DETERMINATION OF HEAVY METALS IN IMPORTED FROZEN FISH AND LOCAL FRESH FISH OBTAINED FROM DIFFERENT MARKETS IN LAGOS STATE, NIGERIA

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ABSTRACT

Fish is an important source of protein for the human body. Despite its nutritional value, it can also be a potential health hazard for the consumer because heavy metals enter into the aquatic environment and subsequently into the food chain. The aim of this study is to compare the concentrations of heavy metals in local fresh fish with that of imported frozen fish obtained in Lagos State, Nigeria. The study involved ten different species of local fish and six species of imported frozen fish. The fishes were dried, digested and analyzed for heavy metals using the Atomic Absorption Spectrophotometer, (AAS).

The concentrations of heavy metals ranged between $0.00-0.20\mu g/g$ (lead), $1.00-2.00\mu g/g$ (copper), $0.00-30.00\mu g/g$ (nickel), $0.00-39.00\mu g/g$ (chromium), $0.00-2.00\mu g/g$ (cadmium) and $0.00-3.00\mu g/g$ (cobalt) for local fresh fish. For imported frozen fish, the heavy metals ranged between $0.00-0.50\mu g/g$ (lead), $2.00-2.61\mu g/g$ (copper), $3.00-310.00\mu g/g$ (nickel), $0.00-95.15\mu g/g$ (chromium), $0.00-0.09\mu g/g$ (cadmium) and $0.00-6.50\mu g/g$ (cobalt). Lead concentration is significantly higher in imported frozen fish, although in trace amounts which is within safe limits. Nickel is present in high concentrations in imported frozen fish when compared with the local fresh fish. These levels are significantly higher than safe consumption limits of the World Health Organization. Copper and cadmium levels were below the limits and are only present in Sardine and Thread fin fish in trace amounts. Cobalt levels are high in imported frozen fish when compared with local fresh fish but still within safe limits. The presence of high concentrations of nickel in imported frozen fish (which is above safe limits) and traces of chromium in the frozen fish may pose a health risk to the consumers.

Keywords: Heavy metals, lead, copper, chromium, Lagos State, Nigeria.

INTRODUCTION

Heavy metal is the generic term for metals that have atomic weigh greater than 40 (Sezentmihalyi and Then, 2007; Canli and Atli, 2003). They enter the environment through natural and anthropogenic sources. The monitoring of heavy metals is essential to assess ecosystem (Mico *et al*, 2006). The main route of exposure for most individuals to heavy metals is through food and water. Chronic exposure to these heavy metals at low concentration can cause great adverse effects (Castro-Gonzalez and Mendez-Armenta, 2008; Censi *et al*, 2006; Tuzen, 2003). The bioaccumulation of heavy metals can threaten the health of many species including the fishes themselves, birds and human beings. Metals can also be mobilized from agriculture lands into food crops via reclamation of metal contaminated rivers and dredging.

Food is one of the major sources of lead exposure. The others are air and drinking water. Another source of ingestion is from the use of lead-based pottery glazes and lead containing vessels. (Ming-Ho, 2005). In human beings, 20-15% of ingested inorganic lead is absorbed while 5 - 15% ingested inorganic lead is absorbed.

Lead is primarily distributed among blood soft tissue and mineralizing tissue once in the stream. The bones of adult contain about 95% of the total body burden of lead. Cadmium is potentially toxic in the human body even at trace concentrations. Long term exposure to cadmium leads to hepatic effects, kidney and skeletal damage together with neurotoxic effects (Khalifa *et al*, 2010; Misera *et al*, 1998). Cadmium has been shown to lead to oxidative damage in tissues by enhancing the peroxide of cell membrane lipids and changing the anti oxidant defense among cells (Bagchi *et al*, 1996; Gputa *et al*, 1991).

