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PROXIMATE, MICRONUTRIENTS, AND HEAVY METALS COMPOSITION OF CLARIAS GARIEPINUS FROM THE BANK OF THE NIGER RIVER, ONITSHA, ANAMBRA STATE, NIGERIA

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Abstract

When compared to other sources of animal protein, fish is relatively more affordable and accessible, even in poorer communities. The proximate, micronutrients and heavy metals composition of catfish (*Clarias gariepinus*) obtained in its fresh form from the bank of Niger River basin in Onitsha and processed with oven and smoke-drying technique under strict supervision was studied. The control sample was a representative sample of already smoke-dried catfish imported to Onitsha from other localities. It was obtained and merged as one from 10 separate retail locations within an open market in Onitsha. The results of the findings showed that drying generally leads to moisture loss in the fresh fish sample and increases nutrient concentrations in the dried fish sample. The moisture ranged from 6.71% - 68.30%. Drying was enhanced with the oven technique thereby improving the protein from 14% -60%, ash from 3.89% - 8.53%, mineral elements, and vitamin A composition. The results further revealed that the catfish sample sourced from the bank of Niger River basin in Onitsha provided the best nutrient quality when compared to the control sample, thereby showing contributing tendency to nutrition and food security in Anambra State. The heavy metals investigated are Lead (Pb), Zinc (Zn), Chromium (Cr) and Cadmium (Cd). The results showed no presence of lead in fresh, processed (both oven and smoke-dried fish samples) and control fish samples, however, traces of Zn, Cr, and Cd were recorded in all the samples. The value of Zn ranged from 2.20 to 2.33mg/kg and these showed no significant difference among the samples. Cr and Cd were significantly higher ($p<0.05$) in processed smoke-dried fish samples when compared to other samples. On a general note, the level of heavy metals obtained from the results in all the samples posed no health threat from consumption of the fish samples as the values are below the recommended permissible limit for heavy metals in food system.

Keywords: catfish, smoke-dried, oven-dried, proximate, micronutrient, heavy metals

INRODUCTION

Fish is considered one of the healthiest foods due to the quality of its nutrients, offering a cheap and highly acceptable source of animal protein with little or no rejection compared to other animal products (*Maulu et al.*, 2021). According to the FAO (2020), approximately 88% of global fish production is for human consumption, with live and fresh fish accounting for 44% and providing fish farmers with significant market worth. The remaining fish production is frozen, dried, salted, smoked, or otherwise cured. Traditional fish processing techniques like salting, brining, drying, and smoking increase consumer access to fish by improving preservation and storage (Adeyemi *et al.*, 2013). The most popular among these methods in Nigeria are smoking, sun-drying, and oven-drying.

In Anambra State, the consumption of dried fish is a popular staple in every household. Dried fish is a significant source of animal protein and other necessary nutrients for maintaining a healthy body, readily available, physically, and economically accessible to all. Consumers prefer dried fish because of its distinct flavour and taste. Dried fish retains significantly more essential nutrients per unit weight than fresh fish (Rasul *et al.*, 2020). However, increasing population growth, lack of processing and storage facilities, and poor post-harvest handling have created an overwhelming gap between the demand and supply of fish (Olayemi *et al.*, 2011).

The catfish (*Clarias gariepinus*) is one of the common and popular fish species in Anambra, and its adoption for consumption is prevalent in every household diet. *C. gariepinus* is considered one of the world's best aquaculture species by many researchers and fish farmers. It has a wide native distribution, high reproductive capacity, rapid growth, the capacity to breathe air, disease resistance, tolerance for high

stocking densities, and high feed-conversion efficiency, among many other positive traits. As the most cultivated catfish on the African continent, it is native to the inland waters of much of Africa and is commercially cultivated in about 15 African nations, including Nigeria, Zambia, Ghana, and South Africa (Wing-Keong, 2021).

Despite the presence of significant aquatic habitat in Onitsha, Anambra's most popular commercial hub, the prevalent dried catfish sold in Anambra open markets are mostly obtained from other riverine community. However, research evidence provides information on the availability of catfish around the Niger River basin in Onitsha (Rupert, 2014), but there is little or no research been conducted to investigate the macro and micronutrient compositions as well as the heavy metal content of *C. gariepinus* obtained from the Niger River basin in Onitsha and link it to the state's nutrition and food security. The present study was designed to bridge the gap.

