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Determination of Some Metals in Selected Species of Imported Frozen Fishes Sold in Kano Fish Market

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Abstract:- This study aims to evaluate the levels of seven metals (viz:Aluminium, Cadmium, Chromium, Iron, Mercury, Lead and Zinc) in the gills, livers and muscles of seven different imported fish species (viz:*Trachurus, Clupea, Scomber, Undulatus, Gadus, Argentine and Oreochromis)* sold at the popular Fish market of Kano Line, Kano State Nigeria and to conduct a risk assessment for human consumers. Atomic Absorption Spectrometer (Perkin Elmer PinAAcle 900H) was used to determine the presence of the metals. A 100% metal recovery range for all assayed metals was detected, with the highest concentration recorded in Iron(Fe) (13.33±0.0022mg/kg) and the lowest concentration was found in Cadmium(Cd) (0.001±0.0009mg/kg). The general order of metal bioaccumulation measured in the fish tissues were in the order; Fe > Zn > Hg > Cr > Pb > Al > Cd in the gills, and Fe >Zn >Al > Hg> Cr >Pd >Cd in the livers, and Zn > Fe > Hg > Pb > Al > Cr > Cd in the fish flesh (muscle). The majority of all the metals analyzed in all the tissues of the fish samples were lower than maximum levels by FAO/WHO guidelines except for Mercury (Hg) in the gills and flesh of *Oreochromis*, and Aluminium (Al) in the livers of all samples and in the gills of *Oreochromis* and *Trachurus*. The estimation of the Target Hazard Risk and Hazard Index (non-carcinogenic risk) indicated no adverse health effects from the consumption of the fishes , although, the elevated levels in *Oreochromis* muscle needs to be closely monitored. The Target Cancer Risk (carcinogenic risk) was also observed to be of low significance, but not ignorable, especially in the Chromium levels of *clupea harengus* and *Oreochromis.* The estimated maximum safe consumption (MSC) levels for the metals showed that Mercury (Hg) may cause significant health effects in humans if *Oreochromis*, *Gadus* and *undulates* are consumed in a large amount.

Keywords:- *Health risk assessment, Target Hazard Quotient, Maximum safe consumption, Metals, Fishes.*

I. INTRODUCTION

The recent proliferation of fish grill spots in Kano metropolis, Kano State Nigeria has led to an increase in the consumption of imported fish. In all the fish spots, one can find different species of barbecued fish which includes Tilapia, Croaker, Silversmelt, Cod fish etc, (Table1). Most of the Commercially imported fish consumed in Kano and environs are gotten from the popular Kasuwar Kifi (Kano line fish market). This fish market serves as a depot for imported commercial fish, from where other retailers come to buy, therefore it was used as a sampling site in order to check for any metal hazard in the fish.

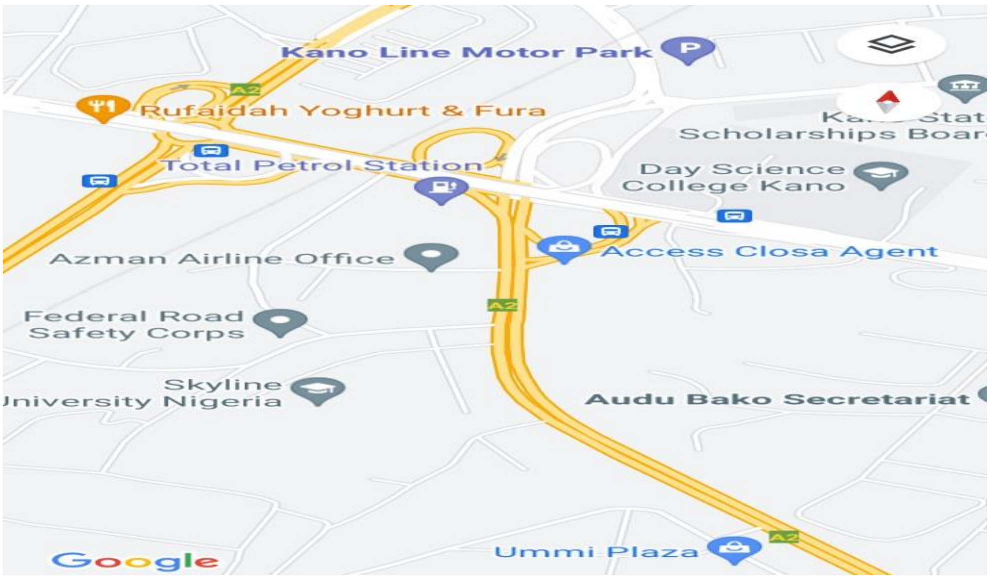

Fig 1: Map showing location of fish market in Kano materopolis, Kano State, Nigeria

Fishes are good source of proteins and vital fatty acids. These fatty acids can help reduce the risk of heart disease and stroke due to their contribution in lowering the cholesterol levels in blood and also provide essential minerals and vitamins (Fazureen,*et al.,2015)*. The American Heart Association recommended the consumption of fish at least twice per week in order to reach the daily intake of omega-3 fatty acid required for the well being of the body (Kris-Etherton *et al.*,,2002), however, the presence of toxic metals in the fish can invalidate their beneficial effect.

The bioaccumulation levels of metals is determined by the ingestion and excretion rates of the fish. Factors responsible for the bioaccumulation are either environmental (water chemistry,salinty,temperature,level of contaminant) or biological (species, age, gender, sexual maturity and diet) or both (Montazer and Ali,2018). Metals can be bioaccumulated in fish via water and food chain. Patrick and loutit (1976) reported the biomagnifications of Cr, Cu,Mn,Fe, and Zn from bacteria to tubified worms, in fish through food chain.