Fishes are generally used to estimate heavy metal pollution in water systems (Papagiannis *et al*, 2004). Many studies have shown the accumulation of heavy metals in fishes (Oksuz *et al*, 2009; Yildirum *et al*, 2009; Fernandes *et al*, 2008; Preveena *et al*, 2008). It has also been reported that consumption of heavy metals contaminated fish reduces the level of antioxidants in the blood (Bolawa, 2015) and also leads to DNA fragmentation in and the blood of rats (Bolawa and Ebuehi, 2015).Cadmium also accumulates in animal milk and fatty tissue (Ozturk *et al*, 2008; Figueora, 2008). Seafood can also be sources of cadmium (WHO 2004, WHO 2006).

Accumulation of high level of copper in the body leads to cirrhosis, renal tubular damage and neurological symptoms (Papagiannis *et al*, 2004). The contamination of human beings through ingestion of contaminated seafood is a major public health concern.

The present study was carried out to determine the levels of heavy metals (Pb, Cr, Cd, Cu, Co, Zn, Ni) and other metals (Mn, Mg, Fe) in imported frozen fish and local fresh obtained from major markets in Lagos, Nigeria.

Materials and Methods

Specimens of ten local fresh fishes and six imported frozen fishes were obtained from different markets in Lagos, Nigeria. Selection was based on relative abundance and availability. All fish samples were taken to the Department of Marine Biology, University of Lagos for identification.

Length and Weight Measurement

The fishes were thawed and weighed on a beam balance. A meter ruler was used for the length measurement. The results were recorded.

Digestion of Fish Samples

The fish samples were washed and oven dried in an oven set to 100° C until the samples were moisture free. The dried samples were grinded and kept in separate plastic containers. 5g of each grinded sample was weighed into a 200 ml beaker followed by the addition of 50 ml of nitric acid. The solution was left for 24 hours after which it was heated at 80°C until all the materials dissolved. The resulting solution was diluted with de-ionized water, filtered and the volume made up to 100 mls with de-ionized water. The resulting solutions were analyzed using Perkin Model flame Atomic Absorption Spectrophotometer (AAS) at the Department of Chemistry, University of Lagos, and the result expressed in $\mu g/g$.

RESULTS

Values of length and weight of fish samples used for the analysis are presented in Tables 1 and 2. Results of metallic analysis of the fishes are presented in Tables 3-6.

SCIENTIFIC NAMES OF FISH	COMMON NAME	MEAN	MEAN	
SAMPLES		LENGTH	WEIGHT	
		(cm)	(g)	
Pomodays jubelini	Grunter	19.00	160.00	
Polydatylus quadrifillis	Threadfin	30.00	240.00	
Elops larceta	Lady fish	24.00	120.00	
Tilapia quineensis	Tilapia	20.00	180.00	
Sphyreara barracuda	Barracuda	32.00	180.00	
Ethmalosa fimbriata	Bonga fish	27.00	200.00	
Mugil cepalus	Mullet	21.00	100.00	
Pseudotholithus typus	Croater	26.00	180.00	
Galeoides decadactylus	Fin Fish	27.00	200.00	
Chrysichthys nigrodidatus	Cat fish	30.00	220.00	
Pangasius sp	Obokun	26.50	100.00	

TABLE 1: WEIGHT AND LENGTH OF FRESH FISH SAMPLES

TABLE 2: LENGTH AND BREADTH OF FROZEN FISH SAMPLES

SCIENTIFIC NAMES OF FISH SAMPLES	LOCAL NAMES	MEAN LENGTH (cm)	MEAN WIDTH (cm)
Etrumes teres	Ojuyobo	36.50	7.40
Pseudotolithus brachygnatus	Croaker	39.20	7.80
Thinnus sp	Kote	29.40	8.20
Sardinella sp	Sardine	22.30	4.40
Scomber japonicas	Titus	30.00	6.20
Merlucclus sp.	Panla	38.50	9.30

