

Assessment of Heavy Metal and Hydrocarbon Contamination in Selected Fish Species from Major Aquatic Bodies of Bayelsa State, Nigeria

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ABSTRACT

Background and Objective: Aquatic ecosystems in the Niger Delta Region are increasingly threatened by petroleum-related pollution and heavy metal contamination, raising concerns about food safety and public health. This study investigated the toxicant profiles of three economically important fish species: *Clarias gariepinus* (African catfish), *Polydactylus quadrifilis* (Giant African Threadfin), and *Oreochromis niloticus* (Nile Tilapia) from freshwater, saltwater, and brackish water habitats in Bayelsa State, Nigeria.

Materials and Methods: A total of twenty-one fish samples (seven per species) were systematically collected from Taylor Creek (freshwater), Brass River/Atlantic Ocean (saltwater), and Nembe Creek (brackish). Heavy metals in fish and water samples were analyzed using Atomic Absorption Spectrophotometry (AAS), while hydrocarbons were assessed using Gas Chromatography-Mass Spectrometry/Flame Ionization Detector (GC-MS/FID) following United States Environmental Protection Agency (USEPA) protocols. Data were analyzed in SPSS v27 using ANOVA and Tukey's HSD ($p < 0.05$).

Results: Significant heavy metal contamination was observed. Lead concentrations in *Oreochromis niloticus* (0.08 ± 0.01 mg/kg) and *Clarias gariepinus* (0.06 ± 0.01 mg/kg) exceeded WHO/FAO limits (0.01 mg/kg) by 8-fold and 6-fold, respectively. Total Hydrocarbon Content (THC) exceeded WHO/FAO standards (0.1 mg/kg) in all species: *Polydactylus quadrifilis* (4.43 ± 0.39 mg/kg), *Oreochromis niloticus* (2.76 ± 0.20 mg/kg), and *Clarias gariepinus* (0.96 ± 0.10 mg/kg). *Polydactylus quadrifilis* also showed detectable concentrations of carcinogenic polycyclic aromatic hydrocarbons (PAHs), including benzo[a]anthracene (0.07 ± 0.00 mg/kg), chrysene (0.06 ± 0.0001 mg/kg), and benzo[a]pyrene (0.03 ± 0.00 mg/kg), all significantly above WHO limits (0.002 mg/kg). **Conclusion:** *Polydactylus quadrifilis* exhibited the highest THC and PAH concentrations, highlighting significant bioaccumulation and the urgent need for remediation. *Oreochromis niloticus* from brackish waters also showed elevated levels of heavy metal contamination, underscoring the need for continuous monitoring to protect food safety and public health.

KEYWORDS

Toxicants, heavy metals, PAHs, THC, bioaccumulation, fish, Bayelsa State

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INTRODUCTION

Bayelsa State's extensive water bodies support diverse fish species that underpin both dietary and economic needs, but decades of oil exploration, gas flaring, industrial effluents, and unregulated anthropogenic activities have transformed these aquatic ecosystems into repositories of heavy metals, polycyclic aromatic hydrocarbons (PAHs), and petroleum-derived toxicants¹.

Bayelsa State and the Niger Delta Region at large stands out as one of the most petroleum-impacted aquatic ecosystems on the African continent. This is due to decades of crude oil extraction, recurrent spillages, gas flaring, and poorly regulated industrial discharges, this has left a lasting legacy of environmental degradation. Bayelsa state has a wide network of rivers, creeks, and coastal waters providing both livelihood and sustenance to a predominantly fishing-dependent population¹.

The toxicant profile of fish is largely influenced by the level of contamination in the aquatic environment where they are found². What determines the levels of contamination include factors such as petroleum hydrocarbon concentrations, heavy metal loads, salinity, and pH, playing major roles across different habitat types, these factors result in habitat-specific differences in contaminant bioaccumulation patterns². Heavy metals and hydrocarbons at high levels in the habitat can bioaccumulate in fish tissues through direct water absorption, dietary intake, and sediment contact³. These toxicants can ultimately creep into human food chain and harbour potentially severe health consequences³.

In this study, three different fish species that thrive in and are adapted to the freshwater, saltwater, and brackish habitats of Bayelsa State were studied. The species of interest are the African Catfish, scientifically known as *Clarias gariepinus* from freshwater habitat; the Giant African Threadfin, scientifically known as *Polydactylus quadrifilis* from saltwater habitat; and the Nile Tilapia, scientifically known as *Oreochromis niloticus* from brackish water habitat. Each species occupies a distinct ecological niche and exhibits different vertical distribution patterns-from benthic-demersal (*Clarias gariepinus*) to demersal-pelagic (*Polydactylus quadrifilis*) to eurytopic (*Oreochromis niloticus*) resulting in differential exposure pathways to environmental contaminants⁴⁻⁶.

The impact of petroleum contamination and heavy metal pollution on fish toxicant profiles varies significantly from one water body to another, even within the same locality. This can be attributed to proximity to oil facilities, frequency of spills, hydrodynamic characteristics, sediment composition, and anthropogenic pressure¹. Studies have documented alarming contamination levels in fish from Niger Delta waters, with concentrations frequently exceeding WHO/FAO safety standards^{3,7}. Bioaccumulation factors for heavy metals and petroleum hydrocarbons in fish tissues can exceed environmental concentrations by 1000-4000 fold, indicating efficient biological concentration mechanisms that magnify environmental contamination⁸.

Recent research suggests that fish species captured from the wild in the Niger Delta region harbour complex mixtures of toxicants, mainly petroleum hydrocarbons and heavy metals⁹. Consumption of such contaminated fish has been epidemiologically linked to a spectrum of health disorders in local populations, including chronic kidney diseases, unexplained neurological tremors, dermatitis, cardiovascular complications, and increased cancer incidence¹⁰. The biochemical mechanisms underlying these health effects are well-established as heavy metals interfere with essential enzyme systems, generate reactive oxygen species leading to oxidative stress, and disrupt cellular signalling pathways involved in DNA repair and apoptosis, while petroleum hydrocarbons alter cellular membrane integrity, interfere with cytochrome P450 enzyme systems, and form DNA adducts that initiate carcinogenic processes¹¹.

