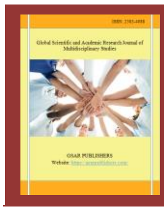

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PROXIMATE COMPOSITION AND CONCENTRATION OF SOME HEAVY METALS IN SMOKED *SYNODONTIS OMIAS* AND *MORMYRUS RUME* FROM GASHUA RIVER

By

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Abstract

The proximate value and the concentration of some heavy metals in Smoked Synodontis omias and Mormyrus rume from Gashua River were determined over a month. The smoked fish samples of Synodontis omias and Mormyrus rume were purchased from Gashua community, Yobe State in northeastern Nigeria, and labeled accordingly. The samples were placed in polythene bags and were immediately transported in plastic boxes to Faculty of Science, Department of Chemistry Laboratory Yobe State University for Proximate analysis. Fish muscles and Gills were removed with a plastic knife, oven dried at about 80°C. Samples were analyzed following the analytical procedures specified by AOAC for heavy metals and proximate composition respectively. The result indicates that the concentration of heavy metals in descending order of magnitude are Cu>Pb>Ni> Cr >As> Cd, and their mean values (±SD) are respectively 3.443±0.0312mg/kg, 1.168±0.0175 mg/kg, 1.137±0.0064 mg/kg, 0.777±0.0032 mg/kg, 0.231±0.0025 mg/kg, 0.130±0.0015 mg/kg in Synodontis omias and Cu> Ni> Cr > Pb> As> Cd, and their mean values (±SD) are 5.427±0.0211 mg/kg, 2.236±0.0074 mg/kg, 1.738±0.0052 mg/kg, 0.955±0.0047 mg/kg, 0.319±0.0011 mg/kg, 0.179±0.0005 mg/kg in Mormyrus rume. The results obtained for proximate composition are moisture (12.57%), protein (34.51%), Nitrogen Free Energy(NFE) (31.93%), fat (15.10%), fibre (0.86%) and ash (5.03%) in Synodontis omias and moisture (8.69%), protein (32.20%), Nitrogen Free Energy (44.60%), fat (10.43%), fibre (0.60%) and ash (3.48%) in Mormyrus rume. The result showed that the concentration of copper, nickel, and chromium are above their FAO stated limits and as such could pose a health risk to consumers. Similarly, the study revealed that Synodontis omias andMormyrus rume are very rich in protein it is therefore recommended to consumers for their protein needs and particularly, to those with protein deficiency as a source of readily available and cheap animal protein. Consumers are, however, warned to check the level (quantity) of consumption so as not to endanger their life.

KEYWORDS *Heavy metal, proximate composition, smoked, Synodontis omias, Mormyrus rume, Gashua River.*

Introduction

Nigeria, a Western African Country has a vast area of freshwater ecosystem, where fishing activities is the main source of livelihood for many. The quest for fish as a food source especially by the local populace is unending, either as a result of its relative affordability and/or because of the nutrients derived from it. Despite the increase in the practice of aquaculture in recent years for adequate fish production due to increasing population, the demand for fish consumption still outweighs aquaculture production. Nigeria produces only about 40 % of the local consumption demand estimated 2.66 million metric tons, importing the balance of 60 % to augment demand. Hence, there is an inevitable need to complement aquaculture with fishing from natural waters which has abundant and diverse fish species. However, fishing from the wild presents its separate challenge as these water bodies are contaminated with chemicals from farmlands, oil spills, and heavy metals from industries.

The high demand for fish is not only because of its taste but also largely due to its nutritional values which is a function of its proximate composition. Fish protein is easily digestible.

Additionally, it is an important source of both essential and non-essential amino acid. Its amino acid content has a high quantity of cysteine than a large amount of other protein source. Beneficial polyunsaturated fatty acids, eicosapentaenoic acid (EPA), and docosahexaenoic acid (DHA) have been reported to be present in adequate quantities in the tissues of fish. These polyunsaturated fatty acids have been reported to have the ability to both prevent, and also cure some diseases of man including cancers, heart diseases, rheumatoid arthritis, and inflammation. The maintenance of acid-base balance is one of the functions of minerals in the body; in addition, they also help in formation of haemoglobin. Furthermore, minerals are involved in catalyzing metabolic reactions, control water balance, and helps formation of bones.

Heavy metals are important component of pollution in the aquatic ecosystem. This is because of their toxicity, accumulation, and ability to bio-magnify along the food chain. The sources of natural aquatic systems contamination of heavy metals are mostly household, manufacturing, and man-made activities.