LEAD AND CHROMIUM IN IMPORTED FROZEN FISH SAMPLES						
NAMES OF FISH SAMPLES	CADMIUM (µg/g)	COBALT (µg/g)	COPPER (µg/g)	LEAD (µg/g)	CHROMIUM (µg/g)	
Ojuyobo	ND	ND	2.00 <u>+</u> 0.11	0.50 <u>+</u> 0.22*	ND	
Croaker	ND	3.60 <u>+</u> 0.34	2.10 <u>+</u> 0.17	ND <u>+</u>	ND	
Kote	ND	5.60 <u>+</u> 0.44	2.61 <u>+</u> 0.15	ND	ND	
Sardine	0.09 <u>+</u> 0.08	3.00 <u>+</u> 0.37	2.20 <u>+</u> 0.12	0.20 <u>+</u> 0.37	ND	
Titus	ND	5.65 <u>+</u> 0.21*	2.30 <u>+</u> 0.11	ND	95.15 <u>+</u> 0.79*	
Panla	ND	6.50+0.37*	2.10 <u>+</u> 0.14	ND	ND	
MPL (WHO)	1.00		30.00	0.50	50	

TABLE 3: CONCENTRATIONS OF CADMIUM, COBALT, COPPER,LEAD AND CHROMIUM IN IMPORTED FROZEN FISH SAMPLES

*p>0.01

TABLE4:CONCENTRATIONSOFZINC,IRON,MANGANESE,MAGNESIUM AND NICKEL IN IMPORTED FROZEN FISH SAMPLES

NAMES OF	Zn	Fe	Mn	Mg	Ni
FISH	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)
SAMPLES					
Ojuyobo	290.00 <u>+</u> 12.60	270.00 <u>+</u> 12.77	20.00 <u>+</u> 1.31*	40.00 <u>+</u> 1.49	3.00 <u>+</u> 0.16
Croaker	340.00 <u>+</u> 14.99*	890.00 <u>+</u> 15.39*	10.00 <u>+</u> 1.27	50.00 <u>+</u> 1.38	300.00 <u>+</u> 14.33*
Kote	370.00 <u>+</u> 14.36*	890.00 <u>+</u> 15.72*	10.00 <u>+</u> 1.99	50.00 <u>+</u> 1.33	310.00 <u>+</u> 14.69*
Sardine	390.00 <u>+</u> 13.52*	240.00 <u>+</u> 12.46	20.00 <u>+</u> 1.48*	120.00 <u>+</u> 11.38*	300.00 <u>+</u> 14.72*
Titus	340.00 <u>+</u> 14.79*	150.00 <u>+</u> 14.22	10.00 <u>+</u> 1.34	140.00 <u>+</u> 11.40*	310.00 <u>+</u> 14.97*
Panla	390.00 <u>+</u> 13.25*	520.00 <u>+</u> 14.87*	3.00 <u>+</u> 0.19	50.00 <u>+</u> 1.46	300.00 <u>+</u> 14.57*
MPL (WH0)	100	100	100		
* . 0.01					

*p>0.01

TABLE 5: CONCENTRATIONS OF CADMIUM, COBALT, COPPER,LEAD AND CHROMIUM IN LOCAL FRESH FISH SAMPLES

Names of Fresh Fish Samples	CADMIUM (µg/g)	COBALT (µg/g)	COPPER (µg/g)	LEAD (µg/g)	CHROMIUM (µg/g)
Bonga fish	ND	3.00 <u>+</u> 0.12*	2.00 <u>+</u> .15	ND	27.00 <u>+</u> 0.33
Lady fish	ND	ND	2.00 <u>+</u> 0.14	ND	ND
Thread fin fish	2.00 <u>+</u> 0.12*	ND	2.00 <u>+</u> 0.17	0.10 <u>+</u> 0.07	ND
Cat fish	ND	3.00 <u>+</u> 0.17*	2.00 <u>+</u> 0.11	ND	39.00 <u>+</u> 0.54*
Mullet fish	ND	2.00 <u>+</u> 0.23	1.00 <u>+</u> 0.09	0.20 <u>+</u> 0.08*	10.00 <u>+</u> 0.37
Barracuda fish	ND	ND	2.00 <u>+</u> 0.14	ND	ND
Tilapia fish	ND	0.10 <u>+</u> 0.09	2.00 <u>+</u> 0.11	ND	19.00 <u>+</u> 0.28
Fin fish	0.30 <u>+</u> 0.01	1.00 <u>+</u> 0.04	2.00 <u>+</u> .15	ND	ND
Grunter fish	ND	ND	2.00 <u>+</u> 0.12	ND	ND
Croaker fish	ND	ND	1.00 <u>+</u> 0.08	ND	ND
MPL (WHO)	0.50	30.00	30.00	0.50	50