Locals and residents of Bayelsa State have traditionally discriminated among fish based on their source water bodies, attributing differences to organoleptic qualities and perceived nutritional values¹². However, these culturally deep-seated preferences lack empirical validation regarding the actual toxicological burdens inherent in fish from the vast aquatic bodies in the state⁸. While numerous studies have investigated fish contamination in the Niger Delta Region, several critical gaps remain and they include: systematic comparison of contamination levels across all three habitat types (freshwater, brackish, saltwater) using the same analytical protocols is lacking; comprehensive toxicological research on *Polydactylus quadrifilis* in Bayelsa State despite its economic importance remains limited; and integrated assessment combining heavy metals, PAHs, BTEX, and THC in the context of human health risk evaluation is absent from existing literature.

This study was therefore designed to comprehensively investigate the toxicant profiles, including heavy metals (lead, cadmium, chromium, nickel, mercury, and arsenic), petroleum hydrocarbons (THC), BTEX compounds, and polycyclic aromatic hydrocarbons (PAHs) in three ecologically and economically important fish species from different water bodies in Bayelsa State. By employing standardized analytical methodologies (AOAC, EPA, APHA) and risk assessment frameworks (Bioaccumulation Factor), this research provides a comprehensive comparative toxicological assessment across freshwater, brackish, and marine ecosystems in Bayelsa State, establishing critical baseline data for environmental monitoring, public health protection, and evidence-based fisheries management in this petroleum-impacted region.

MATERIALS AND METHODS

Study area: Three sampling stations were established to represent the three aquatic habitats studied in Bayelsa State. The freshwater station was situated along Taylor Creek (Freshwater site) located between Polaku and Agbia communities within the Biseni and Gbaran clans of Yenagoa Local Government Area (Latitude 5°01'N-5°02'N, Longitude 6°17'E-6°18'E). While the marine station was situated at the Brass River/Atlantic Ocean interface on Brass Island (Latitude 4°19'01"N, Longitude 6°14'34"E), and the brackish water station was situated along the Nembe Creek in Etieama community, Nembe Local Government Area (Latitude 4°25'50"N, Longitude 6°19'25"E), representing brackish water habitat. The three habitats were chosen because they are established fishing grounds for the target species. The study duration spanned from January 2025 to July 2025^{13,14}.

Sample size: The study utilized a sample size of twenty-one (seven per group) and this was justified by using Mead's resource equation for an experimental design involving three groups¹⁵. In a similar manner, water samples were randomly drawn from randomly selected points in the three study locations¹⁵.

Ethical clearance: Ethical clearance and approval for this study were obtained from the Directorate of Research and Quality Assurance at the Federal University Otuoke, Bayelsa State. Every procedure involving the use of animal specimens complied with the institutional ethical guidelines and also adhered to international standards for humane treatment of research animals such as the Institutional Animal Care and Use Committee (IACUC) framework^{13,14}.

Sample collection: The fish were captured directly from their respective habitats by local fishermen using fishing nets and hooks. Specimens were placed on ice immediately after they were harvested to prevent autolytic and microbial degradation¹⁵.

Sample preparation: Fish samples were prepared using AOAC methods. Skin, bones, scales and viscera were removed, and three cross-sectional slices were removed from the anterior, mid-section and posterior body regions to ensure representative sampling. Samples were then frozen at 20°C for a minimum of 12 hrs. They were then freeze-dried for 72 hrs and then ground using a knife mill to fine powder¹⁵.

Laboratory analysis

Heavy metals: Determination of selected heavy metals in fish and water samples was performed using the EPA 7000B methods¹⁶.

Principle: This analytical technique involves the digestion of the sample and then nebulizing it into a rich flame, where the metal atoms absorb light at specific wavelengths unique to each element. Also, for water samples, use of flame atomic absorption spectrometry for the analysis, where samples are aspirated into a flame and subsequently atomised¹⁶.

Procedure for fish samples: Fish samples were homogenized, and 1-2 g of wet weight were weighed into a digestion vessel. To the digestion vessel, 10 mL of Nitric acid (HNO₃) was added and mixed with the slurry, then covered with a watch glass. Sample was then heated to 95°C and refluxed for 10-15 min without boiling. The samples were then allowed to cool, then 5 mL of concentrated nitric acid was added and refluxed for 30 min. These steps were repeated until no brown fumes were generated, indicating the complete reaction. Afterwards, 30% of hydrogen peroxide was added in 1 mL aliquots until effervescence subsided. The solution was then analyzed using flame atomic absorption spectrophotometry¹⁶.

Procedure for water samples: Water samples were collected in acid-washed containers and then filtered immediately and acidified with nitric acid. Standard solutions of the metals of interest were prepared, and the atomic absorption spectrometer was calibrated using these standards. The prepared samples were then aspirated into an air-acetylene flame using an atomic absorption spectrometer. The spectrometer measured the amount of light absorbed by atomized metals in the flame. The readings were then compared with the calibration curve to determine concentrations, and the metal concentrations were reported in milligrams per litre (mg/L)¹⁶.

Polyaromatic hydrocarbons (PAHs): The PAHs concentration in fish and water samples was determined using EPA 8270 method, which is a standardized approach for PAH analysis in both water and fish tissues using Gas Chromatography-Mass Spectrometry (GC-MS)¹³.

Principle: The EPA 8270 method is designed for the determination of semi-volatile organic compounds, including polycyclic aromatic hydrocarbons (PAHs), in various matrices such as fish tissue. This method was utilized due to its accuracy as it makes use of rigorous sample preparation, extraction, and quality control to ensure accurate quantification of these compounds¹³.

Procedure for fish samples: Homogenized fish tissue samples were subjected to organic solvent extraction (Soxhlet extraction) using established EPA protocols. The PAH compounds were isolated with methylene chloride as the primary extraction solvent. The crude extracts were processed through clean-up procedures following EPA Method 3600 series protocols. Interfering compounds were removed using solid-phase extraction and column chromatography techniques to ensure analytical selectivity and reduce matrix interference effects. Cleaned extracts were fortified with internal standards and analysed using Gas Chromatography-Mass Spectrometry (GC-MS). The analysis was performed on a capillary column system with electron impact ionization detection. Analyte identification was achieved through retention time comparison and mass spectral matching against reference standards¹³.