Fish can easily accumulate heavy metals into their bodies from any of sediment, water of food by virtue of their position in the aquatic food chain. Some of the heavy metals are beneficial to fish, yet their toxicity may overwhelm these health benefits, and man by extension can also be affected further the food chain. There is a rich documentation in literature of the adverse effects of heavy metals in man, ranging from liver and kidney damage, cardiovascular diseases, and in extreme cases, death.

Pollution by heavy metal in aquatic bodies has terrible effects on the environmental balance and the diversity of aquatic species. Aina and Adedipe reported that there has been a steady increase in river pollution in Nigeria. Pollution of the Gashua River occur along the course of the river. Domestic sewage, emission from automobiles, mining processes, discharge of effluents from industries, metallurgical activities, and agricultural production are some of the sources of anthropogenic heavy metal input into the aquatic environment.

Heavy metals bioaccumulate in the food chain, negatively impacting organisms, even leading to death in extreme cases. It is therefore important to analyze the impact of heavy metals in different fish organs. The profiling of the proximate composition of fish is of utmost importance in making sure that fish meet up to standard with the requirements of food regulations and commercial qualifications.

Subsistence fishing within the inland fisheries of Nigeria is a provider of employment, especially as the more profitable jobs are not easy to find. In the communities surrounding the Gashua River, fishing is an important source of livelihood. As the majority of families in these areas are low-income earners, fish presents an alternative and cheap source of protein compared to other protein sources. A lot of fish species are caught from the Gashua River. Amongst these fish species are *Synodontis omias* and *Mormyrus rume.*

The presence of heavy metals is detrimental to fish and by extension, humans and other organism who consume them. Knowledge of the proximate composition of the different fish species is very important, especially if choice is to be made for consumption. The health risks associated with consuming fish that accumulates heavy metals in their bodies far outweighs the nutritional benefits that may be derived from such fish species. Hence, we investigated the proximate composition of two fish species from Gashua River and also analyzed them for some toxic heavy metals with a view to predicting the level of safety associated with their consumption.

Smoking also has its effect on the nutritive value of fish as high temperature denatures protein which is the major nutrient source from fish. Smoke is generated from wood by burning. Smoke has bacteriostatic, bactericidal, and antioxidant functions while heat generated from the wood has dehydrating effect on the fish. The consumption of smoked fish in Nigeria is very high, and consumers sometimes prefer smoked fish to the fresh ones but how nutritive is the smoked fish products using *Synodontis omias* and *Mormyrus rume* remains questionable.

Since there is no formal control of effluents discharged into the Gashua River, it is important to monitor the levels of metals contaminants in Gashua Riverfish and assess the suitability for domestic uses. In order to effectively control and manage water pollution due to heavy metals, it is important to have a clear understanding of the distribution and profiles of heavy metals in the biota. Therefore, the objectives of this present work are to examine the proximate composition and identify some heavy metal in the gills and muscles of smoked *Synodontis omias* and *Mormyrus rume* in Gashua River.

MATERIALS AND METHOD

Study Area

Gashua is a community in Yobe State in northeastern Nigeria, on the Yobe River a few miles below the convergence of the Hadejia River and the Jama'are River. Average elevation is about 299 m. The population of 125,000 according to 2006 census (NPC,2006). Gashua has a latitude of 12°52'35.39"N and a longitude of 11°1'53.7"E respectively. Gashua, Nigeria coordinates 52.8 Km North West to Kumagunnam, 62.4 Km West to Nguru, 97.3 Km East too Geidam, Yobe State.

Sample Collection

The smoked fish samples of *Synodontis omias* and *Mormyrus rume*were purchased fromGashua community in Yobe State in northeastern Nigeria, and labeledaccordingly. The samples were placed inpolythene bags and were immediatelytransported in plastic boxes to Faculty of Science, Department of Chemistry Laboratory Yobe State University for Proximate analysis. Fish muscles and Gills were removed with a plastic knife, oven dried at about 80°C.

Sample preparation and digestion

The fresh fish samples were placed on an already sterilized chopping board and incised vertically to expose the inner portion (the flesh) of the fish. It was then sliced into pieces with a sterilized knife and was separately dried in a laboratory oven at 80°C overnight before being homogenized with ceramic mortar andpestle prior to digestion.

The dried samples were each ground to powder, using laboratory ceramic mortar and pestle, and sieved with 2mm sieve. The powdered samples were digested using the procedure described.

Proximate Analysis
Proximate composition, namely, moisture, crude protein, crude fibre, crude fats, ash and nitrogen free extract (carbohydrate contents) in portions of the various samples were measured according to the standard methods as described in AOAC and other standard techniques obtained from the literature.

