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Original Article

Assessment of Heavy Metal Concentrations in Fresh and Smoked-Dried Catfish from Delta State, Nigeria

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ABSTRACT: *Fish represent a critical source of animal protein, but they also serve as a potential vector for microbial and chemical contaminants. This study evaluated the presence of heavy-metal concentrations (Hg, Pb, Cd) in fresh and smoked Clarias gariepinus sampled from five markets (Amai, Abbey, Kwale, Umutu, Obiaruku) in Ukwuani LGA, Delta State, Nigeria. A total of 50 samples were collected across wet and dry seasons. Heavy metals were quantified using atomic absorption spectrophotometry following acid digestion. The heaviest metal loads were in Amai samples: Hg (0.992 mg/kg), Pb (0.534 mg/kg), and Cd (0.520 mg/kg), exceeding regulatory thresholds. The elevated heavy-metal concentrations suggest a compounded food-safety risk. We recommend strengthened market hygiene, continuous monitoring of fish for both microbial and chemical hazards, and interventions to mitigate environmental metal pollution.*

KEYWORDS: *Clarias Gariepinus, Heavy Metals, Smoked Fish; Fresh Fish, Food Safety; Nigeria.*

1. INTRODUCTION

Fish represents a cornerstone of global food security and nutrition, providing over 3.3 billion people with almost 20% of their average intake of animal protein and essential micronutrients such as omega-3 fatty acids, vitamins, and minerals (FAO, 2022). In Nigeria, as in many developing nations, the demand for fish protein far outpaces supply from domestic capture fisheries, leading to a growing reliance on aquaculture and imported products. Among the most popular and culturally significant fish species consumed is the catfish (*Clarias gariepinus*), prized for its hardiness and taste. A critical challenge to food safety in this context is the preservation of fish, a highly perishable commodity. In West Africa, traditional hot smoking in open-fire kilns remains the most prevalent and affordable preservation method, significantly reducing post-harvest losses and extending shelf life (Adeyeye *et al*., 2018). However, the safety of this widely consumed product is increasingly threatened by anthropogenic pollution. Rapid industrialization, uncontrolled urbanization, mining activities, and the extensive use of agro-chemicals have led to the discharge of toxic heavy metals into aquatic ecosystems (Jaishankar *et al*., 2014). Metals such as lead (Pb), mercury (Hg), and cadmium (Cd) are non-biodegradable, persist in the environment for long periods, and have a high potential for bioaccumulation in the tissues of aquatic organisms like fish.

The human health implications of dietary exposure to these metals are severe and well-documented. Lead (Pb) is a potent neurotoxin particularly harmful to children's cognitive development. Mercury (Hg), especially in its methylmercury form which biomagnifies in the food chain, causes neurological and developmental damage. Cadmium (Cd) is a classified human carcinogen that accumulates primarily in the kidneys, leading to renal dysfunction and bone disease (Godt *et al*., 2006; Clarkson & Magos, 2006). While numerous studies have assessed heavy metals in fresh fish, the impact of the traditional smoking process on metal concentrations is less understood and can be paradoxical. The process could potentially reduce certain metal concentrations through the expulsion of fluid and fat (dripping loss), or it could act as a vector for contamination if the burning fuel, often sourced from industrial or treated wood, is itself polluted (Asante *et al*., 2020). This study was therefore designed to (i) determine and compare the concentrations of Pb, Hg, and Cd in fresh and smoked-dried catfish obtained from five major markets in Delta State, Nigeria, and (ii) evaluate the compliance of these concentrations with the maximum permissible limits set by the Food and Agriculture Organization (FAO) to assess potential public health risks.

2. MATERIALS AND METHODS

2.1. STUDY AREA

Ukwuani Local Government Area is found in Delta State, South – South Geopolitical Zone of Nigeria with the headquarters of the area in Obiaruku. The LGA is made up of several towns and villages which include Amai, Abbey, Kwale, Umutu and Obiaruku. The estimated population of Ukwuani LGA is put at 212, 224 inhabitants with the area predominantly occupied by members of the Ndokwa Ethnic group. The Local Government is best known as the home of agriculture, oil and gas, and hospitality. Fishing also booms in Ukwuani LGA with the area's water bodies being rich in seafood.

