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Analysis of Some Potentially Toxic Elements (PTEs) (Arsenic, Cadmium, Chromium, Copper, Nickel, Lead and Zinc) in Different Smoked Fishes Sold in Gamawa and Hardawa Markets in Bauchi State, Nigeria

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***Abstract*—**The heavy metal contamination of smoked fish species in Bauchi state, Nigeria's northeastern region, was investigated. Zn, Cd, Cu, As, Ni, Pb, and Cr were detected in smoked fish species collected at random from different parts of the Gamawa and Hardawa markets. The concentrations of potentially toxic elements in samples collected after digestion using a conventional procedure in triplicate were analysed using Microwave Plasma Atomic Emission Spectroscopy (MPAES).The ranges of the measured concentrations in the samples were as follows; Zn (63.17 to 117.51 mg/kg), Cd (0.12 to 0.26 mg/kg), Cu (4.19 to 6.39 mg/kg), As (19.60 to 34.98 mg/kg), Ni (3.45 to 7.88 mg/kg), Pb (0.13 to 9.89 mg/kg) and Cr (3.04 to 8.98). The toxic elements Cd and Zn were the least abundant and most abundant in all nine (9) species, respectively. Cu and Cd levels were within the World Health Organization's maximum guidelines in this investigation (WHO), except for samples from Gamawa (Catfish (117.50 mg/kg) and Clarias (112.60 mg/kg)) and Hardawa (Tilapia 116.50 mg/kg), the concentrations of Zn were found to be below the acceptable limits. In every smoked fish sample tested, the amounts of As, Ni, Pb, and Cr were greater than the WHO's maximum tolerable limit. The findings of this study revealed that the fish sold in these markets were substantially contaminated with the PTE (Ni, Pb, As, and Cr), posing a serious health risk to the populace.

***Keywords*—** Clarias, Gamawa, Hardawa, Synodontis, Toxic elements, Tilapia

I. INTRODUCTION

Fish is often regarded as one of the healthiest and most affordable protein sources, with amino acid compositions that are richer in cysteine than most other protein sources [1]. Fish provides roughly 20% of animal protein sources, making it a rich source of protein for both the poor and the wealthy [2,3]. The majority of necessary amino acids, particularly lysine, methionine, and tryptophan, are found in fish but not in plant proteins [2,4]. They are a rich source of critical nutrients that can be used to complement the diets of both infants and adults. Because of its high essential fatty acid (EFA) known as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), fish has become the main source of protein aside from meat and poultry products, contributing a considerable percentage of dietary protein globally [5]. As a result, since fresh fish is very prone to deterioration soon after harvest, proper processing and preservation of fresh fish is critical in avoiding economic losses [6]. Traditional processing methods for preventing or reducing post-harvest losses include fish smoking. It entails applying heat to eliminate water and inhibiting bacteria and enzymatic activity in fish [7]. Furthermore, because to the lower moisture content, high heat causes direct microbial death as well as nutritional concentrations, which may include harmful heavy metals [8].

Heavy metal concentrations have increased as a result of anthropogenic activities, and their buildup lead to heavy metal contamination in the aquatic system [9,10]. Heavy metals, unlike most organic contaminants, cannot be eliminated by biological degradation, and they are easily absorbed and bio accumulated in the protoplasm of aquatic biota [11]. Because heavy metals are non-biodegradable, they can accumulate in the food chain, causing hazardous effects far from the source of pollution [9,12]. Fish may include a variety of chemical pollutants, including heavy metals, posing a risk to consumers' health [13,14]. Because of their severe persistence, high toxicity, tendency to bio accumulate, and availability from a variety of anthropogenic sources, heavy metals are considered harmful to aquatic life [11]. An adverse health risk will arise if the concentration of the metal accumulating in fish tissues exceeds the allowed maximum limit [15]. Heavy metals like as copper, iron, and zinc are required for fish metabolism, whereas mercury, cadmium, arsenic, and lead have no recognized biological function [1,16]. The aim of this research was to find out what potentially toxic elements were included in locally processed and preserved smoked fish items offered in Bauchi State's Gamawa and Hardawa markets, as well as the public health implications.