Determination of moisture content.
The method described by A.O.A.C (1980) was adopted; a clean crucible was dried to a constant weight in air oven at 110°C, cooled in a desiccator and Weighed (W1). Two grams of finely ground sample was accurately weighed into the previously labeled crucible and reweighed (W2). The crucible containing the sample was dried in an oven to constant Weight (W3). The percentage moisture content was calculated thus:

$$\% \text{ Moisture content} = \frac{W2 - W3}{W2 - W1} \times 100$$

Determination of ash content:
The A.O.A.C (1980) method was used. The porcelain crucible was dried in an oven at 100°C for 10 min, cooled in a desiccators and Weighed (W1). Two grams of the finely ground sample was placed into a previously weighed porcelain crucible and reweighed (W2), it was first ignited and then transferred into a furnace which was set at 550°C. The sample was left in the furnace for eight hours to ensure proper ashing. The crucible containing the ash was then removed; cooled in a desiccator and Weighed (W3).

The percentage ash content was calculated as follows:

$$\% \text{ Ash Content} = \frac{W3 - W1}{W2 - W1} \times 100$$

Determination of crude lipid content by Soxhlet method
A clean, dried 100 cm3 Flat bottom flask containing few anti-bumping granules was Weighed (W1) and 60 cm3 petroleum ether (40-60°C) for extraction poured into it. The extractor thimble containing twenty grams (20g) of the sample was fixed into the Soxhlet unit. The round bottom flask and a condenser were connected to the Soxhlet extractor and cold water circulation was connected. The overall setup was place over a heating mantle. The heating mantle was switched on and the heating rate adjusted until the solvent was refluxing at a steady rate (about 500C). Extraction was carried out for 3 hours. The solvent was recovered and the oil dried. The flat bottom flask and oil was then Weighed (W2). The lipid content was calculated thus:

$$\text{Crude Lipid} = \frac{W2 - W1 \times 100}{\text{sample weight}}$$

Determination of crude fibre:
The sample (2 g) was weighed into a round bottom flask, 100 cm3 0.25 M sulphuric acid solution was added and the mixture boiled under reflux for 30 min. The hot solution was quickly filtered under suction. The insoluble matter was washed several times with hot water until it was acid-free. It was quantitatively transferred into the flask and 100 cm3 of hot 0.31 M, Sodium Hydroxide solution was added, the mixture boiled under reflux for 30 min and filtered under suction. The residue was washed with boiling water until it was base free, dried to constant weight in an oven at 100°C, cooled in a desiccator, and weighed (C1). The weighed sample (C1) was then incinerated in a muffle furnace at 550°C for 2 h, cooled in a desiccator, and reweighed (C2).

Calculation: The loss in weight on incineration = C1- C2

$$\textbf{Crude Fibre} = \frac{\textbf{C1 – C2 x 100}}{\textbf{Sample weigh}}$$

Determination of Crude Protein
Crude protein: Samples (2 g) were digested in digestion unit (Digester, model 2020) for 45 min. The digester was then distilled in distillation unit (Kjeldahl System, Distilling unit, model 1026). Finally, it was titrated with 0.2 N HCL and **crude protein** was obtained by multiplying the total nitrogen by a conversion factor of 6.25.

Calculate the percentage nitrogen (wet eight basis) as follows:

$$\% \text{ Nitrogen (wet)} = \frac{(A - B) \times 1.4007}{\text{Weight of sample}} \times 100$$

Where
A = vol. (mL) std. HCl x normality of std. HCl
B = vol. (mL) std. NaOH x normality of std. NaOH
Calculate nitrogen content on dry basis (when moisture content is known) as follows

$$\% \text{ Nitrogen (Dry)} = \frac{\% \text{ Nitrogen (wet)}}{(100 - \% \text{ moisture})} \times 100$$

Calculate the percentage protein (wet or dry basis) as follows:
% Protein = % nitrogen x 6.25 where 6.25 is the protein-nitrogen conversion factor for fish and fish by-products.

Determination of Nitrogen Free Extract (carbohydrate) by (difference)
The total carbohydrate was determined by difference. The sum of the percentage moisture, ash, crude lipid, crude protein and crude fibre was subtracted from 100.

Calculation:
% Total carbohydrate = 100 - (% moisture + % Ash + % fat + % Protein + % Fibre)

Heavy Metals Analysis
The following elements (Chromium Cr, Cadmium Cd, Arsenic As, Nickel Ni, Lead Pb and Copper Cu.) of the two fish samples were determined directly using Atomic Absorption Spectrophotometer (AAS) in the laboratory. This process involves the absorption by free atoms of an element of light at a wavelength specific to that element.