Procedure for water samples: The cleaned and concentrated water extracts were analysed using the same GC-MS conditions specified in the method for fish samples. Analyte identification and quantitation were performed identically to fish tissue samples, using retention time matching, mass spectral confirmation, and internal standard-based calibration curves¹⁷.

Benzene, Toluene, Ethylene, and Xylene (BTEX) Content

Principle: Volatile compounds such as BTEX are analysed using EPA Method 8260 as it is widely regarded as a standard test for investigating these compounds in environmental samples. It offers comprehensive procedures for the detection and quantification of BTEX compounds across various matrices, including fish tissue and water samples¹⁸.

Procedure for fish samples: Fish tissue samples were homogenized, spiked with surrogates and water, and analysed for BTEX compounds using purge and trap Gas Chromatography-Mass Spectrometry (GC-MS). Samples were purged at 40°C, trapped, and then desorbed for introduction into the GC-MS, which was calibrated with BTEX standards. Data quality was ensured by analysing blanks, matrix spikes, and control samples. Compounds were identified and quantified by comparing retention times and mass spectra with standards, following EPA Method 8260 protocols¹⁸.

Total hydrocarbon content (THC): The EPA Method 8015 represents a comprehensive analytical approach for determining total petroleum hydrocarbons (TPH) in both aquatic organisms and water matrices, utilizing Gas Chromatography with Flame Ionization Detection (GC/FID)¹⁸.

Principle: The core principle involves extracting non-halogenated hydrocarbons from the biological matrix, separating compounds by volatility, and quantifying them based on carbon-specific detection¹⁸.

Procedure: A 1-5 g of homogenized fish tissues were collected and allowed to freeze immediately at -20°C, and ground with dry ice to prevent volatile loss. Moisture content was determined by drying at 105°C to constant weight. Samples later underwent extraction with dichloromethane or hexane at 100°C and 1,500 psi, achieving >95% recovery of hydrocarbons in 20 minutes. TraceGOLD TG-5SiIMS (30×0.25 mm ID) was used for separating aliphatic hydrocarbons. Ramp from 40 to 320°C to elute C6-C28 hydrocarbons detection¹⁸.

Analysis of physicochemical properties of the water samples: Electrical Conductivity measures water's ability to conduct electrical current, which is directly related to the concentration of dissolved ions. Total dissolved solids represent the total concentration of dissolved substances (inorganic salts and small amounts of organic matter) in water¹⁹.

The EC and TDS were determined using a smart sensor meter¹⁹. Salinity in water samples is commonly determined using smart sensor meters that measure the electrical properties of the sample, most often its conductivity¹⁹. Turbidity in water samples is determined using a turbidimeter, which quantifies the scattering or attenuation of light caused by suspended particles¹⁹.

Bioaccumulation factor (BAF): Bioaccumulation factors were calculated according to the methodology originally developed by Connell for assessing the accumulation of contaminants in aquatic organisms²⁰.

$$BAF = \frac{C_{fish}}{C_{water}}$$

BAF = Bioaccumulation factor (L/kg)

C_{fish} = Concentration of contaminant in fish tissue (mg/kg wet weight)

C_{water} = Concentration of contaminant in water (mg/L)

Data analysis: The data generated from the study were analysed using SPSS Version 27. The descriptive statistics were expressed as Mean±Standard Deviation. One-way ANOVA was conducted to assess treatment effects, and Tukey's *post hoc* HSD was also utilized to test for pairwise comparisons. Significance levels were set at p<0.05.

RESULTS

Table 1 displays the amounts of heavy metals in fish samples in relation to WHO/FAO standards.

Lead concentrations exceeded WHO/FAO limits (0.01 mg/kg) in two species, with *Oreochromis niloticus* showing significantly the highest concentration (0.08 ± 0.01 mg/kg), which was not significantly different from *Clarias gariepinus* (0.06 ± 0.01 mg/kg), while *Polydactylus quadrifilis* remained significantly below the limit (0.01 ± 0.00 mg/kg).

Arsenic concentrations showed no significant differences between species, with all three species showing identical concentrations (0.01 ± 0.00 mg/kg) exactly at the WHO/FAO threshold of 0.010 mg/kg.

Cadmium concentrations were significantly different between species, with *Oreochromis niloticus* at the WHO/FAO limit (0.03 ± 0.00 mg/kg) and *Clarias gariepinus* near the limit (0.02 ± 0.00 mg/kg), showing no significant difference from each other, while *Polydactylus quadrifilis* was significantly lower (0.01 ± 0.00 mg/kg).

Chromium concentrations were significantly highest in *Polydactylus quadrifilis* (0.01 ± 0.00 mg/kg) compared to *Clarias gariepinus* and *Oreochromis niloticus*, which showed identical concentrations (0.001 ± 0.00 mg/kg).

Mercury concentrations showed no significant differences, with all species showing identical low concentrations (0.001 ± 0.00 mg/kg) well within WHO/FAO limits (0.01 mg/kg).

Table 2 displays heavy metal concentrations in water samples in relation to WHO/FMEnv standards.

Lead concentrations exceeded WHO/FMEnv limits (0.010 mg/L) at all sites and showed significant differences. Site C exhibited the significantly highest concentration (0.02 ± 0.00 mg/L) while Sites A and B showed statistically similar but elevated levels (0.01 ± 0.00 and 0.016 ± 0.00 mg/L, respectively), representing approximately 1-2-fold exceedances.

Arsenic concentrations varied significantly between sites ($F = 518.27$, $p < 0.001$), with Sites B and C showing statistically similar concentrations at or above WHO/FMEnv limits (0.01 ± 0.00 mg/L and 0.01 ± 0.00 mg/L, respectively), both significantly higher than Site A (0.001 ± 0.00 mg/L).

