ANALYSIS OF HEAVY METALS IN SOME FRESH AND MARINE WATER FISH SPECIES SOLD IN DAMATURU METROPOLIS

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ABSTRACT

This study assessed the risk and safety level of heavy metals associated with the haphazard consumption of fresh and marine fish species. Concentrations of Lead, Arsenic, Zinc, Nickel, Cadmium and Chromium in selected fish species (African Catfish: Clarias gariepinus, Nile Tilapia: Oreochromis niloticus, Mackerel: Scomber scombrus japonicas and Herring: Clupea harengus) were determined using a Bulk Scientific U.S.A. Model 210VGP Atomic Absorption Spectrophotometer (AAS).The fish were purchased at Damaturu fish market, that sourced from College Teaching and Research Farm, Suleiman Farm Gashua-Maiduguri by-pass, Alo Dam Maiduguri and Kaneko Sangyo Co. LTD Japan respectively. Highest amount of lead was recorded highest in Oreochromis niloticus (0.0942±0.055) and the least was found in the tissues of Scomber scombrus (0.0457±0.004), Arsenic recorded in Clarias gariepinus (0.0067±0.003) and the Oreochromis niloticus had the lowest value (0.0067±0.003). Nickel was higher in Scomber scombrus and Clupea harengus with similar value 0.0357±0.005 and 0.0330±0.004 respectively while lower amount was found in Oreochromis niloticus and Clarias gariepinus 0.0265±0.004and 0.0237±0.002respectively. Cadmium was only found in Oreochromis niloticus with a value of 0.0030±0.000. Chromium was significantly higher in Clarias gariepinus (0.0447±0.013) compared to Clupea harengus with 0.0062±0.005. Zn was highest in Clupea harengus (72.42mg/g) while, lowest recorded in Oreochromis niloticus with the mean and standard error of 58.250±0.572 mg/g. Only Zn above the Food and Agricultural Organization's (FAO) permitted limits for fresh fish intended for human consumption; the highest levels were found in Scomber scombrus japonicas (69.952.14), while the lowest levels were found in Clupea harengus (58.900.96).Therefore, further research should be carried out to assess the safety margin from other sources, species of fish and elements that poses carcinogenicity and toxicity.

KEYWORDS

Clarias gariepinus, Oreochromis niloticus, Scomber scombrus, Clupea harengus and heavy metals

1. INTRODUCTION

Fish is considered as an imperative source of income for fisherfolks, fishmongers, aquaculturists, and its production creates jobs in developing nations (Felix *et al.*, 2018).

In 2015 and 2016, the marine capture was 81.2 and 79.3 million tons, respectively, with a shortfall of around 2 million tons. China produced 13,189,273 tons in 2014, increased that amount to 15,314,000 tons in 2015, and then declined that amount to 15,246,234 tons in 2016 with a deficit of 15.6%. Between 2015 and 2016, there was a deficit of 0.4%, but between 2015 and 2016, there was a deficit of 67,766 tons (FAO, 2018).In Africa; Morocco produced 1,074 063 tons from 2005 to 2014 and increased to 1,349,937 and 1,431,518 tons in 2015 and 2016 respectively with average of 33.3%, between 2005 and 2014 to 2016 increase with additional 81,581 tons that is 6.0% (FAO, 2018). Nonetheless, it seems that aquaculture has better chances of supplying Nigeria's rising need for fish consumption. It is impossible to overstate aquaculture's potential benefits for local food security and livelihood, particularly for the resource-poor local dwellers.

Distribution of *Clarias gariepinus* and *Oreochromis niloticus* in Nigeria almost occurs in all geopolitical zones, are found in North-east, North-central, North-west, South-east, South-south and South-west (Geidam, 2023; Bala *et al.*, 2009; Essien-Ibok, and Isemin, 2020; Avoaja, 2011and Bolarinwa *et al.* 2015).