*p>0.01

TABLE 6: CONCENTRATIONS OF ZINC, IRON, MANGANESE,MAGNESIUM AND NICKEL IN LOCAL FRESH FISH SAMPLE

NAME OF	ZINC	IRON	MANGANESE	MAGNESIUM	NICKEL
FRESH FISH	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)
SAMPLES					
Bonga fish	470.00 <u>+</u> 14.89*	790.00 <u>+</u> 15.03*	20.00 <u>+</u> 1.30*	50.00 <u>+</u> 1.72	ND
Lady fish	380.00 <u>+</u> 13.55	400.00 <u>+</u> 13.22*	10.00 <u>+</u> 1.22	90.00 <u>+</u> 1.77*	ND
Thread fin fish	400.00 <u>+</u> 14.23*	230.00 <u>+</u> 1.71	10.00 <u>+</u> 1.81	120.00 <u>+</u> 10.68*	ND
Cat fish	430.00 <u>+</u> 14.65*	530.00 <u>+</u> 14.01*	20.00 <u>+</u> 1.65*	90.00 <u>+</u> 1.97*	ND
Mullet fish	430.00 <u>+</u> 14.11*	220.00 <u>+</u> 11.22	10.00 <u>+</u> 1.71	50.00 <u>+</u> 1.99	ND
Barracuda fish	390.00 <u>+</u> 13.78	200.00 <u>+</u> 11.36	4.00 <u>+</u> 0.99	70.00 <u>+</u> 1.79	ND
Tilapia fish	400.00 <u>+</u> 14.91*	680.00 <u>+</u> 14.99*	10.00 <u>+</u> 1.72	120.00 <u>+</u> 10.01*	30.00 <u>+</u> 1.02
Fin fish	480.00 <u>+</u> 14.30*	230.00 <u>+</u> 11.38	10.00 <u>+</u> 1.01	80.00 <u>+</u> 1.96*	ND
Grunter fish	350.00 <u>+</u> 13.22	270.00 <u>+</u> 11.69	20.00 <u>+</u> 1.29*	40.00 <u>+</u> 1.88	ND
Croaker fish	420.00 <u>+</u> 14.74*	170.00 <u>+</u> 11.47	10.00 <u>+</u> 1.58	60.00 <u>+</u> 1.98	ND
MPL (WHO)	100	100	100		
* 0.01	1		1	1	

*p>0.01

DISCUSSION

The research work highlighted the concentrations of heavy metals in fishes. The concentrations of cadmium, chromium, copper, cobalt and lead in imported frozen fish and local fresh fish are presented in Tables 3 and 5. In most of the samples, cadmium was not detectable except in trace amounts in Sardine and Thread fin

fish. These levels were below the Maximum Permissible Levels of the WHO, 1989 (MPL). Chromium was not detected in imported frozen fish samples except in Titus fish in a significantly high amount. In local fish samples, chromium was found in Bonga fish, Cat fish, Mullet fish and Tilapia fish in trace amounts. These levels were below the MPL. Copper is an essential element in human and animals but in high concentration, it is toxic (Tuzen, 2003). It was present in all the fishes examined but in trace amounts. These levels were below the Maximum Permissible Levels. Copper and chromium toxicity has lead to various disorders such as skeletal deformity, hormonal and metabolic disorders including cancer.

Lead was not detected in the fish samples except in Thread fish and Mullet fish (Local fresh fish) and Ojuyobo and Sardine fish (for imported frozen fish). These levels were below the Maximum Permissible Levels of the WHO. Cadmium accumulates in the human body affecting several organs negatively. These include the lungs, brain, liver, kidney etc. (Castro-Gonzalez and Mendez-Armanta, 2008). Food is one of the major sources of lead exposure while the others are air and drinking water (Ming-Ho, 2005). Children are more sensitive to lead due to its effects on the developing nervous system (ATSDR, 2008; Castro-Gonzalez and Mendez-Armenta, 2008). The joint FAO/WHO, expert committee on food addition (JECFA, 2004) established a provisional tolerable weekly intake (PTWI) for lead as 0.025mg/kg body weight (bw) (JECFA, 2004). The WHO provisional guideline of 0.01mg/ is the standard for drinking water (WHO, 2004).