Table 1: Heavy metal levels in fish samples

Parameter mg/kg	WHO/FAO/Limits (mg/kg)	<i>Clarias gariepinus</i>	<i>Polydactylus quadrifilis</i>	<i>Oreochromis niloticus</i>
Lead	0.01	0.06 ± 0.01^a	0.01 ± 0.00^b	0.08 ± 0.01^a
Arsenic	0.01	0.01 ± 0.00^a	0.01 ± 0.00^a	0.01 ± 0.00^a
Cadmium	0.03	0.02 ± 0.00^a	0.01 ± 0.00^b	0.03 ± 0.00^a
Chromium	0.05	0.001 ± 0.00^b	0.01 ± 0.00^a	0.001 ± 0.00^b
Mercury	0.01	0.001 ± 0.00^a	0.001 ± 0.00^a	0.001 ± 0.00^a

Different superscripts a,b indicates significant differences between groups in a row ($p < 0.05$). Shared superscripts indicate no significant difference between groups in a row ($p > 0.05$). Data expressed as mean $\pm$ SD. n = 7 for each species.

Table 2: Heavy metal levels in water samples

Parameter mg/L	WHO/FMEnv Limits	Site A	Site B	Site C
Lead	0.01	0.01 ± 0.00^a	0.01 ± 0.00^a	0.02 ± 0.00^b
Arsenic	0.01	0.001 ± 0.00^b	0.01 ± 0.00^b	0.012 ± 0.00^a
Cadmium	0.003	0.08 ± 0.00^a	0.01 ± 0.00^b	0.01 ± 0.00^c
Chromium	0.005	0.001 ± 0.00^b	0.01 ± 0.00^a	0.002 ± 0.00^b
Mercury	0.000	0.001 ± 0.00^b	0.001 ± 0.00^b	0.003 ± 0.00^a

(Zero tolerance)

Different superscripts a,b indicates significant differences between groups in a row ($p < 0.05$). Shared superscripts indicate no significant differences between groups in a row ($p > 0.05$). Data expressed as mean $\pm$ SD. n = 7 for each site Site A: Taylor creek (Freshwater), Site B: Brass coastline (Saltwater) and Site C: Nembe creek (Brackish water)

Table 3: Levels of BTEX and THC in fish samples

Parameter (mg/kg)	WHO/FAO standards (mg/kg)	<i>Clarias gariepinus</i>	<i>Polydactylus quadrifilis</i>	<i>Oreochromis niloticus</i>
Benzene	0.0001	N.D	N.D	N.D
Toluene	0.0001	N.D	N.D	N.D
Ethylbenzene	0.0001	N.D	N.D	N.D
Xylene	0.0001	N.D	N.D	N.D
Total hydrocarbon content, THC	0.1	0.96±0.10 ^c	4.43±0.39 ^a	2.76±0.20 ^b

N.D: Not detected, N.S: Not significant, Different superscripts a,b,c indicates significant differences between all three groups in a row ($p < 0.05$). Data expressed as mean±SD. n = 7 for each species

Table 4: Concentrations of BTEX and THC in water samples

Parameter (mg/L)	Site A	Site B	Site C	WHO/FAO /FMEnv Limits (mg/L)
Benzene	N.D	N.D	N.D	<0.01
Toluene	N.D	N.D	N.D	<0.7
Ethylbenzene	N.D	N.D	N.D	<0.3
Xylene	N.D	N.D	N.D	<0.5
Total hydrocarbon content, THC	0.001±0.00 ^a	0.001±0.00 ^a	0.001±0.00 ^a	<1

N.D: Not detected, N.S: Not significant, Different superscripts a,b indicates significant differences between groups in a row ($p < 0.05$). Shared superscripts indicate no significant differences between groups in a row ($p > 0.05$), Site A: Taylor creek (Freshwater), Site B: Brass coastline (Saltwater) and Site C: Nembe creek (Brackish water)

Cadmium concentrations showed highly significant site differences ($F = 987.99$, $p < 0.001$), with Site A exhibiting extremely elevated levels (0.09 ± 0.00 mg/L), representing a 30-fold exceedance of WHO/FMEnv standards (0.003 mg/L). Sites B and C showed significantly lower but still elevated concentrations (0.01 ± 0.00 mg/L and 0.005 ± 0.00 mg/L, respectively).

Chromium concentrations differed significantly between sites, with Site B showing the highest concentration (0.010 ± 0.00 mg/L), approaching WHO/FMEnv limits (0.005 mg/L), while Sites A and C remained within acceptable ranges (0.001 ± 0.00 and 0.002 ± 0.00 mg/L, respectively).

Mercury concentrations exceeded zero tolerance levels at all sites and showed significant differences, with Site C exhibiting the highest levels (0.003 ± 0.00 mg/L) compared to Sites A and B (0.001 ± 0.00 mg/L each).

Table 3 presents BTEX and THC concentrations in fish tissues. All BTEX compounds (benzene, toluene, ethylbenzene, and xylene) were not detected in any species, indicating concentrations below detection limits of 0.0001 mg/kg. This resulted in no significant differences between species for these parameters.

Total Hydrocarbon Content (THC) showed highly significant variation between all species). *Polydactylus quadrifilis* demonstrated significantly the highest concentration (4.43 ± 0.39 mg/kg, followed by *Oreochromis niloticus* (2.76 ± 0.20 mg/kg) and *Clarias gariepinus* (0.96 ± 0.10 mg/kg). All THC concentrations significantly exceeded WHO/FAO limits (0.1 mg/kg), with exceedances ranging from 9.6-fold in *Clarias gariepinus* to 44.3-fold in *Polydactylus quadrifilis*.

Table 4 presents BTEX and THC concentrations in water samples from all three sites. All BTEX compounds (benzene, toluene, ethylbenzene, and xylene) were not detected at any site, remaining below WHO/FAO/FMEnv detection limits. This resulted in no significant differences between sites for these parameters. Total Hydrocarbon Content (THC) showed no significant differences between sites, with all locations exhibiting identical low concentrations (0.001 ± 0.00 mg/L) well within WHO/FAO/FMEnv standards (1.00 mg/L).

Table 5 displays PAH concentrations in fish samples in relation to WHO/FAO standards (0.002 mg/kg). Low molecular weight PAHs (naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, fluoranthene, pyrene) were not detected in any species, showing no significant differences. However, high molecular weight PAHs showed highly significant species-specific accumulation patterns.

