

INVESTIGATING THE LEVEL OF HEAVY METAL ACCUMULATION IN SELLECTED FISH SAMPLES

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Abstract: The contamination of food with heavy metals is a significant concern due to the potential health risks if not addressed. This study focuses on assessing the levels of heavy metal pollution in fish samples obtained from two cold rooms in Owo, Ondo State, Nigeria. Fish contamination may originate from aquatic environments, storage conditions, industrial waste, agricultural activities, or geochemical structures, all of which impact water quality and aquatic species. Three types of fish samples from the two cold rooms were analyzed for heavy metal concentrations, revealing varying levels of accumulation. Zinc was the most prevalent in all fish samples, with sample F (1.433 mg/kg, Titus fish from cold room 2) showing the highest concentration, closely followed by sample E (1.431 mg/kg, Titus fish from cold room 1). The heavy metal levels in the samples ranged as follows: Cu (0.195–0.313 mg/kg), Cd (0.013–0.022 mg/kg), Cr (0.029–0.041 mg/kg), Zn (0.995–1.433 mg/kg), and Mn (0.310–0.453 mg/kg). Notably, the heavy metal contamination levels in all fish samples were below the limits recommended by WHO and FAO.

Keywords: contamination proximate, minerals, heavy metals, samples, water and fish.

1. INTRODUCTION

The environmental threat posed by heavy metals is more severe compared to other pollutants due to their non-biodegradable nature, ability to accumulate, and long biological half-lives. Once introduced into the environment, they are challenging to eliminate (Aderinola et al., 2009). The rising use of heavy metals in industrial processes has led to an increased release of these harmful substances into aquatic ecosystems (Aguso et al., 2005). The impact of heavy metals on aquatic environments has become a global concern (Yousafzai, 2008). Heavy metal contamination in water bodies puts public water supplies and fish consumers at risk (Uysal et al., 2009; Okunade et al., 2022). Owing to their persistence in the environment, toxic metals accumulate in the food chain, posing serious health risks to humans when ingested (Baharom & Ishak, 2015).

In developing countries, fish is a vital source of animal protein and essential nutrients required for maintaining a healthy body (Fawole et al., 2007). The diversity and abundance of fish in streams and rivers are remarkable. Fish constitutes approximately 42% of the protein intake in Nigerian diets and is rich in vitamin B12, polyunsaturated fatty acids, and amino acids (Emmanuel et al., 2020). Given the high cost of meat for many Nigerians, fish serves as a complementary protein source in their daily diet (Atta et al., 1997).

The term "fish" encompasses all aquatic animals, including scale/fin fishes, cartilaginous fishes like sharks and rays, amphibians, reptiles such as water snakes, tortoises, and turtles, as well as marine mammals like seals, whales, dugongs, and manatees, which have historically provided food, fuel, and coverings. It also includes mollusks, valued for their meat, shells, pearls, and dyes such as Tyrian purple, crustaceans like shrimp, crabs, and lobsters from both freshwater and marine

environments, and echinoderms like sea urchins and trepang. Fish has been a key component of the human diet for centuries. Nearly all freshwater and marine fish are edible and have long been an essential source of protein, fat, and vitamins A and D. Fish meal, containing about 60% protein and a high level of calcium phosphate, is highly valuable for feeding cattle and poultry. Fish unsuitable for human consumption is often processed into fish manure for agricultural use.

Heavy metals are metallic chemical elements with relatively high densities that are toxic or poisonous even at low concentrations. Examples include mercury, cadmium, arsenic, chromium, thallium, and lead. While some heavy metals, such as copper, iron, zinc, manganese, and selenium, are essential trace elements for maintaining human metabolism, excessive concentrations can lead to poisoning. Heavy metals can contaminate human food sources through water, air, soil, plants, and animals. They are considered a significant pollutant in aquatic environments due to their toxicity and accumulation in marine organisms (Malik, 2004).

