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Determination and health risk assessment of Cd, Cr and Cu in wild *Clarias gariepinus* (cat fish), *Oreochromis niloticus* (tilapia fish) and *Micropogonias undulatus* (croaker fish) sold in Gwagwalada Area Council, FCT Nigeria

Dallatu E. Musa[1,*], Jude E. Emurotu[1], Atumeyi A. Ugbedeojo[1], Ernest O. Onugwu[1], Ibrahim Esther[2]

[1] Chemistry Department, Faculty of Science, Federal University, P.M.B. 1154, Lokoja, Kogi State, Nigeria

[2] Industrial Chemistry Department, Faculty of Science, Federal University, P.M.B. 1154, Lokoja, Kogi State, Nigeria

*E-mail address: emuda4real@yahoo.com , ephraim.dallatu@fulokoja.edu.ng

ABSTRACT

Fish are good sources of protein however when they contain toxic metals, they can pose health risk to human beings. Percentage moisture and ash contents were determined using oven dry weight and furnace methods respectively. Also, the concentrations (mg/ Kg) of Cd, Cr and Cu in the tissue of catfish, tilapia and croaker fish were determined using an atomic absorption spectrophotometer (AAS). Estimated daily intake of Cd, Cr and Cu, hazard quotient, hazard index, and cancer risk were evaluated. The result showed 4.25±0.35 % (catfish), 5.25±0.45 % (tilapia fish) and 4.50±0.00 % (croaker fish) for moisture, 1.75±0.35 % (cat fish), 2.25±0.23 (tilapia fish) and 2.25±0.23 % (croaker fish) for ash content. The concentrations of Cd, Cr and Cu in the species of fish determined were above the threshold WHO/ FAO (0.02 mg/ kg) limit. The THQ for Cu was greater than 1 while Dc and Cr were less than 1. This indicates that the level of Cu in the species of fish determined will lead to a non-carcinogenic effect on consumers.

***Keywords*:** Determination, Heavy Metals, Fish, Moisture, Ash, Health Risk

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1. INTRODUCTION

Heavy metals are metallic elements whose atomic weights and densities are five times greater than that of water in other words, they are metals which possess a specific density of more than 5 g/cm^3 and adversely affect the environment and living organisms (Järup, 2003; Hazrat Ali & Ezzat Khan, 2017; Barakat, 2011; Walker *et al*., 2012; Tchounwou Walker *et al*., 2012; Appenroth, 2010) and according to Morais *et al.* (2012); Jaishankar *et al*., (2014), these metals are quintessential to maintain various biochemical and physiological functions in living organisms when in very low concentrations, however they become noxious when they exceed certain threshold concentrations. Heavy metals often contaminate bodies of water which are the habitats of fish and other aquatic lives through discharge/ disposal of industrial waste water (effluent) into ponds, streams, rivers, sea and oceans; run off of water/ leachates from mining sites into these bodies of water; through feeds and washed off of heavy metal contained fertilizers/ pesticides by rains into bodies of water (Hama Aziz *et al*., 2023; Zaynab *et al*., 2022; Singh *et al*., 2022; Nath *et al.*, 2008). Bioaccumulation of metals in tissues of fish to toxic level could occur. These fish are subsequently harvested, processed and sold for nutritional, medicinal, industrial and many other uses.

Despite the fact that heavy metals have some useful applications like the use of arsenic compounds as rat poisons and insecticides under strict control (Hughes *et al.*, 2011), organoarsenic compounds are added to poultry feed to prevent disease and improve weight gain (Nachman *et al.*, 2013). Mercury is extensively used in thermometers, barometers, pyrometers, hydrometers, mercury arc lamps, fluorescent lamps and as a catalyst (Jaishankar *et al.*, 2014), it is also being used in pulp and paper industries, as a component of batteries and in dental preparations such as amalgams (Chen *et al.*, 2012). According to Ghani (2011), chromium finds its applications in industries such as metallurgy, electroplating, production of paints and pigments, tanning, wood preservation, chemical production and pulp and paper production. About three-fourths of cadmium is used in alkaline batteries as an electrode component, the remaining part is used in coatings, pigments and platings and as a plastic stabilizer (Mutlu *et al.*, 2012), etc.