Scomber scombrus has streamlined, small, and svelte bodies that are suited for quick swimming. During their feeding trip in the late spring and summer, exceptionally plentiful stocks of pelagic fish use the Norwegian Sea as a huge feeding ground and migration route (Huse *et al.* 2012; Utne*et al.* 2012). Moreover, it can be found in the Mediterranean and Black Seas, as well as the northeastern Atlantic Ocean from Norway to Morocco and the Canaries. It occurs in the Northwest Atlantic between Labrador and North Carolina (FAO 1983). Atlantic mackerel (*Scomber scombrus*) is a pelagic fish belonging to the family of *scombridae* (Froese *et al.* 2017).

The freshwater fish species Clarias gariepinus and Oreochromis niloticus, as well as the marine species *Scomber scombrus* and *Clupea harengus*, are frequently consumed in Nigeria. Reports on the safety assessment of imported frozen marine fish species are scarce. As a result, heavy metals can harm a person's health in both freshwater and marine species (Olaifa *et al.,* 2010; Bashir *et al.,* 2013; Faye-ofori *et. al.,* 2015 and Abdullahi *et al.,* 2015).

Ogundiran (2014) discovered that the investigated fish species had appreciable concentrations of Pb, Ar, Zn, Ni, Cd, and Cr that were above the permissible limits. As a result, he suggested that taste, size, freshness, and other related external appearances shouldn't be the only factors considered when choosing which fish to consume. This current study on the elemental constituents of solar-dried samples of *Clarias gariepinus*, *Oreochromis niloticus*, *Scomber scombrus* and *Clupea harengus*, would be determined to gain the comparative knowledge of the risky and safety associated with indiscriminate consumption of freshwater and marine fish species.

2. MATERIAL AND METHOD

2.1. Experimental Site

The experiment was carried out in fisheries technology department of Yobe State College of Agriculture Gujba and the analysis was conducted at Yobe State University Chemistry Research Laboratory Damaturu that is located between latitude $11^0$43 and 37 north and longitude $11^0$58 and 26 east and elevation of 456m above the sea level in the semi and region of Nigeria with tropical continental eliminate the area is characterize by a short period of rainfall (June – September and long period of dry season (October – May).

2.2. Construction of Solar Oven

The solar oven was constructed with readily available materials such as a ceiling, wood, wire mesh, screen, plank, used engine oil, and metal bar plates inserted and attached to the oven wall as a cover adjuster. The oven is box-like in its dimensions, with 62cm in length and width and a height of 34 cm, respectively. Its cover was constructed upward with the groove that held the mirror.

2.3. Sample Collection

The samples of four different species of marine and freshwater fish were purchased at the Damaturu fish market.

2.3.1. Sources of Samples

The different fish samples were purchased from Damaturu fish market: The *Clarias gariepinus, Oreochromis niloticus Scomber scombrus* and *Clupea harengus* were sourced from Suleiman farm at Waziri Ibrahim Estate; Alo-Dam Maiduguri, Damaturu fish market and cold room behind Central Motor Park Damaturu respectively.

2.4. Experimental Materials and Equipment Used

The material used were solar oven, dissecting kits**,** experimental tables**,** hand globes**,** detergent**,** 30 Liters capacity plastic bowl**,** metallic tray**,** analytical balance (0 Hours) with precision of +0.001g, borosilicate, volumetric flasks (25, 50ml, 100 ml and 100ml), measuring cylinder**,** micropipettes (1 – 10ml and 1000ml), Atomic Absorption Spectro-photometry (Buck scientific USA model: 210VGP)**,** hollow Cathode lamps with air Acetylene flame and micro waves digester.

2.5. Laboratory Analysis

2.5.1. Digestion of Fish Samples

The fish muscles were flaked and sampled in accordance with the modified NIVA method described by Abdullahi *et al.* (2015), which was performed on the experimental table. The samples were washed, coded, placed in a solar oven and dehydrated at a temperature between 26 and 38^{0}C. They were then ground into a powder using a porcelain mortar and pestle.

2.5.2. Reagents and Chemicals

Reagents used for the laboratory works were all of analytical grade. For the purpose of diluting the sample and intermediate metal, de-ionized water (made in the lab) with a conductivity of 1.5 us/cm and lower was employed. Standard solution prior to analysis and rinsing glass were and sample bottles. Preparation of 1000ppm stock as standard solution for selected heavy metals such as Cr, Ni, As, Pb, Zn and Cd.

