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Heavy Metals Assessment of Fish Samples Obtained from Selected Cold-Rooms in Ondo State of Nigeria

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Abstract

Heavy metals present in fish samples imported by cold-rooms in Ondo State were investigated. Samples were collected from seven (7) cold-rooms spread across Ondo State. The results indicated that the concentration of Cr>As>Co>Pb. The various concentrations of Chromium (Cr), Arsenic(As), Cobalt (Co) and Lead (Pb) were indicated in Tables 3. The concentration of Arsenic in all the fish samples ranged between 0.033 mg/kg and 0.215 mg/kg. Chromium (Cr) was found present in all the imported fish samples in all the cold-rooms across Ondo State. The concentrations of Cr ranged from 0.10 to 0.713 mg/kg. Cobalt (Co) concentrations in all the fish samples ranged between 0.012 to 0.281 mg/kg. Highest concentration of 0.281 mg/kg was found in *clupea harengus* from KD cold-room in Owo town and the lowest concentration of 0.012 mg/kg was found in *micropogonias* also sold by KD cold-room in Owo town. The concentrations of Lead (Pb) in all the fish samples ranged from 0.006 to 0.120 mg/kg. The highest concentration of 0.120 mg/kg was found present in *scomber-scombrus* and *M.poutassou* from OYI and KD cold-rooms both from Owo town. The results obtained will serve as a baseline for food Agencies in Nigeria to certify safety of fishes imported into this country from overseas before they are sold to the public for consumption.

keywords: Fish Samples; Heavy Metals Assessment; Cold-Rooms; Ondo State Nigeria

1.0 Introduction

Contamination by heavy metals in the aquatic environment has attracted global attention owing to their abundance, persistence and environmental toxicity (Ali and Khan, 2018). The threat of toxic metals in the environment is more serious than those of other pollutants due to their non-biodegradable nature, accumulative properties and long biological half-lives. It is difficult to remove them from the environment once they enter into it (Aderinola *et al.*, 2009). The increasing usage of heavy metals in industries leads to increase in release of harmful heavy metals into the aquatic environment (Aguso *et al.*, 2005; Hajeb *et al.*, 2009). The impact of these heavy metals on water ecosystem has turned out to be a global concern (Yousafzai, 2008).

Metals, particularly heavy metals such as lead, mercury, cadmium, cobalt and arsenic contribute significant potential threat to human health, both occupational and environmental (Oluyemi and Olabanji, 2011). Another significant problem associated with heavy metals in the environment apart from accumulation through the food chain and persistence in nature is their toxicity (King and Jonathan, 2003; Dimeri *et al.,* 2008). These metals accumulate in the tissues of the sea food, concentrate to a high amount and then are passed on, in the food chain. Accumulation of these heavy metals in an aquatic environment has direct consequences to the ecosystem and men at large (Kawser *et al.,* 2016).

As a result of Cadmium poisoning, Itai-itai disease in Japan, a degenerative bone disease, occurred by substitution of calcium in the bone. The outbreak occurred when Cadmium released as industrial waste due to mining in Toyama Prefecture in Japan around 1912. "Itai-itai" disease was coined by locals for the severe pains the people with the condition felt in the spine and joints. Cadmium was subsequently passed through the food web to fish consumers. Fish also bio-accumulate Cadmium through passive transport in the gills. Cadmium has been found to be related to osteoporosis (skeletal damage) in both animals and humans according to studies (Hans *et al.,* 2020). Short term Cadmium inhalation can cause serious lung damage and respiratory discomfort and higher doses of Cadmium ingestion can cause stomach irritation, resulting in vomiting and diarrhea. It may also lead to anemia, high blood pressure, circulation problem, decalcification of bones and muscle atrophy (Martyna, 2016). Lead (Pb) is a highly toxic metal whose widespread use has caused extensive environmental contamination and health problems in many parts of the world. In early 2010, ducks began to disappear in Zamfara state, Nigeria. A few months later, public health officials learned that hundreds of children had become sick in this state. Report stated that children suffered from vomiting, abdominal pain, headaches and seizures. Many of these children later died. Infact, one-fourth of the children in the community had died in the past year. The team found unsafe levels of lead inside most of their homes, water and community wells. Children in villages had dangerous levels of lead in their blood. Hundreds of children and animal died throughout the region. It was the largest known outbreak of lead poisoning in history (CDC, 2010). Lead poisoning interferes with formation of hemoglobin, prevents uptake of iron, the poison may lead to brain damage, kidney dysfunction, gastro-intestinal tract malfunctioning and impairment of central nervous system (Philip and Akudinobi, 2020).