Table 5: Concentrations of PAHs in fish samples

Parameter mg/L	<i>Clarias gariepinus</i>	<i>Polydactylus quadrifilis</i>	<i>Oreochromis niloticus</i>	WHO/FAO Standards (mg/kg)
Naphtalene	N.D	N.D	N.D	<0.002
Acenaphthene	N.D	N.D	N.D	<0.002
Acenaphthylene	N.D	N.D	N.D	<0.002
Fluorene	N.D	N.D	N.D	<0.002
Phenanthrene	N.D	N.D	N.D	<0.002
Fluoranthene	N.D	N.D	N.D	<0.002
Pyrene	N.D	N.D	N.D	<0.002
Benz(a)anthracene	0.001±0.00 ^b	0.07±0.00 ^a	0.001±0.00 ^b	<0.002
Chrysene	N.D	0.06±0.0001 ^a	N.D	<0.002
Benzo(a)fluoranthene	0.001±0.00 ^b	0.04±0.0001 ^a	0.001±0.00 ^b	<0.002
Benzo(b)fluoranthene	N.D	0.02±0.0001 ^a	N.D	<0.002
Benzo(a)pyrene	0.003±0.00 ^b	0.03±0.00 ^a	0.003±0.00 ^b	<0.002
Indeno(1,2,3-cd) pyrene	N.D	0.05±0.0001 ^a	N.D	<0.002
Dibenz(a,h)anthracene	N.D	N.D	N.D	<0.002
Benzo(ghi)perylene	N.D	N.D	N.D	<0.002

N.D: Not detected, N.S: Not significant, Different superscripts a,b indicates significant differences between groups in a row ($p < 0.05$), Shared superscripts indicate no significant differences between groups in a row ($p > 0.05$), Data expressed as mean±SD. n = 7 for each species

Table 6: Concentrations of PAHs in water samples

Parameter (mg//L)	Site A	Site B	Site C	WHO/FAO Standards
Naphtalene	N.D	N.D	N.D	<0.0002
Acenaphthene	N.D	N.D	N.D	<0.0002
Acenaphthylene	N.D	N.D	N.D	<0.0002
Fluorene	N.D	N.D	N.D	<0.0002
Phenanthrene	N.D	N.D	N.D	<0.0002
Fluoranthene	N.D	N.D	N.D	<0.0002
Pyrene	N.D	N.D	N.D	<0.0002
Benz(a)anthracene	N.D	N.D	N.D	<0.0002
Chrysene	N.D	N.D	N.D	<0.0002
Benzo(a)fluoranthene	N.D	N.D	N.D	<0.0002
Benzo(b)fluoranthene	N.D	N.D	N.D	<0.0002
Benzo(a)pyrene	N.D	N.D	N.D	<0.0002
Indeno(1,2,3-cd) pyrene	N.D	N.D	N.D	<0.0002
Dibenz(a,h)anthracene	N.D	N.D	N.D	<0.0002
Benzo(ghi)perylene	N.D	N.D	N.D	<0.0002

N.D: Not detected, N.S: Not significant, Site A: Taylor creek (Freshwater), Site B: Brass coastline (Saltwater) and Site C: Nembe creek (Brackish water)

Table 7: Physiochemical properties of water samples

Parameter (Units)	Site A (Freshwater)	Site B (Saltwater)	Site C (Brackish)	f-value	p-value	WHO/DPR/UESPA Standards
TDS (mg/L)	74.57±1.97 ^c	1150±13.43 ^b	4800±13.43 ^a	40057.85	<0.001	300-900 mg/L
EC (µS/cm)	72.90±2.03 ^c	1500±2.03 ^b	15000±25.07 ^a	58781.63	<0.001	50-1500 µS/cm
Turbidity (NTU)	18.11±0.96 ^a	10.46±0.81 ^b	3.55±0.21 ^c	686.30	<0.001	5-10 NTU
Salinity (ppt)	0.1±0.00 ^c	32.00±1.70 ^a	13.00±0.62 ^b	1645.05	<0.001	<0.5 ppt (freshwater), 0.5-30 ppt (brackish water) and 35 (marine)
pH	6.70±0.09 ^c	7.5±0.09 ^b	7.8±0.04 ^a	349.06	<0.001	6.5-9.0

Different superscripts a,b,c indicates significant differences between sites. Data expressed as mean±SD. n = 7 for each site. $P < 0.001$ means there is very much significant difference, Site A: Taylor creek (Freshwater), Site B: Brass coastline (Saltwater) and Site C: Nembe creek (Brackish water)

Table 6 displays the findings of the PAH analysis for water samples. All analyzed PAH chemicals (naphthalene to benzo(ghi)perylene) were undetected at the three sampling locations, remaining below WHO/FAO standards (<0.0002 mg/L).

Table 8: Bioaccumulation factor of heavy metals in fish samples

Parameters L/kg	<i>Clarias gariepinus</i>	<i>Polydactylus quadrifilis</i>	<i>Oreochromis niloticus</i>
Lead	4.36	0.37	3.26
Arsenic	0.001	0.001	0.001
Cadmium	3.56	0.0001	0.17
Chromium	1	0.04	0.5
Mercury	1	1	1

BAF values <100 is considered low, BAF values within the range of 100-1000 are moderate and BAF values >1000 are considered high

Table 9: Bioaccumulation factor of total hydrocarbons in fish samples

Parameter L/kg	<i>Clarias gariepinus</i>	<i>Polydactylus quadrifilis</i>	<i>Oreochromis niloticus</i>
THC	959.40	4343.10	2764.80

BAF values <100 is considered low, BAF values within the range of 100-1000 are moderate and BAF values >1000 are considered high

The physicochemical parameters presented in Table 7 show clear and statistically significant variations among the three sampling sites ($p < 0.001$). Total dissolved solids (TDS) were lowest at Site A (74.57 mg/L), moderate at Site B (1150 mg/L), and highest at Site C (4800 mg/L). Site A values fall below the recommended range (300-900 mg/L), while Site B slightly exceeds and Site C greatly exceeds permissible limits, indicating a high level of dissolved substances in the brackish environment.

