

Analytical Aspects of Essential Compounds and Nutritional Impact of Economic Important Fish Species (*Heterotis niloticus* and *Macolor niger*) in Water Bodies

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Abstract

The biological composition of fish food and water can affect the minerals and nutrient composition of the fish, showing the relationship between the fish, its habitat and what they eat. This has necessitated the research on the amino acid, mineral and proximate compositions of *Heterotis niloticus* and *Macolor niger* from coastal water bodies to investigate the nutritional status of these two prominent and economic important fish species. A total of 120 specimens of weight between 500 and 700g were examined. Water and benthic sediments from the three locations (Badagry creek, Ikorodu and Lagos island area of Lagos, Nigeria) were analyzed for quality assessment. The amino acid and Proximate compositions were determined by method describes by Association of Analytical Chemist (AOAC). Mean body mineral constituent in the fish differed significantly ($p < 0.05$) between the two species except from arsenic, lead and nickel. Lagos lagoon has the lowest percentage of iron in the water (0.08 ± 0.00), while Ikorodu coastal water has the largest percentage (0.31 ± 0.00), fat constituents values of 16.86 ± 1.08 (*H. niloticus*) and 0.99 ± 0.08 (*M. niger*) were detected in both species. Among the 8 essential amino acids detected; Leucine has the lowest mean value of 7.93 ± 0.04 in *H. niloticus* while *M. niger* had the highest concentration of 9.25 ± 0.28 in *H. niloticus* and *M. niger*. All the amino acids were discovered to be significantly different at $p < 0.05$. Both fish species contains all the essential amino acids in the permissible and appreciable concentrations. Due to the abundant nutrients found in the two species examined, it is recommended that *H. niloticus* and *M. niger* are safe for human consumption.

Keywords: Proximate; Minerals; Amino acids; *Heterotis niloticus*; *Macolor niger*

Abbreviations: AOAC: Association of Analytical Chemist; EAA: Essential Amino Acids; NEAA: Non Essential Amino Acids; FAA: Functional Amino Acid; TDS: Total Dissolved Solids; TSS: Total Suspended Solids; QCS: Quality Control Sample; CRM: Certified Reference Material; LSD: Least Significant Difference; DNMRT: Duncan's New Multiple Range Test

Introduction

Fish are potential source of animal protein and significant nutrients in human diets. Fish meat contain low lipids and higher water than poultry meat and is well favored than white or red meats [1]. The nutritional value of fish tissues constitutes moisture, dry matter, protein, lipids, vitamins, minerals in addition to the caloric value of the fish. Minerals are important nutrients and also components of metabolic enzymes that contribute to the biomass of the fish [2]. From the nutritional point of view, fish compose of very high nutritional quality which is rich in most vitamins, proteins, minerals, fats and amino acids and is a nutritious part of human diet. An idea which had been justified by some biological experiments that is nutritionally equivalent to meat, milk and eggs [3]. Despite the recognition of the essential roles of minerals for various life processes, research on mineral and trace element nutrition of fish

has progressed rather slowly. Although about 29 of the 90 naturally occurring inorganic elements are considered to be essential for all farmed animals including fish, only few of them have been studied in detail in fish [4]. Dietary requirements are established from macro-minerals such as Ca, K, Mg, Na, P and micro-minerals such as Cu, Fe, I, Mn, Se, Zn for one or more fish species [5]. Studies have dealt with the functions, deficiency, availability, utilization, toxicity, interaction with other nutrients and environment on the fore said minerals to several fish species [6-9]. It is recognized that nutrient requirement of an animal should be determined in terms of a specific response criterion at a given age, sex, weight gain and body composition [8]. This applies to studies on mineral and trace element requirements of fish as well. However, it is much more complicated in fish due to the close interaction with the aquatic environment unlike in terrestrial animals [10]. Factors that may affect the minimal dietary levels of mineral and trace element of fish can be one or a combination of the following: biological factors such as species, life stage, sex, trophic level, feeding habits and the nutritional status of the fish; dietary factors such as diet composition, availability and nutrient interactions; and environmental factors such as water mineral concentration, salinity and temperature of the rearing system [8,11,12]. The health status also affects the micronutrient and macronutrient content of fish tissues [13,14].

Dietary amino acids (AA) are crucial for fish as energy substrates, for endogenous protein synthesis and to regulate metabolic pathways. More than half of the AA consumed by fish may be deposited into body protein, and the requirement of Essential Amino Acids (EAA) corresponds to the AA tissue

content [15]. Protein is a significant component of fish diets and is generally higher in carnivorous than herbivore fish. In salmonid diets, protein makes up 35-55% of the diet, with highest inclusion levels at early life stages [5]. Most of the AA are protein bound but can also be supplied in the form of crystalline AA to fulfill the AA requirement, as regulated by national legislation of feed additives, especially when using alternative protein sources [16]. Amino acid have traditionally been classified as essential (EAA) or nonessential (NEAA) relating to whether the organism can produce the Amino acid endogenously from the dietary NEAA. Recently, the term Functional Amino Acid (FAA) have received more attention relating to AA that modulate key metabolic pathways thus affecting immune response, health, reproduction, cell signaling, animal welfare and more [17]. Amino acid classified as NEAA such as glutamine, glutamate and proline have been demonstrated to have functional properties in both fish and mammalian metabolism, suggesting that fish have requirement also for NEAA to obtain maximum performance [18,19]. In the case of NEAA, both the dietary content of the AA and its substrates are of importance. The AA here includes arginine, glutamate, glutamine, tryptophan, histidine, sulfur amino acids (SAA; methionine, cysteine and taurine) and branched chained AA (BCAA; leucine, isoleucine and valine). Notably, other AA including glycine, lysine, threonine and aromatic AA are also involved in metabolic pathways. The major aim of this study was to investigate the proximate, minerals and amino acids compositions of the *Heterotis niloticus* and *Macolor niger*. This study compared the proximate, minerals and amino acids compositions of the most consumed fish species in specific locations in Lagos, Nigeria (Figure 1).

