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Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) and Heavy Metals in Rivers and Creeks around Bonny River, Nigeria

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Abstract
This study assessed polycyclic aromatic hydrocarbons (PAHs) and heavy metals in the Bonny River by analyzing water, sediment, and biota samples from fifteen strategically selected stations: Jetty to Mguodeya, Eagle Island opposite Emenike waterfront, 107 Emenike Str waterfront by slaughter, Waterfront by Hospital Management Board, Abonnema Wharf Rd, Oil terminal, Wait and Bush Jetty, Nembe Jetty, Old PH Tourist Beach 1, PH Tourist Beach 2, Borokiri Sandfill 1, Fed. Housing Estate (Jetty), Fed. Housing Estate (Abandoned House), Rd 2 Old PH TWP, 42 Eastern Bye-pass, and Amadi Sandfill. The research design adopted in this study was a descriptive approach aimed at analyzing the presence and concentration of polycyclic aromatic hydrocarbons (PAHs) in surface water, sediments, and biota samples from the selected sampling points along the Bonny River. Standard sampling methods were followed. Sample collection involved obtaining 15 surface water samples, 15 sediment samples, and 15 biota samples, ensuring a comprehensive representation of the aquatic environment. The collected samples were preserved and prepared for analysis, with selected physicochemical parameters of the water, sediments and biota measured using suitable laboratory equipment. PAHs were extracted from the samples using appropriate solvents and methods, followed by a clean-up process to eliminate impurities and unwanted compounds, ensuring accuracy in the subsequent analysis. The concentration of PAHs were determined using Gas Chromatography-Mass Spectrometry (GC-MS). Principal Component Analysis (PCA) was employed for source apportionment of the PAHs. The heavy metals were analysed using the Atomic Absorbtion Spectrophotometer (AAS). The ecological risk assessment was conducted to evaluate the potential impact on the environment. Findings revealed significant pollution with electrical conductivity (5850.7±0.15-16490.80±2.15 µS/cm), total dissolved solids (2925.37±2.14-8245.38±3.14 mg/L), and other contaminants exceeding permissible limits, indicating serious environmental contamination. Heavy metal analysis highlighted high levels of cadmium (mean 1.535±3.22 mg/kg) and lead (mean 29.279±3.12 mg/kg) in sediments, with seafood such as crabs showing elevated cadmium (mean 0.182±0.02 mg/kg), chromium (mean 0.972 mg/kg), and lead (mean 4.391±0.18 mg/kg). Carcinogenic risk indices for seafood ranged from 1.99E-04 to 1.50E-03 for adults and from 7.80E-04 to 5.83E-03 for children, exceeding safety thresholds. Ecological risk assessments indicated significant bioaccumulation in oysters, crabs, and periwinkles, with non-carcinogenic risk values and carcinogenic indices surpassing acceptable limits. PAH analysis showed elevated B(a)Pteq values, with oysters having the highest

levels and exceeding EU limits for PAHs in smoked fish, underscoring the need for enhanced monitoring and pollution control to protect public health.

Keywords: *Polycyclic Aromatic Hydrocarbons (PAHs), Heavy Metals, Bonny River, Ecological Risk Assessment, Gas Chromatography-Mass Spectrometry (GC-MS), Principal Component Analysis (PCA)*

1 Introduction

Surface water has been, and is still being used, for many purposes, which include drinking, irrigation, animal farming, recreation and serves as habitat to numerous organisms. The aesthetic properties of most rivers and streams have made them sites for tourist attraction and recreation. It has also served as sources of employment, particularly for the fishing industry. Generally, in most countries of the world, surface water is used as the main source of water for the provision of potable water after necessary treatment. The treatment costs for potable water production are reduced greatly when water of a desirable quality is used as a source. Therefore, freshwater sources like rivers and streams, need to be protected from contamination with benefits not limited to humans alone, but also to prevent environmental deterioration and reduction in biodiversity. Access to safe water is entrenched in the constitution of the federal republic of Nigeria, as a basic human right of Nigerian citizens (Okukpon & Anozie, 2018), yet, it has been estimated that 60 million people in Nigeria do not have access to safe drinking water, and this problem is more pronounced in rural areas (Atser & Udoh, 2015). Thus, many residents of the affected rural or disadvantaged communities depend largely on surface water for their domestic water needs.