Mercury (Hg) is a common environmental toxin and pollutant and causes significant changes in body tissues as well as a variety of negative health effect (Bhan and Sarkar, 2005). Methyl mercury is the most frequently encountered compound of the organic form in the environment and is formed by methylation of mercury by micro-organisms found in the soil and water (Dispp *et al.,* 2004). A serious mercury poisoning occurred in Japan, in the city of Minamata, Minamata Prefecture, Japan in 1956. It was caused by release of methyl mercury in the Industrial Wastewater from a chemical factory owned by the Chisso Corporation, which continued from 1932-1968. It was also confirmed that some of the mercury sulphate in the Wastewater was also metabolized to methyl mercury by bacteria in the sediment (Hamay and Noyes, 1975). This highly toxic chemical bio-accumulated and biomagnified in all the fishes in Minamata Bay and the Shiranui Sea, which when eaten by the local population resulted in mercury poisoning. Death of cats, dogs, pigs and humans continued for 36 years (Vail *et al.,* 2009). By March 2001, over 1,784 people had died from consumption of contaminated fishes from the bay and sea.

Scientists has been investigating in order to mitigate exposure to heavy metals pollution which is a general problem facing the world at large (Thompson *et al.,* 2019). This research was to find out the degree of heavy metal contamination from imported fish samples sold in cold-rooms spread over Ondo State of Nigeria to ascertain their safety when consumed by the populace.

2.0 2.0 Materials and Methods

2.1 Study Area

Four (4) different study locations were chosen in the South-West Geopolitical region of the Federal Republic of Nigeria. One of the sampling site was Owo town with latitude of 7.1889 ºN and a longitude 5.5923 ºE. The second sampling site was Akure town also with a latitude of 7.2571 ºN and a longitude 5.2058ºE. It is the largest city and capital of Ondo State. The third sampling site was Ikare town with a latitude of 7.5248 ºN and longitude of 5.7669 ºE. The fourth sampling site was Ondo town with a latitude of 7.1000 ºN and longitude 4.1817 ºE, it is a trade center for the surrounding region. Ondo state is in South-West of Nigeria with a coastline of about 80 km which runs in a northwest to southeast direction.

Figure 2.1: Map of Ondo State showing the sampling locations (Source: google map data, 2017)

Figure 2.2: Map of Africa showing Nigeria (Source: google map data, 2017)

Table 2.1: Table Showing the Samples and Location of Collection

S/N	Sample Local Name	Sample Botanical Name	Collection Point	Cold Room	State
1	Shawa	*Clupea harengus*	Owo(1)	Oyinkansola(1)	Ondo
2	Panla	*Micromesistius poutassou*	Owo(1)	Oyinkansola(1)	Ondo
3	Titus	*Scomber scombrus*	Owo(1)	Oyinkansola(1)	Ondo
4	Panla	*Micromesistius poutassou*	Ikare	Mary	Ondo
5	Shawa	*Clupea harengus*	Ikare	Mary	Ondo
6	Shawa	*Clupea harengus*	Akure	Kingdom	Ondo
7	Titus	*Scomber scombrus*	Akure	Kingdom	Ondo
8	Croaker	*Micropogonias undulates*	Akure	Kingdom	Ondo
9	Panla	*Micromesistius poutassou*	Akure	Kingdom	Ondo
10	Panla	*Micromesistius poutassou*	Ondo Town(1)	Isiko	Ondo
11	Titus	*Scomber scombrus*	Ondo Town(1)	Isiko	Ondo
12	Shawa	*Clupea harengus*	Ondo Town(1)	Isiko	Ondo
13	Panla	*Micromesistius poutassou*	Ondo Town(2)	Okedibo	Ondo
14	Croaker	*Micropogonias undulates*	Ondo Town(2)	Okedibo	Ondo
15	Panla	*Micromesistius poutassou*	Owo(2)	Fransco and Shine	Ondo
16	Shawa	*Clupea harengus*	Owo(2)	Fransco and Shine	Ondo
17	Panla	*Micromesistius `poutassou*	Owo(3)	Oyinkansola(2)	Ondo
18	Shawa	*Clupea harengus*	Owo(3)	Oyinkansola(2)	Ondo
19	Titus	*Scomber scombrus*	Owo(3)	Oyinkansola(2)	Ondo