Data Analysis

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Data analysis from the study were entered into Microsoft Excel and analysed using SPSS for Windows version 16.0 software. Treatment means of the two smoked fish samples were compared using one-way Analysis of Variance (ANOVA) at 5% level of significance reported as mean standard deviations (± SD). The values were compared with Food and Agriculture Organization (FAO) Standard (2004).

RESULTS

Proximate analysis

The results of proximate composition of smoked fish samples of *Synodontis omias* and *Mormyrus rume*are shown in Table 1; the moisture, protein, carbohydrate, fibre, and fat content *Synodontis omias*were higher than in the *Mormyrus rume*while carbohydrate are higher in *Mormyrus rume* than in the *Synodontis omias*.

The value of the moisture content of the smoked fish samples indicates that lowervalues of moisture content were recorded in all the species, with the highest value (12.57±0.02%) from *Synodontis omias*, while the lowest (8.69±0.03%) was in *Mormyrus rume*. For the Ash content, highest value of ash (5.03±0.01%) was observed in *Synodontis omias* and the lowest (3.48±0.00%) in *Mormyrus rume.* For the crude fat, highest value of crude fat was recorded in *Synodontis omias*(15.10±0.01) when compared to other species with a mean value of (10.43±0.00%).

The least percentage crude protein of 32.20±0.00 was recorded for *Mormyrus rume,* while the highest was recorded for *Synodontis omias* (34.51±0.00). higher values of 0.86±0.00 crude fibre was recorded in smoked *Synodontis omias*and0.60±0.00 in *Mormyrus rume*when compared to the carbohydrates contents, the highest value of NFE (Nitrogen Free Energy) was recorded in *Mormyrus rume* with a mean concentration of*(*44.60±0.03) when compared to *Synodontis omias* with a mean concentration of*(*31.93±0.03).

The table below shows that NFE content (44.60%) was highest in *Mormyrus rume*and(31.93%) in *Synodontis omias*, followed by protein (34.51%) in *Synodontis omias*and (32.20%) in *Mormyrus rume*, fat (15.10%) and (10.43%),moisture content (12.57%) and (8.69%), ash content (5.03%) and (3.48%), andfibre (0.86%) and (0.60%) which is the least.

Determination of crude lipid content by Soxhlet method

A clean, dried 100 cm3 Flat bottom flask containing few anti-bumping granules was Weighed (W1) and 60 cm3 petroleum ether (40-60°C) for extraction poured into it. The extractor thimble containing twenty grams (20g) of the sample was fixed into the Soxhlet unit. The round bottom flask and a condenser were connected to the Soxhlet extractor and cold water circulation was connected. The overall setup was place over a heating mantle. The heating mantle was switched on and the heating rate adjusted until the solvent was refluxing at a steady rate (about 500C). Extraction was carried out for 3 hours. The solvent was recovered and the oil dried. The flat bottom flask and oil was then Weighed (W2). The lipid content was calculated thus:

$$\text{Crude Lipid} = \frac{W2 - W1 \times 100}{\text{sample weight}}$$

Determination of crude fibre:

The sample (2 g) was weighed into a round bottom flask, 100 cm3 0.25 M sulphuric acid solution was added and the mixture boiled under reflux for 30 min. The hot solution was quickly filtered under suction. The insoluble matter was washed several times with hot water until it was acid free. It was quantitatively transferred into the flask and 100 cm3 of hot 0.31 M, Sodium Hydroxide solution was added, the mixture boiled under reflux for 30 min and filtered under suction. The residue was washed with boiling water until it was base free, dried to constant weight in an oven at 100°C, cooled in a desiccator and weighed (C1). The weighed sample (C1) was then incinerated in a muffle furnace at 550°C for 2 h, cooled in a desiccator and reweighed (C2).

Calculation: The loss in weight on incineration = C1- C2

$$\textbf{Crude Fibre} = \frac{\mathbf{C1 - C2 \times 100}}{\textbf{Sample weigh}}$$

Determination of Crude Protein

Crude protein: Samples (2 g) were digested in digestion unit (Digester, model 2020) for 45 min. The digester was then distilled in distillation unit (Kjeldahl System, Distilling unit, model 1026). Finally, it was titrated with 0.2 N HCL and **crude protein** was obtained by multiplying the total nitrogen by a conversion factor of 6.25.

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Where

A = vol. (mL) std. HCl x normality of std. HCl

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Calculate the percentage protein (wet or dry basis) as follows:

% Protein = % nitrogen x 6.25

where 6.25 is the protein-nitrogen conversion factor for fish and fish by-products.

Determination of Nitrogen Free Extract (carbohydrate) by (difference)

The total carbohydrate was determined by difference. The sum of the percentage moisture, ash, crude lipid, crude protein and crude fibre was subtracted from 100.