These metals have a history of being harmful to human health, even at low quantities and they can build up in the body over time, creating serious health issues for instance, lead exposure has been reported by Jaishankar *et al.* (2014); Kumar (2018) to harm the brain system, kidneys and reproductive system, Hayat *et al.* (2019); Wang *et al.* (2021); Nawrot *et al.* (2010) report that cadmium exposure can result in lung and prostate cancer, kidney damage and brittle bones (Rafati et al., 2017).

Nausea, mouth ulcers, skin ulcers, skin rashes, vomiting, diarrhea and arthritic pain have been reported by Krewski *et al.* (2007); Jaishankar *et al.* (2014) as symptoms for higher amounts of aluminium in human body, its exposure is probably a risk factor for the onset of Alzheimer disease (AD) in humans, as hypothesized by the WHO (1997) and other complications associated with aluminium toxicity are lung problems, anemia, impaired iron absorption, nervous system problems (Krewski *et al.*, 2007). The inorganic forms of arsenic such as arsenite and arsenate are reportedly said to be highly carcinogenic causing cancer of lungs, liver, bladder and skin (Matschullat, 2000; Smith *et al.,* 2000; Hoque, 2011). Cadmium and its compounds are being classified as group 1 carcinogens for humans by the International Agency for Research on Cancer (Henson and Chedrese, 2004) and can cause both acute and chronic intoxications (Chakraborty *et al.* 2013).