Contamination with polycyclic aromatic hydrocarbons (PAHs) and Heavy metals in the aquatic environment has attracted global attention owing to its abundance, persistence and environmental toxicity (Ali *et al.*, 2016; Rakib *et al.*, 2022). Both natural and anthropogenic activities are responsible for the abundance of PAHs and heavy metals in the environment (Kabir *et al.*, 2020; Islam *et al.*, 2021). However, anthropogenic activities can effortlessly generate PAHs and Heavy metals in sediment and water that pollute the aquatic environment (Ali *et al.*, 2016). The increasing pollution by PAHs and heavy metals have a significant adverse health effect for invertebrates, fish, and humans (Zaynab *et al.*, 2021). The metal pollution of aquatic ecosystems is increasing due to the effects from urbanization and industrialization (Hu *et al.*, 2013).

The assessment of PAHs and heavy metals in water, sediments, and biota represents a crucial endeavor in environmental science, providing a comprehensive understanding of the interactions between contaminants and different components of aquatic ecosystems. In the context of Bonny River, this multifaceted analysis serves as a fundamental tool for evaluating the impact of anthropogenic activities on the river's environmental health. Water, being a primary medium for the transport of pollutants, was scrutinized for concentrations of PAHs and Heavy metals such as lead, cadmium, arsenic, etc. The results demonstrated discernable contamination levels, reflecting the influence of industrial discharges and urban runoff (Aleru *et al.*, 2019; Akankali *et al.*, 2021). This component of the study not only identifies potential risks to aquatic life but also highlights the implications for human populations relying on the Bonny River for drinking water and agricultural activities.

The comprehensive analysis of PAHs and heavy metals in the Bonny River, prompted by escalating industrialization and urbanization in the Niger Delta region, has provided critical insights into environmental contamination and potential risks to ecosystems and human health (Moslen *et al.,* 2019). Anthropogenic activities, notably oil and gas exploration and industrial discharges, introduce significant quantities of PAHs and heavy metals such as lead, cadmium, mercury, and arsenic into the river (Okogbue *et al.*, 2018). For instance, oil and gas exploration in the Niger Delta releases PAHs and heavy metals into water bodies through drilling fluids and produced water, contributing to the contamination of the Bonny River (Erakhrumen, 2015). The results from the analysis revealed elevated concentrations of these contaminants, with sediments acting as reservoirs for persistent pollutants. Fish and benthic organisms were found to bio accumulate metals like mercury and cadmium, posing potential risks to both the aquatic food web and local communities dependent on the river for sustenance.

This research study therefore is to make available the current status of the potable nature, ecological and health risk of the Bonny River tributaries which have immense uses due to their adjacent sites to residential occupations. Understanding the interactions between river water, sediments, and biota is essential for a holistic assessment of ecological resilience in the Bonny River ecosystem. This research aims to integrate findings from these components to develop a comprehensive understanding of the ecological dynamics in the face of heavy metal contamination.

2. Methodology

The methodology outlines the procedural framework and approach for the investigation, designed to address research questions and reduce disparities (Venkatesh *et al.*, 2016). This study employs an experimental design to evaluate the impact of an intervention on specific variables or a population without random assignment. Focusing on the Bonny River in Rivers State, Nigeria, the research involves analyzing water, sediment, and biota. Samples were systematically collected from multiple locations along the river and assessed in the laboratory for physicochemical properties, microbial content, heavy metals, and polycyclic aromatic hydrocarbons (PAHs). The analysis aims to enhance understanding of the river's quality, contributing valuable insights to existing knowledge.

The Bonny River, situated along the southern border of Rivers State, Nigeria, flanked at latitudes 4° 27' 5.76"N to 4° 49'N and longitudes 7° 00' to 7° 10' 14.66"E. It shares a climate similar to the tropical equatorial latitude, with an average precipitation of 2719mm and a temperature ranging from 22°C to 32°C throughout the year (Gobo, 1998; Gobo *et al.,* 2012). This vital water source serves drinking, commercial, and industrial activities in the Port Harcourt metropolis, contributing to the degradation of water quality over time.

The map of the study area is shown in Figure 3.1 below.

