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Evaluation of Some Potential Toxic Elements (Arsenic, Cadmium, Chromium, Copper, Nickel, Lead and Zinc) in Smoked Fish Samples Sold at Azare and Darazo Markets in Bauchi State

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Abstract- The increased and sustained usage of fish is due to the fact that it contains not only all of the essential amino acids that humans require, but also polyunsaturated fatty acids not present in other protein sources. In other studies, the concentrations of potentially hazardous components in various fish species were shown to be greater as a result of environmental pollution. This study looked at potential toxic elements in smoked Butter catfish, Alesties fish, Clarias fish, Synodantis fish, and Clupid fish from Azare and Darazo markets in Bauchi state. Microwave Plasma Atomic Emission Spectroscopy (MPAES) was used to detect the quantities of possibly hazardous elements in samples obtained after digestion using a standard method in triplicate. The findings revealed that Zinc and Arsenic had the highest heavy metal load in butter catfish, with mean values of 122.616 mg/kg and 35.163 mg/kg, respectively, whereas zinc (116.213 mg/kg) and lead (29.706 mg/kg) had the highest in clarias. Zinc and arsenic were the two heavy metals with the highest mean values in clupid fish, with 75.650 mg/kg and 19.446 mg/kg, respectively. Synodantis has the highest levels of zinc (75.410 mg/kg) and arsenic (20.253 mg/kg). Cadmium was the least abundant of the heavy metals found in all five species, with mean concentrations of 0.270, 0.156, 0.213, 0.187, and 0.160 mg/kg for butter catfish, clarias, clupid, synodantis, and tilapia fish, respectively. In this study Cu and Cd levels recorded were within the maximum acceptable limit. Concentration of Zinc was found to be within the recommended guidelines of WHO/FAO, except for sample from Azare (clarias) and Darazo (butter catfish and clupid fish). The mean concentrations of Ni, Pb and Cr in the sampled were higher than the maximum acceptable limit prescribed by WHO/FAO/FEFA. The concentrations of Ni, Cr, Pb was found to be higher in all smoked fish except for butter catfish and clupid fish from Darazo which was not detected.

***Keywords*—**Azare, fish, *clarias gariepinus,* toxic elements, tilapia

I. INTRODUCTION

Due to its high protein content, nutritional worth of unsaturated fatty matter, and affordability for the masses as compared to beef, fish is a perishable but significant food item, especially in third-world countries [1-2]. In Nigeria, fish is a valuable and inexpensive source of nutrition for humans, and dried catfish has long been a popular delicacy [1]. Fish are the most diverse group of vertebrates, with over 32,000 species known; nonetheless, only a small number of species are commonly eaten by humans [3-4]. Fish has become the main source of protein outside of meat and poultry products due to its high content of essential fatty acids (EFAs) such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) and contributes a significant percentage of dietary protein globally [5]. Fish is a good supply of polyunsaturated fatty acids, omega-3, calcium, iodine, phosphorus, iron, trace minerals like copper, and a good amount of B vitamins, all of which are good for your health [3]. As soon as the fish is removed from the water, it begins to deteriorate due to a variety of reasons including enzymatic activity, bacterial development, and chemical oxidation of fat, all of which induce rancidity and/or off-flavour [6].

The long-term viability of the environment has recently been questioned. The majority of this is due to human activities, with natural factors playing a minor contribution. Pollution has an impact on the three major components of the environment: soil, water, and air. Human activities frequently result in contamination of land [7]. The majority of debris ends up in the aquatic ecosystem as a result of runoff. As a result, the characteristics of entering surface waters in several Nigerian coastal sites have changed. Human activity has impacted the soil in a number of ways, including heavy metals and microbiological features [8]. For example, chemicals originating from agricultural operations (pesticides and herbicides) and industrial effluents, such as metals, end up in a variety of water bodies, where they can cause a variety of harmful consequences in aquatic animals [9].