MATERIALS AND METHOD

Collection of samples

Freshly harvested catfish used for the study was obtained from bank of Niger River in Onitsha. Another dried catfish sample imported to Onitsha from other riverine community and sold in "Ose Okwodu" open market in Onitsha was used as a control sample to establish relative differences and similarities in the investigated parameters of the fish samples. This sample was however obtained from ten different retail locations within the market and merged to serve as a representative sample for the market

Processing and preparation of the fish for analysis

Approximately 3kg of the live catfish sample obtained from bank of the Niger River in Onitsha were slaughtered, eviscerated, washed with tap water, and divided into three portions. One of the portions was analyzed as fresh while the other two portions were oven-dried and smoked respectively. Prior to the drying process, the fish samples were brined using a teaspoon of salt per fish as described by Olayemi *et al*. (2011). Smoking of the fish sample was performed using burning charcoal with the aid of a charcoal pot under strict supervision. The smoking process was terminated when the fish were properly dried after 15 hrs. The oven drying process was conducted at 70°C for 24 hrs to obtain a sample with constant weight and complete drying as described by Ali and Mozhgan (2015). After the drying process, all dried samples were milled accordingly in a dry blender, packaged using Ziploc polyethylene bag, and kept in the freezer until needed for further analysis. Samples were analyzed in triplicates.

Macro and micronutrients analysis

Proximate, macrominerals (Ca, P & K), and vitamins of the fish samples were investigated. All analysis was carried out at the Food Technology Department, Federal Polytechnic Oko, Anambra State. The proximate, minerals and vitamins evaluation were carried out according to AOAC (2000).

Heavy metal analysis

The analytical procedure followed that of Muinde *et al.* (2013) with some modifications. 5g of each of the individual fish samples were weighed using electronic weighing balance into a 50 mL Pyrex beaker for digestion using 10 mL mixture of concentrated HCl and HNO_3, in the ratio of 3:1 (Aqua regia) for 3h at 60°C using a hot plate inside the fume chamber. After digestion, the content of the flask was filtered into a 50 mL standard flask and made up to the mark with deionized water and then transferred into the laboratory sample bottles and kept at room temperature until analysis. Sample blanks were prepared by taking 10 mL of the reagent mixture through the same procedure. Aliquots of the filtrates were analyzed for Zinc (Zn), lead (Pb), chromium (Cr), and cadmium (Cd) using Atomic Absorption Spectrophotometer (AAS). The calibration of the instrument was carried out using standard solutions.

Statistical Analysis

All the analyses were conducted in triplicates. Data were subjected to analysis of variance, and Duncan's multiple range test was performed to compare the means at a 5% level of significance. All analyses were performed using statistical software, SPSS version 25

RESULTS AND DISCUSSION

The results of the proximate, micronutrients and heavy metals evaluation of fresh and dried fish samples are presented in the Tables 1, 2 and 3 respectively.

Table 1: Results of the proximate composition of cat fish samples from bank of River Niger, Onitsha

Samples	Parameters (%)				
	Moisture	Protein	Fat	Carbohydrate	Ash
Fresh catfish	68.30±0.10[a]	14.0±0.000[d]	9.0±0.000[c]	4.81±0.010[c]	3.89±0.044[c]
Open market catfish	9.35±0.012[b]	45.75±0.025[c]	29±0.000[a]	8.43±0.020[a]	7.47±0.026[b]
Smoke-dried catfish	8.31±0.005[c]	50.11±0.015[b]	29.2±0.010[a]	4.93±0.012[bc]	7.45±0.030[b]
Oven-dried catfish	6.71±0.020[d]	60.55±0.020[a]	19±0.000[b]	5.21±0.020[b]	8.53±0.020[a]

Values are mean of three replicates. Samples with the same superscripts along the column are not significantly (P<0.05) different

Proximate composition

The moisture content of the fish samples ranged from 6.71% to 68.30%. Comparing the dried samples to the fresh sample revealed a significant decrease in the moisture content for dried samples. The high moisture observed in the fresh fish can make it prone to early spoilage if not immediately preserved (Adeyeye *et al.*, 2016). High moisture content has been associated with an increase in microbial susceptibility (Elleuch *et al*., 2011; *Olayemi et al.*, 2011, Adeyeye *et al*., 2016). The moisture differences observed among the dried samples could be due to variations in drying temperature and heat source, duration of drying, and storage condition. The higher moisture content observed in smoke-dried fish sample obtained from the open market could be attributed to absorbed moisture by the fish during storage (Ali and Mozhgan, 2015).