Keywords:

OY1 - Oyinkansola 1   OY2 - Oyinkansola 2   KD - Kingdom   OK – Okedibo

FS - Franco and Shine   IS - Isiko   MA - Mary

2.2 Methods

2.2.1 Dry Ashing Method

About 50g of the sample was weighed and transferred into a porcelain crucible (Emmanuel *et al.,* 2020; Ogundeleolusola *et al.,* 2019). The crucible was transferred into the muffle furnace and ashed at a temperature between 400-700 ºC between 3-4hrs. The crucibles were removed and kept in a desiccator ready for analysis.

2.2.2 Determination of Heavy Metals

The analysis of the heavy metals was carried out with a Buck model 211 VGP atomic absorption spectrophotometer. In all cases, air-acetylene was the flame used and hollow cathode lamp of the individual was metal was the resonance line source. The calibration plot method was adopted for the analysis. For each element, the instrument was auto zeroed using blank (de-ionized water) after which the standard was aspirated into the flame starting from the lowest concentration. The corresponding absorbance values were obtained and the graph of absorbance against concentration was plotted by the instrument. The digested samples were analyzed in duplicates with the average concentration of the metal present being displayed in mg/kg by the instrument after extrapolation from the standard curve.

2.3 Statistical Analysis

All analyses were done in triplicate to evaluate experimental reproducibility and reported as Mean ± Standard Deviation. The data obtained were subjected to one-way analysis of variance (ANOVA) using SPSS version 21. Duncan's multiple range test was used to determine means that were significantly different at a level of significance (α) of 0.05.

3.0 Results and Discussion

The concentrations of all the heavy metals investigated in all the fish samples collected from nineteen (19) different locations in Ondo State showed that the concentrations of Cr>As>Co>Pb. The concentrations of Arsenic (As), Chromium (Cr), Cobalt (Co) and Lead (Pb) in various imported fish samples from cold-rooms OY1, OY2, KD in Owo town, OK, FS, IS in Ondo town, MA in Ikare town were as indicated in tables 1a,1b,1c,1d and 1e respectively. The highest concentration of As, 0.215 mg/kg was found in *M.poutassou* from cold-room KD in Owo town, while the lowest concentration of 0.033 mg/kg was found in *Clupea harengus* in IS cold-room in Ondo town. The concentration of Arsenic (As) in all other fish samples from all cold-rooms were low, all below 1.4mg/kg as recommended by FAO/WHO (1989). Man can be contaminated by Arsenic through food, beverages and air (Mahipal *et al.*, 2016). Most of the paints, dyes, soaps, metal semi-conductors and drugs contain Arsenic (Smedley and Kinniburgh, 2002). Arsenic poisoning in human being can cause cancer of the lungs, liver, bladder and skin.

Chromium (Cr) was found present in all the imported fish samples from all the cold-rooms across Ondo State. Chromium concentrations ranged from 0.10 to 0.713 mg/kg. The highest concentration of 0.713 mg/kg was found in *M.poutassou* sold by KD cold-room and the lowest concentration of 0.10 mg/kg was found in *Scomber scombrus* sold by KD cold-room in Owo town. The concentration of Chromium in all the fish samples from all the cold-room were high, far higher than the limit of 0.05mg/kg recommended by FAO/WHO (1993). All the fish samples sold by all the cold-rooms were not fit for consumption for containing high concentrations of Chromium, above the recommended limit of FAO/WHO (1993).

Cobalt (Co) concentrations in all the samples ranged between 0.012 to 0.281 mg/kg. Highest concentration of 0.281 mg/kg was found in *clupea harengus* from KD cold-room and the lowest concentration of 0.012 mg/kg was found in *micropogonias* also sold by KD cold-room in Owo town. High concentration of Cobalt 0.132 mg/kg was also detected in *M.poutassou* from Y2 cold-room in Owo town. Cobalt was also found at high temperature in *Scomber* 0.10 mg/kg also from OY2 cold-room in Owo town. About twenty (20) different fish samples were surveyed and most of them had higher concentration of Cobalt, rendering them unfit for consumption. The affected cold-rooms were from Owo, Akure, Ondo and Ikare towns. Maximum permissible limit recommended by FAO/WHO is 0.05mg/kg (FAO/WHO, 2006).