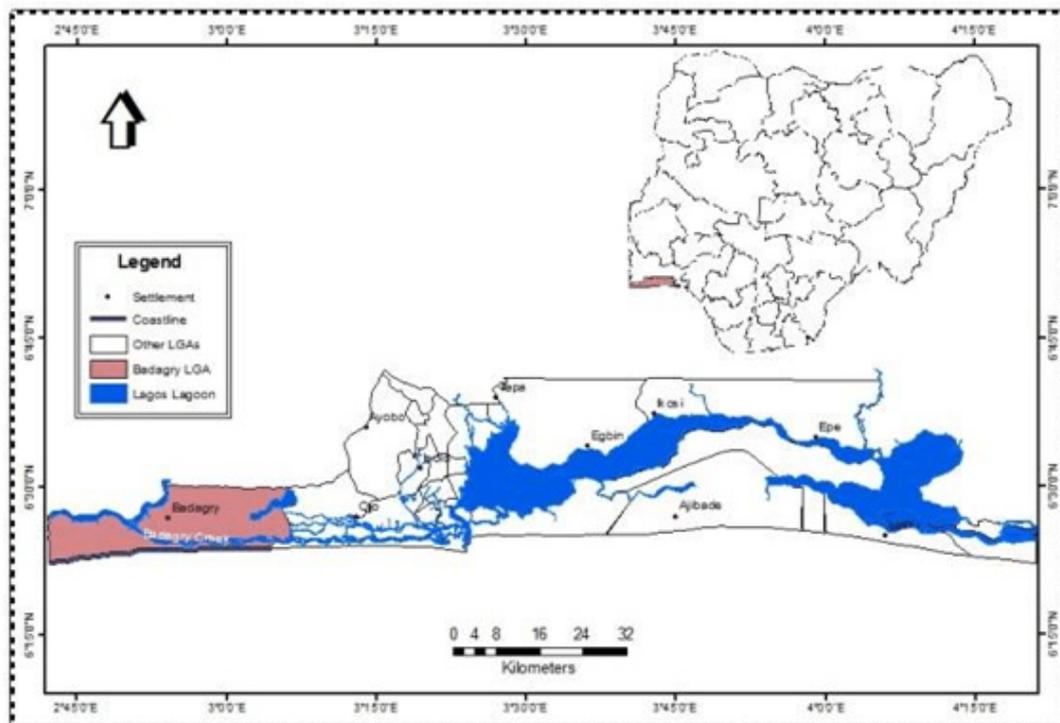


Figure 1: Map showing Badagry creek, Lagos lagoon and Ikorodu coastal areas of Lagos State.

Materials and Method

Study area

The study emphasized on three major areas which are: Badagry creek, (approximately 60km long and 3km wide and lies between longitude 2°42' and 3°23'E and latitude 6°23' and 6°28'N. It is part of a continuous system of Lagoons and creeks along the coast of Nigeria from the border with the Republic of Benin to the Niger delta. Its water depth ranges from 1-3m. The creek experiences two broad seasons: the dry season (December-May) and the wet season (June-November). Most of the year, it is characterized by fresh and slightly brackish water. The creek is approximately equidistant from the entrances of Lagos and Cotonou harbour. As a result, it is influenced by tides and floods from the Lagos Lagoon and Cotonou harbour through Lake Nokue and Lake Porto-Novo. Badore is situated in Ibeju Lekki, Lagos, Nigeria, its geographical coordinates are 6°26'0" North, 3° 51'0" East and its original name (with diacritics) is Badore. Ikorodu is bounded to the south by the Lagos Lagoon, to the north by a boundary with Ogun State, and to the east by a boundary with Agbowo-Ikosi, a town in Epe Division of Lagos State. The town has grown significantly in the past 40 years and is divided into sixteen or seventeen "Ituns" or minor areas. The main industries in the town are trading, farming and manufacturing. Nearby major towns include Imota, Isiu, Liadi, Egbin, Ijede, Igbogbo and Bayeku, all of which constitute their own Local Council Development Area with their own traditional rulers (Obas).

Sample collection and preparation

20 fish each (120 in all) and between 500 and 700g were collected for analysis in each location. The samples were brought to the Department of Fisheries, Lagos State University Laboratory for digestion and water parameter testing. The fin, liver and flesh of the fish were removed and washed with ultra-pure water. 1g of each sample was taken, weighed and digested with *Aqua regia* in a flume tank on low heat. The digested samples were then stored in a sampling bottle and carried out for analysis at dISI analytical in Surulere, Lagos.