Calculation:

% Total carbohydrate = 100 - (% moisture + % Ash + % fat + % Protein + % Fibre)

Heavy Metals Analysis

The following elements (Chromium Cr, Cadmium Cd, Arsenic As, Nickel Ni, Lead Pb and Copper Cu.) of the two fish samples were determined directly using Atomic Absorption Spectrophotometer (AAS) in the laboratory. This

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process involves the absorption by free atoms of an element of light at a wavelength specific to that element.

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Data analysis from the study were entered into Microsoft Excel and analysed using SPSS for Windows version 16.0 software. Treatment means of the two smoked fish samples were compared using one-way Analysis of Variance (ANOVA) at 5% level of significance reported as mean standard deviations (± SD). The values were compared with Food and Agriculture Organization (FAO) Standard (2004).

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The value of the moisture content of the smoked fish samples indicates that lowervalues of moisture content were recorded in all the species, with the highest value (12.57±0.02%) from *Synodontis omias*, while the lowest (8.69±0.03%) was in *Mormyrus rume*. For the Ash content, highest value of ash (5.03±0.01%) was observed in *Synodontis omias* and the lowest (3.48±0.00%) in *Mormyrus rume.* For the crude fat, highest value of crude fat was recorded in *Synodontis omias*(15.10±0.01) when compared to other species with a mean value of (10.43±0.00%).

The least percentage crude protein of 32.20±0.00 was recorded for *Mormyrus rume*, while the highest was recorded for *Synodontis omias* (34.51±0.00). higher values of 0.86±0.00 crude fibre was recorded in smoked *Synodontis omias*and0.60±0.00 in *Mormyrus rume*when compared to the carbohydrates contents, the highest value of NFE (Nitrogen Free Energy) was recorded in *Mormyrus rume* with a mean concentration of*(*44.60±0.03) when compared to *Synodontis omias* with a mean concentration of*(*31.93±0.03).

The table below shows that NFE content (44.60%) was highest in *Mormyrus rume*and(31.93%) in *Synodontis omias*, followed by protein (34.51%) in *Synodontis omias*and (32.20%) in *Mormyrus rume*, fat (15.10%) and (10.43%),moisture content (12.57%) and (8.69%), ash content (5.03%) and (3.48%), andfibre (0.86%) and (0.60%) which is the least.

Table 1: Proximate Composition of Selected Fish Samples from River Gashua

Proximate Component	Smoked Synodontis Omias (mg/kg)	Smoked Mormyrus rume (mg/kg)	P-Value (mg/kg)
Moisture	12.57±0.02	8.69±0.03	0.0051
Ash	5.03±0.01	3.48±0.00	0.0001
Lipid	15.10±0.01	10.43±0.00	0.0006
Fiber	0.86±0.00	0.60±0.00	-
Protein	34.51±0.00	32.20±0.00	-
NFE	31.93±0.03	44.60±0.03	0.0010

Heavy Metal Analysis

The heavy metal concentration in smoked *Synodontis omias* and *Mormyrus rume* (Table 2) illustrates that Cu has the highest concentration of heavy metal with a mean value of 3.443±0.031mg/kg and 5.427±0.021mg/kg and which is higher than 0.03 mg/kg of the Food and Agriculture Organisation (FAO) limit in the fish. There is a significant difference (0.001) among the two samples; two big fishes (gill and muscles). Cd with the lowest mean value of 0.130±0.0015mg/kg and 0.179±0.0005mg/kg and lower than 1.5 mg/kg of FAO limit. The $P < 0.05$; hence there are no significant differences (0.004) among the Cd values of each sample. In addition, Cr (0.777 ± 0.0032mg/kg, and 1.738 ± 0.0052mg/kg), Ni (1.137±0.0064mg/kg and 2.236±0.0074mg/kg), Cu (3.443 ± 0.031mg/kg and 5.427 ± 0.021mg/kg), As (0.231 ± 0.002mg/kg and 0.319 ± 0.001mg/kg) and Pb (1.168 ± 0.018mg/kg and 0.955 ± 0.005 mg/kg) content in muscles and gills of smoked *Synodontis omias* and *Mormyrus rume* are lower than FAO limit of 1.0, 0.6, 0.03, 0.5, and 1.3g respectively. Furthermore, with the *P value* of Cr (0.010), Ni (0.022), Cu (0.0001), As (0.003) and Pb (0.03); there are no significant differences among the values of fishes (gills and muscles) in the Cr, Zn and Pb; but there are no significant differences in the values of Ni and Cu in fishes. Heavy metal concentration in muscles and gills of smoked *Synodontis omias* and *Mormyrus rume* shows that Cu has the highest concentration (3.443±0.031mg/kg and 5.427±0.021 mg/kg) and is higher than the 0.03 mg/kg of the Food and Agriculture Organisation (FAO) limit. There are significant differences (0.01) among the two samples. Cd has the lowest mean value of 0.130±0.0015mg/kg and 0.179±0.0005 mg/kg and is higher than the 0.03 mg/kg of FAO limit. $P > 0.05$; hence, there are no significant differences among the Cd values of each sample. The mean value of Cr (0.777 ± 0.0032mg/kg, and 1.738 ± 0.0052mg/kg), Ni (1.137±0.0064mg/kg and 2.236±0.0074mg/kg), Pb (1.168 ± 0.018mg/kg and 0.955 ± 0.005mg/kg), As (0.231 ± 0.002mg/kg and 0.319 ± 0.001mg/kg) and Cd (0.130±0.0015mg/kg and 0.179±0.0005 mg/kg) content in muscles and gills of smoked *Synodontis omias* and *Mormyrus rume* are lower than FAO limit of 1.0, 0.6, 1.3, 0.5, and 1.5 mg/kg respectively. However, with *P value* of Cr (0.01), Ni (0.02), Cu (0.001), As (0.003) and Cd (0.004); there are no significant differences among the values of the two fishes' samples in Cu and Pb