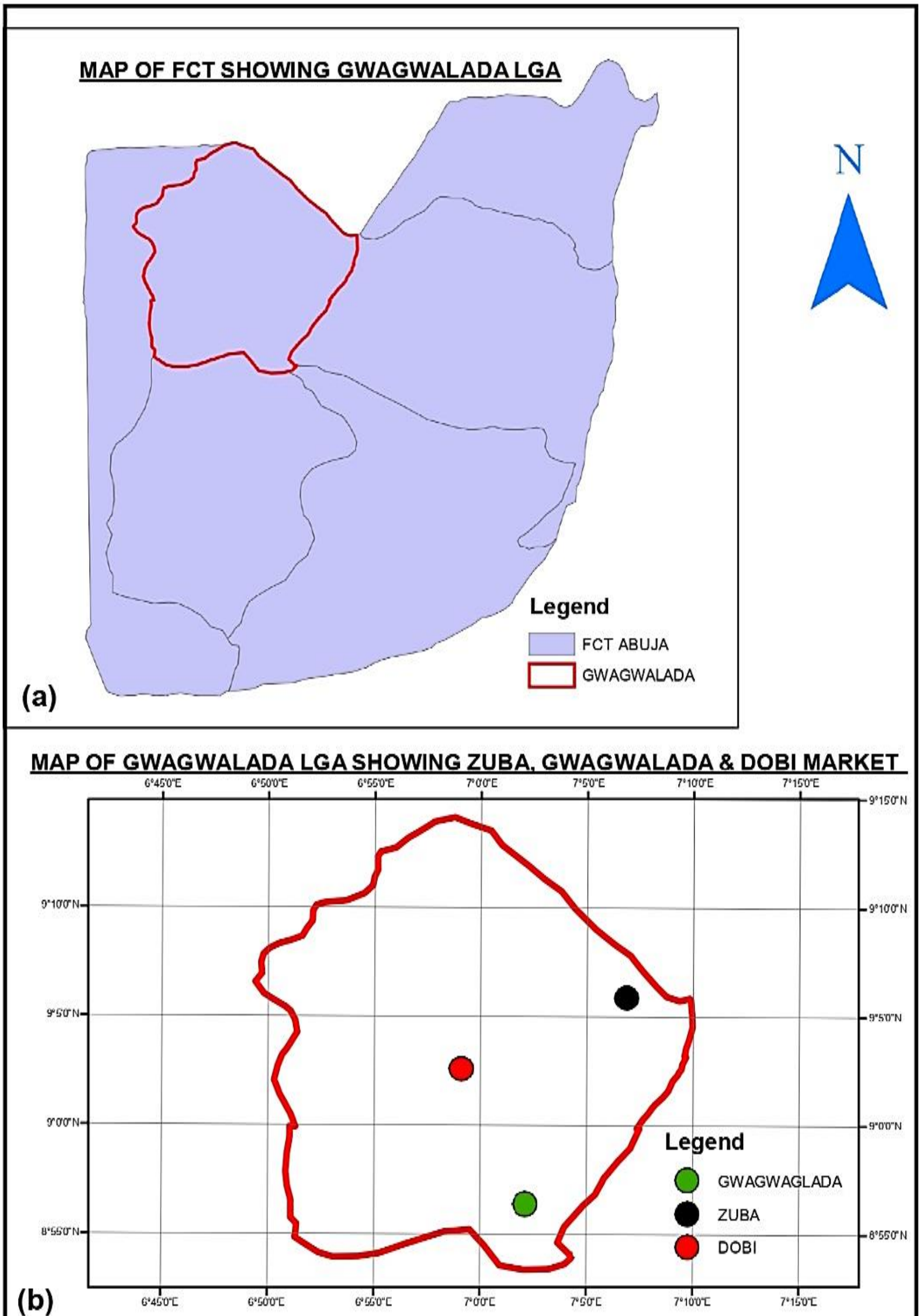

Plate 1(a,b). Maps of Federal Capital Territory, Abuja Showing Gwagwalada Area Council and Map of Gwagwalada Area Council Showing the Sampling areas: Dobi, Gwagwalada and Zuba.

Chromium(VI) compounds, such as calcium chromate, zinc chromates, strontium chromate and lead chromates, are highly toxic and carcinogenic in nature (National Toxicology Program, 2021). Emerit *et al.* (2001) reported that iron can catalyze the reactions involving the formation of radicals which can damage biomolecules, cells, tissues and the whole organism. Iron poisoning has always been a topic of interest mainly to pediatricians (Albretsen, 2006). Children are highly susceptible to iron toxicity as they are exposed to a maximum of iron-containing products (Albretsen, 2006). Lead poisoning is a classic disease and the signs that are observed in children and adults are mainly pertaining to the central nervous system and the gastrointestinal tract (Markowitz, 2000; ATSDR, 2000).

The non- biodegradable heavy metals bio- accumulate in living organisms thereby causing various damages, diseases and disorder such as gastrointestinal and kidney dysfunction, nervous disorders, skin lesions, vascular damage, birth defects thus, heavy metals contamination in fishes can pose serious health risks to consumers hence the need to determine heavy metals in some wild fish sold in three major markets of Gwagwalada Area Council, FCT – Abuja owing to the fact that these fish might have been harvested from rivers of neighboring states wherein mining activities of solid minerals containing heavy metals and brought in for sale at these markets.

Analyzing levels of heavy metals in fish allows for an assessment of potential dietary exposure to these heavy metals. By understanding the concentration of these metals in fish, researchers and regulatory bodies can estimate the extent of heavy metal intake by individuals, helping in risk assessment and mitigation strategies. Regulating the amounts of heavy metals in food and water sources has been attempted. For instance, the World Health Organization (WHO) has established restrictions on the allowable levels of heavy metals in food, supplements and drinking water (FAO/WHO, 2007). The European Union has also created guidelines for the highest allowed levels of heavy metals in food (European Commission, 2018).

Methods and Approaches for determining and assessing health risk of Cd, Cr and Cu

The aim of this study to assess the levels of some heavy metals in wild fish sold in the three major markets of Gwagwalada Area Council, FCT – Abuja. This was achieved through fish sample collection, sample preparation, heavy metal analysis using atomic absorption spectrophotometer (ASS) and comparison of results with safety standard specifications. Findings of this study are useful to the society, humanity, researchers since its contribution lies in enhancing food safety, protecting human health, advancing scientific knowledge and promoting responsible agricultural practices.

2. EXPERIMENTAL / RESULTS/ (MATERIALS AND METHODS)

Assorted glass wares, crucibles with lids, crucible tongs, laboratory knife, spatula, pestle and mortal and weighing balance; oven: AS ONE 1-5197-01 FC-1000, pH meter: MSP43, Atomic Absorption Spectrophotometer (AAS) Machine ED-XRF Analyzer and Muffle Furnace: GPC AMS2750E were used. Analytical grade nitric acid (HNO_3), hydrochloric acid (HCl), hydrogen peroxide (H_2O_2), buffer tablets of pH 4.7 and 9, potassium hydroxide (KOH), and sodium carbonate (Na_2CO_3) were used. Standards of cadmium (Cd), chromium (Cr) and copper (Cu) were also used. These reagents were purchased from BDH.