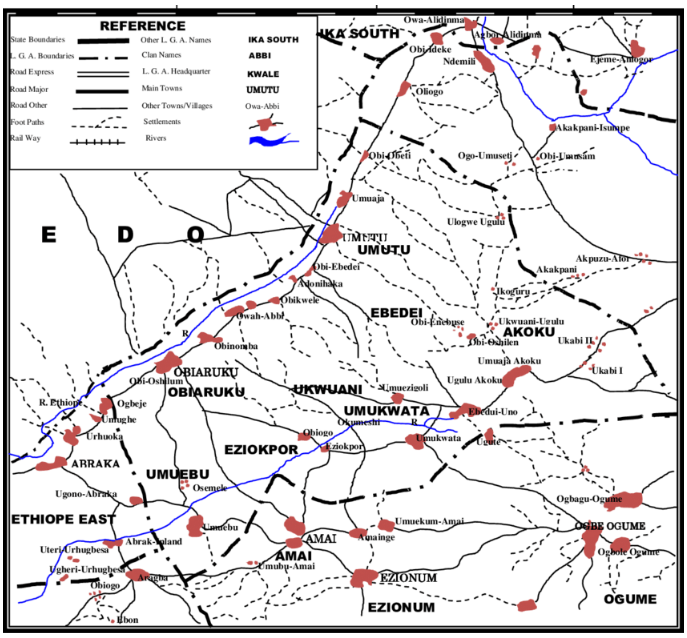

FIGURE 1 Map of Ukwuani Local Government Area

***Source*: Ukwuani Local Government Secretariat, 2022.**

2.2. SAMPLE COLLECTION

A total of 50 samples of the African sharptooth catfish (Clarias gariepinus) were purposively collected from five major markets: Amai, Umutu, Abbey, Obiaruku, and Kwale. These markets were selected due to their high volume of fish trade and representation of different catchment areas. From each market, five fresh (wet) and five traditionally smoked-dried catfish samples of comparable size (average weight: 250g ± 50g) were purchased between January and March 2023. This ensured a total of 25 fresh and 25 smoked samples. All samples were individually wrapped in clean, pre-labeled polyethylene bags, placed in an ice chest, and transported to the laboratory for analysis.

2.3. SAMPLE PREPARATION AND DIGESTION

In the laboratory, each fish sample was thoroughly washed with distilled water to remove external contaminants. Edible muscle tissues were carefully dissected using a stainless-steel knife, avoiding bones and internal organs to standardize the analysis. The muscle tissues were then oven-dried at 105°C for 24 hours until a constant weight was achieved. The dried samples were pulverized into a fine, homogenous powder using an agate mortar and pestle to prevent metallic contamination. Approximately 2.0 grams of each homogenized sample was accurately weighed into a 100 mL Pyrex digestion flask. A mixture of 10 mL of concentrated analytical-grade nitric acid (HNO_3, 69%) and 4 mL of perchloric acid ($HClO_4$, 70%) was added. The flask was covered with a watch glass and placed on a hot plate at a temperature of 90°C for 1 hour, which was then gradually increased to 150°C until a clear, digestate was obtained and dense white fumes evolved, indicating complete oxidation of organic matter. The digestate was allowed to cool, filtered through Whatman No. 42 filter paper, and the volume made up to 50 mL with distilled deionized water in a standard volumetric flask. A procedural blank, containing only the acids, was prepared simultaneously following the same protocol to correct for any background contamination.

2.4. INSTRUMENTAL ANALYSIS

The concentrations of heavy metals (Lead-Pb, Mercury-Hg, and Cadmium-Cd) in the digested samples were determined using an Atomic Absorption Spectrophotometer (AAS) (Model: Agilent 240FS AA). The instrument was calibrated using standard solutions prepared from certified stock solutions (1000 mg/L) for each metal. Specific hollow cathode lamps for each element were used at their respective wavelengths. For mercury analysis, which requires higher sensitivity, a Cold Vapor AAS (CV-AAS) attachment was used following reduction with stannous chloride. All measurements were carried out in triplicate to ensure precision, and the mean value was recorded for each sample.

2.5. QUALITY ASSURANCE AND QUALITY CONTROL (QA/QC)

Rigorous quality control measures were implemented. The accuracy of the analytical procedure was verified by analyzing certified reference material (CRM) DORM-4 (Fish Protein) obtained from the National Research Council of Canada. The recovery rates for the metals in the CRM ranged between 92% and 105%, which was deemed acceptable. The precision of the method, expressed as the relative standard deviation (RSD) of the triplicate measurements, was consistently below 10%.

2.6. DATA ANALYSIS

The data for each metal, location, and processing type were pooled, and descriptive statistics (mean and standard error of the mean, SE) were calculated using Microsoft Excel 365. The mean concentrations were systematically compared against the maximum permissible limits (MPL) for heavy metals in fish as established by the Food and Agriculture Organization (FAO, 1983).

3. RESULTS

Table 1 represent the concentrations of three heavy metals (mean ± SE) in a total of 50 fresh and smoked catfish purchased from Amai, Umutu, Abbey, Obiaruku and Kwale. In Amai, the fresh and smoked fish Pb (lead) concentration were 0.249mg/kg and 0.534, in Hg (Mercury) were 0.433mg/kg and 0.992mg/kg (0. 992mg/kg was above the recommended limit of Food and Agricultural Organization but was within permissible limits of heavy metals in fish) while Cd (Cadmium) was 0.320mg/kg and 0.520mg/kg. In Umutu, the fresh and smoked fish Pb (lead) concentration were 0.219mg/kg and 0.001mg/kg, in Hg (Mercury) were 0.401mg/kg and 0.246 mg/kg while Cd (Cadmium) was 0.180mg/kg and 0.247mg/kg. In Abbey, the fresh and smoked fish Pb (lead) concentration were 0.001mg/kg and -0.007mg/kg, in Hg (Mercury) were 0.109mg/kg and 0.100 mg/kg while Cd (Cadmium) was 0.347g/kg and 0.120mg/kg. In Obiaruku, the fresh and smoked fish Pb (lead) concentration were 0.001mg/kg and 0.001mg/kg in Hg (Mercury) were 0.203mg/kg and 0.362mg/kg while Cd (Cadmium) was 0.136mg/kg and 0.158mg/kg. In Kwale, the results were within the normal range as recommended by Food and Agricultural Organization limits (FAO) and permissible limits in fish.