Metal pollutants in fresh water and marine are known to disturb the delicate balance of the aquatic ecosystem due to their biomagnication capabilities. Fishes are known for their ability to concentrate metals in their muscles and since they are important in human diet, they need to be carefully examined to ensure that unnecessary high level of some toxic metals are not being transferred to man by their consumption (Adeniyi and Yusuf,2007). Quite a number of studies have shown that high metal bioaccumulations in fish resulted in sub lethal effects and even death in some fish populations (Almeida *et al.*, 2002; Jones *et al.*, 2001 and McGeer *et al.*, 2000, Dhary Alewy *et al.*,2020).Also, high concentrations of toxic metals in human cells may cause cellular dysfunction leading to systemic pathologies in the central nervous system, hematopoiesis, kidney function, immune system , respiratory and cardiovascular system (Dhary Alewy *et al.*,2020; Kim *et al.*, 2019).

Therefore the presence of some toxic metals in commercial fish can pose potential health risks to humans. Hence, it is important to identify the levels of metal content in fish in order to ensure that it does not pose any hazard to humans and also maintain concentrations under permissible levels by adhering to the maximum safe consumption (MSC) limits of the fish (Sivaperumal, 2007) .

S/N	SAMPLE	LOCAL NAME	SPECIE	MEAN WEIGHT(g)	MEAN LENGTH(cm)	ORIGIN	STATUS
1	Horse Mackerel	Sadin	*Trachurus Trachurus*	700 ± 4.5	41 ± 1.00	Pacific, Chile	Frozen
2	Herring	Shawa	*Clupea Harengus*	300 ± 10	26 ± 0.50	Russia	Frozen
3	Mackerel	Sukumbia	*Scomber Scomberus*	400 ± 8.5	30 ± 1.50	Pacific, Peru	Frozen
4	Croaker	Kroka	*Micropogonias Undulatus*	800 ± 5.0	42 ± 1.00	Uruguay	Frozen
5	Stock Fish	Kwalla	*Gadus morhua*	400 ± 11	41± 1.00	USA	Frozen
6	Silver Smelt	Ajentan	*Argentina Silus*	500 ± 7.5	41.5 ± 1.25	Germany	Frozen
7	Tilapia	Karpasa	*Oreochromis aureus*	1000 ± 10	35 ± 1.00	China	Frozen

Table 1: SUMMARY OF THE FISH SAMPLES ANALYSED

II. MATERIALS AND METHOD

Analytical grade reagent was used throughout the study. Seven different species of imported fish sold at the popular fish market, Kasuwar Kifi at Kano line, Kano State Nigeria were used for this study. The Fish species include: Horse Mackerel (HML), Herring (HRR), Mackerel (MKL), Croaker (CRK), Silvermelt (SMT),Stockfish (STF) and Tilapia (TLP).

A. *Sample treatment*

Fish samples were purchased and immediately transferred into a plastic box containing ice and transported to the laboratory where they were frozen at -20°C for the hold time. The Samples were defrosted and then the length and weight was taken. The scales were removed, rinsed with distilled water and each separated into head and trunk from which the gills, flesh and liver were obtained using a stainless steel knife for dissection. The fish parts were rinsed with deionized water and dried at 80^0C for 24 hours in an oven until constant weight was observed. This was then milled using porcelain mortar and pestle to ensure homogeneity and each properly labeled. (Oluwa *et al.*, 2010; Adeniyi and Yusuf, 2007)

B. Sample analysis

5g of each sample was weighed and transferred into a porcelain crucible and ignited in a muffle furnace at temperature 550^0C for 2 hours. The ashed residue was dissolved in $5cm^3$ of concentrated nitric acid (70% w/v, S.G 1.42, 63.01g/mol) in a beaker and made up to $50cm^3$ volume. The solution was then transferred to the sample bottles and labeled. (Oluwa *et al.*, 2010). Atomic Absorption Spectrometer (Perkin Elmer PinAAcle 900H) was used to determine the presence of the metals.

C. Statistical analysis

All analyses were performed in triplicates. The means of the replicates and evaluation of significant differences between different samples were determined using descriptive statistics and analysis of variance (ANOVA), respectively. Two-way and one-way analysis of variable (ANOVA) were used to test for significant differences in the concentrations of metals in the samples. For comparison of means, ANOVA test and post hoc test Tukey were used. Results of the test were considered significant if the calculated *P* values were ≤ 0.05. Pearson correlation was used to examine the relationship between the metals in the fish. The data was analyzed using AnalyStat version 1.6.50g

D. Health risk assessment

a) Estimated daily intake:

According to USEPA (2015), the estimated daily intake for each heavy metals in fish food is given by:

$$EDI\ (mg\ kg^{-1}day^{-1}) = \frac{EF \times ED \times FIR \times C}{ABW \times ATn} \quad - - - - \quad 1$$

EF is the Exposure frequency (365 days $year^{-1}$). ED is the Exposure duration (30 years for adults), equivalent to the average lifetime; FIR is the Fish ingestion rate (kg $person^{-1}$ day^{-1}) = 20.8g, due to the 7.6kg per capita consumption in Nigeria . C is the Metal concentration in fish (mg kg^{-1}). RfD is the Oral reference dose (mg kg^{-1} day^{-1}). ABW is the Average body weight (kg) = 60 kg for adults. ATn is the Average exposure time for non-carcinogens (365 days $year^{-1}$ × ED). (Bassey and Chukwu 2019)

b) Target hazard quotient:

Target hazard quotient (THQ) is the ratio of potential exposure to a contaminant and the acceptable level of the same contaminant at which no adverse effect is expected.(Jasmina *et al.*, 2020). THQ is given by

$$THQ = \frac{EF \times ED \times FIR \times C}{RFD \times ABW \times ATn} \times 10^{-3} \quad - - - - - \quad 2$$

Where ; RFD = Reference oral dosage for contaminant (mg kg^{-1} day^{-1}).RFD for Zn = 0.3, Cr = 0.003, Fe = 0.7, Cd = 0.001, Pb = 0.004, Hg = 0.0001 mg kg^{-1} day^{-1}(Bassey and Chukwu, 2019)

c) Hazard index

Hazard index (HI) is the sum of the total THQ for individual metals and used to assess the total potential health effect due to exposure to a mixture of metals. It is generally accepted that when HI > 1 , then adverse effects are possible (Jasmina *et al*, 2020). It is given by

$$HI = \sum_{i=1}^{n} THQ \quad - - - - - - - - - - - \quad 3$$

HI < 1.0 Indicates unlikely lifetime non-carcinogenic health risk to the human consumer

HI ≥ 1.0 Indicates an increasing potential lifetime non-carcinogenic health risk to humans
(Samson *et al*, 2020)

d) Target cancer risk

This refers to the potential risk of cancer development in humans over a lifetime of heavy metals exposure to contaminated fish (muscles or flesh) and is given by

$$TCR = \frac{EF \times ED \times FIR \times C \times CPso}{ABW \times ATc} \times 10^{-3} \quad - - - - - \quad 4$$

Where ; ATc is the Average time for carcinogen (365 day^{-1} $year^{-1}$ for 70 years) CPso = Carcinogenic potency slope of metals CPso for Pb = 0.0085, Cd = 0.38 , Cr = 0.5 Ni = 1.7 (Samson *et al*, 2020)

e) Maximum safe consumption level.

The maximum safe consumption (MSC) is the acceptable consumption limit per week within which no adverse effect is expected for the consumer of the fish. It is usually computed using the provisional tolerable weekly intake (PTWI) as follows;

$$MSC = \frac{BW \times JL}{C} \quad - - - - - - \quad 3.5$$

Where; MSC is the maximum safe consumption of food/week items in relation with a contaminant. BW is the body weight (kg) of the human for whom the assessment of the MSC is carried out. JL is represents the PTWI of a trace metal . According to the FAO/WHO (2004), the PTWI for Cd, Pb, and Hg are 7, 25, and 4 μg/kg/week, respectively PTWI for Al= 1, Cr= 0.7, Fe= 5.6, , Zn= 7 (Lavent *et al*,2018; Hatem 2017; WHO 2013) . *C* = is the concentration of metal in fish muscle in µg/kg (Mohammad *et al*, 2021)

III. RESULT AND DISCUSSION

fish sample	**Tissue**	**Al**	**Cd**	**Cr**	**Fe**	**Hg**	**Pb**	**Zn**
Croaker	**gills**	**0.108±0.0319**	**0.037±0.0050**	**0.692±0.0078**	**7.256±0.0136**	**0.476±0.0819**	**0.587±0.0007**	**5.175±0.0271**
	liver	**1.074±0.0257**	**0.010±0.0020**	**0.212±0.0250**	**8.817±0.3259**	**0.363±0.0246**	**0.113±0.0134**	**2.783±0.0087**
	flesh	**0.150±0.0369**	**0.006±0.0008**	**0.046±0.0171**	**1.411±0.0067**	**0.267±0.0228**	**0.103±0.0107**	**1.037±0.0025**
H.Mackerel	**gills**	**0.492±0.0167**	**0.090±0.0025**	**0.635±0.0441**	**13.33±0.0022**	**0.215±0.0616**	**0.479±0.0215**	**3.505±0.0045**
	liver	**0.144±0.0251**	**0.561±0.0021**	**0.152±0.0184**	**3.784±0.0188**	**0.193±0.1093**	**0.167±0.0057**	**5.223±0.0438**
	flesh	**0.036±0.0118**	**0.009±0.0013**	**0.023±0.0285**	**1.233±0.0075**	**0.186±0.0234**	**0.082±0.0146**	**0.871±0.0015**
Herring	**gills**	**0.102±0.0409**	**0.045±0.0015**	**0.114±0.0143**	**1.635±0.0075**	**0.410±0.1331**	**0.151±0.0102**	**0.913±0.0056**
	liver	**0.643±0.0263**	**0.021±0.0008**	**0.011±0.0383**	**2.703±0.0116**	**0.201±0.0631**	**0.081±0.0093**	**0.361±0.0007**
	flesh	**0.490±0.0100**	**0.008±0.0005**	**0.078±0.0226**	**1.972±0.0008**	**0.260±0.0949**	**0.122±0.0053**	**1.066±0.0060**
Mackerel	**gills**	**0.226±0.0122**	**0.085±0.0013**	**0.436±0.0322**	**4.329±0.0102**	**0.295±0.0782**	**0.356±0.0071**	**3.282±0.0096**
	liver	**0.320±0.0252**	**0.393±0.0014**	**0.168±0.0351**	**5.933±0.0076**	**0.198±0.0309**	**0.144±0.0098**	**4.278±0.0014**
	flesh	**0.024±0.0154**	**0.005±0.0014**	**0.023±0.0354**	**1.115±0.0072**	**0.127±0.0603**	**0.085±0.0088**	**1.260±0.0048**
Stock Fish	**Gills**	**0.108±0.0297**	**0.006±0.0007**	**0.290±0.0433**	**2.102±0.0020**	**0.290±0.0831**	**0.277±0.0044**	**1.489±0.0018**
	liver	**0.172±0.0104**	**0.018±0.0006**	**0.012±0.0347**	**2.664±0.0249**	**0.400±0.0877**	**0.073±0.0100**	**3.676±0.0137**
	flesh	**0.036±0.0110**	**0.001±0.0009**	**0.041±0.0189**	**0.526±0.0050**	**0.341±0.1624**	**0.131±0.0122**	**0.867±0.0033**
SilverSmelt	**Gills**	**0.001±0.0205**	**0.012±0.0010**	**0.231±0.0367**	**2.341±0.0128**	**0.329±0.0689**	**0.230±0.0086**	**2.491±0.0076**
	liver	**0.701±0.0023**	**0.701±0.0023**	**0.042±0.0089**	**0.956±0.0022**	**0.398±0.1188**	**0.080±0.0182**	**2.623±0.0009**
	flesh	**0.092±0.0890**	**0.008±0.0017**	**0.043±0.0144**	**0.514±0.0045**	**0.162±0.0447**	**0.126±0.0111**	**1.320±0.0160**
Tilapia	**Gills**	**0.916±0.0134**	**0.025±0.0017**	**0.517±0.0313**	**6.486±0.0064**	**1.881±0.1367**	**0.400±0.0203**	**0.406±0.0364**
	liver	**1.812±0.0265**	**0.007±0.0004**	**0.186±0.0469**	**8.164±0.0083**	**0.394±0.1634**	**0.068±0.0113**	**1.967±0.0072**
	flesh	**0.108±0.0293**	**0.007±0.0004**	**0.086±0.0064**	**0.704±0.0013**	**0.519±0.0763**	**0.110±0.0087**	**1.372±0.4729**