Shawa Fish (*Clupea harengus*)

Shawa, a fish species primarily belonging to the Clupeidae family, is commonly known as herring. These fish typically move in large schools around fishing banks and coastal areas, particularly in the shallow, temperate waters of the North Pacific and North Atlantic Oceans, including the Baltic Sea and the west coast of South America. The Atlantic herring is the most abundant among these species, accounting for over half of all herring captured. In the United Kingdom, herring were historically referred to as "silver darlings."



Image of Shawa fish (*Clupea harengus*)

Titus Fish (*Scomber scombrus*)

Mackerel, a common name for various pelagic fish species, primarily belongs to the Scombridae family. These fish inhabit both temperate and tropical seas, living mostly along the coast or in oceanic environments. Mackerel species are characterized by their deeply forked tails and distinctive vertical, tiger-like stripes on their backs (Daan, 1973). They migrate in large schools along the coast to spawn in shallow waters. After spawning, they return in smaller schools to feeding grounds near areas of upwelling. Some mackerel then move offshore into deeper waters to spend the winter in relative inactivity (Daan, 1973).



Image of Titus fish (*Scomber scombrus*)

Panla Fish (*Micromesistius poutassou*)

Panla fish, commonly known as hake, refers to fish from the Merlucciidae family, found in both northern and southern oceans. Hake are medium-to-large fish, typically weighing between 0.5 to 3.6 kilograms (1 to 8 pounds), though some can reach up to 27 kilograms (60 pounds). They grow to about 1 metre (3 ft 3 in) in length and can live for up to 14 years. Found in the Atlantic and Pacific Oceans, hake typically inhabit depths of 200 to 350 metres (660 to 1,150 ft). During the day, they stay in deeper waters and move to shallower depths at night. As indiscriminate predators, hake feed on prey near or at the bottom of the sea. Male and female hake are visually similar (Daan, 1973). After spawning, their eggs float on the sea's surface where larvae develop before migrating to the sea bottom, favoring depths of less than 200 metres (656 ft) (Daan, 1973).



Image of Panla fish (*Micromesistius poutassou*)

Fish Consumption and Safety Concerns in Owo

In Owo, fish is consumed daily in nearly every household as it is one of the most affordable sources of protein. However, there is increasing concern about the safety of fish, both imported and locally sourced, due to potential contamination of water bodies. The extent of contamination and the enforcement of regulatory measures remain uncertain. This raises the need for further research to determine whether fish serve as reservoirs of heavy metals resulting from exposure to contaminants during farming or storage.

2. MATERIALS AND METHODS**Sample Collection and Preparation**

Fish samples were collected from two cold rooms (C1 and C2) located in Owo, Owo Local Government Area of Ondo State, Nigeria. These samples were taken to the Department of Aquaculture at Rufus Giwa Polytechnic, Owo, where they were taxonomically identified by experts using standard reference materials. The fish samples were packed in ice and transported to the Chemistry Laboratory at Rufus Giwa Polytechnic. Their length and weight were recorded, and they were smoked separately without adding salt. The smoked samples were then pulverized individually and stored in airtight containers for laboratory analysis.

Materials

The materials used included HCl, H₂SO₄, a weighing balance, filter paper, heating mantle, crucible, thread, beakers, conical flask, distilled water, reagent bottles, chloroform, water bath, acetic acid, and pipette, among others.

Determination of Heavy Metal Composition**Ashing**

Approximately 20 g of each pulverized sample was placed in a crucible and ashed in a muffle furnace at 550 °C for 4 hours. The crucibles were removed and stored in a desiccator to prevent the samples from absorbing additional moisture.

Digestion

Each ashed sample was mixed with nitric acid (HNO₃) and hydrochloric acid (HCl) in a 1:3 ratio. The mixture was diluted to 100 ml with distilled water in a measuring cylinder, transferred to a beaker, sieved, and stored in a sample bottle at room temperature for Atomic Absorption Spectrophotometer (AAS) analysis.