Figure 2.1: Study Area showing the Sampling Stations
(Source: Researcher's Design)

Table 2.1: Sample Stations and their Locations

Sample Stations	Co-ordinates	Acronym of Sought Parameters	Description Address	Prevalent Human Activities
Station 1	Lat. 4.78891 (N4^{0}47'19.89'') Long. 6.97793 (E6^{0}58'40.2'')	W1 and S1	Jetty to Mgbuodeya (6 Rd E, Eagle Island, PH)	Floating waste accumulated through traffic of people travel from Eagle Island to Mgbuodaya.
Station 2	Lat. 4.78293 (N4^{0}46'58.572'') Long. 6.98682 (E6^{0}59'12.57'')	W2 and S2	14 E1, Rd 27, Eagle Island opposite Emenike waterfront	A newly acquired sandfill environment
Station 3	Lat. 4.78537 (N4^{0}47'7.326'') Long. 6.98948 (E6^{0}59'22.116'')	W3 and S3	107 Emenike Str waterfront by slaughter	Demolished/destroyed houses and presence of a meat slaughter using tyres to raost meat
Station 4	Lat. 4.78405 (N4^{0}47'2.562'') Long. 6.99858 (E6^{0}59'54.8942'')	W4 and S4	(Waterfront by Hospital Management Board	Petroleum usage by marine operators
Station 5	Lat. 4.77513 (N4^{0}46'30.48'') Long. 7.0043 (E7^{0}0'15.684'')	W5 and S5	Abonnema Wharf Rd, Old PH Rd., PH	Petroleum usage by marine operators
Station 6	Lat. 4.75611 (N4^{0}45'22.008'') Long. 7.00452 (E7^{0}0'16.284'')	W6 and S6	Oil terminal, Wait and Bush Jetty, PH (Has Naval Base)	Illegal bunkering
Station 7	Lat.4.75755(N4^{0}45'27.216'') Long. 7.02443 (E7^{0}1'27.87'')	W7 and S7	Nembe Jetty, Borokiri, PH	Illegal bunkering

Station 8	Lat. 4.75794 (N4^{0}45’28.53’’) Long. 7.04325 (E7^{0}2’35.754’’)	W8 and S8	Old PH Tourist Beach 1 (Jetty Area)	Human activities dues to human actives and boat wrecks
Station 9	Lat. 4.76008 (N4^{0}45’36.288’’) Long. 7.04277 (E7^{0}2’33.966’’)	W9 and S9	PH Tourist Beach 2 (Residential area)	Cooking with firewook and human waste
Station 10	Lat. 4.737(N4^{0}44’13.212’’) Long. 7.02521 (E7^{0}1’30.762’’)	W10 and S10	P2PG + JJW, New Rd, Borokiri Sandfill 1	Human activities: fishing, selling and domestic waste
Station 11	Lat. 4.73495 (N4^{0}44’5.826’’) Long. 7.02775 (E7^{0}1’39.888’’)	W11 and S11	Fed. Housing Estate, Plot 2, Rd 5, Borokiri, PH (Jetty)	Illegal bunkering
Station 12	Lat. 4.73412 (N4^{0}44’2.832’’) Long. 7.02918 (E7^{0}1’44.988’’)	W12 and S12	Fed. Housing Estate, Plot 2, Rd 5, Borokiri, PH (Abandoned House)	Boat wrecks and constructions waste
Station 13	Lat. 4.73446 (N4^{0}44’3.612’’) Long. 7.0309 (E7^{0}1’55.35’’)	W13 and S13	Rd 2 Old PH.	Wrecks and illegal bunkering
Station 14	Lat. 4.7731 (N4^{0}46’23.148’’) Long. 7.0208 (E7^{0}1’14.892’’)	W14 and S14	42 Eastern Bye-pass (Opp. NDDC Perm Site Complex, PH)	Activities of ship repair yards, mechanics workshops and illegal bunkering
Station 15	Lat. 4.79001 (N4^{0}47’24.178’’) Long. 7.02918 (E7^{0}1’45.432’’)	W15 and S15	Amadi-Ama Sandfill, PH	Human waste management, assembling and separation action

The study involved collecting samples from 15 strategically selected points along the Bonny River, with locations identified using a Garmin GPS. Sampling focused on water, sediments, and biota, ensuring representation of the river's diverse environments. Surface water samples were gathered by submerging containers just below the top 1-5 cm layer. They were stored in specific containers based on the type of analysis—plastic containers for physicochemical and heavy metal analyses, amber glass bottles for PAHs, and sterile vials for microbial assessments. Preservation methods, such as acidifying with HNO_3 or H_2SO_4, ensured sample stability. Sediment samples were collected using a stainless steel Eckman's grab sampler, while biota samples, including oysters, crabs, and periwinkles, were carefully extracted and preserved. Biota tissues were processed and stored at -20°C for subsequent analysis. Samples were transported to the laboratory in coolers to maintain integrity.