Table 2: Mean concentration of metals (mg/kg) in fish tissue

The distribution of Aluminium concentration (Table 2) in the tissues analyzed were in the order TLP>CRK>SMT>HRR>HML>MKL>STF. The livers of all the samples analyzed accumulated the highest concentrations while the flesh (muscles) had the least concentrations. Tilapia had the highest Aluminium concentration in the liver (1.812±0.0265 mg/kg) and gills (0.916±0.0134mg/kg) while the flesh of Silversmelt (SMT) accumulated the least concentration of Aluminium (0.001±0.0205 mg/kg) with significant variation ($p<0.05$) in the liver samples. For Aluminium, as a result of the acidification of soils, soluble Aluminium (Al) can reach the aquatic environment easily (Arturo, *et al.*2017). Pollution from anthropogenic activities is also an important means through which Al is being released into the marine environment. Effluents from food additive industries also contributes to aluminium levels in the water ways. The Al flesh result obtained in this study were lower than the WHO (2017) and SON(2015) permissible limit of 0.2mg/kg except in Herring. They were also lower than those reported by Ismaniza and Idaliza (2012).

The Cadmium concentrations in all fish tissue samples analyzed were bioaccumulated in the order HML>MKL>HRR>CRK>TLP>SMT>STF. The livers of all samples analyzed were found to have the highest bioacculumation while the flesh had the least. The liver of Horse Mackerel (HML) was found to have the highest Cadmium concentration (0.561± 0.0021mg/kg) while the lowest cadmium concentration (0.001±0.0009mg/kg) was found in the flesh of Stock Fish (STF). Significant difference ($p<0.05$) was observed in the livers compared to the flesh. Fish livers and kidneys are said to be the detox centers of the body as well as a reflector of metal contamination and bioaccumulation in the entire fish body (Samson, *et al.*, 2020) that is why they tend to accumulate more metals than other organs. Cd in the liver leads to hepatotoxicity, and when it gets to the kidneys, it accumulates in the renal tissue causing nephrotoxicity. Cd can bind with cystein, glutamate, histidine and aspartate ligands and lead to the deficiency of iron (Moiseenko, 2020). In this study, even though the flesh levels of cadmium concentration were all below the FAO/WHO (2003) permissible limit of 0.05mg/kg, the livers and gills of Mackerel and Horse Mackerel were above the limit. The flesh result were all lower than that obtained by Samson *et al*,(2020) at Abuja fish market and also lower than those recorded by Montazer and Ali (2018).

The concentrations of Chromium in all tissues of fish samples analyzed generally bioaccumulated in the order CRK>HML>TLP>MKL>STF>SMT>HRR. The gills of all samples analyzed accumulated the highest concentrations while the flesh had the lowest concentrations. The gills of

Croaker (CRK) was found to have the highest Chromium concentration (0.692±0.0078mg/kg) while the lowest concentration (0.011±0.0383mg/kg) was found in the liver of Herring (HRR), even though in general, the flesh of all samples accumulated the least Chromium. Significant variation ($p<0.05$) was observed in the gills compared to the flesh. Chromium is used as metal alloys and pigments for paints, cement, paper, rubber, and other materials especially in the dyeing and tanning industries (Montazer and Ali, 2018). Effluents from these industries into the water ways pollutes the aquatic environment with fishes being hit the most. Excess chromium damages the gills of fishes swimming near the point of chromium disposal. Exposure to a low concentration of Cr may cause skin irritation and cause ulceration. More so, long term exposure is capable of causing kidney and liver damage and also disruptions of circulatory and nerve tissues (ATSDR, 2000). Bioaccumulation of Cr in aquatic life is hazardous and may contribute to the danger of eating fish. Chromium(III) is beneficial in the body as it helps in some metabolic processes in the body, while Chromium(VI) is carcinogenic (Sehar *et al.,*2014). The concentrations of chromium in this study were found to be below the FAO/WHO(1983) limit of 1mg/kg in fish food. This result is quite similar to those reported by Zheng *et al.,* (2007) and Eisenberg and Topping (1986).