As a result of anthropogenic activities, heavy metal concentrations have risen, resulting in heavy metal contamination in the aquatic system [10-11]. Heavy metals, unlike most organic pollutants, cannot be degraded by biological means, and they are readily absorbed and rapidly accumulated in aquatic biota protoplasm [12]. Heavy metals are non-biodegradable, so they can accumulate in the food chain and cause health problems far from the source of pollution [10,13]. Metal buildup can develop as a result of contamination of fish habitat water bodies, as well as elemental heavy metals, which are predominantly produced by anthropogenic activities [14]. Heavy metal ions are transported through the fish's blood and bond to proteins when the fish dwells in a contaminated water body. Due to the ions' great affinity for cysteine bonds in protein molecules, significant sulfhydryl connections are formed between the muscles, gills, or liver of the fish and the metal ions [15] (). Non-biodegradable metals, on the other hand, have a tendency to remain in the fish, and as the fish grows, the metals continue to form strong sulfhydryl bonds, resulting in bioaccumulation. When a smaller fish with bio-accumulated metals is eaten by a larger fish, the metal ions in its tissues are bio-magnified, causing the larger fish to accumulate more heavy metals in its organs [16]. These dangerous metals are subsequently passed down the food chain to humans, causing bioaccumulation and bio-magnification. Bioaccumulation in humans causes difficulty swallowing, muscle spasms, hypoxia, diarrhea, and, in the worst-case scenario, death [14].

Smoked fish have a bio-accumulative tendency that can cause metal build-up in their tissues. Chemical contaminants, such as heavy metals, may be present in fish, posing a health concern to consumers [17-18]. Heavy metals are detrimental to aquatic life because of their long persistence, high toxicity, susceptibility to bioaccumulate, and availability from a range of anthropogenic sources [12]. If the concentration of metal accumulating in fish tissues surpasses the permissible maximum limit, it poses a health risk [19]. Heavy metals like copper, iron, and zinc are necessary for fish metabolism, whereas mercury, cadmium, arsenic, and lead have no biological role [20-21]. The goal of this research was to find out how much potentially harmful materials were present in locally processed and preserved smoked fish items offered in Bauchi State's Azare and Darazo markets, as well as the public health implications.

II. RELATED WORK

Many studies about fresh and smoked fish samples were carried out in Akwa Ibom [22], Yola [23], Ikirun [24], Uke [25], Bangi [26], Abeokuta [27], Minna [28,29] to evaluate the concentration of potentially toxic elements. So to the best of our knowledge studies on potentially toxic elements in smoked fish have not been adequately carried out in recent time in the present study areas.

III. MATERIALS AND METHODS

Smoked fish was sampled from Azare and Darazo markets in Buchi state. Seven samples of different smoked fish including; 1 *Tilapia (Oreochromis niloticus),* 1 *Claries (Clarias gariepitnus),* 2 *Butter catfish (Schilbe mystus),* 2 clupid (*Clupea harengus*) and 1 *Synodonties (Synodoutis clrias)*were purchased from the Azare and Darazo. 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 *Synodonties (Synodoutis clrias)* respectively. The samples were then taken to the laboratory for analysis of heavy metals.

Sample Preparation

Samples were prepared using a standard method of analysis as described by [30]. Laboratory analysis of these toxic elements in fish was conducted using the Microwave Plasma Atomic Emission Spectroscopy (MPAES) was used to detect the quantities of possibly hazardous elements in samples obtained. SPSS version 20 was used to carry out the statistical analysis. Data were expressed as mean ± standard deviation.

IV. RESULTS AND DISCUSSION

Table 1-2 shows the heavy metals (Zn, Cd, Cu, As, Ni, Pb and Cr) load of five species of smoked fish from the Azare and Darazo markets: butter catfish, tilapia fish, clarias fish, synodantis fish, and clupid fish. In butter catfish, zinc and arsenic had the highest heavy metal load with a mean value of 122.62mg/kg and 35.16mg/kg, respectively, while Zinc (116.21mg/kg) and Lead (29.71mg/kg) were the highest in clarias. In clupid fish, zinc and arsenic had the highest heavy metal value with a mean value of 75.65mg/kg and 19.45mg/kg, respectively, while Zinc (75.41mg/kg) and Lead (20.25mg/kg) were the highest in synodantis. The concentration of cadmium was low among the heavy metals detected in all five species with a mean concentration of 0.27, 0.16, 0.21, 0.19 and 0.16 mg/kg for butter catfish, clarias, clupid, synodantis and tilapia fish respectively.