Reagents and standard solutions

Analytical reagent grade chemicals were used in all tests. Except otherwise stated, all reagents used for QC procedures were from Hach Chemical Company, USA. Reagents and certified reference standards were procured from authorized dealers: Analytical grade nitric acid, hydrochloric acid, sulphuric acid, Ethanol (AR; 99.9%) and acetone (AR), were procured from Sigma-Aldrich Co., USA. All the volumetric glass ware used was Type "A". Calibrated micropipettes with range 100-1000µl, and 1-5ml were used (where applicable). Standard reference solutions of 1000µg/ml, each metal, (traceable to NIST) were procured from Inorganic Ventures (Christiansburg, VA; USA). Filter paper was used for filtration, where necessary.

Sample treatment

Mild digestion for determination of SO_4^{2-} , PO_4^{3-} in water:

An aliquot (50ml) of well-mixed sample was transferred into a conical flask. To this was added 5mL of 6M HCl, and then heated on a hot plate until the volume has been reduced to about 30ml. The digestate was cooled and then filtered through Whatman #1 filter paper. The residue on filter was washed with distilled water. The filtrate was quantitatively transferred to a 50ml volumetric flask, diluted to volume with distilled water and saved for the determination of sulphate, silica and phosphate.

Pretreatment for determination of NO_3^- and NO_2^- : A 50ml aliquot of well-mixed sample was filtered through a 0.45µm membrane filter. The filtrate was saved for the determination of nitrate and nitrite. Other sample pre-treatment methods are discussed under individual methods for measurements

Methods for Measurements

pH (Electrode method (Hach Method 8156, SM4500H+B, EPA150.1): Procedure

pH was determined on a liquor to fun filtered water samples using a combination pH electrode (IONIXPC-50) multi-parameter test meter. Test results were validated using traceable pH buffer solutions (pH 4.01±0.02, 7.00±0.02, 10.0±0.02; Hach Chemicals, Loveland, USA)

Electrical conductivity (Direct measurement method (SM2510B, Hach Method 8160)

Electrical conductivity was determined by potentiometric method, using a multi-parameter conductivity meter (IONIXPC-50), in the EC mode. Test results were validated against certified conductivity standards (18.0, 1000, and 1990µS/cm; Hach Chemicals, USA).

Procedure: The multi-meter was set to the EC mode and then used for the determination of E Conaliquots of the samples, and LCS.

Total Dissolved Solids (TDS); (Direct measurement method)

TDS was determined by potentiometric method, using a multi-parameter meter (IONIXPC-50), in the TDS mode. Test results were validated against certified conductivity standards (18.0, 1000, and 1990µS/cm; Hach Chemicals, USA).

Procedure: The multi-meter was set to the (TDS) mode and then used for the determination of TDS on aliquot soft the samples and LCS.

Salinity (Direct measurement method)

Salinity was determined by potentiometric method, using a multi-parameter conductivity meter (IONIXPC-50), in the salinity mode. Test results were validated against certified salinity standards (0.10, 0.50, 1.0 and 2.0 ppt; Sigma Aldrich, USA)

Procedure: The multi-meter was set to the Salinity mode and then used for the determination of salinity on aliquot soft the samples, and LCS.

Total Suspended Solids (TSS) (Gravimetric Method (SM2450D; Hach Method 8158)

An aliquot (50-100ml) of the sample was filtered through a 47mm, 0.45µm glass fibre filter. The residue on the filter was dried at 103°C, for 1 hour, cooled in a desiccator to 25°C and weighed.

Turbidity (Nephelometric method): Procedure

Turbidity of the water sample was measured on a 10ml aliquot, of a homogeneous sample, by ratio turbidimetry of a primary nephelometric light scatter signal (90°) and transmitted light scatter signal.

Total acidity (Buret titration method SM2320, Hach Method 8010)

Total Acidity of unfiltered samples was determined by buret titration using standard NaOH.

Total alkalinity (Buret titration method SM 2320B, Hach Method 8203)

Total Alkalinity of unfiltered samples was determined by buret titration with standard sulphuric acid (0.02N) to colorimetric end-point, corresponding to H4.3, and includes all forms of alkalinity (carbonate, bicarbonate and hydroxide alkalinities).

Carbon dioxide (Buret titration method)

Carbon dioxide of unfiltered samples was determined by buret titration with standard NaOH (0.02M) to colorimetric end-point, corresponding to H8.3.

Total hardness: (Buret Titration Method SM 2340C, Hach Method 8226)

Total hardness was determined by the buret titration method. An aliquot (10-50ml) of the test sample was treated with a pH 10 buffer (Hach) and the nitrate with standard 0.08 MEDTA titrant, using calm agite a send-point indicator. The total hardness was calculated as follows:

Dissolved Oxygen (DO): Membrane electrode method (SM 4500G, US EPA 360.1, Hach Method 8151): Dissolved oxygen was determined by membrane electrode method using a dissolved oxygen meter with Clark- Type amperometry sensor.