The concentrations of Iron in all the fish tissues analyzed were in the order HML>CRK>TLP>MKL>STF>HRR>SMT. The gills of all samples analyzed accumulated the highest concentrations of Iron while the flesh had the lowest. The gills of Horse Mackerel (HML) was found to have the highest Iron concentration (13.33±0.002mg/kg) while the lowest concentration (0.514±0.0045mg/kg) was found in the flesh of Silversmelt (SMT). Silversmelt also had the lowest Iron concentration in the liver with 0.956±0.0022mg/kg compared to all the fish samples analyzed. Significant difference ($p<0.05$) was observed across all samples analyzed. The gills bioaccumulated more Iron concentrations, as it is said to be the site for ion exchange during respiration (Fazureen, *et al.*, 2015). Samson *et al.*, (2020) reported an iron level of 221 mg/kg in the livers of *clarias gariepinus* sold at Abuja fish market. Ismaniza and Idaliza (2012) found more iron concentrations in fish species inhabiting the rocky bottoms and muddy part of lake, indicating that benthic fishes are prone to have more iron than pelagic fishes. Iron is a very important essential metal. It is present in the red blood cells as hemoglobin and in the muscle cells as myoglobin. It is essential for transferring oxygen through the blood from the lungs to the tissues for metabolic processes (UCSF, 2021). The Iron results obtained in this study were found to be within the FAO/WHO (2006) limits of 14.80 mg/kg in fish food. The Fe concentrations obtained in this work compares favorably to that reported by Oluwa *et al.,* (2010)

The bioaccumulation of Mercury in all tissues of fish analyzed were in the order TLP>CRK>HRR>STF>SMT>HML>MKL. The highest Mercury concentration was found in the gills of all samples analyzed while the flesh (muscles) had the lowest. The gills of Tilapia (TLP) accumulated the highest Mercury concentration (1.881±0.1367mg/kg)while the flesh of Mackerel (MKL) was found to have the lowest (0.127±0.0603mg/kg) . There was significant difference ($p<0.05$) across all samples analyzed. It was observed that the two fishes caught in Pacific Ocean (Table 1), Horse Mackerel (HML) and Mackerel (MKL), were the ones with the lowest Mercury concentrations suggesting that the waters in the area are less contaminated with mercury. Mercury (Hg) is a non-essential element. The levels of Hg increase as the fish increases in size (Farkas *et al* 2003), and it is usually at maximum in predatory species (Watras *et al* 1998). Hg toxicity causes organ damage in fish species and can lead to the destruction of fetal development in humans. (Fazureen *et al.,*2015). It can also cause kidney damage in human (WHO,2015). Its primary source in human is by consumption of fish. The majority of the samples analyzed were well below the FAO/WHO (2003) limit of 0.5 mg/kg in fish samples except for the gills and flesh of Tilapia. The result obtained in this study is higher than that reported by Zheng *et al.,* (2007) .

The accumulation of Lead in all tissues of fish analyzed was in the order CRK>HML>TLP>MKL>STF>SMT>HRR. The lead concentrations in all samples analyzed were found to be highest in the gill tissues and lowest in the flesh tissues. The gill of Croaker (CRK) was found to have the highest Lead concentration (0.587±0.0007mg/kg) while the liver of Tilapia was found to have the lowest (0.068±0.0113 mg/kg), even though in general, the flesh of all samples analyzed contained the lowest lead concentrations compared to the livers and gills. Significant variation ($p<0.05$) was observed across all tissues analyzed. Moiseenko and Gashkina (2020) showed that Pb is more actively accumulated in fish organism at low Ca concentrations in the waters and at low pH, which means Pb accumulation by fish depends more strongly on its concentration in the water and is enhanced in waters with lower pH than through the food chain, this explains why in this study, the gills of all samples analyzed were found to have more Pb than the Livers. Data obtained for all samples analyzed in this study showed that the Pb levels were all below the FAO/WHO (2003) acceptable limit of 0.2 mg/kg for fish food except for the gills of Croaker,Tilapia,Mackerel and Horse Mackerel. The result obtained in this work is quite similar to those obtained by Sina *et al.,* (2010) and Zheng *et al.,* (2007).

The bioaccumulation of Zinc in all tissues analyzed was in the order CRK>HML>MKL>SMT>STF>TLP> HRR. The Livers of all samples analyzed were found to have the highest Zinc concentrations while the Flesh contained the lowest. The liver of Horse Mackerel (HML) bioaccumulated the highest Zinc concentration (5.223±0.0438mg/kg) while the liver of Herring (HRR) had the lowest (0.361±0.0007mg/kg), although in general, the flesh of all samples analyzed were found to have the lowest Zinc concentrations compared to the livers and gills. Significant difference ($p<0.05$) was observed across all tissues analyzed. Previous studies, Zheng *et al*, (2007) have shown that pelagic fishes are more prone to contain more Zinc in comparison to benthic fishes. It was also claimed that the Zinc content of a fish are considerably reduced during the course of cooking and packaging (Sehar *et al*, 2014). When people are exposed to little Zn they can experience decrease in sense of taste and smell, loss of appetite, slow wound healing and skin sores while Zn deficiencies can even cause birth defects in humans(Sehar *et al.*,2014). Sub-lethal levels of Zinc in fish have been known to unfavorably affect hatchability, existence and hematological strictures of fish (Kori and Ubogu.,2008). For all the samples analyzed, the concentration of Zinc was also below the FAO/WHO (2006) limit of 12 mg/kg. The Zinc flesh result obtained is similar to that of Zarith and Mohd (2015) and also that of Oluwa *et al.,* (2010).