The protein, fat, carbohydrate, and ash content of the fresh fish sample as shown in Table 1 was significantly lowered ($p<0.05$) when compared to the dried samples. The increase in the nutrients composition of the dried samples can be attributed to an increase in the dry matter content per unit weight as a result of dehydration during the drying process (Suryanti and Suryaningrum, 2017), and the results as shown in Table 1 clearly revealed an inverse relationship between the moisture contents and other nutrients composition in the fish samples, with protein accounting for the highest dry matter. The protein content of the dried samples ranged from 45.75% - 60.55% with the highest value recorded in the oven-dried sample. This finding was in line with the results of earlier researchers who recorded significantly higher protein contents in oven-dried fish when compared with smoke-dried fish (Ime-Ibanga and Fakunle, 2009, Chukwu and Shaba, 2009, Akinneye *et al*, 2010, Omoruyi *et al*., 2017).

The fat content of the dried samples showed no significant difference ($p<0.05$) in both smoked dried samples (that is, smoke-dried catfish obtained from the open market and smoke-dried catfish obtained from the bank of the Niger River basin). The values obtained for both samples were significantly higher ($p<0.05$) than that of oven-dried sample. This was in line with the work of Omoruyi *et al.* (2017) who recorded a 21.19% fat content in smoked dried fish sample when compared to the oven-dried fish sample of 16.10%. Fat may be exuded as a result of moisture evaporation and prolonged heat treatment during the oven drying process. (Chukwu and Shaba, 2009) because the oven drying technique was performed for a period of 24h as against the 15h termination period in the smoke-drying technique.

The values recorded for ash in the present study ranged from 3.89% - 8.53%. The mean values for dried fish samples were significantly higher ($p<0.05$) than the fresh fish. The oven-dried fish sample revealed a higher ash content when compared to both smoked fish samples (control and smoke processed fish samples). The mineral constituents of any food, including fish, can be measured by its ash content. The higher ash value recorded in oven-dried fish sample in the present study depicts a higher mineral profile in comparison to other samples. It is known that fish have different concentrations of minerals and trace elements depending on their feeding habits, environment, ecosystem, and migration even within the same area (Omoruyi *et al*., 2017).

Carbohydrate is a good source of instant energy. Additionally, it supports the body's development and growth (Omoruyi *et al*., 2017). The fish samples generally have low carbohydrate content, with the highest value recorded in smoked fish sample obtained from the open market.

Samples	Parameters (mg/100g)					
	Calcium	Phosphorus	Potassium	Vit.C	Vit.A	Vit.B_2
Fresh catfish	15.0±0.152^c	13.53±0.020^c	12±0.000^d	11±.000^b	36±0.044^c	0.28±0.023^b
Open market catfish	15.15±0.017^c	37.15±0.035^a	29.79±0.055^c	12.17±0.026^a	53.15±0.02^b	0.24±0.004^b
Smoke-dried catfish	45±2.00^b	37.15±0.020^a	35.12±0.026^b	10.15±0.020^c	55±0.00^b	1.19±0.010a
Oven-dried catfish	47±0.00^a	35±0.000^b	45.50±0.030^a	10±0.001^c	77±0.020^a	0.10±0.006^c

Table 2: Results of the micronutrients analysis of catfish samples from bank of River Niger, Onitsha
Values are mean of three replicates. Samples with the same superscripts along the column are not significantly (P<0.05) different

Micronutrients

The results of the selected macrominerals (Ca, P & K) investigated in the current study showed that drying evidently concentrates the mineral elements. Ca and K mean values are significantly higher (p<0.05) in the oven-dried sample (47mg/100g & 45mg/100g respectively), followed by the smoke-dried sample obtained from the bank of Niger River basin (45mg/100g & 35.12mg/100g respectively). The least value for Ca & K was recorded in the smoke-dried sample sourced from the open market (control sample). Variations in the concentrations of mineral elements from one sample of fish to another could be due to the chemical forms of the element, their concentrations in the local environment, and the fish processing condition (Akinnye *et al.,* 2010). The phosphorus of both smoked fish samples is recorded to be 37.15mg/100g which was significantly different (p<0.05) and higher in value when compared to the oven-dried fish. Mineral nutrients are essential for maintaining life as they help the body develop and function properly. The development and mineralization of bones, as well as the healthy function of tissues and the central nervous system, depend on calcium (Maulu *et al*., 2021). Along with supporting calcium in the development of robust, healthy bones and teeth, phosphorus aids in the body's ability to store and use energy. Potassium controls muscle contractions and nerve impulses, preserve the body's fluid balance and ensures continued proper nerve and muscle function.

Fish is an essential source of vitamins, especially vitamin A and D as well as the B complex. Fresh fish contains a small amount of vitamin C, which is necessary for tissue preservation, wound healing, and helping the nervous system absorb iron (Maulu *et al*., 2021). The present study revealed the availability of vitamins, A, B_2, and C. Vitamin A content ranged from 36mg/100g to 77mg/100. A significant increase was observed due to drying, with the highest value recorded in the oven-dried sample.