Biochemical oxygen demand: 5-days BOD Test (APHA 5210-OB) BOD was determined by measuring dissolved oxygen before and after 5 days of incubation of 60ml aliquots of the samples, in the dark at 20 °C. A 150ml aliquot of the sample was aerated with an aeration pump. The dissolved oxygen of an aliquot of this oxygen-enriched sample was determined ($DO_{initial}$). A second aliquot (60ml) was immediately incubated, in a BOD bottle, at 20 °C for 5 days in an incubator.

Chemical Oxygen Demand (COD): Closed Reflux, Colorimetric Method (HACH Method 8000, SM 5220C, 5220D).

Phosphate (Ascorbic Acid Method (Hach Method 8048, SM 4500-PE): Ortho phosphate reacts with molybdate in an acid

medium to produce a mixed phosphate/molybdate complex. Ascorbic acid then reduces the complex to an intense blue color. Measurement is made at 880nm, using as spectrophotometer

Nitrate (cadmium reduction method (Hach 8192, SM 4500B, E): Cadmium metal reduces nitrates in the sample to nitrite. The nitrite ion reacts, in acidic medium, with sulfanilic acid to form an intermediate diazonium salt, which couples with chromotropic acid to form a pink solution, which absorbs at 507nm. Reagents (Hach Chemical Company, USA)

Nitrate standard (0.4mg/LNO₃-N, prepared from 100mg/LNO₃-N; Hach chemicals): To a 15ml aliquot of the prepared sample was added the contents of one NitraVer6 Nitrate Reagent Powder Pillow (Hach). The mixture was shaken and allowed to stand for 5min. To 10ml of the clear solution was added the content of NitraVer3 reagent, and the solution shaken to dissolve the mixture. The mixture was allowed to stand for 15min for complete color development. Thereafter, measurement was made with as spectrophotometer at 507nm.

Nitrite diazotization method (Hach method 10019, EPA Method 354.1): Nitrite ion reacts, in acidic medium, with sulfanilic acid to form an intermediate diazonium salt. The salt couples with anchromotropic acid to form a pink solution, which absorbs at 507nm.

Chloride (Burette titration method (SM4500-ClB, Hach method 8225): Chloride was determined by buret titration. An aliquot (10-20ml) of the test sample was titrated with standard silver nitrate titrant, using potassium chromate as end-point indicator.

Sulphate (turbidimetric methods (SM4500E; Hach 8051): Sulphate was determined by turbidimetric method, in which an aliquot of sample filtrate that passed through 0.45µm membrane filter was reacted with bariumchloride (HACH Sulfa Ver4 reagent powder). The amount of turbidity in test solution is proportional to sulphate concentration and was determined at 450nm, using as spectrophotometer.

Determination of metals and trace elements by ICP-OES (EPA Method 200.7): EPA Method 200.7 is applicable to the analyses of the metals, dissolved and stabilized in aqueous acidic media, and then analyzed by the use of an ICP. The method was used for determination of the specified metals in water, sediment & fish.

Quality Control Sample (QCS): Analysis of a QCS was required for initial and periodic verification of calibration standard solutions, in order to verify instrument performance. The QCS was obtained as Certified Reference Material (CRM) and prepared in the same acid mixture as the calibration standards. The concentration of the analytes in the QCS solution was 1.0mg/L, for each metal

Methods of measurements: Standard multi-element calibration solutions of the metals (1.0-5.0mg/L, each) were prepared for the ICP-OES calibration curves. The solutions were prepared from the stock standard reference solution of the individual metal (1000µg/ml) by appropriated dilution, in a

volumetric flask, with deionized water. Except otherwise stated in the procedures, the chemicals used for the analysis of the samples were of analytical grade.

Analytical data for the simultaneous determination of the elements: The metals were determined on the prepared sample solutions by ICP-OES spectrometry. An Agilent SPS-3 Auto sampler was used to deliver the sample solutions to the ICP. A 3-second rinse was used to assist with wash out of high concentration of the elements. A reagent blank was determined against a 5-point calibration curve plotted for the standard solutions of metals. Conversion from mg/L of test solution to mg/kg of the sediment or fish sample was obtained from the relationship.

Proximate Analysis

Moisture content

The method described by [20] was adopted. The method is based upon removal of water from the sample and its measurements by loss of weight. A clean crucible was weighed and dried in the oven (W1): 1.0g of each of the samples was weighed into the crucible (W2) and dried at 105 °C for 20 hours. The crucible was then transferred from the oven to desiccators, cooled and reweighed (W3). The percentage moisture content was calculated thus:

$$\% \text{ Moisture content} = 100 - (W3 - W1 / W2 \times 100)$$

Crude protein

Crude protein in the sample fish fillet was quantified following the procedure of (20) by Kjeldahl method. About 2g of each of the samples were mixed with 10ml of the concentration H_2SO_4 in a heating tube. One tablet of selenium catalyst was added to the tube mixture heated inside a fume cupboard. The digest was transferred inside distilled water; 10ml of the digest was mixed with equal volume of 45% NaOH and poured into a Kjeldahl distillation apparatus. The mixture was distilled and the distillate collected into 4% boric acid solution containing 3 drops of methyl red indicator. A total of 50ml distillate was collected and titrated as well. The sampling was duplicated and the average value taken. The nitrogen content was calculated and multiplied with 6.25 to obtain the crude protein content.

This is given as the percentage Nitrogen = $(100 \times N \times 14 \times VF) / T / 100 \times Va$

Where: N=Normality of the titrant.