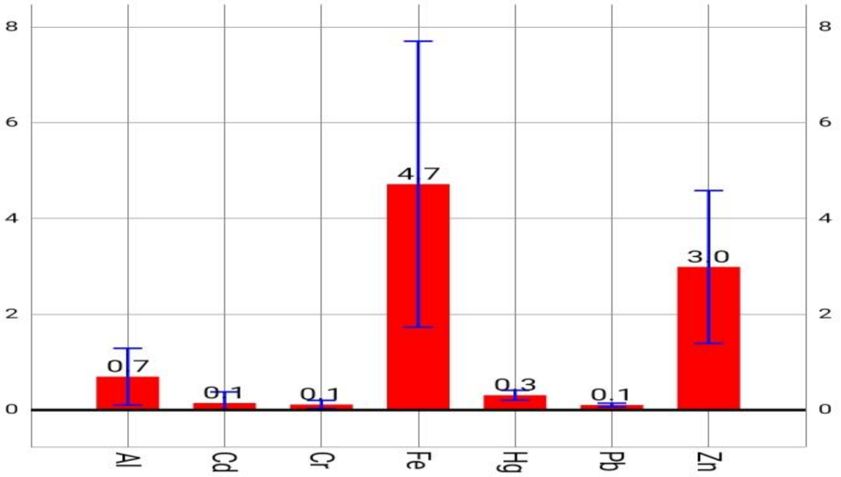

Fig. 2: mean anova results

Figure 2 shows mean anova analysis. For all the samples analyzed, the variations of the metal concentrations in the fish tissues differs significantly ($p<0.05$) which means that the concentrations of the metals across all samples analyzed varied with each other, but the degree of variation in Fe and Zn were more than the others.

Significant ($p<0.05$) liver bioaccumulation ($P<0.0001^*$) occurred in Zn and Fe compared to their muscle levels, with insignificantly ($p>0.05$) higher Pb and Hg liver levels over muscle concentrations. The higher recorded liver bioaccumulations of Fe and Zn compared with muscles of the sampled fish is in agreement with earlier report by Samson *et al.*(2020) in the fish sold at Abuja fish market.

IV. HEALTH RISK ASSESSMENT

For this study, a 100% metal recovery range for all assayed metals was recorded, hence a detailed health risk assessment is necessary to check if the combination of metals present in a given sample of fish could pose a health risk either from a carcinogenic or a non-carcinogenic perspective. Furthermore, since the fish flesh is the greatest mass of the fish consumed, it was suitable for the health risk assessment. This was carried out by investigating the estimated daily intake(EDI), target hazard quotient (THQ), target cancer risk (TCR), and establishing the maximum safe consumption levels (MSC).

Sample	**Al**	**Cd**	**Cr**	**Fe**	**Hg**	**Pb**	**Zn**
Croaker	0.052	2.1×10^{-3}	0.016	0.489	0.093	0.036	0.3595
H.Mackerel	0.012	3.1×10^{-3}	7.97×10^{-3}	0.427	0.064	0.028	0.302
Herring	0.170	2.8×10^{-3}	0.027	0.684	0.090	0.042	0.3696
Mackerel	0.008	1.7×10^{-3}	7.97×10^{-3}	0.387	0.044	0.029	0.4368
Stock Fish	0.012	3.5×10^{-3}	0.014	0.182	0.118	0.045	0.3006
Silver Smelt	0.032	2.8×10^{-3}	0.015	0.178	0.056	0.044	0.4576
Tilapia	0.037	2.4×10^{-3}	0.023	0.244	0.180	0.038	0.4757

Table 3: Estimated daily intake(mg/kg/day)

Table 3 shows the estimated daily intake of the metals. The EDI was determined based on the average concentrations of the metals of interest in each fish sample and the daily intake in grams of the respective fish sample. The Target hazard qoutieent is represented in table 4.0. THQ is the ratio of potential metal contaminant to acceptable level of which no health risk is expected within a period of time. it is used to assess the non-carcinogenic risk posed by the consumption of the metals in the flesh of the sampled fish.

Sample	Al	Cd	Cr	Fe	Hg	Pb	Zn
Croaker	5.2×10^{-5}	2.1×10^{-3}	5.3×10^{-3}	6.9×10^{-4}	0.31	9×10^{-3}	1.2×10^{-3}
H.Mackerel	1.2×10^{-5}	3.1×10^{-3}	2.7×10^{-3}	6.1×10^{-4}	0.21	7×10^{-3}	1×10^{-3}
Herring	1.7×10^{-4}	2.8×10^{-3}	9×10^{-3}	9.8×10^{-4}	0.3	10.5×10^{-3}	1.23×10^{-3}
Mackerel	8×10^{-6}	1.7×10^{-3}	2.7×10^{-3}	5.5×10^{-4}	0.146	7.25×10^{-3}	1.5×10^{-3}
Stock Fish	1.2×10^{-5}	3.5×10^{-3}	4.7×10^{-3}	2.6×10^{-4}	0.39	11.25×10^{-3}	1×10^{-3}
Silver Smelt	3.2×10^{-5}	2.8×10^{-3}	5×10^{-3}	2.5×10^{-4}	0.19	0.011	1.53×10^{-3}
Tilapia	3.7×10^{-5}	2.4×10^{-3}	7.7×10^{-3}	3.5×10^{-4}	0.6	9.5×10^{-3}	1.59×10^{-3}
Global THQ	3.23×10^{-4}	1.84×10^{-2}	0.0371	3.6×10^{-3}	2.146	0.0655	9.05×10^{-5}