The determination of a given metal concentration in the experimental solution was based on its respective calibration curve. the calibration curves for Chromium, Nickel, Arsenic, lead, zinc and cadmium were plotted, while a stock solution of each metals ion of 1000ppm was prepared by dissolving 1.5g, 80g of Pb $(NO_3)_2$, 2.1032g of Cd (NO_3) and other metals so as to get exactly 1.0g of the desired metal in 100ml of solution in de-ionized water and then was diluted to 1 liter in a volumetric flask.

2.5.3. Standard Working Solution

A working solution of 100 ppm was prepared from the already prepared 1000 ppm solution. The volume of the stock solution was estimated and diluted to the required concentration using a sample formula (C1V1 = C2V2). Pb (NO3)2, Cr (NO3)2, H2O, Cd (NO3)2, and other standard stock solutions totaling 10 ml were pipetted into 100 ml calibrated flasks, added, and then diluted with de-ionized water. The solution was then carefully mixed. The other standard working solution was prepared from 100 ppm by pipetting out an appropriate volume into calibrated flasks and making up the volume with de-ionized water.

2.5.4. Laboratory Analysis

2.5.4.1. Preamble

The instruments used were all calibrated, and their status was checked both before and during the experiments. The equipment like digestive flasks, volumetric flasks, and measurements cylinders were all carefully cleaned with detergent and tap water before being rinsed with de-ionized water.The volumetric flasks were submerged in 10% (v/v) and the digestion tubes in 1% (w/v) po tassium dichromate in 98% (v/v) $H2SO_4$. HNO_3 for 24 hours, then rising with deionized water, dr ying in an oven, and storing the apparatus somewhere free of dust until analysis. These equipmen ts were washed and immersed in deionized water before each usage.

2.5.5. Determination of Metal Content

2.5.5.1. Preparation of Calibration Curve

The concentration of the metals in the sample solution was calculated using calibration curves. The instrument was calibrated using a series of working standards. The working standard solutions of each metal were prepared from standard solutions of their respective metals, and their absorbance was taken using the AAS calibration curve from each metal ion to be analyzed, which was prepared by plotting the absorbance as a function of metal ion standard concentration.

2.5.6. Determination of Metal Contents in Samples

Each sample was replicated and the concentration of the ions present on the sample was calculated. Their absorbance was read using AAS (Buck Scientific model 210GP), and the results were compared on their respective standard calibration curves. The instrument was manually read and recorded for each solution as the metals were determined using the absorption concentration mode. Both the spiked samples and the digested blank solution's element determination used the same analytical process.

2.6. Experimental Design and Setup

The four different treatments A1, A2, A3 and A4 as flesh, gills and visceral organs respectively in triplicated (R1, R2, R3 and R4) in a completely randomized design (CRD).

2.7. Statistical Analysis

All data obtained were subjected to analysis of variance as described by a special package for social sciences (SPSS 2012) means were separated using a Duncan multiple test range (1955).

3. RESULTS AND INTERPRETATION

The samples of four different species of marine and freshwater fish were purchased at the Damaturu fish market. The comparative analysis heavy metals of the sampled fishes are shown in Table 1. Lead value obtained was 0.0497 for *Clarias niloticus*, 0.0942 for *Oreochromis niloticus*, 0.0457 for *Scomber scombrus* and 0.0626 *Clupea harengus* as shown in Table 1. Arsenic value obtained was 0.0067 for *Clarias niloticus*, 0.0003 for *Oreochromis niloticus*, 0.000 for *Scomber scombrus* and 0.0012 *Clupea harengus* as shown in Table 1. The Zinc value obtained was 71.880 for *Clarias niloticus*, 58.250 for *Oreochromis niloticus*, 66.778 for *Scomber scombrus* and 63.373 *Clupea harengus* as shown in Table 1 respectively. The Nickel Value obtained was 0.0237 for *Clarias niloticus*, 0.0256for *Oreochromis niloticus*, 0.0357 for *Scomber scombrus* and 0.0330 *Clupea harengus* as shown in Table 1. Cadmium obtained was 0.0000 for *Clarias niloticus*, 0.0030 for *Oreochromis niloticus*, 0.0000 for *Scomber scombrus* and 0.0000 *Clupea harengus* as shown in Table 1.The Chromium value obtained was 0.0447 for *Clarias niloticus*, 0.0253 for *Oreochromis niloticus*, 0.0335 for *Scomber scombrus* and 0.0062 *Clupea harengus* as shown in Table 1. The heavy metal of four sampled fish was graphically represented by figures 1, 2, 3, 4 and 5 respectively.