VF=Total volume of the digest=100ml

T=Titre value

VA=Aliquot volume distilled

Total lipids (Bligh and dryer method): 5-10g wet sample were weighed in pre-weighed 100ml conical flask. 20ml methanol (MeOH) and 10ml chloroform ($CHCl_3$) were added. Samples were homogenized for 2 minutes with an Ultra Turrax. 10ml $CHCl_3$ were added a second time. The mixtures were vigorously mixed for 1minute. About 18ml of distilled water was added (including

the water already in the sample). The mixture was vortex again for 1 minute. The two layers were separated by centrifugation for 10 minutes at 450g in a thermostatic centrifuge. The lower layers were transferred to a pear-shaped tank with a pasteur pipette. A second extraction was done with 20ml 10% (v/v) MeOH in $CHCl_3$ by vortexing for 2 minutes. The lower $CHCl_3$ phase was added to the first extract. The samples were added to the first extract. The residues were further dried at 104°C for 1 hour.

Crude fibre: The method described by [21] was used for this analysis. The 1.0g of the finely ground samples was weighed out into a round bottom flask, 100ml of 1.25% sulphuric acid solution was added and the mixture was boiled under a reflux for 30 minutes. The insoluble matter was washed several times with hot water until it was acid free. It was quantitatively transferred into the flask, 100ml of hot 1.25% sodium hydroxide (NaOH) solution was added and the mixture boiled again under reflux for 30 minutes under suction.

The loss in weight of sample on incineration = $C1 - C2 \times 100$

Weight of original sample: % crude fiber = $C1 - C2$

Total ash: The (21) method was used for the determination of total ash content. The porcelain crucible was dried in an oven at 100°C for 10 minutes. Cooled in desiccators and weighed (W1). About 2g of the sample was placed into the previously weighed crucible and reweighed (W2) and then placed in a furnace for 4 hours at 600°C to ensure proper ashing.

$$\% \text{ Ash content} = (W2 - W1) \times 100 / W3 - W1$$

Amino acids: Extraction and the instrumentation analyses were carried out by following the modified method [22] in the simultaneous identification and determination of total content of amino acids in food supplements tablets by gas chromatography as described by [2].

Statistical Analysis

Proximate data were analyzed using graph pad prism. V statistical package was employed in the analysis. Differences were considered significant at ($p < 0.05$). The results were expressed as mean \pm SD. The determined differences among treatments were partitioned by the Least Significant Difference (LSD) and the Duncan's New Multiple Range Test (DNMRT) [23].

Results

The mean and the standard deviation of the water parameters and mineral composition are presented in (Table 1) below. The Temperature of Lagos Island ($25.15 \pm 0.07^\circ C$), Ikorodu ($25.2 \pm 0.14^\circ C$) and Badagry ($25.15 \pm 0.07^\circ C$), were not significantly different but the pH were however significantly different for Lagos Island (7.42 ± 0.23), Ikorodu (6.03 ± 0.02) and Badagry (6.11 ± 0.08). The concentration of dissolved oxygen was highest in Lagos Island with mean value of (4.95 ± 0.35 mg/L). Arsenic, Cadmium, Lead and Nickel were not detected in the three stations. The mean concentration of arsenic, cadmium, copper, nickel in the three sampling stations showed no significant difference ($p > 0.05$). The percentage concentration

of zinc and iron was found to be statistically difference ($p < 0.05$) (Table 2). (Table 3) revealed the percentage mineral composition of zinc and iron which were found to be statistically different ($p < 0.05$), while arsenic, cadmium, copper, lead, nickel showed no significant difference ($p > 0.05$). Badagry had the lowest arsenic concentrate with value of ($0.06 \pm 0.01 \text{ mg/kg}$) (Table 4), while Lagos Island had the highest concentration of arsenic (0.11 ± 0.04). The zinc content

generally ranged from a minimum of ($415.5 \pm 40.45 \text{ mg/kg}$) in Lagos Island and maximum of ($1826.35 \pm 63.29 \text{ mg/kg}$) in Ikorodu. The moisture content of *M. niger* had the highest concentration ($77.61 \pm 0.60\%$) while *H. niloticus* had mean value of ($55.68 \pm 3.87\%$). The highest concentration of protein was observed in *H. niloticus* ($21.33 \pm 1.15\%$) while the lowest was in *M. niger*. There were significant differences in all the samples ($p < 0.05$) (Table 5).

Table 1: Water parameters and mineral compositions of Sample locations

Means with different superscript for a given parameter in the same role are significantly different ($p < 0.05$)