Table 2: Heavy Metals Composition of Selected Fish Samples from River Gashua

Heavy Metals	Smoked *Synodontis omias*	Smoked *Mormyrus rume* (mg/kg)	P-Value (mg/k	FAO Standard

	(mg/kg)		g)	(mg/kg)
Chromium	0.777±0.0032	1.738±0.0052	0.010	1.0
Cadmium	0.130±0.0015	0.179±0.0005	0.0004	1.5
Arsenic	0.231±0.0025	0.319±0.0011	0.0003	0.5
Nickel	1.137±0.0064	2.236±0.0074	0.0222	0.6
Copper	3.443±0.0312	5.427±0.0211	0.0001	0.03
Lead	1.168±0.0175	0.955±0.0047	0.0335	1.3

Values are means of three replicates ± SD. Sample A = *Synodontis omias*, Sample B = *Mormyrus rume*

DISCUSSION

Proximate analysis

Moisture

The proximate analysis revealed that the moisture content of *T. guineensis* which is comparatively lower than the result observed in brackish and freshwater tilapia (*O. niloticus*) respectively by Olaniyi *et al.*, *(*2016). It is however comparative lower to the result reported by Adefemi (2011) but is significantly higher than moisture content reported by Ikape, *et al.*, (2018) in proximate and macro element composition of four fish species from lower River Benue Makurdi, Benue State.

The loss in moisture of smoked fish samples is as a result of the application of heat which decreases water activity in fish tissue, while high moisture content provides a conducive environment for spoilage by microbes (Akintola *et al.* 2013). The lowest moisture content recorded in smoked fish samples entails a longer shelf life of the product. It has been reported by Abolagba and Osifo (2008) that the principle of fish smoking is the removal of moisture content as a result of heat application from smoking.

Protein

The quality of fish protein is superior to that which could be obtained from milk, meat and eggs. The increase in protein content of smoke-dried sample as shown in Table 1 may be due to product dehydration which concentrated the protein during smoke-drying thereby increasing the nutritive value of the fish.Fish protein is of high quality and contains sufficient amounts of all the essential amino acids required by the body for growth, maintenance of lean muscle tissue and active metabolism (Olayemi *et al.,* 2011). A Similar finding was reported by Adebowale *et al.* (2008) who compared the crude protein level of*Clarias gariepinus* to the processed smoke-dried sample.

Generally, the proteins are important for normal function, growth, and maintenance of body tissue and hence protein content is considered to be an essential tool for the evaluation of biochemical and physiological standards of a given organism (Belton *et al.,* 2014). From the nutritional point of view, protein is the mostimportant constituent of fish. Protein content in most fish averages 18-20%, though the general variation is in the range of 15-24%. Variations in protein content occur in relation to age, fat content, spawning, starvation etc (Hossain, 2011). In this study protein content was slightly higher in the muscle and gill of *Synodontis omias* (34.51%)than in the *Mormyrus rume* (32.20%).The protein composition obtained in this study is slightly higher than the result reported by Davies and Jamabo (2016), Adejonwo *et al.,* (2010) and Nurnadia *et al.,* (2011). However, it is also higher than the one recorded by Akinjogunla *et al.,* (2017).But the value obtained in this study is higher than the one reported by Shemishere *et al.,* (2018).