Cadmium accumulates in the human body affecting several organs negatively. These include the lungs, brain, liver, kidney etc. (Castro-Gonzalez and Mendez-Armenta, 2008). Cadmium toxicity also leads to negative hepatic, immunological and haematological effects (Apostoli and Catalani, 2011). The joint WHO/FAO has recommended the PTWl for cadmium as 0.007mg/kg bw (JEFCA, 2004). The EPA maximum contaminant level for Cadmium in drinking water is 0.005mg/L whereas the WHO adopted the provisional guideline of 0.003mg/L (WHO, 2004). Lots of studies have attributed high metal accumulation in fishes to the feeding habit of the fish. Khaled in 2004, showed that S. rivulatus, which is an herbivore, accumulated high concentrations of metals in their muscles than Sargus sargus, which is a carnivore. Al-Bausaidi et al, in 2011, also showed that high cadmium concentrations in T. albacores were due to their feeding habits at high tropic levels. These feeding habits could be one of the reasons why Sardinella sp., a filter feeder, accumulates high concentrations of heavy metals with the exception of lead, in all organs (Abdallah, 2008). With agreement with these results on Sardinella sp., Aiturigi and Albedair (2012), found high concentrations of zinc,

cadmium, iron and manganese in sardine collected from the Saudi market. Chen and Hsien in 2001 found that the muscles of *Sardinella lemuru* contains high concentrations of zinc, iron, copper and manganese among other fishes collected from Taiwan waters. Agatha in 2010, found heavy metals present in tissues of Bonga fish.

Cadmium concentrations in fish has been showed to be positively linked to the age of the fish, since cadmium is difficult to excrete from the liver once it is accumulated (Eisler, 2010; Khaled, 2004). In this study, Thread fin fish weighs 240g and it was seen to accumulate the highest amount of cadmium. This study supports the findings of Eisler, (2010) and Khaled, (2004).

Zinc is a powerful antioxidant (Bolawa, 2015). When taken as a daily supplement, it was found to ameliorate the harmful effects of heavy metals in rats (Bolawa *et al*, 2014). The presence of zinc in fish has beneficial effects on the human body. Although in high concentrations, zinc is toxic. Zinc levels within the range of 12.7 mg/kg-389.73 mg/kg have been reported in Mackerel fish (Law *et al*, 1992). The concentrations of zinc found in this study were below the Maximum Permissible Levels. In this study, local fresh fish samples contained higher zinc concentration than imported frozen fish samples.

Iron is an essential element to human health although, high concentrations of iron have been found in the liver of Alantic Horse mackerel (Thompson, 1992). In this study the lowest level of iron was found in Titus fish and local Croaker fish. Kote fish, Croaker fish (imported species), Bonga fish, Cat fish and Tilapia fish all contain high concentrations of iron. The highest level of iron was found in imported Croaker (890.00 μ g/g) and local Bonga fish (790.00 μ g/g). These levels are above the Maximum Permissible Limits of the WHO.

Manganese and magnesium were present in all the fish samples analyzed but below the Maximum Permissible Limits. According to Thompson (1992), manganese concentration in fishes is usually lower than 28mg/kg.

Nickel was not detected in any local fresh fish except in Tilapia fish samples whereas nickel was detected in all the imported frozen fish samples, with values ranging from $3.00 \ \mu g/g - 310 \ \mu g/g$. In this study, a high level of nickel was found in all the imported frozen fish samples examined. This is a danger sign and can lead to health complications in the general public if consumed over a period of time. Preventive measures should be taken by countries from which these fishes

are being imported from, to reduce the nickel concentrations in their water bodies. Metal accumulation in fish is a sign of exposure to contaminated aquatic environment and could be used to assess the environmental condition of the area from which they are gotten from.

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