II. MATERIALS AND METHODS

Smoked fish samples were collected from Gamawa and Hardawa markets in Bauchi state. Nine (9) samples of different smoked fish including; 2 *Tilapia (Oreochromis niloticus),* 1 *Claries (Clarias gariepitnus),* 2 *Butter catfish (Schilbe mystus),* 2 clupid (*Clupea harengus*) and 1 *Synodantis (Synodoutis clrias)* were purchased from the Gamawa and Hardawa markets. The smoked fish samples were placed in a polyethene bags and labelled appropriately based on the location. Fish species were then further coded as A, B, C, D and E, representing the species, *Tilapia (Oreochromis niloticus), Claries (Clarias gariepitnus), Butter catfish (Schilbe mystus),* clupid (*Clupea harengus*) and *Synodantis (Synodoutis clrias)* respectively. The samples were then taken to the laboratory for analysis of toxic elements.

Each sample had twenty (20) grams of smoked fish weighed and transferred to a macro-kjeidahl digestion flask. The sample was mixed with 20ml of concentrated nitric acid and 20ml of water. The flaskh's contents were boiled for about 15 minutes until the total volume was reduced to roughly 20ml. After cooling the digested fish solution, 10ml of concentrated sulphuric acid was added and the mixture was heated once more. As the contents began to blacken, little amounts of nitric acid were added, and the heating was continued until white vapors emerged. The solution was then cooled, and 10ml of saturated ammonium oxalate solution was added, followed by another boil until white smoke was generated. The oxalate treatment helped to remove yellow colouring caused by nitro compounds, lipids, and other substances, resulting in a colourless final solution. Because the ammonium oxalate was added before the metals were assayed, every trace of nitric acid was eliminated. After the sample had turned colourless, it was made to the 100ml mark with distilled water and kept for analysis. The analysis was carried out in triplicate. As a negative control, a blank was used that had been treated with all of the chemicals [17]. SPSS version 20 was used to carry out the statistical analysis. Data were expressed as mean±standard deviation.

III. RESULTS AND DISCUSSION

Table 1, 2, 3 and 4, shows the mean concentration and standard deviation of five smoked fish species (catfish, clarias, clupid, synodantis and tilapia) from Gamawa and Hardawa markets in Bauchi state. The different species had variable levels of heavy metals, which could be attributable to their different feeding patterns as well as their bioaccumulation factor. The ranges of the measured concentrations in the samples were as follows; Zn (63.17 to 117.51 mg/kg), Cd (0.12 to 0.26 mg/kg), Cu (4.19 to 6.39 mg/kg), As (19.60 to 34.98 mg/kg), Ni (3.45 to 7.88 mg/kg), Pb (0.13 to 9.89 mg/kg) and Cr (3.04 to 8.98).

Table 1: Gamawa mean±standard deviation for Zn, Cd and Cu concentration in mg/kg

Fish Name	Zn	Cd	Cu
Butter catfish	117.51±91.61	0.15±0.06	4.71±1.70
Synodontis fish	70.26±36.22	0.12±0.08	6.39±4.12
Clarias fish	112.58±42.74	0.20±0.11	4.34±1.60
Clupid fish	90.99±11.14	0.26±0.10	5.36±1.03
Tilapia fish	63.63±21.25	0.23±0.09	5.53±1.54
WHO	100	1	30

Table 2: Gamawa Mean±Standard Deviation for As, Ni, Pb and Cr Concentration in mg/kg

Fish Name	As	Ni	Pb	Cr
Butter catfish	34.98±2.75	5.77±1.09	1.09±0.65	7.26±0.92
Synodontis fish	19.60±6.61	5.76±2.69	1.10±0.24	6.32±4.08
Clarias fish	25.68±10.83	3.45±1.82	1.36±0.47	7.12±4.80
Clupid fish	21.27±2.92	6.79±0.88	0.13±0.13	5.29±1.62
Tilapia fish	22.99±17.24	7.88±6.04	4.46±2.02	8.98±5.33
WHO	0.02	0.5	0.5	0.15

Table 3: Hardawa Mean±Standard Deviation for Zn, Cd and Cu Concentration in mg/kg