Table 1: Heavy Metals of Four Different Fish Species from Damaturu Metropolis

Heavy Metals	***Clarias gariepinus***	***Oreochromis niloticus***	***Scomber scombrus***	***Clupea harengus***	**WHO/**FAO(2017) **Standard(Mg/Kg/L)**
Lead	0.0497 ± 0.003^{b}	0.0942 ± 0.055^{a}	0.0457 ± 0.004^{b}	0.0626 ± 0.008^{ab}	0.3
Arsenic	0.0067 ± 0.003^{a}	0.0003 ± 0.003^{b}	0.0000 ± 0.000^{a}	0.0012 ± 0.000^{ab}	0.01
Zinc	71.880 ± 2.664^{a}	58.250 ± 0.572^{b}	66.778 ± 1.602^{ab}	63.373 ± 5.305^{ab}	0.01-0.05
Nickel	0.0237 ± 0.002^{b}	0.0265 ± 0.004^{ab}	0.0357 ± 0.005^{a}	0.0330 ± 0.004^{a}	0.07
Cadmium	0.0000 ± 0.000^{ab}	0.0030 ± 0.000^{a}	0.0000 ± 0.000^{ab}	0.0000 ± 0.000^{ab}	0.003
Chromium	0.0447 ± 0.013^{a}	0.0253 ± 0.065^{ab}	0.0335 ± 0.002^{ab}	0.0062 ± 0.005^{b}	0.05

Note: Different letters as superscripts indicate significant differences among the treatments