Table 1: Azare mean standard deviation for Zn, Cd, Cu, Ni, As, Pb and Cr concentration in mg/kg

Sample	Zn	Cd	Cu	As	Ni	Pb	Cr
Butter	99.08±32.25	0.27±0.15	4.71±2.48	21.55±2.48	4.68±1.99	4.44±3.51	6.72±3.47
Clarias	116.21±75.91	0.16±0.01	4.34±0.49	23.72±4.16	4.67±0.50	29.71±38.74	6.90±2.23
Clupid	75.65±20.62	0.21±0.21	5.43±0.26	19.45±2.03	4.66±0.97	0.88±0.85	7.63±1.68
Synodantis	75.41±47.95	0.19±0.02	3.86±0.26	20.25±5.34	2.58±2.66	4.80±3.17	8.41±0.89
Tilapia	53.36±2.14	0.16±0.01	4.48±0.57	20.06±0.69	1.16±0.06	8.42±0.40	2.96±0.07
WHO	100	1	30	0.02	0.5	0.5	0.15

Table 2: Darazo Mean±Standard Deviation for Zn, Cd, Cu, Ni, As, Pb and Cr Concentration in mg/kg

Sample	Zn	Cd	Cu	As	Ni	Pb	Cr
Butter catfish	122.62 ±59.85	0.10±0.07	4.35± 1.39	35.16 ±0.68	3.76± 2.48	ND	8.71± 1.55
Clupid fish	122.62 ±59.85	0.10±0.07	4.12± 1.14	ND	3.76± 2.48	ND	5.08± 1.10
WHO	100	1	30	0.02	0.5	0.5	0.15

Heavy metals are found in the earth's crust as natural constituents and are persistent environmental contaminants since they cannot be reduced or removed. Although these components are in short supply, they are not without significance. The concentrations of seven (7) heavy metals in catfish, clarias, clupid, synodantis and Tilapia sold in Azare and Darazo markets were determined in this study.
Zn was discovered in all fish samples studied (Butter catfish, Alesties fish, Clarias fish, Synodantis fish, and Clupid fish). Butter catfish and clupid fish from Darazo had the maximum concentration of 122.62mg/kg, while tilapia from Azare had the lowest concentration of 53.36mg/kg. As shown in Fig. **1**, the values of Zn in clarias from Azare, butter catfish, and Clupid from Darazo were found to be higher above the suggested limits of 100mg/kg. The findings contradict with the study of [31] who reported Zn value of 15.05, 16.80 and 17.85mg/kg in *M. rume rume, M. cyprinoides and L. coubie*. Zinc is a cofactor for almost 300 enzymes in all aquatic creatures, making it an important vitamin for both animals and humans. Zn is a component of numerous enzymes and is responsible for a number of biological functions that necessitate a rather high level to sustain [32]. Zn deficiency can cause lack of appetite, growth retardation, skin changes, and immunological abnormalities, and they are toxic at greater concentrations [3,33]. Electrolyte imbalance, nausea, anemia, and lethargy have all been documented as side effects of Zn toxicity [32].