Fish Name	Zn	Cd	Cu
Butter catfish	95.05±27.94	0.17±0.06	4.19±0.42
Tilapia fish	116.44±96.27	0.20±0.06	5.87±10.72
Clupid fish	78.60±73.35	0.18±0.06	4.52±0.42
Clarias fish	63.17±20.89	0.25±0.08	4.97±0.78
WHO	100	1	30

Table 4: Hardawa Mean±Standard Deviation for As, Ni, Pb and Cr Concentration in mg/kg

Fish Name	As	Ni	Pb	Cr
Butter catfish	29.56±2.96	2.66±0.11	5.40±0.84	3.04±0.19
Tilapia fish	31.38±1.40	4.62±0.85	3.71±0.80	7.20±1.57
Clupid fish	26.76±1.23	4.32±0.36	9.89±0.53	4.05±31.09
Clarias fish	25.28±2.86	3.61±1.053	3.23±0.31	3.62±1.42
WHO	0.02	0.5	0.05	0.15

Zinc was found in all of the fish samples, with the highest quantities found in clarias, followed by tilapia and clupid, and the lowest concentrations found in catfish and synodantis (Figure 1 and 2). Edosomwan *et al.*, [18], recorded lowest Zn mean value of 3.18±3.36 mg/kg and 2.2±0.85 mg/kg in *Channa obscura* and *Clarias gariepinus* respectively. This finding also contradicts with the study of Eneji *et al* [19], who observed value of Zn to be 7.15 mg/kg 5.66 mg/kg and 5.24 mg/kg in gill, intestine and tissue of *T. zilli.* Concentration of Zn in catfish and clarias (samples from Gamawa) and Tilapia (sample from Hardawa) was higher than the maximum permissible limit of 100 mg/kg prescribed by World Health Organization [20]. Although zinc is an essential element, it can be hazardous to fish at high amounts, causing death, growth retardation, and reproductive problems. Zinc can have antagonistic, additive, or synergistic effects when it interacts with other elements [1]. According to [21,22], high intake of Zn induces production of Cu binding proteins in intestine which traps Cu within intestinal cells and prevents its systemic absorption. Within this area of the Gamawa and Hardawa markets, zinc does not appear to be a contamination threat to fish.

The results of this study show that the mean concentration of Cd varied from 0.12 to 0.26 mg/kg, similar to [23-25] but lower than [26]. Clupid fish and synodontis from Gamawa had the highest and lowest Cd concentration (0.26 mg/kg) and (0.12 mg/kg) (Fig. **3** and **4**). Cd levels in fish intended for human consumption have been established at 1.0 mg/kg by the FAO/WHO [27]. The Cd concentration found in this study is below the maximum permitted levels. Because the samples studied in this study had less cadmium than many previous studies, they do not pose a health danger when it comes to cadmium levels. Cd concentrations in the liver of swordfish (*Xiphias gladius*) reached 46.9 mg/kg, according to [28]. Cd, like some other HMs such as Pb and Hg has no biological function in human system. Some adverse effects of acute cadmium toxicity are kidney damage, testicular tissue destruction, high blood pressure and red blood cells destruction [29]. Any considerable amount of cadmium in the body produces rapid poisoning, liver and kidney damage, Cd-containing compounds are also carcinogenic [30].

The mean concentrations of Cu in samples analyzed ranged from 4.19 to 6.39 mg/kg (Fig. **5** and **6**). Higher concentration of 6.39 mg/kg was reported in *Synodontis* specie from Gamawa, whereas lowest concentration of 4.19 mg/kg was detected in catfish from Hardawa. In their study, [31] observed the mean value of Cu to be 0.05–0.07 mg/kg in some selected smoked *Clarias gariepinus* cultured fish in earthen ponds in some locations, Lagos state. In Cameroon, [32] recorded a highest mean value for Cu ranging from 0.35 to 0.36 mg/kg in *Arius heudelotii*. The recommended concentration of copper in fish established by [20,33] is 30 mg/kg. The samples analyzed in this research were all found to be below the standard limit of 30 mg/kg as presented in figure **5** and **6**. Copper being micronutrient is needed in trace amount for proper body functions [9] and it is an important element, helps the body's enzyme systems function properly. Copper is also required for hemoglobin production and is found in numerous enzymes [34]. When taken in excessive amounts, this element can be harmful to humans and animals and at high concentration; Cu can affect the brain, liver, or kidneys resulting in mental illness and death [10].