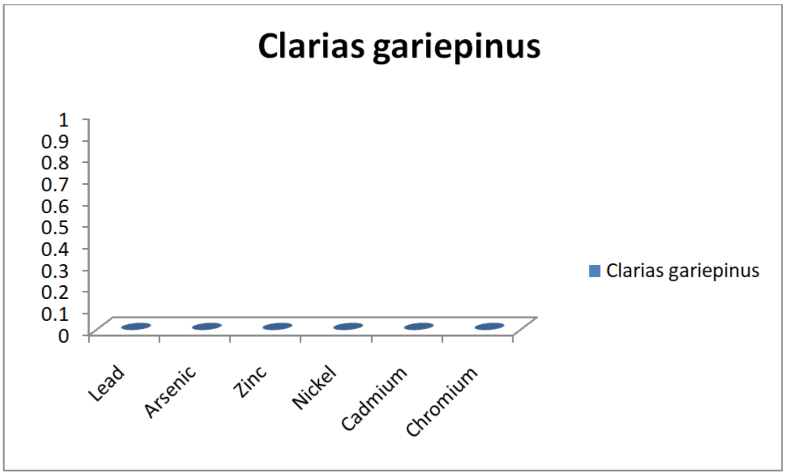

Figure:1 Heavy Metal of *Clarias gariepinus* Sold in Damaturu Metropolis

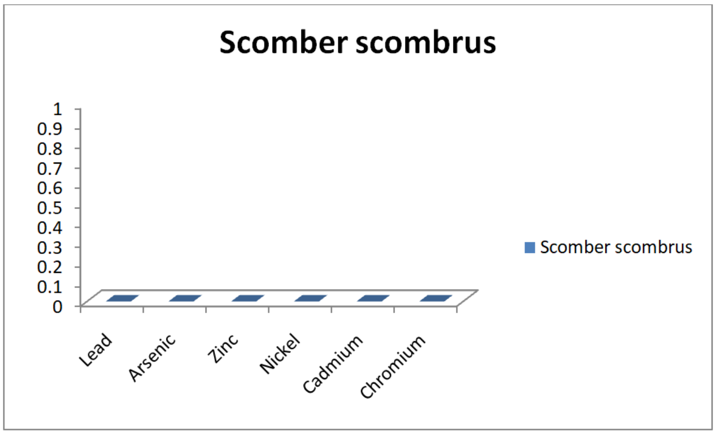

Figure: 2 Heavy Metal of *Scomber scombrus* Sold in Damaturu Metropolis

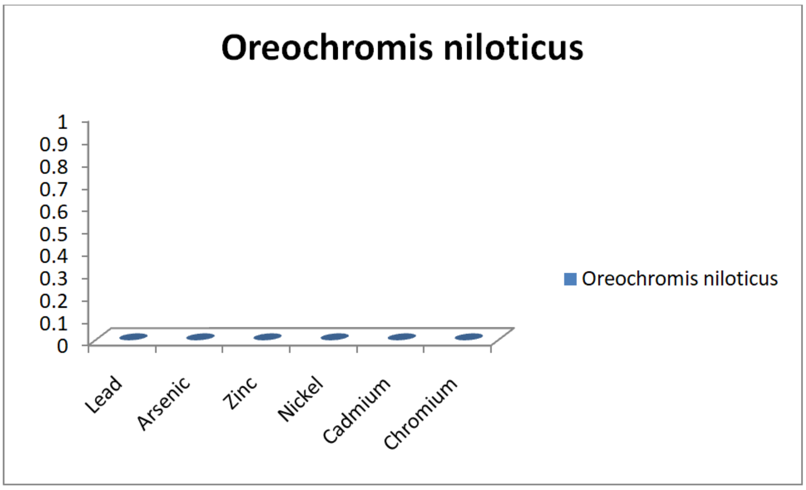

Figure:3 Heavy Metal of *Oreochromis niloticus* Sold in Damaturu Metropolis

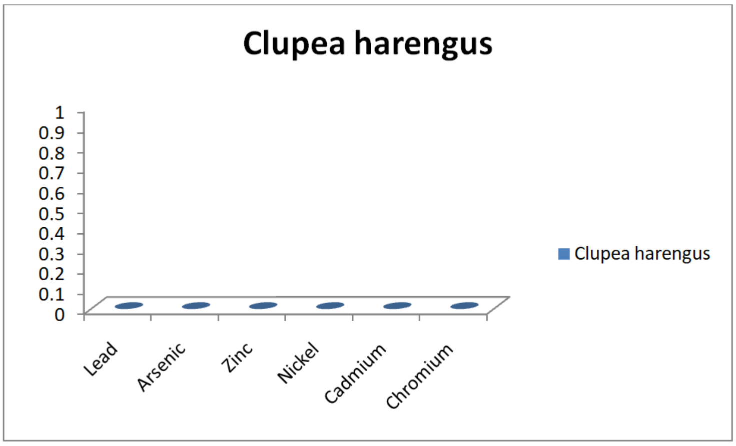

Figure:4 Heavy Metal of *Clupea harengus* Sold in Damaturu Metropolis

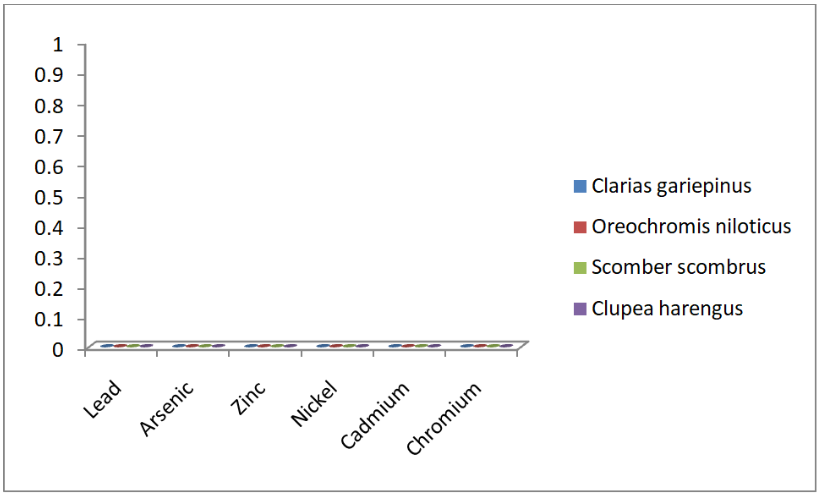

Figure:5 Heavy Metal of Both Four fishes Sold in Damaturu Metropolis

4. DISCUSSION

The mean and standard error of the lead concentrations in *Oreochromis niloticus* were 0.0942±0.055, while the lowest concentrations were found in the tissues of and *Scomber scombrus* with values of 0.0497±0.003 and 0.0457±0.004, respectively. These results were desirable compared to those of Peter *et al*. (2018), who found that the mean lead concentrations in muscles with 6.69±3.89 mg/kg exceeded the Food and Agriculture Organization (WHO/FAO, 2017).The concentrations of arsenic were recorded higher in *Clarias gariepinus* with mean and standard error of 0.0067±0.003 and the *Oreochromis niloticus* had the lowest concentration with mean and standard error of 0.0067±0.003 and negative in *Scomber scombrus* which was within the range of acceptable limit. Zinc concentrations were found to be lower in Oreochromis niloticus with mean and standard error of 58.2500.572 and higher in *Clupea harengus* with mean and standard error of 71.880±2.664 that were compared to Okayi, (2011) who reported values ranged from 0.01-3.8 mg/l, with a mean of 1.39±1.44 and a standard deviation in mg/l, indicating high values that are over the acceptable limit for freshwater bodies. The concentrations of nickel were significantly higher in Scomber scombrus and *Clupea harengus*, with similar values of 0.0357±0.005 and 0.0330±0.004 respectively, while the lowest concentrations were found in