Parameter	Lagos Island	Ikorodu	Badagry	WHO Limit 2011
Temperature ($^{\circ}\text{C}$)	25.15 ± 0.07^a	25.2 ± 0.14^a	25.15 ± 0.07^a	<40
pH	7.42 ± 0.23^a	6.03 ± 0.02^b	6.11 ± 0.08^c	6.5-6.9
Electrical Conductivity ($\mu\text{S/cm}$)	52450 ± 70.71^a	109 ± 0.71^c	1245.65 ± 2.33^b	<0.01
Total Dissolved Solids (mg/L)	37550 ± 70.71^a	58 ± 4.95^c	884.6 ± 0.57^b	<1000
Salinity (ppt)	32.31 ± 0.13^a	0.08 ± 0.00^c	0.62 ± 0.01^b	
Total Suspended Solids (mg/L)	3.5 ± 2.12^b	18 ± 0.00^a	5.5 ± 0.71^b	
Turbidity (NTU)	4.6 ± 5.18^c	13.31 ± 0.62^a	1.66 ± 0.69^b	
Acidity (mg/L, CaCO_3)	14.05 ± 8.41^b	119.5 ± 5.66^a	71.6 ± 0.57^c	
Alkalinity (mg/L, CaCO_3)	117.05 ± 12.80^a	56.75 ± 0.49^c	58.55 ± 2.19^b	
Carbon Dioxide (mg/L, CO_2)	9.2 ± 3.68^c	85.73 ± 2.12^b	87.9 ± 6.79^a	100
Dissolved Oxygen (mg/L)	4.95 ± 0.35^a	1.45 ± 0.35^c	2.65 ± 0.49^b	5
Biochemical Oxygen Demand (mg/L)	2 ± 1.41^b	35 ± 2.83^a	4 ± 1.41^b	6
Chemical Oxygen Demand (mg/L)	7 ± 7.07^c	84.5 ± 4.95^a	11.5 ± 3.54^b	30
Total Hardness (mg/L, CaCO_3)	6069.15 ± 12.80^a	23.15 ± 1.63^c	123.6 ± 16.55^b	
Calcium (mg/L)	347.56 ± 13.94^a	4.85 ± 0.07^b	17 ± 2.26^c	<200
Magnesium (mg/L)	1262.91 ± 5.50^a	2.6 ± 0.28^c	19.95 ± 2.28^b	0.05mg/l
Arsenic (mg/L)	0 ± 0.00^a	0 ± 0.00^a	0 ± 0.00^a	0.010mg/l
Cadmium (mg/L)	0 ± 0.00^a	0 ± 0.00^a	0 ± 0.00^a	0.003
Chromium (mg/L)	0.01 ± 0.00^a	0 ± 0.00^a	0.04 ± 0.00^a	0.05
Copper (mg/L)	0 ± 0.00	0.01 ± 0.00^a	0.02 ± 0.02^a	0.1mg/l
Iron (mg/L)	0.08 ± 0.00^c	0.31 ± 0.00^a	0.11 ± 0.00^b	1.0mg/l
Lead (mg/L)	0 ± 0.00^a	0 ± 0.00^a	0 ± 0.00^a	0.01
Nickel (mg/L)	0 ± 0.00^a	0 ± 0.00^a	0 ± 0.00^a	0.1 $\mu\text{g/l}$
Zinc (mg/L)	0.06 ± 0.01^c	0.33 ± 0.04^a	0.13 ± 0.04^b	1.0mg/l
Chloride (mg/L Cl^-)	17716.4 ± 9.05^a	64.3 ± 5.80^c	336.3 ± 3.96^b	10 $\mu\text{g/l}$
Phosphate (mg/L, PO_4^{3-})	0.09 ± 0.01^b	0.36 ± 0.04^a	0.07 ± 0.02^b	
Nitrate (mg/L, NO_3^-)	7.58 ± 0.90^b	3.55 ± 0.02^c	8.54 ± 5.06^a	50
Nitrite (mg/L, NO_2^-)	0 ± 0.00^b	0 ± 0.00^b	0.15 ± 0.06^a	<0.01
Sulphate (mg/L, SO_4^{2-})	2196.4 ± 9.62^a	9.25 ± 0.35^c	41.85 ± 0.49^b	

Table 2: Mineral composition in the gills, flesh and liver of *Heterotis niloticus* in Badagry, Lagos Island and Ikorodu sample stations.

The means with different super script for a given parameter in the same role are significantly different ($p < 0.05$).

Mineral (mg/kg)	Gill			Flesh			Liver		
	BDG	ISLAND	IKD	BDG	ISLAND	IKD	BDG	ISLAND	IKD
As	0.02 ± 0.00^a	0.02 ± 0.00^a	0.18 ± 0.00^a	0.02 ± 0.00^a	0.02 ± 0.00^a	0.02 ± 0.00^b	0.02 ± 0.00^a	0.02 ± 0.00^a	0.02 ± 0.00^b

Cd	0.22±0.06 ^a	0.43±0.48 ^a	0.04±0.00 ^a	0.04±0.01 ^c	0.03±0.01 ^c	0.02±0.00 ^b	0.06±0.04 ^b	0.09±0.02 ^b	0.02±0.00 ^b
Co	0.12±0.04 ^a	0.41±0.42 ^a	0.04±0.60 ^b	0.04±0.01 ^b	0.02±0.00 ^c	0.02±0.00 ^c	0.12±0.02 ^a	0.15±0.08 ^b	0.62±0.85 ^a
Cr	0.13±0.05 ^a	0.68±0.76 ^a	0.34±0.04 ^a	0.06±0.01 ^b	0.08±0.08 ^c	0.02±0.00 ^c	0.04±0.01 ^b	0.46±0.16 ^b	0.06±0.05 ^b
Fe	979±130.11 ^b	194±45.24 ^c	564±870.50 ^b	155±79.20 ^c	956.5±89.80 ^a	592±56.57 ^c	816±69.30 ^a	676±151.32 ^b	1542.5±1287.64 ^a
Pb	0.10±0.03 ^a	0.1±0.03 ^a	0.63±0.07 ^a	0.02±0.00 ^b	0.02±0.00 ^b	0.02±0.00 ^c	0.06±0.02 ^c	0.03±0.01 ^b	0.09±0.10 ^b
Ni	0.06±0.02 ^a	0.1±0.03 ^a	0.4±0.00 ^b	0.02±0.00 ^b	0.02±0.00 ^b	0.02±0.00 ^a	0.02±0.00 ^b	0.02±0.00 ^b	0.02±0.00 ^a
Zn	177.15±76.16 ^b	121.7±28.85 ^c	1289.11±150.85 ^c	43.7±10.04 ^c	232.35±53.81 ^b	1437.3±56.57 ^b	647.3±132.79 ^a	669.35±25.67 ^a	1588.15±269.90 ^a