The amount of As in various smoked fish species ranged from 19.60 to 34.98 mg/kg. The highest As level was found in a Gamawa catfish sample (34.98 mg/kg), while the lowest As level was found in a Gamawa synodontis sample (19.60 mg/kg) (Fig. **7** and **8**). A study conducted by Meche *et al* [35], recorded lower values of 0.23, 0.93 and 0.73 mg/kg in *Pimelodus maculates*, *Hypostomus punctatus* and *Serrasalmus spilopleura* respectively. The concentration of the samples analyzed was found to be higher than the maximum permissible limit for food. One of the biggest risk factors for public health is arsenic, which is a toxic element, arsenic exposure can occur at work or through contaminated food and water. Arsenic may act as an endocrine disruptor at extremely low quantities, according to new research [37]. Chronic inorganic arsenic exposure can harm the gastrointestinal tract, respiratory tract, skin, liver, cardiovascular system, hematological system, and neurological system, among other organs [38].

In smoked fish samples examined, Ni concentrations varied from 3.45 mg/kg to 7.88 mg/kg. Highest and lowest concentration was observed in Tilapia fish and clarias from Azare (Fig. **9** and **10**). Nickel content recorded in the fish species exceeded the **permissible limit of 0.5 mg/kg [39].** In another study, [40] recorded mean value of 16.3±4.10 mg/kg and 6.73±4.84 mg/kg in the muscle and liver of **Tiger grouper** *(E. fuscoguttatus)* sample analyzed. Nickel normally occurs at very low levels in the environment [41]. When nickel is discharged into the environment, it quickly forms complexes with a wide range of ligands, making it more mobile than most heavy metals [42]. At low concentrations, nickel is a crucial metal for many species, but at greater concentrations, it is toxic. Nickel exposure can cause nickel allergy, contact dermatitis, and organ system toxicity, among other things. High levels of Ni can cause reproductive toxicity, hepatotoxicity, gene toxicity, neurotoxicity, nephrotoxicity, and an increased risk of cancer [40,43]. Similarly, Forti *et al* [41] reported that Ni causes inflammation, fibrosis, emphysema, and cancers in the lungs.

The lead concentrations in this study ranged from 0.13 to 9.88 mg/kg. The clupid fish from Gamawa and Hardawa, respectively, had the highest (9.89 mg/kg) and lowest (0.13 mg/kg) mean Pb content (Fig. **11** and **12**).This study's findings are comparable to those of Ako and Salihu [45], who found low amounts of lead in smoked and oven-dried foods in Minna, Nigeria. . This study contradicts with the finding of Ajani and Balogun [46], who recorded higher mean value, ranged between 14.86 to 18.06 mg/kg in *Chrysichthys nigrodigitatus*. The samples analyzed were found to be higher than the maximum permissible limit prescribed by WHO. The presence of Pb a non-essential metal even in trace amounts in fish tissue portends grave danger if consumed in large quantities [47] and Pb levels that are too high in the body might create serious problems in the haematological, neurological, and renal systems [48]. Lead availability may be influenced by agricultural, industrial, and domestic sewage discharge, atmospheric deposition, feeding behaviors, fish species, age, and size, food, and physicochemical characteristics of the aquatic environment [49, 50].

As indicated in Figure **13** and **14**, the Cr concentration in the examined fish samples ranged from 3.04 mg/kg in Hardawa market smoked fish to 8.98 mg/kg in Gamawa market smoked fish. The permissible level of Cr in fish food, according to WHO [51] and FEPA [52] data, is 0.05–0.15 mg/kg body weight. All of the samples examined in this study were found to be greater than this standard limit. Cr toxicity occurs when people are exposed to high levels of chromium in the environment for an extended period of time [53,54]. Cr is involved in oxidation processes and has some biological functions. In humans, Cr insufficiency is usually linked to gastrointestinal and neurological system issues [55] and it is linked to lung cancer [54]. Cr, like other metals, has been demonstrated to elevate glycogen levels in a variety of organs, indicating metal stress [56]. According to Aslam and Yousafzai [57], the toxicity of Cr is proportional to its concentration and temperature; any increase in these parameters increased the toxicity, i.e. rose with growing concentration and temperature, but decreased with increasing salinity and sulfate concentration.