Gwagwalada has an area of 1,043 km^2 and a population of 157,770 at the 2006 census. It is projected to have a 6.26% growth between 2020 and 2025, the largest increase on the African continent.

The latitude of Gwagwalada, Nigeria is 8.950833, and the longitude is 7.076737. Gwagwalada, Nigeria is located at *Nigeria* country in the *Towns* place category with the gps coordinates of 8° 57' 2.9988" N and 7° 4' 36.2532" E. Figures 1a and b are maps of Federal Capital Territory, Abuja showing Gwagwalada Area Council and map of Gwagwalada Area Council showing the sampling areas: Dobi, Gwagwalada and Zuba (Avery, 2021).

Samples and sampling: The samples were dried wild cat, tilapia and croaker fish. About 500 g each of the fish were randomly bought on 15th November, 2023 from fish vendors in Dobi, Zuba and Gwagwalada markets into five washed and rinsed - labeled plastic sampling containers, covered and transported to laboratory for analysis.

Sample preparation: Substances other than fish were identified and removed from the samples and the samples were washed, rinsed with distilled – deionized water in order to remove dust and any other particles adhered to the samples which might contain heavy metals.

Determination of moisture content: This was done according to the oven dry basis method procedure reported by Onwuka (2005); Boyd (2021); Ahn *et al*. (2014); Ibeabuchi *et al*. (2020). About 3.0 g of pulverized dried samples was weighed into a dried and weighed crucible as W_1. This was placed in an oven and heated at 105 °C for 30 minutes. It was removed, allowed to cool in desiccators and weighed as W_2. The crucible with its content was again transferred back to the oven, heated, removed after 30 minutes, allowed to cool and weighed – this was repetitively done until constant or stable values for mass of crucible with content after cooling was obtained as W_3. The percentage moisture content was calculated using the formula

$$\%\ Moisture\ content = \frac{Mass\ of\ Moisture}{mass\ of\ sample} \times 100$$

This was done in triplicates.

Preparation of standard and working standards: This was done in line with the procedures reported by Ibitoye (2005; 2008); Nabil (2011). 100 ppm solution (stock) of each heavy metal was prepared in 100 cm^3 using distilled – deionized water, made up to mark and labeled as such. Thereafter, dilution principle equation, $C_1V_1 = C_2V_2$ was used to prepare working standards of 2.0 ppm, 4.0 ppm, 6.0 ppm, 8.0 ppm and 10.0 ppm for each metal in map100 cm^3 and labeled respectively.

Thermal digestion (ashing) of samples: The ash content was determined using the ignition method in line with the procedure reported by Onwuka (2005); Boyd (2021); Ahn *et al*. (2014); Ibeabuchi *et al*. (2020). A crucible was thoroughly washed and pre-heated in a muffle furnace at 450 °C. About 10.0 g of pulverized sample was weighed and placed in the pre-heated cooled and weighed crucible and then reweighed. The crucible was covered with its lid and then placed in the muffle furnace. Its temperature was allowed to rise to 550 °C and the ashing was carried out for three hours after which crucible was removed from the furnace, allowed to cool in a desiccators and reweighed. The percentage ash content was calculated using the formula:

$$\%\ Ash\ content = \frac{Mass\ of\ ash}{mass\ of\ dried\ sample} \times 100$$

This was done in triplicates.

Preparation of sample solutions: Ash of each sample was dissolved and filtered into 100 cm^3 volumetric flask with distilled – deionized water, made up to mark and labeled according to the procedure reported by Ibitoye (2005; 2008).

Atomic absorption spectrophotometric determination of heavy metals: This was done in line with the procedures reported by Ibitoye (2005; 2008). Hollow cathode lamp of each heavy metal was fixed and its wavelength was set. The instrument was switched on for fifteen minutes in order to stabilize it followed by the compressor to supply air at a regulated pressure. The fuel, acetylene was then on and regulated. The ignition control knob was pressed for flame to alight.