Table 3: Mineral composition in the gills, flesh and liver of *Macolor niger* in Badagry, Lagos Island and Ikorodu sample stations.

Means with different superscript of a given parameter in the same role are significantly difference (p<0.05).

Mineral (mg/kg)	Gill			Flesh			Liver		
	BDG	ISLAND	IKD	BDG	ISLAND	IKD	BDG	ISLAND	IKD
As	0.02±0.00 ^a	0.02±0.00 ^a	0.02±0.00 ^a	0.02±0.00 ^a	0.02±0.00 ^a	0.02±0.00 ^a	0.02±0.00 ^a	0.02±0.00 ^a	0.02±0.00 ^a
Cd	0.625±0.30 ^c	1.6±0.62 ^a	0.22±0.06 ^a	0.02±0.00 ^a	0.02±0.00 ^c	0.04±0.01 ^c	0.04±0.02 ^b	0.07±0.04 ^b	0.06±0.04 ^b
Co	0.065±0.04 ^c	0.13±0.08 ^b	0.12±0.04 ^a	0.02±0.00 ^a	0.02±0.00 ^c	0.04±0.01 ^b	0.07±0.01 ^b	0.16±0.06 ^a	0.12±0.02 ^a
Cr	0.58±0.20 ^c	1.03±0.18 ^a	0.13±0.05 ^a	0.02±0.00 ^a	0.05±0.03 ^c	0.06±0.01 ^b	0.06±0.04 ^b	0.08±0.04 ^b	0.04±0.01 ^b
Fe	365.5±127.99 ^b	612.50±242.54 ^b	979±130.11 ^b	12±29.70 ^a	30±8.49 ^c	155±79.20 ^c	764.50±160.51 ^c	1097.50±33.23 ^a	816±69.30 ^a
Pb	0.175±0.06 ^a	0.73±0.34 ^a	0.10±0.03 ^a	0.02±0.00 ^b	0.02±0.00 ^b	0.02±0.00 ^b	0.02±0.00 ^b	0.02±0.00 ^b	0.06±0.02 ^c
Ni	0.125±0.06 ^a	0.70±0.01 ^a	0.06±0.02 ^a	0.02±0.00 ^b	0.02±0.00 ^b	0.02±0.00 ^b	0.02±0.00 ^b	0.02±0.00 ^b	0.02±0.00 ^b
Zn	196.8±48.93 ^b	637.70±117.80 ^b	177.15±76.16 ^b	39.8±13.36 ^c	99.05±17.18 ^c	43.7±10.04 ^c	234.4±51.76 ^a	746.60±147.64 ^a	647.3±132.79 ^a

Table 4: Concentration of Sediments in the Study locations.

The means with different superscript for a given parameter in the same role are significantly different (p<0.05).

Minerals	Lagos Island	Ikorodu	Badagry
As (mg/kg)	0.11±0.04 ^a	0.42±0.53 ^b	0.06±0.01 ^c
Cd (mg/kg)	7.89±1.37 ^a	2.56±0.46 ^b	0.92±0.64 ^c
Cu (mg/kg)	5.13±1.27 ^a	8.11±0.57 ^b	4.83±0.09 ^c
Cr (mg/kg)	3.35±3.60 ^a	16.47±19.14 ^b	0.55±0.05 ^c
Fe (mg/kg)	28173±10156.88 ^a	15080±169.71 ^b	2592±49.00 ^c
Pb (mg/kg)	3.7±1.02 ^a	10.09±0.04 ^b	4.98±0.55 ^c
Ni (mg/kg)	0.29±0.15 ^a	1.74±0.03	0.4±0.22 ^c
Zn (mg/kg)	415.5±40.45 ^a	1826.35±63.29 ^b	497.8±25.5 ^c

Table 5: Proximate Analysis of Sampled Fish.

Means with different superscript for a given parameter in the same role are significantly different (p<0.05)

Parameters	<i>H. niloticus</i>	<i>M. niger</i>
Moisture	55.68±3.87 ^a	77.605±0.60 ^b
Carbohydrate	4.925±0.15 ^a	1.76±0.53 ^b
Protein	21.33±1.15 ^a	18.47±0.60 ^b
Crude fiber	1.14±0.57 ^a	1.34±0.16 ^b
Crude fat	16.86±1.08 ^a	0.99±0.08 ^b
Ash	1.43±0.13 ^a	0.61±0.11 ^b

H. niloticus has the highest concentrate of isoleucine in the table above of (5.4±0.14). *M. niger* has the highest concentrate of essential amino acid except in histidine and isoleucine. All the sampling species were all statistically different (p<0.05). *M. niger* has the

highest value of glutamine acid of (8.15±0.16). The result in (Tables 6 & 7) above shows that *M. niger* has the highest concentrate of non-essential amino acid except in serine. All the sampling species were all statistically different (p<0.05).