Electrical conductivity (EC) followed a similar trend, increasing from Site A (72.90 $\mu\text{S}/\text{cm}$) to Site B (1500 $\mu\text{S}/\text{cm}$) and reaching a maximum at Site C (15000 $\mu\text{S}/\text{cm}$). While Site A falls within acceptable limits, Site B is at the upper threshold and Site C far exceeds the standard range, reflecting elevated ionic concentration.

Turbidity showed an inverse pattern, with the highest value recorded at Site A (18.11 NTU), exceeding the recommended limit (5-10 NTU), suggesting higher suspended particles in freshwater. Site B (10.46 NTU) is near the permissible limit, whereas Site C (3.55 NTU) falls within acceptable levels.

Salinity values confirmed the classification of water types, with Site A (0.1 ppt) representing freshwater, Site C (13.00 ppt) indicating brackish conditions, and Site B (32.00 ppt) approaching marine levels. These values align reasonably with standard classifications, although Site B exceeds the typical brackish range.

The pH values ranged from slightly acidic at Site A (6.70) to slightly alkaline at Site C (7.8), with all sites remaining within the acceptable range (6.5-9.0), indicating no immediate concern regarding acidity or alkalinity.

Table 8 displays the bioaccumulation potential of heavy metals in fish tissues. Lead showed moderate to high bioaccumulation capacity, with *Clarias gariepinus* demonstrating the highest BAF (4.36 L/kg), followed by *Oreochromis niloticus* (3.26 L/kg), while *Polydactylus quadrifilis* showed low bioaccumulation (0.37 L/kg).

Cadmium exhibited species-specific bioaccumulation patterns, with *Clarias gariepinus* showing moderate bioaccumulation (3.56 L/kg), while *Polydactylus quadrifilis* and *Oreochromis niloticus* demonstrated minimal accumulation (<1.0 L/kg).

Arsenic, chromium, and mercury showed consistently low bioaccumulation factors (<1.0 L/kg) across all species, indicating limited environmental persistence in fish tissues.

Table 9 displays the bioaccumulation potential of THC in fish tissues. All three species demonstrated high bioaccumulation potential (BAF >1000), indicating efficient biological concentration of hydrocarbon compounds.

DISCUSSION

The heavy metal analysis in fish (Table 1) indicates contamination levels that surpass international safety requirements, signifying considerable anthropogenic pollution in the study area. Lead concentrations in *Oreochromis niloticus* (0.08 ± 0.01 mg/kg) and *Clarias gariepinus* (0.06 ± 0.01 mg/kg) are significantly above the WHO/FAO limit of 0.01 mg/kg by 8-fold and 6-fold, respectively, but *Polydactylus quadrifilis* remained within limits (0.01 ± 0.00 mg/kg). This trend indicates that contamination patterns are habitat-specific, with freshwater and brackish species exhibiting greater lead loads than saltwater species, this may be attributed to the mobilization of sediment-bound lead and diminished dilution effects in confined aquatic environments²¹. Arsenic concentrations were consistent throughout all species (0.01 ± 0.00 mg/kg), precisely at WHO thresholds, suggesting pervasive yet regulated arsenic pollution, potentially from atmospheric deposition or geological origins. Cadmium levels neared WHO thresholds (0.03 mg/kg) in *Oreochromis niloticus* (0.03 ± 0.00 mg/kg) and *Clarias gariepinus* (0.02 ± 0.00 mg/kg), but *Polydactylus quadrifilis* demonstrated a lower concentration of 0.01 ± 0.00 mg/kg²¹. Also, the strong affinity of Cadmium for sulfhydryl groups in proteins is known to induce metallothionein and causes oxidative stress, perhaps resulting in damage in the liver and kidneys. Chromium contents were below WHO thresholds in all species, however *Polydactylus quadrifilis* exhibited marginally increased values (0.01 ± 0.00 mg/kg), and potentially indicating saltwater habitat sediment contamination due to movements of ships. Mercury concentrations were negligible (0.001 ± 0.00 mg/kg) in all species, well under WHO thresholds, suggesting efficient mercury excretion or limited environmental mercury presence. These findings correspond with Green *et al.*²¹ who reported increased lead concentrations in freshwater fish from the Niger Delta, linked to petroleum exploration and industrial discharges²¹. Nonetheless, mercury concentrations from this study are low and at safe levels, this may be due to accelerated elimination kinetics and metallothionein-facilitated detoxification in tropical fish species²²⁻²⁴.

The analysis of heavy metals in water (Table 2) showed large differences in all sites. Lead concentrations exhibited the following concentrations: Site C (0.02 ± 0.00 mg/L) > Site B (0.01 ± 0.00 mg/L) > Site A (0.01 ± 0.00 mg/L), with all sites surpassing WHO standards (0.010 mg/L), signifying pervasive lead pollution resulting from petroleum operations and industrial effluents. The elevated concentrations at Site C (Nembe Creek) indicate significant industrial discharges and diminished dilution within the semi-enclosed brackish ecosystem. The distribution of arsenic indicated that Site C and Site B (0.01 ± 0.00 mg/L) had higher levels than Site A (0.001 ± 0.00 mg/L). All sites were within WHO guidelines, however freshwater levels were significantly low, implying inputs of arsenic from saltwater and anthropogenic sources. Cadmium concentrations demonstrated the hierarchy Site A (0.08 ± 0.00 mg/L) > Site B (0.01 ± 0.00 mg/L) > Site C (0.005 ± 0.00 mg/L), with freshwater and saltwater levels significantly beyond WHO guidelines (0.003 mg/L) by a factor of 30, suggesting acute cadmium contamination potentially attributable to agricultural runoff or industrial effluents²⁴. Chromium concentrations were heightened at Site B (0.01 ± 0.00 mg/L), nearing WHO thresholds (0.0050 mg/L), potentially indicating how shipping activities and anti-fouling paint operations pollute the environment²¹. Mercury concentrations were elevated at Site C (0.003 ± 0.00 mg/L), beyond the zero-tolerance threshold, suggesting inputs of mercury related with petroleum contamination. These findings correspond with Anyanwu *et al.*²⁵, who recorded increased heavy metal concentrations in Niger Delta water bodies due to petroleum drilling activity²⁵.

