contaminated with Hg can manifest with stomach upset, chills, weakness, cough, dyspnea, renal failure, poor appetite, and may mimic viral diseases. Acrodynia and erethism are two distinct clinical syndromes associated with chronic exposure [20].

Health risk assessment of heavy metals

The results of the study indicate that Hazard Quotient (HQ) was greater than 1 suggesting an unacceptable level of non-carcinogenic adverse health risk in all the sampling stations where the heavy metals were detected except for sampling station H, in which Cr and As are less than 1 suggesting an acceptable level of non – carcinogenic adverse health risk of the heavy metals.

Hazard index (HI) values of the heavy metals (Pd, Cd, Cr, As, and Hg) were all greater than 1, indicating an unacceptable level of non-carcinogenic adverse health effects. Hence, the results of the high HI values recorded in the smoked fish in the study area might lead to aggregate risk through ingestion as the higher values of HI were reported to pose a great health risk to the individual exposed to the contaminated food [15-17].

The result of the high level of HI can have a more adverse effects on a special categories of people in the populations (people with weak systems (underlying health issues), sensitive, and pregnant women) the potential human health risks of heavy metal accumulation through smoked fish consumption. Though, smoked fish intake is just a proportion of food consumed, supplementary or complementary food that may include vegetables [15, 17], meat, rice [24] and tobacco [25].that are consumed can also contribute to and/or increase amounts of heavy metals [15-17].

CONCLUSIONS

The different levels of heavy metal contaminations on smoked fish from the study area calls for strict enforcement of the regulated standards as it possesses health implications, particularly cadmium contaminations (in all the stations) and Lead (in station E and F).

ACKNOWLEDGEMENTS

Conflict of interests

No conflict.

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