Table 4: Target hazard quotient

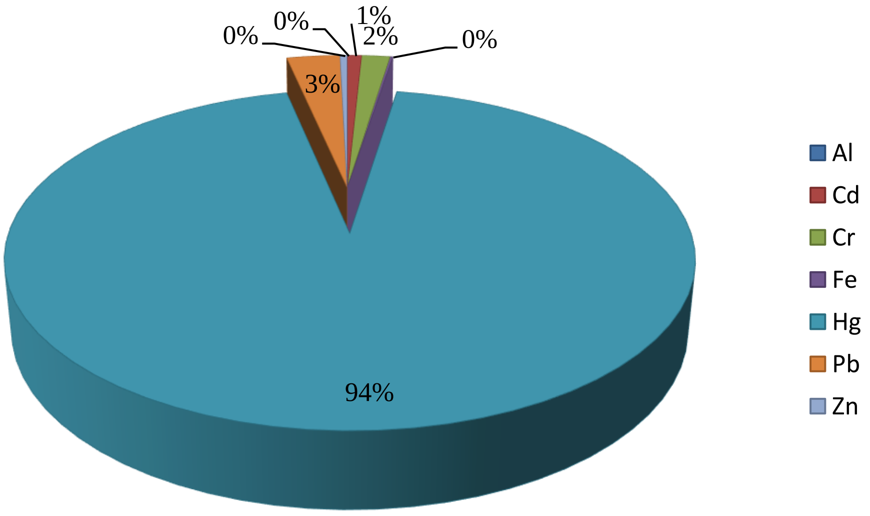

Fig 3.0: The distribution of the Global Target Hazard Quotient

For Aluminium,, the THQ values ranged from 8×10^{-6} in Mackerel to 5.2×10^{-5} in Croaker (Table 4), which accounts for about 0.014% (Fig3.0)of the Global THQ for all fish samples analyzed. The THQ values for cadmium ranged from 1.7×10^{-3} in Mackerel to 3.1×10^{-3} in Horse Mackerel. This is about 0.81% of the Global THQ analyzed. THQ Chromium ranged from 2.7×10^{-3} in Horse Mackerel to 9×10^{-3} in Herring. This accounts for about 1.63% of the Global THQ for all samples analyzed. The THQ values for Iron ranged from 2.5×10^{-4} in Silversmelt to 9.8×10^{-4} in Herring. This is about 0.15% of the Global THQ. The values of THQ for Mercury ranged from 0.19 in Silversmelt to 0.6 in Tilapia, which accounts for about 94% of the Global THQ which calls for concern. This means that there is a 94.49% risk chance of developing mercury related problems if all fish species are consumed by a single person after 30 years especially when the maximum safe limits are exceeded. Furthermore, the THQ values for Lead ranged from 7×10^{-3} in Horse Mackerel to 11.25×10^{-3} in Stock Fish, which accounts for about 2.88% of the Global THQ. Also, the THQ values of Zinc ranged from 1×10^{-3} in Horse Mackerel and Stock Fish to 1.59×10^{-3} in Tilapia. This represents about 0.0039% of the Global THQ values.

In this study, the THQ and Hazard Index (summation of elemental THQ) results were all less than 1 (Table 5.0) in adult consumers for all heavy metals analyzed, which means people would not experience any significant non-carcinogenic health risk from intake of this fish species sold at the fish market except they exceed the maximum safe consumption level

However, it should be noted that the value of THQ depends largely on metal concentration in fish and the fish ingestion rate. Therefore, excess fish consumption of these fish species may easily increase the THQ Values to THQ > 1. In this study, the major risk contributor is Hg (Fig 3.0), with the highest THQ value of 0.6 in Tilapia fish (Table 4.0) and Hazard Index of 0.6215(Table 5.0), similar to the result obtained by Mohammed *et al.*, (2021)

Sample	Hazard Index
Croaker	0.3253
H.Mackerel	0.2244
Herring	0.3247
Mackerel	0.1597
Stock Fish	0.4006
Silver Smelt	0.2104
Tilapia	0.6215

Table 5: Hazard Index for all fish samples analyzed

A. *Target Cancer risk (TCR)*

The target cancer risk (TCR), which is the potential risk of cancer development due to carcinogens present in fish samples in humans over a lifetime of exposure(usually 70 years) to contaminated fish (muscles or flesh). The acceptable range of TCR is 10^{-6} to 10^{-4}, a TCR $\leq 10^{-6}$ is considered inconsequential and a TCR $\geq 10^{-3}$ is considered to be of high risk. (Samson E, *et al*, 2020). For all fish samples analyzed (Table 6), non was up to 10^{-4}. The highest TCR obtained in this study was that of chromium 10^{-5} in Herring and Tilapia, similar to what Samson *et al.*(2020) reported in *Claries gariepinus* sold at Kado fish market Abuja. This indicates that all fish samples were safe for consumption and they do not pose any cancer risk.