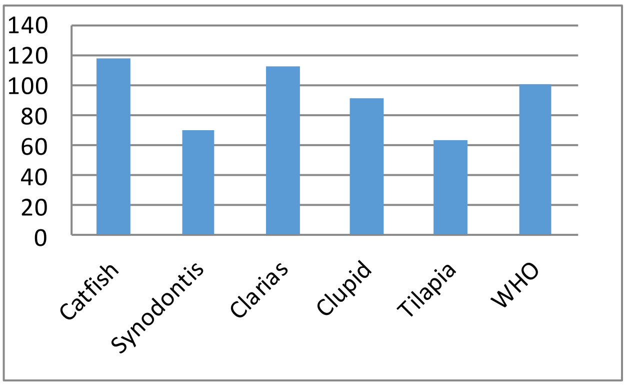

Figure 1: Zn Mean Concentration of Gamawa Samples

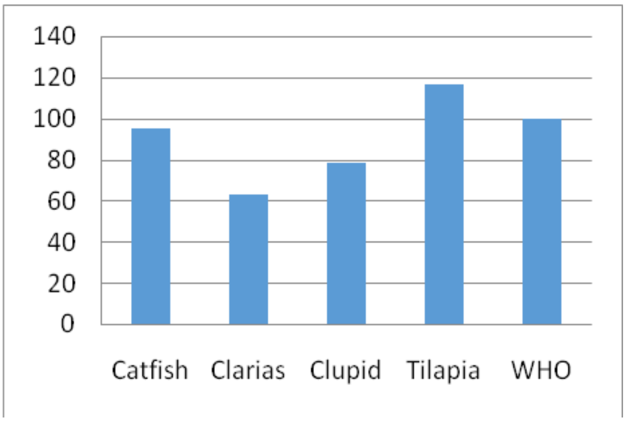

Figure 2: Zn Mean Concentration of Hardawa Samples

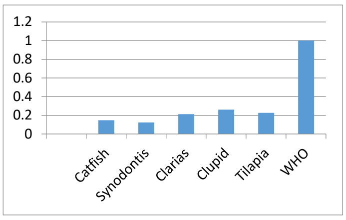

Figure 3: Cd Mean Concentration of Gamawa Samples

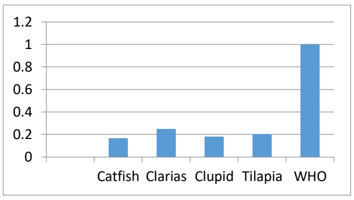

Figure 4: Cd Mean Concentration of Hardawa Samples

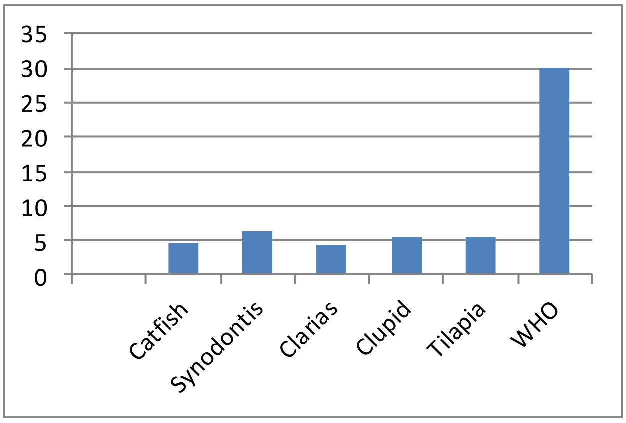

Figure 5: Cu Mean Concentration of Gamawa Sample

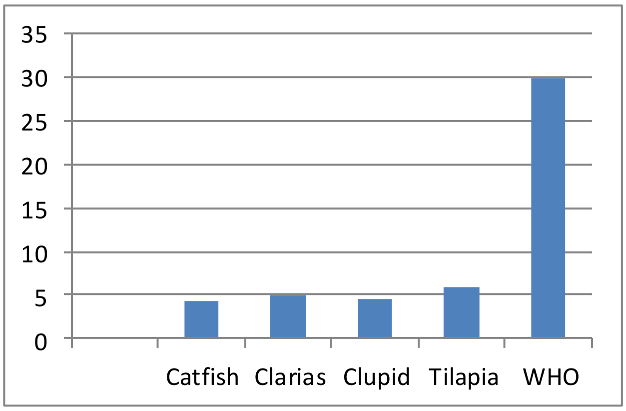

Figure 6: Cu Mean Concentration of Hardawa Samples

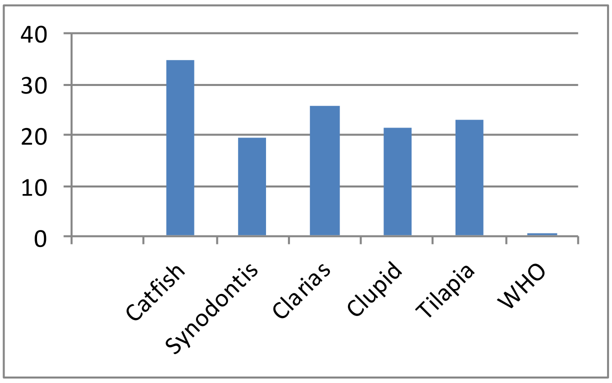

Figure 7: As Mean Concentration of Gamawa Samples

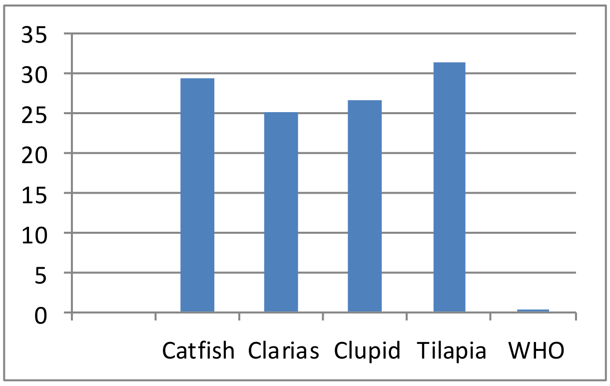

Figure 8: As Mean Concentration of Hardawa Samples