A blank, 0.0 mg/ L or ppm was introduced and aspirated into the flame. The blank control was adjusted to set zero absorbance or 100 % transmittance and working standards of the heavy metal in question were introduced and aspirated, agreeable absorbance readings were recorded against their concentrations (ppm). Similarly, sample solutions were respectively introduced, aspirated and their absorbance were recorded. Absorbance of samples and concentration of Cd, Cr and Cu in the samples were read up from the atomic absorption spectrophotometer's monitor.

Quality assurance: All apparatus/ glass wares were washed and rinsed with distilled – deionized water, all all instruments were calibrated before use, analysis and measurements were done in replicates and, analytical weighing balance was used. Adequate precautions were also taken when handling samples to prevent cross-contamination.

Health risk assessment: This was done by adopting the procedure reported by Ametepey *et al.* (2018). Potential health risks associated with long term consumption of fish contaminated with heavy metals were assessed by calculating the average daily dose (ADD) of heavy metals, hazard index (HI), target hazard quotient (THQ) and non-carcinogenic risk (NCR). Table 1 shows the parameters that characterized the ADD.

$$ADD = \frac{Ci \times IR \times EF \times ED}{BW \times AT} \quad (1)$$

where Ci is metal concentration in fish, IR is ingestion rate, EF is exposure frequency, ED is exposure duration, BW is body weight of consumer and AT is average time. The health risk was assessed in relation to its non-carcinogenic as well as carcinogenic effects based on the calculation of ADD estimates and defined toxicity according to the following relationships (USEPA IRIS 2011; Wongsasuluk *et al*. 2014).

Table 1. Input Parameters to Characterize ADD Value

Exposure parameters	Symbols	Units	Value
Concentration Ingestion rate	C IR	mg / kg g/day	Table 3 2.2
Exposure frequency	EF	days/year	365
Exposure duration	ED	Years	70
Adult BW	BW	Kg	70
Child BW	BW	Kg	16
Average time	AT	Years	25,550 days

Source: Wongsasuluk *et al*. 2014; USEPA IRIS, 2011

Estimation of non-carcinogenic risk of heavy metals consumption was determined using target hazard quotient values. Target hazard quotient is a ratio of the determined dose of a contaminant to oral reference dose considered detrimental. If the ratio is greater than or equal to 1, an exposed population is at risk. The non-carcinogenic risk of heavy metals was calculate using Eq. 2:

$$Hazard\ Quotients(HQ) = \frac{ADD}{RfD} \quad (2)$$

where ADD is average daily dose and RfD is reference dose.

Hazard index is used to estimate the potential human health risk when more than one heavy metal is consumed. HI was calculated as the sum of HQs.

$$HI = (THQi + THQii + THQiii + THQn) \sum THQ \quad (3)$$

The individual metal toxicity responses (dose response) are 5.0×10^{-4} for Cd, 3.0×10^{-3} for Cr and 4.2×10^{-2} for Cu all in mg/kg/day as the Oral Reference Dose (RfD) (USEPA IRIS 2011; Wongsasuluk et al. 2014). The risk assessments of a mixture of chemicals, the individual HQs are summed to form hazard index (HI): According to Lim et al. (2008) an HI / HQ > 1 means an unacceptable risk of non-carcinogenic effects on health, whilst HI / HQ < 1 means an acceptable level of risk.

Table 2. Moisture Content of Dried Sampled Fishes.

Samples	Moisture content (%)
Cat fish	4.250±0.354
Tilapia fish	5.250±0.453
Croaker fish	4.500±0.000

Tables 2, 3 and 4 show moisture and ash content, and concentration (mg/Kg) of Cd, Cr, Pb and Fe in cat, tilapia and Titus fish respectively.

The data in Table 2 are graphically presented in Fig. 1.