Sample	Cd	Pb	Cr
Croaker	7.98×10^{-7}	3.06×10^{-7}	8.0×10^{-6}
H.Mackerel	1.18×10^{-6}	1.62×10^{-7}	3.98×10^{-6}
Herring	1.06×10^{-6}	3.57×10^{-7}	1.35×10^{-5}
Mackerel	6.46×10^{-7}	2.465×10^{-7}	3.98×10^{-6}
Stock Fish	1.33×10^{-6}	3.825×10^{-7}	7.0×10^{-6}
Silver Smelt	1.06×10^{-6}	3.74×10^{-7}	7.5×10^{-6}
Tilapia	9.12×10^{-7}	3.23×10^{-7}	1.15×10^{-5}

Table 6: The Target Cancer Risk for all samples analyzed

B. *Maximum Safe Consumption (MSC)*

For the maximum safe weekly consumption (Table 6.0), Hg appears as the only metal of concern regarding the consumption of Tilapia fish, where the maximum amount of Tilapia*(Oreochromis*) that should be eaten by a 60kg adult person to reach the PTWI for Hg is 0.46kg per week. This result shows that Hg may cause more harm to human if the maximum safe consumption level is exceeded, since it has an overall lowest PTWI compared to other metals obtained in this study. This also means that in order to avoid the negative effect of Hg from its bioaccumulation in body of its consumers, the consumption of this Tilapia fish should not exceed 0.46kg per week. This is quite lower than the 1.6kg reported by Mohammed *et al.,* (2021). The lowest calculated PTWI for Pb and Cd are 11.45kg in Stock fish and 46.67kg Horse Mackerel respectively per week consumption. This is relatively safe since it may not be possible for 60kg consumer to exceed this level in one week's consumption.

Sample	Al	Cd	Cr	Fe	Hg	Pb	Zn
Croaker	400	70	913	238.13	0.89	14.56	405.01
H.Mackerel	1,666.67	46.67	1,826	272.50	1.29	18.29	482.20
Herring	122.49	52.5	538.5	170.39	0.92	12.29	393.99
Mackerel	2,500	84	1,826	301.35	1.89	17.65	333.33
Stock Fish	1,666.67	420	1,024.4	638.78	0.70	11.45	484.43
Silver Smelt	652.17	52.5	974.7	653.69	1.48	11.90	318.18
Tilapia	555.56	60	488.4	477.27	0.46	13.64	306.12

Table 7: The maximum safe consumption (MSC) for all fish samples analyzed (kg/week).

V. CONCLUSION AND RECOMMENDATIONS

A. Conclusion

Seven metals in the gills, livers and flesh(muscle) tissues of seven different imported fish species sold at the popular fish market of Kano line, Kano State Nigeria , were determined to investigate their levels and human health risk. All the metals (Al,Cd,Cr,Fe,Hg,Pb,Zn) were detected in all the fish samples analyzed, with the highest concentration recorded in Iron(Fe) and the lowest concentration was found in Cadmium(Cd). The general order of metal bioaccumulation measured in the fish tissues were in the order; Fe > Zn > Hg > Cr > Pb > Al > Cd in the gills, and Fe >Zn >Al > Hg> Cr >Pd >Cd in the livers, and Zn > Fe > Hg > Pb > Al > Cr > Cd in the fish flesh(muscle). The majority of all the metals analyzed in all the tissues of the fish samples were lower than maximum levels of FAO/WHO (2003) guidelines except for Mercury(Hg) in the gills and flesh of Tilapia (*Oreochromis aurens*), and Aluminium (Al) in the livers of most samples and in the gills of Tilapia (*Oreochromis aurens*) and Horse Mackerel (*Trachurus trachurus).* The pattern of the metals accumulation for all fish tissues was found to be more in the gills and livers, which was as a result of breathing (gills) and feeding pattern, since the gills is the site for ionic exchange and also, the liver is the store-house for minerals.

The estimation of the Target Hazard Risk and Hazard Index (non-carcinogenic risk) conducted in this study indicated no adverse health effects from the consumption of the fishes , although, the elevated levels in the Tilapia muscle needs to be closely monitored. The Target Cancer Risk (carcinogenic risk) was also observed to be of low significance, but not ignorable, especially in the Chromium levels in Herring(*clupea harengus*) and Tilapia(*Oreochromis aurens*).The Chromium exposure through the fish consumption may increase the probability of developing cancer in future if not checked. According to the estimated maximum safe consumption (MSC) levels, Mercury(Hg) may cause significant health effects in humans if Tilapia(*Oreochromis aurens*), Stock fish(*Gadus* morhua) and Croaker(*micropoginias undulates*) are consumed in a large amount.

B. Recommendations

The detection of the metals in all assayed fish samples suggest that these fish species are from an aquatic environment prone to contamination. Although, to some reasonable extent, the fishes are safe for consumption, this should not be without proper routine monitoring of the contaminant levels, before they are allowed into the shores of this country. Taking into cognizance the results obtained from this study, the following recommendations will prove useful

- Health management officials in the various source countries should implement regulatory agencies task with the periodic biomonitoring of the source waters from which they export these fish. They can also advise the people into the fishing business to stop fishing from water bodies that are receiving industrial effluents
- NAFDAC and the Nigerian Customs should begin to investigate imported fish before they are allowed into Nigerian markets to ensure they are not contaminated with toxic heavy metals and this should be done regularly on every single imported container of fish
- The Mercury(Hg) level in Tilapia (*Oreochromis aurens*) in this study was quite high and therefore it should be consumed in moderation (not more than 0.5kg per week) in order to avoid any future health complications.
- Due to the limitations of this study, this result should be taken as preliminary, therefore further research to additionally validate these results are recommended.

- List of Tables

- List of Figures

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