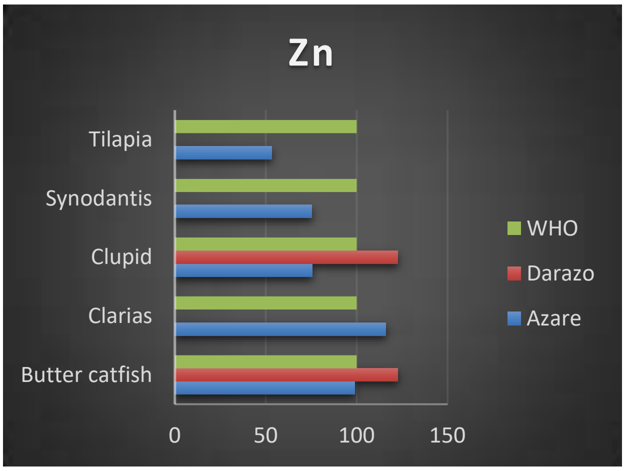

Fig. 1: Mean Concentration of Zinc in Azare and Darazo

Cd levels range from 0.10 to 0.27 mg/kg in this study. The greatest Cd value was 0.27mg/kg in butter catfish from Azare, while the lowest Cd value was 0.10mg/kg in butter catfish and clupid fish samples from Darazo (Fig. **2**). Cd levels in fish intended for human consumption have been established at 1.0mg/kg by the FAO/WHO [34]. The cadmium levels detected in this investigation are significantly below the maximum permissible values. The results are slightly greater than those of [35], who found 0.01mg/kg and 0.05mg/kg of *Clarias gariepinus* muscle and kidney, respectively. The levels were low compared to the 0.30-0.54 mg/kg found in Lake Geriyo fish in Adamawa state [36]. Eneji et al., [37] found that *Tilapia zilli* and *Clarias gariepinus* obtained from the River Benue had higher Cd values of 0.351mg/kg and 0.325mg/kg, respectively. Reference [26] found a higher Cd level of 0.70 in *Oreochromis niloticus* liver tissue. Cd damages the kidneys and causes chronic toxicity symptoms such as impaired kidney function, low reproductive capability, hypertension, tumors, and hepatic dysfunction [38]. Furthermore, Cd inhibits calcium uptake in the gills and, by altering normal tissue distribution, may disrupt the metabolism of essential trace elements such as zinc and copper [34].

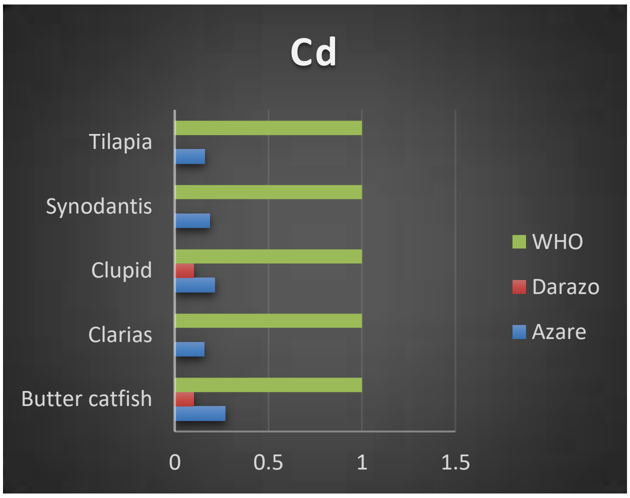

Fig. 2: Mean Concentration of Cd in Azare and Darazo

One of the elements required for human health is copper. Its prevalence in the environment could be due to the buildup of household and agricultural waste [35]. Cu binds to specific proteins to generate enzymes that act as catalysts in the body's processes and are also necessary for the synthesis of haemoglobin [39]. According to [40-42], at high doses, copper causes nausea, diarrhea, vomiting, and headaches, whereas chronic copper toxicity causes gastrointestinal bleeding, haematuria, intravascular haemolysis, and acute renal failure. The Cu amounts in the smoked fish items investigated are shown in Fig. **3**. Clupid fish samples from Azare had the highest mean Cu content (5.43mg/kg), while synodantis samples from the same locality had the lowest Cu concentration (3.86mg/kg). The results are better than those obtained in a previous study by [35], who found Cu values of 0.84, 1.37, and 0.66 in water, sediment, and fish, respectively. In a similar work, [43], detected lowest value of 0.21 and 0.25 in *Nibea soldado* and *Pristipomoides filamentosus.* Cu levels in this study were less than 30 mg/kg, which is below the [44-45] permitted limit, therefore fish purchased from these markets can be ingested without concern of Cu poisoning.