Atomic Absorption Spectrophotometer (AAS) Analysis

The samples were analyzed for heavy metals, including cadmium, manganese, copper, zinc, and chromium. The heavy metal concentrations in each fish sample were determined using values obtained from AAS analysis. The AOAC (2010) method was applied for ash content determination and heavy metal analysis using an atomic absorption spectrophotometer (AAS Model: 2000).

3. RESULTS AND DISCUSSION**RESULTS:****Table 1: Showing the Location of Collection**

S/N	Sample Local Name	Sample Botanical Name	Collection Point	Cold Room	State
1	Shawa	<i>Clupea harengus</i>	Owo	Coldroom (1)	Ondo
2.	Panla	<i>Micromesistius poutassou</i>	Owo	Coldrooms (1)	Ondo
3	Titus	<i>Scomber scombrus</i>	Owo	Coldroom (1)	Ondo

Table 2: Showing the Location of Collection

S/N	Sample Local Name	Sample Botanical Name	Collection Point	Cold Room	State
1	Shawa	<i>Clupea harengus</i>	Owo	Coldroom (2)	Ondo
2.	Panla	<i>Micromesistius poutassou</i>	Owo	Coldrooms (2)	Ondo
3	Titus	<i>Scomber scombrus</i>	Owo	Coldroom (2)	Ondo

Table 3: Showing the Length and Weigh of the Fish Samples

Fish Sample	L(Cm)	L (Inches)	Wt(G)	Wt (Kg)	Location
A (Panla)	22.01	8.700	355	0.36	Cold Room 1
B (Panla)	20.03	8.673	350	0.35	Cold Room 2
C (Shawa)	22.07	8.688	410	0.41	Cold Room 1
D (Shawa)	22.40	8.818	420	0.42	Cold Room 2
E (Titus)	22.50	8.858	430	0.43	Cold Room 1
F (Titus)	23.09	9.090	700	0.7	Cold Room 2

Table 4: Showing Results of Heavy Metal Composition of the fish Samples (mg/kg)

Fish samples	Cu	Cd	Cr	Mn	Zn
A (Panla 1)	0.311	0.020	0.041	0.322	1.041
B (Panla 2)	0.313	0.022	0.040	0.328	0.995
C (Shawa 1)	0.195	0.015	0.029	0.310	1.210
D (Shawa 2)	0.198	0.013	0.031	0.314	1.214
E (Titus 1)	0.256	0.015	0.030	0.453	1.431
F (Titus 2)	0.260	0.017	0.033	0.450	1.433
WHO Limit (mg/kg) (1993).	4.00	0.05	0.050	5.00	99.4
FAO limit (mg/kg) (1999)	4.00	0.02	0.02	4.00	99.4

4. DISCUSSION

Heavy Metal Contamination in Fish Samples

The levels of heavy metal contamination in the fish samples are summarized in the table above. Zinc was the most abundant metal across all samples, with sample F (Titus fish from Cold Room 2) exhibiting the highest concentration at 1.433, closely followed by sample E (Titus fish from Cold Room 1) at 1.431. The lowest zinc concentration was found in sample B (Panla fish from Cold Room 2) at 0.995, which is significantly lower than the value reported by Igwemmar et al. (2013) in their study on fish samples. Zinc levels in the fish samples followed a descending order: F > E > D > C > A > B. The zinc content in Panla fish from Cold Room 2 (0.995) was lower than that of the other samples. Nwaedozie (1998) reported a zinc concentration of 6.60 ppm in tilapia, which is notably higher than the values observed in this study, likely due to differences in fish species. Igwemmar et al. (2013) reported a zinc concentration of 2.81 in Titus fish, slightly higher but comparable to the values observed in this study for Titus fish from Cold Rooms 1 and 2 (1.431 and 1.433, respectively).

The variations in zinc levels could be attributed to differences in fish species, location, stage of maturity, storage duration, and sample preparation methods. The zinc concentrations in all fish samples (Shawa, Titus, and Panla) were below the WHO and FAO recommended limit of 99.4 mg/kg in food. Zinc contamination is known to affect the hepatic distribution of other trace metals in fish.