Table 6 & 7: Essential and Non-essential amino acid composition in sampled fish.

Means with different superscript for a given parameter in the same role are significantly different (p<0.05).

Essential Amino acid		
Amino acid	<i>H. niloticus</i>	<i>M. niger</i>
Histidine	2.5±0.10 ^b	2.82±0.06 ^a
Methionine	2.48±0.45 ^b	3.26±0.21 ^a
Valine	4.34±0.05 ^b	4.54±0.04 ^a
Leucine	8.4±0.08 ^b	9.08±0.06 ^a
Isoleucine	5.4±0.14 ^a	5.2±0.09 ^b
Lysine	7.93±.04 ^b	9.25±0.28 ^a
Phenylalanine	5.52±0.23 ^b	6.14±0.16 ^a
Tryptophan	1.09±0.10 ^b	1.42±0.04 ^a
Non Essential Protein		
Cystheine	0.31±0.02 ^b	1.47±0.13 ^a
Aspartic Acid	7.66±0.45 ^b	9.32±0.08 ^a
Asparagine	5.14±0.06 ^b	6.19±0.22 ^a
Serine	4.02±0.03 ^b	3.36±0.09 ^c
Glutamic Acid	9.51±0.25 ^b	14.2±0.23 ^a
Glycine	3.84±0.08 ^b	4.44±0.52 ^a
Alanine	5.72±0.12 ^b	6.46±0.09 ^a
Tyrosine	2.76±0.01 ^b	3.39±0.37 ^a
Glutamine	5.07±0.06 ^b	8.15±0.16 ^a
Arginie	5.21±0.09 ^b	6.21±0.04 ^a
Proline	3.16±0.05 ^b	3.31±0.22 ^a

Discussion

The physico-chemical parameters of the three stations; Ikorodu, Badagry and Lagos island waters investigated are presented in Table 1 above. There were variations in the physical and chemical characteristics of the sampled water. The reported values referred to the mean values of the water quality concentrations of the minerals, proximate analysis and amino acids of sampled stations. Physico-chemical characteristics; such as temperature, Ikorodu (25.2±0.14°C), Badagry (25.15±0.07°C) and Lagos Island (25.15±0.07°C) were within the [24] regulatory limit. pH value of Ikorodu (6.03±0.02) and Badagry (6.11±0.08) were also within the [24] regulatory limit, but values obtained for Lagos island (7.42±0.23) water sample was slightly alkaline exceeding the regulatory limit. The alkaline level obtained in Lagos Island could have resulted from decaying organic matter [2,3,25]. Virtually all parameters analyzed deviated from the WHO standard values of 2011. Electrical conductivity, magnesium and chloride exceeded the WHO permissible limit, and this may be attributed to high level of anthropogenic activities around the respective sampling stations respectively.

Copper was not detected in Lagos Island, 0.01mg/l was detected in Ikorodu and 0.02mg/l in Badagry, all of these were within the WHO standard. Copper is essential for good health, but high intakes can cause health problems such as liver and kidney damage [25,26]. Iron was largest in Ikorodu (0.31mg/l). Fish is a major source of iron for adult and children and iron deficiency causes anemia [21]. The level of magnesium and chloride is higher than WHO standard limit. The proximate composition of *H. niloticus* and *M. niger* shows high level of crude protein of 19.86%, 21.33%, and 18.47% respectively. The high to moderate level of protein shows that they are good source of protein but the differences reported in the obtained values maybe as a result of feed consumed by the fishes and their ability to absorb and convert nutrient from their diet or water into biochemical substances needed by the fishes [27,28]. The recorded variation in the concentration of the fish nutritional component could be as a result of the rate/concentrations at which the minerals are available in the water. This is supported by the findings of [2]. Amino acids are important biomolecules that serves as the building block of protein and are intermediaries in various metabolic pathways. They serve as precursors for the synthesis of

biologically important substances including nucleotide, peptide hormones and neurotransmitters. Leucine is an essential amino acid and it was the most obtained in all fish samples compared to other amino acids. Leucine concentration (Table 2) detected in *H. niloticus* and *M. niger* were 8.4 ± 0.08 and 9.08 ± 0.06 respectively with *M. niger* having the highest concentration of leucine. The most concentrated non-essential amino acids were glutamic acid and aspartic acid.

Conclusion

The more balanced the fish minerals composition, the more value they add to man as our health is governed predominantly by the nutritional value of the food consumed. Therefore, human activities that alter the ecosystem should be discouraged and prohibited around our coastal water bodies to avoid buildup of heavy metals in aquatic habitat. It is strongly recommended that the culture of these species in Nigeria should be encouraged, its inclusion in the meal of growing children are highly advocated with caution and fish meat should be properly assessed for quality assurance before consumption.

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