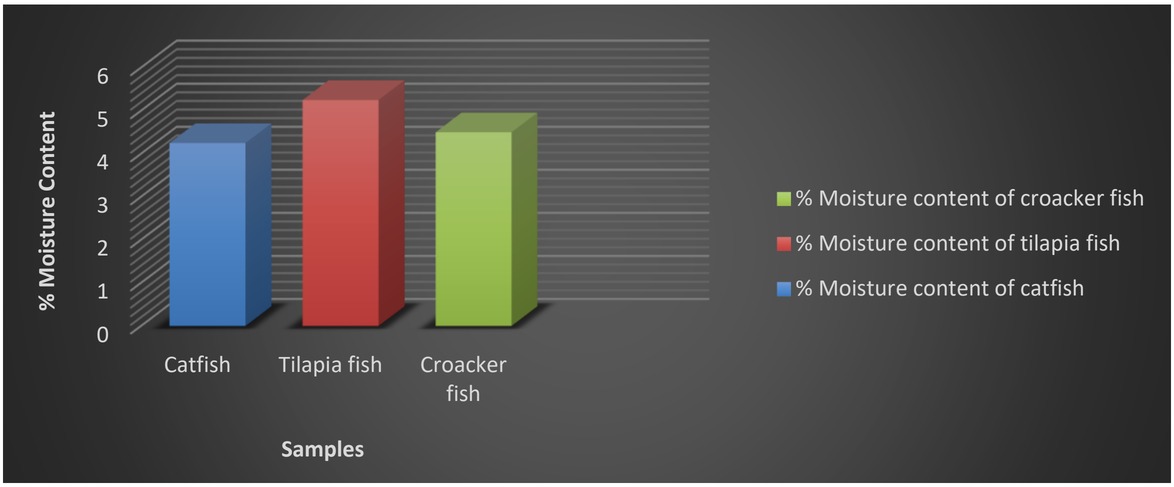

Figure 1. Bar Chart for % Moisture Content of the Sampled Fish

Table 3. Ash Content of Sampled Fishes

Samples	Ash content (%)
Cat fish	1.750±0.354
Tilapia fish	2.250±0.231
Croaker fish	2.250±0.231

The data in Table 3 are graphically presented in Fig. 2.

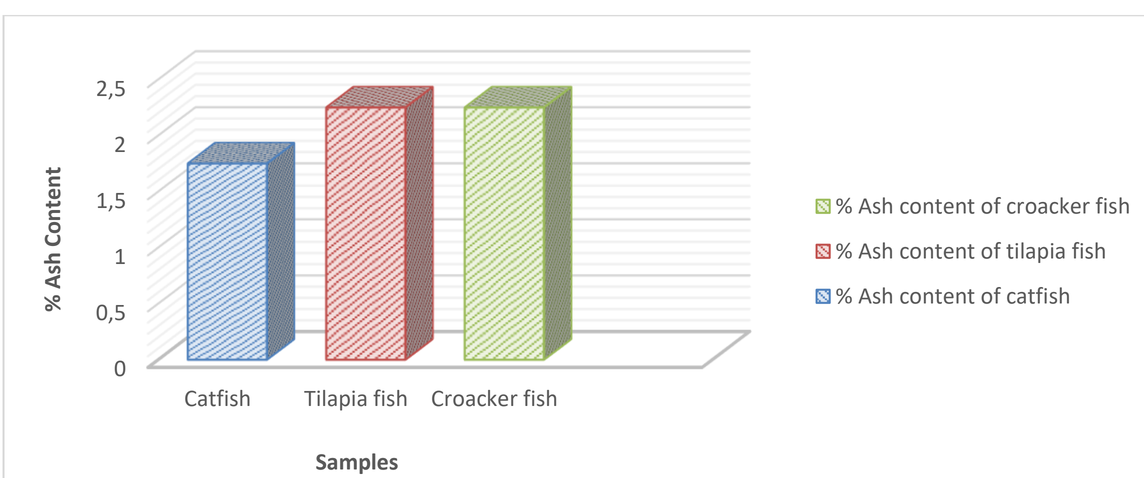

Figure 2. Bar Chart for % Ash Content of the Sampled Fish

The data in Table 4 are graphically presented in Fig. 3.

Table 4. Concentration (mg/ Kg) of Cd, Cr, Cu and Pb in Sampled Fishes

Sampled Fish	Results	Cd	Cr	Cu
Cat	Min.	0.04	0.43	1.45
	Max.	0.07	0.47	2.50
	Mean	0.06±0.02	0.45±0.03	1.98±0.74
Tilapia	Min.	0.05	0.25	2.23
	Max.	0.06	0.64	2.31
	Mean	0.06±0.01	0.45±0.28	2.27±0.06
Kroaker	Min.	0.04	0.15	2.30
	Max.	0.06	0.54	2.34
	Mean	0.05±0.01	0.345±0.28	2.32±0.03
WHO/FAO (2007)		0.02	5	2-3