The cadmium (Cd) concentrations in the samples revealed that sample D (0.013, Shawa fish from Cold Room 2) had the lowest value, followed by sample C (0.015, Shawa fish from Cold Room 1) and sample E (0.015, Titus fish from Cold Room 1). The highest cadmium concentration was recorded in sample B (0.022, Panla fish from Cold Room 2), slightly higher than sample A (0.020, Panla fish from Cold Room 1). The cadmium levels followed the order: B > A > F > C > E > D, with samples C and E having identical concentrations (0.015). All cadmium concentrations were below the WHO (1993) standard limit of 0.05 and similar to the FAO (1999) recommendation of 0.02. These findings align with the absence of cadmium reported by Chima et al. (2017) in selected fish samples and the values reported by Ukulu et al. (2018), which ranged from 0.015 to 0.221. Cadmium toxicity can cause renal dysfunction, pulmonary disease, glucose intolerance, severe liver and kidney damage, and even death (ATSDR, 2011; Voogt et al., 1980).

Manganese (Mn) was present in all fish samples, with the lowest concentration observed in sample C (0.310, Shawa fish from Cold Room 1) and the highest in sample E (0.453, Titus fish from Cold Room 1), followed by sample F (0.450, Titus fish from Cold Room 2). Despite being the same species, the slight difference in manganese levels between samples E and F may be attributed to their origin from different cold rooms. All manganese concentrations were below the WHO (5.00 mg/kg) and FAO (4.00 mg/kg) limits for food. Manganese, while essential in trace amounts, can interfere with iron metabolism, particularly hemoglobin formation.

Copper (Cu) accumulation was also noted in the samples, with sample B (0.313, Panla fish from Cold Room 2) showing the highest concentration. Samples A, F, E, D, and C followed in descending order with concentrations of 0.311, 0.260, 0.256, 0.198, and 0.195 mg/kg, respectively. The lowest copper concentration was observed in sample C (0.195, Shawa fish from Cold Room 1). All copper levels were below the WHO and FAO limit of 4.00 mg/kg. Alinnor and Obiji (2010) reported higher copper concentrations in fish samples, ranging from 1.247 to 8.00 ppm. Copper is an essential element that enhances enzymatic activity in the body.

Chromium (Cr) levels were highest in sample A (0.041, Panla fish from Cold Room 1) and sample B (0.040, Panla fish from Cold Room 2), with the lowest levels recorded in sample C (0.029, Shawa fish from Cold Room 1) and sample E (0.030, Titus fish from Cold Room 1). All chromium levels complied with the WHO (1993) and FAO (1999) recommendations of 0.05 mg/kg and 0.02 mg/kg, respectively. Chromium, a heavy metal essential for metabolic activities in trace amounts, can lead to toxicity and diseases when excessively accumulated in the body through food and water.

5. CONCLUSION AND RECOMMENDATION

Conclusion

Fish is undeniably an affordable source of protein, but contamination with heavy metals can reduce its value. This study evaluated the concentration of heavy metals in selected fish samples. The results revealed that the levels of heavy metals in Shawa fish 1 & 2, Titus fish 1 & 2, and Panla fish 1 & 2 were below the levels of concern, as they were found to be lower than the WHO and FAO recommended limits for food. Consequently, the fish samples (Panla, Shawa, and Titus) available in the market during the research period were deemed safe for consumption.

Recommendation

Public awareness should be raised about the risks and harmful effects of heavy metal contamination in food. The heavy metal levels in the analyzed fish samples were within safe limits as per WHO and FAO recommendations, confirming that they are safe for consumption. This study concludes that the fish samples investigated are safe for consumption, as their heavy metal concentrations fall below the WHO-recommended thresholds. Further studies are recommended to assess the heavy metal concentrations in other fish species from different locations.

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