TABLE 1 Mean Concentration of Heavy Metals In Fresh And Smoked Dried Catfish

Catfish Location	Sample Type		Pb Mg/Kg +Ve Samples		Hg Mg/Kg +Ve Samples		Cd Mg/Kg +Ve Samples
		No	Means ±SE		Means ±SE		Means ±SE
Amai	Fresh	5	0.249		0.433		0.320
	Smoked	5	0.534		0.992		0.520
Umutu	Fresh	5	0.219		0.401		0.180
	Smoked	5	0.001		0.246		0.247
Abbey	Fresh	5	0.001		0.109		0.347
	Smoked	5	-0.007		0.100		0.120
Obiaruku	Fresh	5	0.001		0.203		0.136
	Smoked	5	0.001		0.362		0.158
Kwale	Fresh	5	-0.009		0.187		0.0193
	Smoked	5	-0.004		0.0599		0.0138
MPL	mg/kg		2.0				

Hg = Mercury,
Cd= Cadmium,
Pb= Lead,
MPL= maximum permissible limits for metals in fish
ND, Not-Detected
SE= Standard error of mean
pl = permissible limit

4. DISCUSSION

This study reveals a complex and location-dependent profile of heavy metal contamination in both fresh and smoked catfish from Delta State, Nigeria. The data indicates that the smoking process, often perceived merely as a preservation technique, can significantly alter the heavy metal load, acting in some cases as a pathway for contamination rather than a neutral process. The concentrations of Pb, Hg, and Cd varied considerably across the five locations, reflecting differences in environmental pollution and post-harvest practices.

The most striking finding of this study is the significant elevation of heavy metal concentrations in smoked fish from Amai. The Hg level in smoked samples (0.992 mg/kg) was more than double the concentration in fresh samples (0.433 mg/kg) and substantially exceeded the FAO permissible limit of 0.5 mg/kg. This suggests that the smoking process itself in Amai is a critical point of contamination. The source is likely the wood or other fuel used for smoking, which may have been contaminated with mercury, possibly from industrial or agricultural waste (e.g., fungicides or coal) (Fiedler *et al*., 2019). Upon combustion, mercury can volatilize and subsequently deposit onto the fish surface, leading to concentration. Similarly, the near-doubling of Cd and Pb in smoked versus fresh fish from Amai further supports the hypothesis of a contaminated fuel source. This finding aligns with studies like that of Asante *et al.* (2020), who reported that fish smoked with rubber wood and other industrial waste materials showed markedly higher levels of Cd and Pb compared to those smoked with clean wood.

Conversely, the data from Umutu and Abbey present a different narrative. In Umutu, smoking was associated with a dramatic reduction in Pb (from 0.219 mg/kg to 0.001 mg/kg) and a decrease in Hg. A plausible explanation for this is the "dripping loss effect," where fat and juices containing lipophilic or soluble metal complexes are expelled during the heating process (Adeyeye *et al*., 2018). The type of wood used in Umutu, potentially a cleaner, non-contaminated source, would not add metals while this purging occurs. The variation in Cd levels across locations underscores the influence of pre-smoking environmental exposure. For instance, the high Cd in fresh fish from Abbey (0.347 mg/kg) points to potential environmental contamination from phosphate fertilizers or electronic waste, which are known sources of cadmium (Godt *et al*., 2006). The subsequent reduction in Cd after smoking in Abbey could again be attributed to the dripping loss effect.

When compared to international standards, the implications for public health become clear. The elevated Hg in Amai's smoked fish is a significant concern due to mercury's well-documented neurotoxicity, particularly its harmful effects on fetal and child development (Clarkson & Magos, 2006). The Cd levels in Amai's smoked fish (0.520 mg/kg), which also exceed the FAO limit, pose a long-term risk of kidney and bone damage, as cadmium has a biological half-life of 10-30 years (Godt *et al*., 2006). While the Pb concentrations were within permissible limits across all samples, chronic exposure even to low levels can contribute to cumulative health risks.

5. CONCLUSION

Conclusion, this discussion highlights that the safety of smoked fish is not a given. It is a product of two major factors: the initial environmental contamination of the fish and the subsequent contamination or decontamination during the smoking process. The stark contrast between the hazardous levels found in Amai's smoked products and the safe levels in Kwale's underscores the urgent need for targeted regulatory interventions. These should include monitoring of smoking materials and educating processors on the critical link between fuel source and food safety.

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