Fat (Lipid)

The fat content increase could be as a result of heat produced by smoking which results in moisture content losses, increasing the concentration of nutrient in the reaming mass of fat as related to lipid oxidation, which produced volatile compounds known to be unsaturated and very prone to oxidation. These findings are in line with Dirar, (2013) who reported that during fish smoking, fish loses its moisture content, which results in an increase in the concentration of nutrient in the remaining mass of fats. And also is in line with Olayemi *et al*., (2011) who reported that during smoking fish losses its moisture content which result in increase in the concentration of nutrient in the remaining mass of fats.The fat content obtained in *C. gasar* by Akinjogunla *et al.,* (2016) and Nurnadia *et al.,* (2011) are both lower than the observed value in this investigation.

Ash

Ash is the inorganic residue that remains after matter has been burnt off which was found in little non-significant traces in the fish sample. Ash is the measure of the mineral content of any food including fish (Omotosho *et al.*, 2001). Smoke drying increased significantly the ash content which could be attributed to the fish species, season and food availability. Similar findings were reported by Kumolu-Johnson *et al.*, (2010) who observed significant difference in ash content of some smoked *Clarias gariepinus.* The ash content of the smoked dried sample increased was similar to the works of Akinmeye *et al.,* (2010) on Spp, *Sardinella* Spp and *Heterotis niloticus.*

Fibre

The fibre content in this study was higher than the result reported by Akinjogunla *et al.,* (2017), but lower than the one reported by Woke *et al.,* (2016) in *C. gasar* collected from Andoni River.

Heavy Metal Analysis

The highest concentration factor of Cr, Cd, As, Ni and Cu were found in gills and muscle of *Synodontis omias* and Cr, Cd, As, Ni and Cu *Mormyrus rume* respectively.

Lead (Pb)

The mean concentration of Lead in this investigation was in agreement with the value reported by Abu and Nwokoma (2016);but higher than the range obtained in fish tissue from Sombreiro River by Wokoma (2014). Lead, copper, cadmium, and zinc form poisonous "ligands" with organic molecules

*Corresponding Author: **Onyia, Lucky Uche.**

*(*El-Badry, 2016). Lead toxicities induce weakness, irritability, muscle pain, coma, and kidney, liver, and brain injury. Cadmium toxicity causes Japanese Itai-Itai disease, bone disease, anosmia, and tooth discoloration *(*Sanders, *et al.* 2009*;* Sankar and Kumar, 2014*; and* Agumassie, 2018).

Pb is a confirmed toxic metal with no known beneficial effect on the human body. Current mean Pb concentrations are less than those reported by Ahmed *et al.* (2019). Besides, Staniskiene *et al.* (2006), and Copat *et al.* (2012), obtained a comparable Pb concentration in their published work.The mean value of lead recorded in this study was lower than the permissible limit stipulated by FAO.

Cadmium (Cd)

The mean concentration of Cadmium reported respectively by Ekweozor *et al.* (2017), in the muscle of *O.niloticus* from Okujuagu-Ama creek, is higher than the mean recorded in the present study. However, the result from this study was lower than the permissible limits of FAO. Toxic effects of Cadmium in man include renal damage and dysfunction, proteinuria, bone lesions, prostate and lung cancer. It is also embryo toxic and teratogenic. Cd is transported in the blood and is reported to accumulate in the liver and kidney. It poses a great toxic effect on the human kidney, the respiratory and skeleton systems. It also has carcinogenic effects on humans making it to be classified as a human carcinogen. According to M'Kandawire (2017), cadmium concentration above 0.5 mg/kg in fish is hazardous and can be harmful to the consumer of such fish as well as affect the protein and carbohydrate metabolism in the fish. Cadmium toxicity caused Japanese Itai-Itai sickness, bone disease, anosmia, and tooth discoloration *(*Selda, and Nursah, 2012; Bosch, *et al.* 2016).

Nickel (Ni)

The observed mean concentration of Nickel in this investigation is higher than the permissible limits of the FAO. The mean nickel concentration was higher than the reported ranges in *Clarias gariepinus* as reported by Wokoma, (2014) and Bob-Manuel *et al.,* (2015) respectively. Though, lower than the value found in the tissues of *Chrisichthyes nigrodigitatus* from Sombreiro River by Wokoma (2014), and the range reported by Obot *et al.* (2016) in *Ilisha africana* from the lower Cross River estuary both in the Niger Delta. It is however slightly higher than the value revealed in the heart of *Clarias gariepinus* by Babatunde *et al.,* (2012). Nickel is often associated with allergies and at high concentrations can induce lung and nasal cancers.