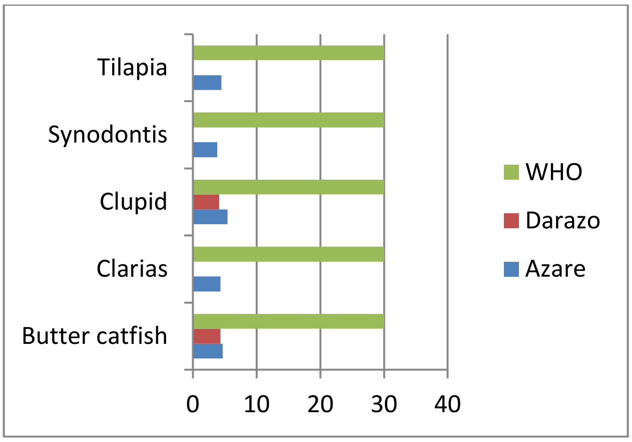

Fig. 3: Mean Concentration of Cu in Azare and Darazo

Smoked clarias fish collected from Azare had the highest mean Pb concentration, 29.71mg/kg and lowest concentration was found to be 0.88mg/kg (Fig. **4**). Of the two samples of catfish and clupid fish from Darazo analyzed, Pb was not detected as presented in Fig. **4** below. Despite the fact that all of the fish analyzed had high Pb levels ranging from 0.88mg/kg to 29.71mg/kg, these levels were higher than the WHO suggested limit of tolerance. The findings of this study are similar to those of [28], who found low levels of lead in both smoked and oven-dried foods in Minna, Niger State, Nigeria. Ibanga et al., [22], also reported lower Pb concentrations in smoked fish samples, with mean values ranging from 0.150 to 0.250 mg/kg, in Akwa Ibom State, Nigeria. Higher levels of lead have been shown to impair ATP-dependent active transport pathways, as well as cellular oxidation-reduction reactions and protein synthesis. Pb levels in smoked fish were greater than the WHO allowed limit of 0.5 mg/kg [5], indicating that the metal has contaminated these consumer products.

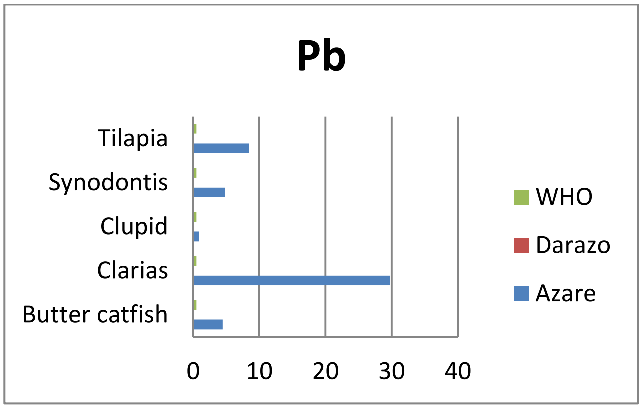

Fig. 4: Mean Concentration of Pb in Azare and Darazo

In smoked fish samples examined, Ni concentrations varied from 1.160 mg/kg to 4.680 mg/kg in Tilapia fish and butter catfish from Azare (Fig. **5**). The Ni concentrations in most samples were similar to those reported by [46] for *Trachurus trachurus*, *Gobius cephalarges*, *Spicara smaris*, and *Engraulis encrasicolus*, which were 6.14, 5.96, 7.68, and 3.60 respectively. The finding contradicts with the study of [47], who determined least value of 0.47 and 0.56mg/kg in *O. niloticus* during the winter and summer respectively. Nickel quickly forms complexes with a wide range of ligands once released into the environment, making it more mobile than most heavy metals [48]. Nickel is an important metal for many species at low amounts, but it is hazardous at higher concentrations. Nickel allergies, contact dermatitis, and organ system toxicity are all possible side effects of nickel exposure. Nickel can cause respiratory issues and is carcinogenic [49].

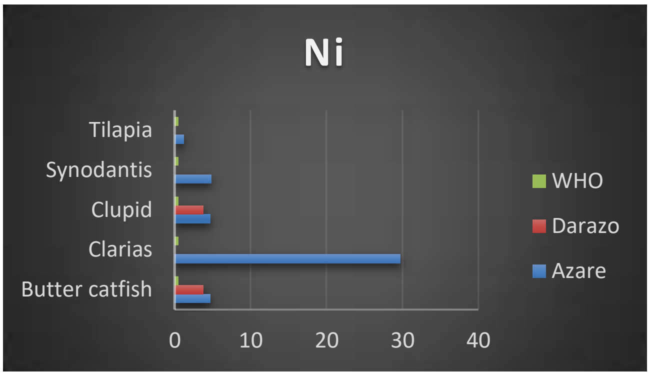

Fig. 5: Mean Concentration of Ni in Azare and Darazo

Butter catfish from Darazo had the greatest Cr concentration (8.71mg/kg), whereas Tilapia fish from Azare had the lowest (2.96mg/kg) (Fig. **6**). The value reported in this study will be less than the Median International Standard for fish food's acceptable limit of 1.0 mg/kg. The concentration is higher than in *Tilapia zilli* [50] and similar to *Clarias camerunensis* and *Oreochromis niloticus* [51]. Chromium plays an important part in oxidation processes and has some biological roles. Chromium deficiency in humans is frequently associated with gastrointestinal and central nervous system problems [8]. Cr along with other metals has been shown to raise glycogen levels in many organs, indicating metal exposure stress [32]. Chromium toxicity is proportional to its concentration and temperature; any rise in these parameters increased its toxicity, i.e. increased with rising concentration and temperature, but decreased with increasing salinity and sulfate concentration [52].