Table 3: Results of the heavy metals analysis of cat fish samples from bank of River Niger, Onitsha

Samples	Parameters (mg/kg)			
	Lead	Zinc	Chromium	Cadmium
Fresh catfish	ND	2.33±0.0026^a	0.20±0.000^c	0.07±0.000^{ab}
Open market catfish	ND	2.30±0.030^a	0.29±0.010^b	0.07±0.008^{ab}
Smoke-dried catfish	ND	2.20±0.020^b	1.19±0.012^a	0.08±0.001^a
Oven-dried catfish	ND	2.20±0.000^b	0.15±0.020^d	0.06±0.010^b

Values are mean of three replicates. Samples with the same superscripts along the column are not significantly (P<0.05) different; Key: ND – Not detected

Heavy metals

The results of the heavy metal composition of fresh, oven-dried, smoke-dried and open market catfish were presented in Table 3. The results revealed that lead (Pb) was not detected in all the fish samples. Pb exposure from contaminated food can result in stunted growth and development often with the following symptoms; stomach upset, loss of appetite, headaches, sleeping problems, anemia, kidney dysfunction, hearing problems, memory loss, severe abdominal pain, and stumbling when walking (Jan *et al*., 2015). The absence of lead in the fish samples suggests that the studied fishes are safe from lead poisoning.

The zinc composition of the fish samples varied between 2.20 (smoked and oven dried catfish) to 2.33 mg/kg (fresh catfish) with no detectable significant difference, however, mean values suggests that smoking and oven drying slightly reduced the concentration of the zinc. The values obtained from the study agreed with the findings of Adeyeye *et al* (2016) who reported a zinc range of 1.38 to 2.62 mg/100g in drum-smoked and kiln-smoked fish samples. Zinc is necessary for the activity of over 300 enzymes that aid in metabolism, digestion, nerve function and many other processes. In addition, it is critical for the development and function of immune cells. Nevertheless, excessive zinc intake can lead to toxicity, manifesting in symptoms such as irritability, muscular stiffness, and pain (Abukakar *et al*., 2023).

The mean Chromium (Cr) concentration ranges from 0.15 to 1.19 mg/kg in the fish sample. All the samples assessed were within the permissible limits of 0.15-1mg/kg as set by FAO (Ekweozor *et al*., 2017; Tore *et al*., 2021; Wangboje and Miller, 2018), except for smoke processed fish samples obtained from bank of Niger river. This is consistent with the findings of Nzitiri *et al*. (2023) who reported a Cr composition of 0.026 - 1.144 mg/kg. The concentration of Cr in the oven-dried fish samples was lower than the rest of the samples which suggests that oven drying was able to reduce the Cr concentration of the fish than the rest of the processing methods. Cr from ingested contaminated food can bind to proteins to form complexes that are transported to the kidneys where it damages the kidneys (Jan *et al*., 2015). Other health effects include; diarrhoea, vomiting, stomach upset, fractures in bone, mutagenicity and carcinogenicity effects, fertility and teratogenicity, and damaging to the nervous and immune systems (Ali *et al*., 2014).

From the results of this study, the mean concentration of Cadmium (Cd) ranges from 0.06 – 0.08 mg/kg. Again, it is noteworthy that the Oven-dried catfish sample recorded a lesser mean concentration of Cd. The results of Cd concentration in this study were lower than those obtained by Nzitiri *et al*. (2023) (0.160– 1.006 mg/kg). Several studies indicate that most foods typically contain 0.005–0.1 mg/kg of Cd, with seafood occasionally exceeding this range. Approximately 50% of Cd in the ocean originates from industrial waste and certain fertilizers (Athanasia *et al.*, 2023). 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 (Oloruntoba *et al*., 2017). However, all the accessed fish samples were below the national threshold of 0.1 mg/kg as set by NAFDAC (2019), making them safe from Cadmium toxicity.

CONCLUSION

Drying generally provides positive influences on the nutrient composition of fish following dehydration that increases the dry matter. The oven drying technique proved more effective in enhancing fish nutrients as observed in the protein values, mineral elements and vitamin A. In Africa, where protein and energy malnutrition has become a major public health concern, the high protein content of dried fish is significantly valuable and the use of oven drying technique will help reinforce the nutritional values. The processed fish samples obtained in their fresh form from the bank of Niger River basin provide better nutrient quality when compared to the smoked fish sample sourced from the open market (control sample) thereby making a vital contribution to the Anambra food and nutrition security. The levels of heavy metal contamination of the fresh and processed fish samples from the study area were also below the permissible limit, thereby securing the consumption of the catfish caught along the bank of the River Niger in Onitsha from metals toxicity and poisoning.

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