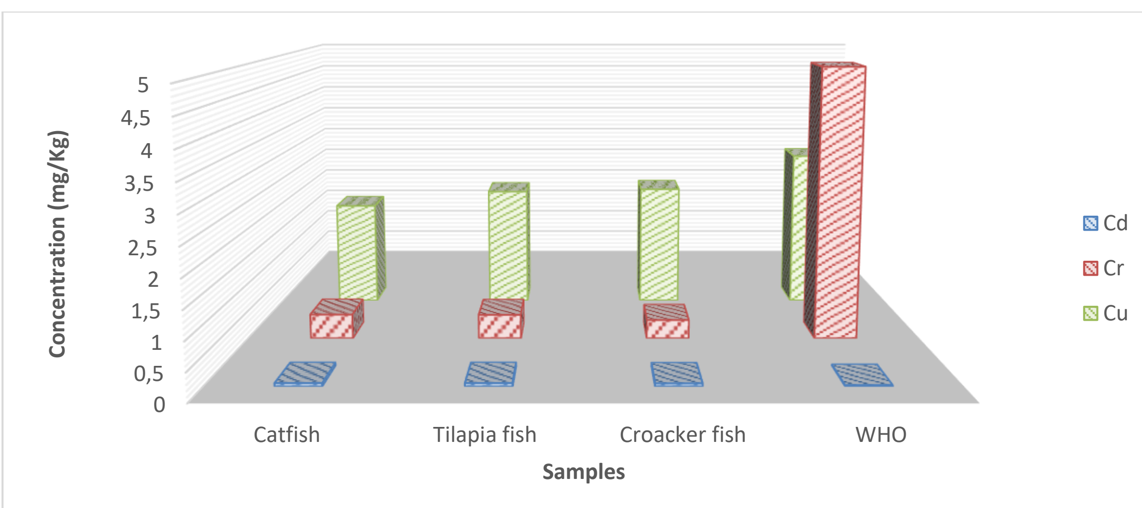

Figure 3. Bar Chart for Concentration (mg/Kg) cadmium (Cd), chromium (Cr) and Copper (Cu) in Cat, Tilapia and Titus Fish

Result for moisture content presented in table 2 shows tilapia fish having the highest moisture content, 5.25±0.45 % followed by croaker 4.50±0.00 % and the lowest moisture content sample was cat fish with 4.25±0.35 %. The moisture content plays a significant role in the flow and other mechanical properties of the food. However, it depends largely on the method, extent of drying and the humidity in the surrounding atmosphere (Lawal, 2004). Drying is removal of water from fish to such an extent where most of microbes, enzymes and moulds will be inactive and will not grow due to reduced moisture and water activity. In general, moisture content of 15-20% is aimed (FDA, 2001). Water activity levels below 0.6 lead to complete restriction for microbial growth Pathogen growth in the finished product as a result of inadequate drying of fishery products can cause consumer illness. Examples of dried fish products are: salmon jerky; octopus chips; dried shrimp; and, stock fish. (FDA, 2001)

Result for ash content presented table 3 indicates that tilapia and croaker fish have the same percent ash content, 2.25±0.23 % with cat fish having the lowest, 1.75±0.35 %. This result could be attributed to the varying composition of the mineral contents of the samples.

Table 4 shows concentrations (mg/ Kg) of Cd, Cr and Cu in sampled fish where cat and tilapia fish are of higher concentration of Cd, 0.06±0.02 and 0.06±0.01 respectively while croaker fish contained 0.05±0.01 all of which are above the threshold of WHO/ FAO (2007), 0.02 mg/Kg: this might pose health risk to consumers. No known beneficial function of cadnium in the human body (Genchi *et al*., 2020; Sinicropi *et al*., 2010; Friberg *et al*., 2019) however, it is a cumulative toxin (Chen *et al*., 2014; Lane *et al*., 2015; Oladipo *et al*., 2016). Cat fish has the highest concentration of Cr (0.45±0.03 mg/ Kg) followed by tilapia fish, 0.45±0.28 mg/ Kg and lowest in croaker fish, 0.35±0.28 mg/ Kg and, these are all below the WHO/ FAO (2007) specifications (5 mg/ Kg).