The concentrations of Lead (Pb) in all the fish samples ranged from 0.006 mg/kg and 0.120 mg/kg. The highest concentration was 0.120 mg/kg was present in *Scomber scombrus* and *M.poutassou* from OY1 and KD cold-rooms in Owo town. The lowest concentration of 0.006 mg/kg was found present in *Scomber scombrus* obtained from KD cold-room also from Owo town. Lead (Pb) was found in all the fish samples in all the cold-rooms but at varying concentrations but all the concentrations were below 0.4 mg/kg recommended by FAO/WHO (2011). Consequently, all the fish samples were safe for consumption. But Lead (Pb) can bio-accumulate making its consumption very unsafe.

Lead (Pb) is a non-essential element and can be very toxic to humans above the FAO/WHO recommended dose (Salem *et al.,* 2000). Lead will interfere with essential nutrients such as Calcium (Ca) and Zinc (Zn) to cause renal failure and liver damage in humans (Salem *et al.*, 2000). Lead poison can also result in neurological, hematological, behavioral, renal, cardiovascular, reproductive effects at levels above the tolerant limit of 0.4mg/kg (FAO/WHO, 2011).

Table 3.1: Heavy Metal (mg/kg) content in Imported Fish Samples Obtained from OY1 Cold Room 1.

Metal (mg/kg)	FAO/WHO Limit	*Clupea harengus* /Shawa	*M.poutassou/*Panla	*Scomber scombrus/*Titus
As	1.4 (1989)	0.069 ± 0.002	0.070 ± 0.003	0.096 ± 0.001
Cr	0.05 (1993)	0.276 ± 0.003	0.248 ± 0.006	0.283 ± 0.001
Co	0.05 (2006)	0.013 ± 0.000	0.019 ± 0.003	0.019 ± 0.001
Pb	0.4 (2011)	0.035 ± 0.001	0.035 ± 0.001	0.018 ± 0.001

Number of replicates = 3; Mean ± Standard Deviation; Mean with different superscript across columns are significantly different at ($P>0.05$)

Table 3.2: Heavy Metal (mg/kg) content in Imported Fish Samples Obtained from OY2 Cold Room 2.

Metal (mg/kg)	FAO/WHO Limit	*Clupea harengus/*Shawa	*M.poutassou*/Panla	*Scomber scombrus* /Titus
AS	1.4 (1989)	0.181 ± 0.004	0.038 ± 0.002	0.178 ± 0.001
Cr	0.05 (1993)	0.351 ± 0.007	0.24 ± 0.003	0.383 ± 0.002
Co	0.05 (2006)	0.094 ± 0.002	0.015 ± 0.002	0.100 ± 0.002
Pb	0.4 (2011)	0.079 ± 0.002	0.041 ± 0.004	0.120 ± 0.002

Number of replicates = 3; Mean ± Standard Deviation; Mean with different superscript across columns are significantly different at ($P>0.05$)

Table 3.3: Heavy Metal (mg/kg) content in Imported Fish Samples Obtained from KD Cold Room.

Metal (mg/kg)	FAO/WHO Limit	*Clupeaharengus*/ Shawa	*M.poutassou*/ Panla	*Scomber scombrus/* Titus	*Micropogonias undulates/*Croaker
AS	1.4 (1989)	0.098 ± 0.004	0.215 ± 0.004	0.075 ± 0.002	0.090 ± 0.002
Cr	0.05 (1993)	0.227 ± 0.005	0.713 ± 0.004	0.10 ± 0.003	0.110 ± 0.004
Co	0.05 (2006)	0.281 ± 0.004	0.132 ± 0.002	0.044 ± 0.003	0.012 ± 0.002
Pb	0.4 (2011)	0.034 ± 0.002	0.113 ± 0.004	0.006 ± 0.002	0.012 ± 0.002

Number of replicates = 3; Mean ± Standard Deviation; Mean with different superscript across columns are significantly different at (P>0.05)

Table 3.4: Heavy Metal (mg/kg) content in Imported Fish Samples Obtained from OK Cold Room.