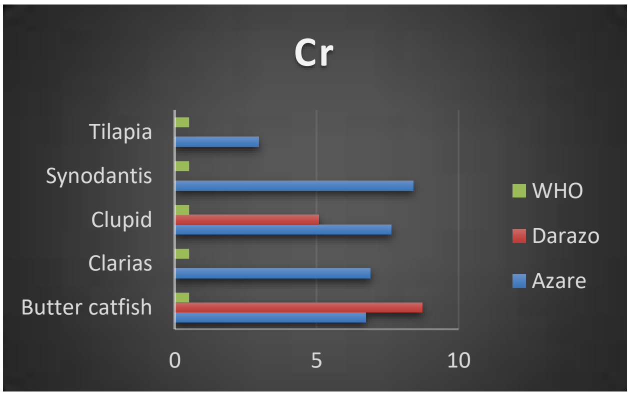

Fig. 6: Mean Concentration of Cr in Azare and Darazo

Arsenic can be found in our diet in several chemical forms. However, inorganic arsenic is more hazardous than organic arsenic due to its molecular structure. It's difficult to accurately measure the different types of arsenic that exist (Ahmed et al., 2015). Chronic inorganic arsenic exposure can harm the gastrointestinal tract, respiratory tract, skin, liver, cardiovascular system, hematological system, and neurological system, among other organs [53]. Arsenic may act as an endocrine disruptor at extremely low quantities, according to new research [13]. The amount of Arsenic in various smoked fish species ranged from 20.06 to 35.16mg/kg. The butter catfish has the highest levels of arsenic, followed by Clarias and synodantis (Fig. **7**). A study conducted by [54], recorded lower values of 0.23, 0.93 and 0.73 mg/kg in *Pimelodus maculates*, *Hypostomus punctatus* and *Serrasalmus spilopleura*. The concentration of the samples analyzed was found to be higher than the maximum permissible limit.

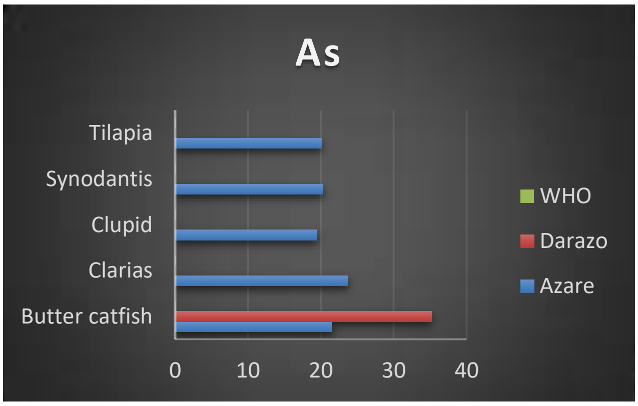

Fig. 7: Mean Concentration of As in Azare and Darazo

V. CONCLUSION

The study revealed that Zinc and Arsenic had the highest heavy metal load in butter catfish, with mean values of 122.62mg/kg and 35.16mg/kg, respectively, whereas zinc (116.21mg/kg) and lead (29.71mg/kg) had the highest in clarias. Zinc and arsenic were the two heavy metals with the highest mean values in clupid fish, with 75.65mg/kg and 19.45mg/kg, respectively. Synodantis has the highest levels of zinc (75.41mg/kg) and arsenic (20.25mg/kg). Cadmium was the least abundant of the heavy metals found in all five species, with mean concentrations of 0.27, 0.16, 0.21, 0.19, and 0.16 mg/kg for butter catfish, clarias, clupid, synodantis, and tilapia fish, respectively. In this study Cu and Cd levels recorded were within the maximum acceptable limit. Concentration of Zinc was found to be within the recommended guidelines of WHO/FAO, except for sample from Azare (clarias) and Darazo (butter catfish and clupid fish). The mean concentrations of Ni, Pb and Cr in the sampled were higher than the maximum acceptable limit prescribed by WHO/FAO/FEFA. The concentrations of Ni, Cr, Pb was found to be higher in all smoked fish except for butter catfish and clupid fish from Darazo which was not detected.

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