Wilbur *et al*. (2012); Liu *et al*. (2018); Sharma *et al*. (2011) reported that chromium is an essential nutrient required for normal energy metabolism nevertheless, human health is adversely affected due to the exposure of chromium (Guertin, 2004) and certain effects of Cr like mouth ulcers, indigestion, acute tubular necrosis, vomiting, abdominal pain, kidney failure and even death have been reported by (Beaumont *et al*., 2008). On the other hand, concentration of Cu was higher in croaker fish, 2.32±0.03 mg/Kg followed by tilapia, 2.27±0.06 mg/Kg and low in cat fish, 1.98±0.74 mg/Kg relative to the WHO/ FAO (2007) permissible specification, 2 - 3 mg/Kg. Importance of copper to humans have been widely reported among which are a study carried out by Bonham *et al*. (2002); Uriu-Adams and Keen (2005) whose findings are that Cu appears to have many important functional roles in body that apparently relate, among others, to the maintenance of immune function, bone health and haemostasis also, Bost *et al*. (2016); Pham *et al*. (2013) have it that copper is a vital micronutrient for humans, but an excess of it in the body, particularly in cells, can lead to cytotoxicity emphasizing that the free hydrated form (such as Cu^{2+}) has the potential to be toxic by altering membrane permeability and protein synthesis, as well as various enzymatic activities and, Royer and Sharman (2023) added that copper metabolism plays an important role in physiologic homeostasis however, its toxicity induces several pathologic processes that are detrimental to human health.

Table 4 also shows that concentration of cadmium (Cd) in sampled cat, tilapia and croaker fish is higher than the FOA/ WHO permissible limit (0.02 mg/ Kg) hence non – carcinogenic risk of Cd was determined by calculating average daily dose (ADD) using equation 1 subsequently, hazard quotients (THQ) using equation 2. THQs for adults and children are 3 and 13.8 respectively. These are greater than 1 and in line with USEPA IRIS (2011); Wongsasuluk *et al*. (2014) therefore, the health of adults and children who consume these cat, tilapia and croaker fish sold in Dobi, Gwagwalada and Zuba markets of Gwagwalada Area Council is at risk. On the other hand, concentration of Cu in the sampled fish is averagely in between the minimal and maximal permissible level, 2 -3 mg/Kg (Table 3). Calculated THQ – Cu for adults and children are 1.62 (> 1) and 0.23 (<1) respectively hence health of adults is merely at risk but the children's health is not at risk. For Cr, its concentration (mg/ Kg) in the sample fish; cat fish: 0.45±0.03, tilapia fish: 0.45±0.28, croaker fish: 0.35±0.28 (Table 3) is far below the permissible limit (5 mg/ Kg) thus, Cr does not pose health risk to both adults and children consuming these fish.

3. CONCLUSION

Tilapia fish has the highest moisture content, 5.25±0.35 % followed by croaker 4.50±0.00 % and the lowest moisture content sample was cat fish with 4.25±0.35 %. Ash content shows tilapia and croaker having the same percent ash content, 2.25±0.35 % with cat fish having the lowest, 1.75±0.35 %.

The concentrations (mg/ Kg) of Cd, Cr and Pb in sampled fish shows cat and tilapia fish containing higher concentration (mg/Kg) of Cd, 0.06±0.02, 0.06±0.01 respectively and low in croaker fish: 0.05±0.01 all of which are above the threshold of WHO/ FAO (2007), (0.02 mg/Kg). Cat fish has the highest concentration of Cr (0.45±0.03 mg/ Kg) followed by tilapia fish, 0.45±0.28 mg/ Kg and lowest in croaker fish, 0.35±0.28 mg/ Kg. These are all below the WHO/ FAO (2007) specifications (5 mg/ Kg). However, Cu is higher in croaker fish, 2.32±0.03 mg/ Kg, follow by 2.27±0.06 mg/ Kg in tilapia but low in cat fish, 1.98±0.74 mg/ Kg – these are relatively low below permissible levels of Cu.

Health of adults and children who consume the sampled cat, tilapia and croaker fish sold in Dobi, Gwagwalada and Zuba markets of Gwagwalada Area Council is at risk due to concentration of Cd and Cu in them: these might pose health risk to the consumers. But while health of adults is at risk due to Cr content, that of children is not.

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