Chromium (Cr)

Chromium is an essential metal in the human body especially in enhancing insulin activity, above recommended limits however. Cr and its compounds are well known toxins especially Cr(VI) which is due to its oxidizing potential, easily permeates biological membranes and causes renal damage, diseases of the central nervous system, cancer etc. in man. Cr is an essential trace metal and it plays a crucial role in glucose metabolism(Fang *et al.*,2014).

The mean concentration of Chromium reported by Bob-Manuel *et al*., (2015) in organs of *Clarias gariepinus* from Okilo Creek, Rivers State, Nigeria, is higher than the value recorded in this study. However, it is in parity with the mean value recorded in Catfish by Orosun *et al.,* (2016). However, Cr value in this study is in line with the value reported by Aliyu *et al.,* (2015) in Kaduna Metropolis, Nigeria and Adeyeye and Ayoola (2012) in the liver of *Tilapia zilli* from Eko-ennde dam Nigeria. However, not all metals are toxic to humans; some metals, such as nickel, zinc, and chromium, are useful in human metabolic processes in small amounts (Sfakianakis *et al*., 2015).

Copper (Cu)

The mean concentration of Copper (Cu) is in parity with the mean concentration reported by Wokoma (2014) in the tissues of *Psuedotolithusel angatus* from Sombreiro River, Niger Delta, and Upadhi *et al.,* (2013) in *Tilapia zilli*. In Ghana's Asafo market, its levels ranged between 0.02-0.156 (Kwaansa-Ansah, *et al.* 2019),far less than the current recorded values. Copper is crucial to the body because it aids in synthesizing haemoglobin and other vital enzymes, but an excess can cause hepatic and renal injuries (Travis, 2013; Vu *et al.*, 2017*).*

However, Cu concentration in muscles and gills of smoked *Synodontis omias* and *Mormyrus rume*as revealed by this investigation is higher than the permissible limits of FAO.

Arsenic (As)

The mean concentration of Arsenic (As) observed in muscles and gills of smoked *Synodontis omias* and *Mormyrus rume* in this work was higher than the range of value recorded in *Ilisha africana*(Obot *et al.,* 2016) from lower Cross River Estuary, Nigeria as well as the range of value found in gills of Grey Mullet(Stancheva *et al.,* 2013). The result from this work is lower than the permissible limits of FAO.

Arsenic exposure is associated with various health risks, including cancers. Wastes are usually discharged into the aquatic system in most cases, contain heavy metals such as lead, aluminum, cadmium, and arsenic known to be very toxic or carcinogenic, even at deficient concentrations to humans (Kabir *et al*., 2012).

Ingestion from contaminated food associated lead to blood in the urine, hair loss, stomach upset, convulsions, vomiting, diarrhoea, and it's also reported to affect the skin, liver, lungs, and kidneys which may lead to a coma or even death(de Carlho *et al.*,2023).
Another explanation for the detected high Cu levels is the hot weather-induced copper precipitation as CuS due to temperature rises (Hegazy *et al*., 2016***)***.

Metal concentrations in fish can vary spatially and temporally due to factors like water quality, habitat, migration patterns, and seasonal variations. A study in a specific location or period may not capture the full range of metal concentrations under investigation (Darweesh *et al.* 2019*).*

In addition to these variables, the tropic level, feeding practices, age, dimensions, length of time exposed to the polluting elements, and metabolic activity of aquatic organisms may impact their accumulation of heavy metals. For example, a study by *Liao et al.* (2021) found that the accumulation of heavy metals in fish was influenced by their trophic level, with higher trophic level fish having higher tissue heavy metals concentrations.

The concentration pattern of the muscles and gills of *Synodontis omias* and *Mormyrus rume* were in the order of Cu>Pb>Ni> Cr >As> Cd respectively.

Conclusion

The analysis of proximate composition and heavy metals concentration of smoked *Synodontis omias* and *Mormyrus rume*from Gashua River revealed that the fish is highly nutritious with a high protein content which makes it good for consumption. The outcome of this study indicated that moisture contents of fish are of great importance, as most of the biochemical reactions and physiological changes in fish depend on moisture content. Protein content in smoked fish samples was observed to increase, as a result of an increase in the dry matter content per unit weight following sample dehydration during smoking. Therefore, the increase in protein content, ash content and ash content can be due to an increase in the dry matter content per unit weight following sample dehydration.

However, the result also showed that smoked *Synodontis omias* and *Mormyrus rume* from Gashua River has a high body load of some heavy metals (copper, lead and nickel). The study also showed the accumulation of Cu, Pb and Ni to levels higher than safe limits, as their concentrations exceed the permissible limit set by the FAO. Consumers are therefore advised to exercise restraint in the consumption of this fish (smoked *Synodontis omias* and *Mormyrus rume*) from the Gashua River so as to avoid potential health hazards.

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