Metal (mg/kg)	FAO/WHO Limit	*Micromesistius poutassou/* Panla	*Micropogonias undulates/* Croaker
AS	1.4 (1989)	0.045 ± 0.007	0.091 ± 0.001
Cr	0.05(1993)	0.168 ± 0.004	0.287 ± 0.002
Co	0.05 (2006)	0.015 ± 0.005	0.052 ± 0.001
Pb	0.4 (2011)	0.028 ± 0.003	0.069 ± 0.002

Number of replicates = 3; Mean ± Standard Deviation; Mean with different superscript across columns are significantly different at (P>0.05)

Table 3.5: Heavy Metal (mg/kg) content in Imported Fish Samples Obtained from FS Cold Room.

Metal (mg/kg)	FAO/WHO Limit	*Micromesistius poutassou/* Panla	*Clupea harengus/*Shawa
AS	1.4 (1989)	0.176 ± 0.002	0.051 ± 0.002
Cr	0.05 (1993)	0.471 ± 0.001	0.301 ± 0.002
Co	0.05(2006)	0.338 ± 0.002	0.119 ± 0.003
Pb	0.4 (2011)	0.106 ± 0.004	0.024 ± 0.002

Number of replicates = 3; Mean ± Standard Deviation; Mean with different superscript across columns are significantly different at (P>0.05)

Table 3.6: Heavy Metal (mg/kg) content in Imported Fish Samples Obtained from IS Cold Room

Metal (mg/kg)	FAO/WHO Limit	*Micromesistius poutassou/* Panla	*Scomber scombrus/* Titus	*Clupea harengus/*Shawa
AS	1.4 (1989)	0.20 ± 0.002	0.075 ± 0.004	0.033 ± 0.002
Cr	0.05 (1993)	0.057 ± 0.002	0.135 ± 0.007	0.163 ± 0.003
Co	0.05 (2006)	0.012 ± 0.002	0.068 ± 0.003	0.083 ± 0.004
Pb	0.4 (2011)	0.016 ± 0.001	0.021 ± 0.001	0.033 ± 0.002

Number of replicates = 3; Mean ± Standard Deviation; Mean with different superscript across columns are significantly different at (P>0.05)

Table 3.7: Heavy Metal (mg/kg) content in Imported Fish Samples Obtained from MA Cold Room

Metal (mg/kg)	FAO/WHO Limit	*Micromesistius potassou/* Panla	*Clupea harengus/*Shawa
AS	1.4 (1989)	0.200 ± 0.005	0.039 ± 0.003
Cr	0.05 (1993)	0.471 ± 0.006	0.021 ± 0.004
Co	0.05 (2006)	0.105 ± 0.004	0.035 ± 0.005
Pb	0.4 (2011)	0.111 ± 0.004	0.046 ± 0.004

Number of replicates = 3; Mean ± Standard Deviation; Mean with different superscript across columns are significantly different at (P>0.05)

4.0 Conclusion

The study revealed that the concentration of Chromium (Cr) was higher than that of Arsenic (As), Arsenic (As) higher than that of Cobalt (Co) and that of Cobalt higher than that of Lead (Pb). The concentration of Chromium was high in all the imported fish samples in all the cold-rooms in Ondo State, higher than the FAO/WHO (1993) limit of 0.05mg/kg. Therefore, this batch of fish samples investigated were not fit for consumption, having been polluted heavily by Chromium, a heavy metal. Arsenic (As) was found present in all the imported fish samples but at a concentration less than FAO/WHO (1989) limit of 1.4mg/kg. Though the fish samples can be consumed but continuous consumption may be dangerous because Arsenic (As) may bio-accumulate in human body. High concentrations of Cobalt (Co) were detected in many imported fish samples from many cold-rooms, some above the limit recommended by FAO/WHO (2006) of 0.05mg/kg. Those above the recommended limit were not approved for consumption while those below the recommended limit were strongly recommended for consumption. Cobalt (Co) may bio-accumulate in the human body and cause serious toxicity in future. Lead (Pb) was found present in all the fish samples but their concentrations were below the FAO/WHO (2011) recommended limit of 0.4mg/kg. The fish samples were recommended for consumption but continuous consumption of similar samples were not recommended because Lead (Pb) bio-accumulates and bio-magnifies in humans. Lead (Pb) pollution by inhalation is dangerous because Lead is toxic and carcinogenic.

5.0 Recommendation

Most fish samples investigated contained heavy metals, rendering them unfit for consumption, through the fish samples have already been sold to the public. The public has been polluted with these heavy metals thereby putting their lives in danger. The Federal Ministry of Health and the State counterparts must be informed of the result of this assessment so that necessary sanctions be brought against the erring cold-rooms by the Ondo State Government.

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