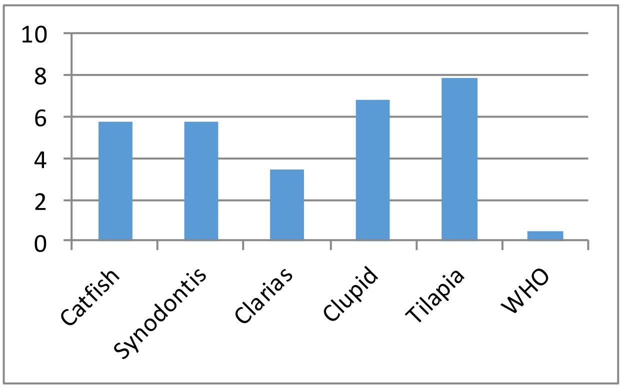

Figure 9: Ni Mean Concentration of Gamawa Samples

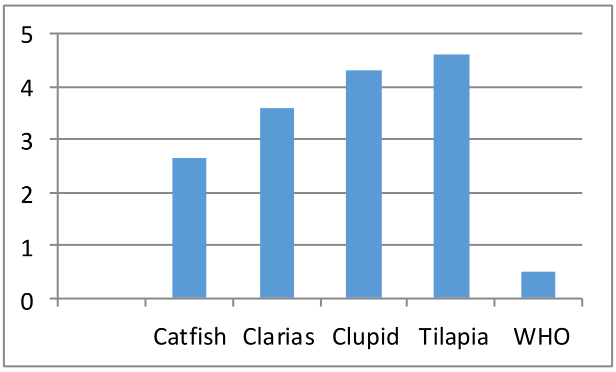

Figure 10: Ni Mean Concentration of Hardawa Samples

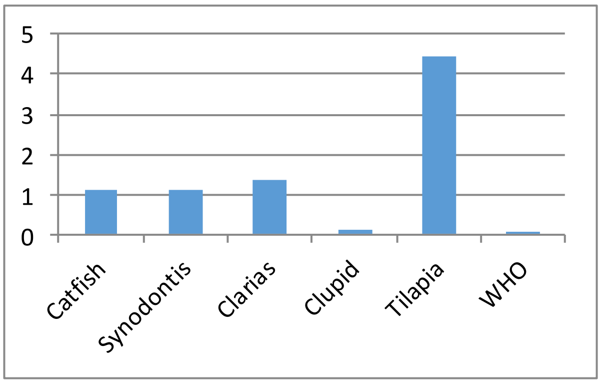

Figure 11: Pb Mean Concentration of Gamawa Samples

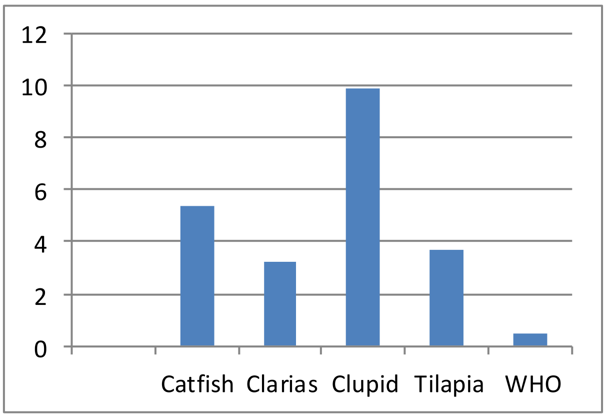

Figure 12: Pb Mean Concentration of Hardawa Samples

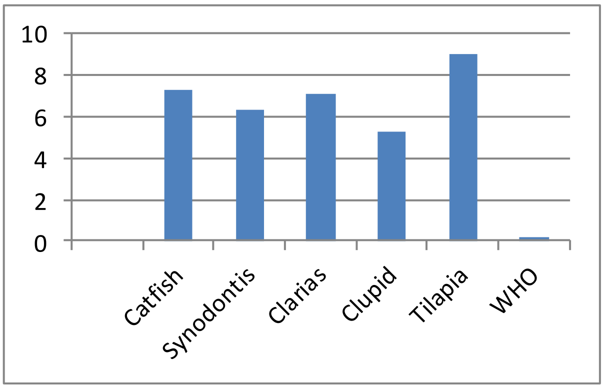

Figure 13: Cr Mean Concentration of Gamawa Samples

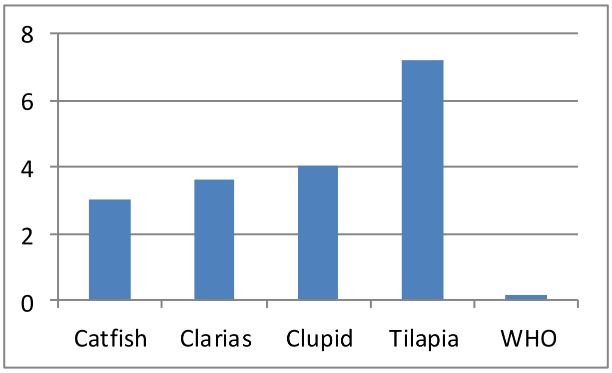

Figure 14: Cr Mean Concentration of Hardawa Samples

IV. CONCLUSION

The toxic elements Cd and Zn were the least abundant and most abundant in all nine (9) species, respectively. Copper and Cd levels were within the World Health Organization's maximum guidelines in this investigation (WHO). Except for samples from Gamawa (Catfish (117.51 mg/kg) and clarias (112.58 mg/kg)) and Hardawa (Tilapia 116.45 mg/kg), the concentrations of Zn were found to be below the maximum acceptable limits. In all the smoked fish sample tested, the amounts of As, Ni, Pb, and Cr were found to be greater than the WHO maximum tolerable limit. The above-mentioned high level of Pb over the WHO MPL could be attributable to metal deposition in water bodies as a result of agricultural and/or anthropogenic activities near the water source where the fish was gathered prior to preservation.

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