The BTEX and THC analysis (Table 3) revealed selective hydrocarbon bioaccumulation, suggesting the presence of petroleum contamination in the study area. Benzene, toluene, ethylbenzene, and xylene were undetected across all fish species, despite WHO/FAO criteria of 0.0001 mg/kg, these results can be attributed to the fact that these compounds are highly volatility and can be easily removed from biological systems via gill ventilation and metabolic breakdown. This absence corresponds with the hydrophilic characteristics of BTEX chemicals and their tendency to partition into aqueous phases rather than lipid tissues²⁶. Total Hydrocarbon Content (THC) showed significant species-specific accumulation in this

manner: *Polydactylus quadrifilis* (4.43 ± 0.39 mg/kg) > *Oreochromis niloticus* (2.76 ± 0.20 mg/kg) > *Clarias gariepinus* (0.96 ± 0.10 mg/kg) had values that greatly beyond WHO/FAO limits (0.1 mg/kg) by a factor of 9.6 to 44.3. The significant accumulation in *Polydactylus quadrifilis* is indicative of its high fat content and possibly increased exposure in saltwater environments settings influenced by offshore petroleum operations. From a molecular standpoint, hydrocarbon bioaccumulation can cause massive problems as it can compromise cellular membrane integrity, hinder mitochondrial function, and trigger oxidative stress via cytochrome P450-mediated metabolism, resulting in the production of reactive oxygen species²⁶. The results surpass those documented by Yaguo *et al.*²⁷ in comparable Niger Delta ecosystems, this suggests that petroleum contamination on the increase²⁷.

The investigation of water BTEX and THC (Table 4) offers essential insights into the origins of petroleum contamination and the environmental destiny processes in the three aquatic ecosystems. Benzene, toluene, ethylbenzene, and xylene were undetected at any location, despite sensitive detection methods (GCMS) and sensitive thresholds (<0.01-0.7 mg/L), suggesting either rapid volatilization from aqueous surfaces, increased biodegradation by microbes or because of air partitioning of these volatile organic chemicals. This absence contrasts with their widespread industrial application and implies the presence of effective natural attenuation processes or the timing of sampling following contamination occurrences²⁶. Total Hydrocarbon Content (THC) was consistently low at all locations (0.001 mg/L), much beneath WHO thresholds (<1 mg/L), suggesting active bioaccumulation, swift dilution due to size of water bodies, volatilization, or biodegradation of petroleum hydrocarbons in the aquatic ecosystem²⁶. Also, the dramatically wide disparity between low water THC and elevated fish tissue THC (9.6-44.3 times above limits) can only be attributed to chronic bioaccumulation across all trophic levels resulting from persistent low-level exposure, food web biomagnification, and lipophilic partitioning into biological matrices²⁷. This water-tissue disparity is typical of hydrophobic organic pollutants that preferentially accumulate in biota instead of persisting in aqueous phases and from an environmental biochemistry standpoint, petroleum hydrocarbons experience weathering processes such as photooxidation, evaporation, and microbial degradation, which swiftly diminish water column concentrations while leftover chemicals accumulate in sediments and across food webs²⁷. These findings correspond with literature as Yaguo *et al.*²⁷ recorded low hydrocarbon concentrations in water and heightened fish tissue levels in Niger Delta habitats too²⁷.

Assessment of Polyaromatic Hydrocarbons (PAHs) in fish samples (Table 5) also indicate contamination patterns that are species specific with carcinogenic chemicals present at certain levels that are still considered hazardous. Low molecular weight polycyclic aromatic hydrocarbons (naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, fluoranthene, pyrene) were undetected in all species, likely because of their increased volatility and augmented metabolic clearance. However, higher molecular weight PAHs exhibited alarming contamination especially in *Polydactylus quadrifilis*: Benzo(a)anthracene (0.07 ± 0.00 mg/kg), chrysene (0.06 ± 0.0001 mg/kg), benzo(b)fluoranthene (0.02 ± 0.0001 mg/kg), benzo(a)pyrene (0.03 ± 0.00 mg/kg), and indeno(1,2,3-cd)pyrene (0.05 ± 0.0001 mg/kg), all significantly surpassing WHO standards (<0.002 mg/kg) by 10-35 times. Benzo(a)anthracene and benzo(a)pyrene were identified at low concentrations in *Clarias gariepinus* and *Oreochromis niloticus* (0.001-0.003 mg/kg), however these concentrations still surpass safety thresholds because of how highly carcinogenic these compounds are. This unique concentration in *Polydactylus quadrifilis* backs the claim that there is a pollution crisis specifically in the marine environment and increased lipophilic partitioning into adipose tissues and maybe diminished metabolic clearance of intricate aromatic compounds²⁷. From a toxicological standpoint, these PAHs are subjected to cytochrome P450-mediated biotransformation, resulting in the generation of reactive epoxide metabolites that covalently bind to DNA, hence inducing mutagenic and carcinogenic effects²⁸. The lack of dibenzo(a,h)anthracene and benzo(ghi)perylene in all species indicates either a restricted environmental occurrence or selective accumulation in non-muscle tissues²⁸.

The water PAH analysis (Table 6) indicates a total absence of all 15 key PAH chemicals at the three sampling sites, despite sensitive detection methods (GC-MS/FID) and very sensitive limits (<0.0002 mg/L) and notable PAH buildup in fish tissue. The contradiction between water and fish tissues illustrates the pronounced hydrophobic characteristics of PAHs and their preference for soil, living organisms and other biological matrices rather than aqueous phases²⁹. This trend signifies that PAH accumulation is fast in soil organic matter, suspended particles, and biological lipid compartments, with water column concentrations falling below analytical detection thresholds²⁹. Bioaccumulation in fish tissues transpires via dietary absorption from contaminated sediments and prey species, rather than through direct water absorption, elucidating the discrepancy between water and tissue concentrations²⁹.