Oreochromis niloticus and *Clarias gariepinus*, with mean and standard error values of 0.0265±0.004 and 0.0237±0.002 respectively. This is in agreement with Joseph *et al.*, (2012), who found the lowest value (0.68 mg/g) in the flesh of *Oreochromis niloticus* and in contrast to Abdullahi *et al.*, (2015) that obtained the concentration in muscles of EU sourced samples with 6.042±0.005 which exceeded maximum acceptable level.

The concentration of cadmium only found in *Oreochromis niloticus* with the mean and standard error of 0.0030±0.000 and negative in *Clarias gariepinus*, *Scomber scombrus* and *Clupea harengus* respectively. This was in contrast with Peter *et al.*, (2018) revealed that cadmium concentrations that analysed in muscles of Oreochromis niloticus as 1.30±0.71 mg/kg which was above the acceptable limit of 0.003mg/l (FAO, 2017).

The concentrations of chromium were significantly greater in *Clarias gariepinus* (0.0447±0.013), followed by *Scomber scombrus* (0.0335±0.002) and *Oreochromis niloticus* (0.0253±0.065) but *Clupea harengus* had the least concentration of 0.0062±0.005 with the mean and standard error, which is in contrast with the Faye-ofori *et al* (2015) which reported that the concentrations of chromium in the muscle of *Clarias gariepinu*s are above the stated limits thus making the consumption of catfish based on his study as potential health hazard.

5. Conclusion

Conclusively, with the exception of Zn, the levels of metals bio-accumulated in tissues of *Clarias gariepinus, Scomber scombrus* and *Clupea harengus* were not exceeded recommended guideline in accordance with (WHO/FAO, 2017). As is negative in the composite tissues of *Scomber scombrus* while Cd concentrations were recorded negative in *Clarias gariepinus, Scomber scombrus*, and *Clupea harengus* respectively.

6. Recommendations

1. It is recommended to use these fish species for human because it can't pose public health problems or serious threat to human upon their consumption due to negligible amounts of elemental bioaccumulation.
2. Therefore, further research should be carried out to assess the safety margin from other species, on other metals and sources respectively.

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