The physicochemical examination of water quality (Table 7) demonstrates distinct environmental fingerprints that substantially affect fish health and the bioavailability of contaminants in the three aquatic environments. Total Dissolved Solids (TDS) exhibited a pronounced gradient: Site C (4800 ± 13.43 mg/L) > Site B (1150 ± 13.43 mg/L) > Site A (74.57 ± 1.97 mg/L), with Site C significantly surpassing WHO standards (300-900 mg/L) by a factor of 5.3, indicating hypersaline conditions due to its saltwater nature, hydrocarbon brine release and contamination from anthropogenic activities. The increased ionic strength imposes strain on fish osmoregulatory systems, resulting in cellular dehydration and metabolic impairment. Electrical Conductivity (EC) mirrored TDS trends: Site C (15000 ± 25.07 μ S/cm) > Site B (1500 ± 2.03 μ S/cm) > Site A (72.90 ± 2.03 μ S/cm), with Site C surpassing WHO thresholds (50-1500 μ S/cm) by a factor of ten, indicating significant ionic pollution that disturbs ionic equilibrium and adversely affects renal function in local fish populations. Turbidity exhibited an inverse correlation: With Site A (freshwater) having the highest turbidity (18.11 ± 0.96 NTU), followed by Site B (brackish water) with a turbidity of (10.46 ± 0.81 NTU) and Site C (saltwater) having the lowest value of (3.55 ± 0.21 NTU), with freshwater turbidity surpassing WHO guidelines (5-10 NTU), signifying suspended particle matter capable of adsorbing pollutants and diminishing photosynthetic activity. Salinity in the habitats showed: Site B (32.00 ± 1.70 ppt-saltwater) > Site C (13.00 ± 0.62 ppt-brackish) > Site A (0.1 ± 0.00 ppt-freshwater), consistent with anticipated ranges for their respective ecosystems. The pH values exhibited a gradient: Site C (7.8 ± 0.04) > Site B (7.5 ± 0.09) > Site A (6.70 ± 0.09), with Site A nearing acidic conditions that elevate metal toxicity via altered speciation and increased bioavailability. The interrelated water quality parameters provide synergistic stress conditions that undermine fish immunological function, affect enzyme activity, and alter contaminant uptake kinetics³⁰.

The examination of the heavy metal bioaccumulation factor (Table 9) reveals significant bioaccumulation potential that is unique to the species in this study, this indicates how serious environmental pollution and biological concentration mechanisms are. The bioaccumulation parameters for lead followed this pattern: *Clarias gariepinus* (4.36) > *Oreochromis niloticus* (3.26) surpasses *Polydactylus quadrifilis* (0.37), with freshwater species demonstrating high bioaccumulation (BAF 100-1000), whilst saltwater species are classified in the low group (BAF < 100). This trend illustrates that there is improved lead bioavailability in freshwater ecosystems owing to less competition from major ions and heightened gill permeability in hypoosmotic settings. Arsenic bioaccumulation factor was negligible across all species (<0.001), suggesting general low concentration, effective excretion processes or selective accumulation in non-muscular tissues like the liver and kidneys. Cadmium bioaccumulation followed this pattern: *Clarias gariepinus* (3.56) > *Oreochromis niloticus* (0.17) exhibits more accumulation potential than *Polydactylus quadrifilis* (<0.0001), with *Clarias gariepinus* demonstrating substantial cadmium accumulation despite lower tissue concentrations, indicating species-specific cadmium management. Bioaccumulation of chromium and mercury exhibited consistent values (1.0) across species, suggesting baseline accumulation due to widespread environmental presence rather than substantial contamination sources. Bioaccumulation factors are determined by the ratio of tissue concentration to water concentration, offering insight into biological concentration mechanisms and environmental outcomes. Values below 100 signify modest bioaccumulation, those between 100 and 1000 denote moderate accumulation, and values beyond 1000 suggest a strong potential for bioaccumulation²⁷.

The investigation of THC bioaccumulation potential (Table 10) reveals consistently elevated bioaccumulation in all three fish species, signifying pervasive petroleum contamination and efficient biological concentration of hydrocarbon chemicals from aquatic ecosystems. *Polydactylus quadrifilis* demonstrated the greatest bioaccumulation factor (4343.1), signifying significant bioaccumulation that signifies both lipophilic partitioning into adipose tissues (19.45%) and biomagnification within the marine food web. *Oreochromis niloticus* exhibited considerable bioaccumulation (2764.8), signifying notable hydrocarbon absorption despite its aqueous environment and reduced lipid content (13.15%). *Clarias gariepinus* showed significant bioaccumulation (959.4), the lowest among species, although nevertheless demonstrating a high capacity for environmental concentration. All bioaccumulation factors surpass 1000, categorizing all species inside the "High Bioaccumulation Potential" classification, which signifies environmental persistence, sluggish clearance kinetics, and progressive tissue accumulation over time. The calculation of the bioaccumulation factor (tissue concentration ÷ water concentration) reveals biological concentration ratios of approximately 1000-4000 times, signifying a remarkable effectiveness in hydrocarbon sequestration from dilute environmental sources. The significant bioaccumulation potential is indicative of the lipophilic characteristics of petroleum hydrocarbons, protracted metabolic clearance, and persistent environmental exposure due to ongoing petroleum operations. The consistent high categorization among species signifies widespread ecosystem contamination necessitating extensive cleanup initiatives and prolonged biomonitoring activities²³.

CONCLUSION

This comprehensive nutritional assessment reveals significant species-specific and habitat-dependent variations in both proximate and essential mineral profiles. The findings demonstrate that all three fish species are good sources of nutrition and are suitable for addressing conditions such as protein-energy malnutrition in local communities. The presence of essential minerals such as calcium and magnesium in freshwater species makes these species valuable for supporting child and maternal diets. The low concentrations of some minerals suggest dietary diversification to meet daily requirements.

SIGNIFICANCE STATEMENT

This study provides a comprehensive comparative assessment of heavy metals and petroleum hydrocarbons across freshwater, brackish, and marine fish species in Bayelsa State, highlighting severe contamination levels that exceed international safety standards. The findings reveal significant bioaccumulation of toxicants, particularly in *Polydactylus quadrifilis* and *Oreochromis niloticus*, indicating potential public health risks through fish consumption. The work establishes critical baseline data for environmental monitoring and emphasizes the urgent need for pollution control and remediation strategies in petroleum-impacted aquatic ecosystems.

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