Field measurements of unstable parameters, including pH, electrical conductivity (EC), total dissolved solids (TDS), salinity, and dissolved oxygen (DO), were conducted onsite using calibrated instruments to ensure data accuracy. Laboratory analyses were carried out at a government-certified facility in Port Harcourt, adhering to guidelines from the Federal Ministry of Environment and established standards like APHA and ASTM. Analytical methods included spectrophotometry for total suspended solids (TSS), direct Nesslerization for ammonia, cadmium reduction for nitrates, and turbidimetric methods for sulfates. These rigorous procedures provided comprehensive insights into the physicochemical, microbial, and contaminant profiles of the Bonny River's ecosystem.

The study employed standardized analytical methods to assess phosphate, biochemical oxygen demand (BOD), chemical oxygen demand (COD), microbial load, and heavy metal concentrations in water, sediment, and biota samples, alongside polycyclic aromatic hydrocarbons (PAHs). Phosphate was quantified via ascorbic acid reaction and spectrophotometry, while BOD and COD were determined using 5-day BOD tests and closed reflux methods, respectively. Microbial analysis employed the spread-plate technique, and heavy metals were assessed post-sample digestion using Atomic Absorption Spectroscopy (AAS). PAHs were extracted through liquid-liquid and sonication-based methods followed by gas chromatography-flame ionization detection (GC-FID). Quality assurance included strict adherence to APHA and EPA protocols, calibration with certified standards, and extensive use of blanks, duplicates, and reference materials, ensuring high accuracy, reproducibility, and reliability of data.

Photo Splash of Field Sampling Exercise

Plate 2.1a: Samples in ice ches

Plate 2.1b: Bonny River

Plate 2.1c: Part of the Bonny River used as waste dumpsite

Plate 2.1d: Author with sample from the Bonny River

Photo Splash of Laboratory Analysis at Endpoint Laboratories, Port Harcourt.

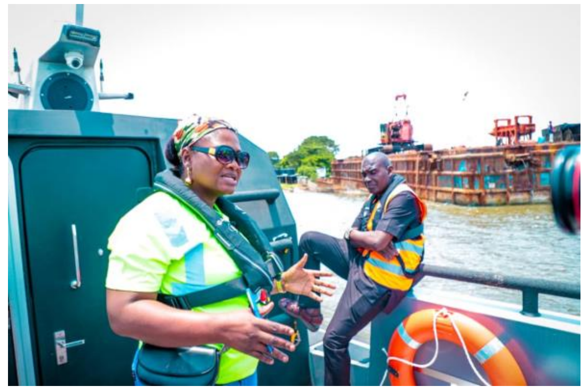

Plate 2.2a: Heavy metals Analyses using the AAS

Plate 2.2b: At Port Harcourt Tourist Beach Plate

3. Results and Discussion

The physicochemical parameters of Bonny River water samples from 15 locations were evaluated against NSDWQ (2015) and WHO (2011) standards. The pH ranged from 6.09 to 7.64, aligning with acceptable limits (6.5–8.5), while temperature (26.87–29.30°C) met ambient criteria. Electrical conductivity (5850.7–16490.8 µS/cm) and total dissolved solids (2925.37–8245.38 mg/L) showed significant spatial variation ($p < 0.05$). Salinity ranged from 1.95 to 5.50 PSU, with total suspended solids averaging 23.43 mg/L. Nutrient levels showed nitrate (5.18 mg/L) and sulfate (238 mg/L) within WHO limits, but phosphate (2.88 mg/L) and chloride (2209 mg/L) exceeded guidelines. BOD5 (2.24–7.41 mg/L) and COD (56.74–112.52 mg/L) indicated organic pollution. Cations such as calcium (220.53–532.76 mg/L) and magnesium (88.35–221.53 mg/L) displayed significant spatial disparities. Microbial counts varied widely (2.0×10^2 to 1.8×10^6 cfu/L), highlighting notable contamination differences across locations.

Table 3.1: Results of Physicochemical Parameters of Surface Water Samples from the different Stations of the Bonny River.

	PARAMETERS															
STATIONS	pH	Temperature (°C)	EC (µ∫/cm)	TDS (mg/L)	Salinity (PSU)	TSS (mg/L)	Chloride (mg/L)	Nitrate (mg/L)	Sulphate (mg/L)	Ammonia (mg/L)	Phosphate (mg/L)	BOD5 (mg/L)	COD (mg/L)	Ca (mg/L)	Mg (mg/L)	Microbial Count (cfu/mL)
W1	6.09^{a}±0.01	27.56^{ab}±0.30	9800.50^{ab}±5.62	4900.25^{ab}±3.40	3.27^{ab}±0.52	25.87^{bc}±1.81	1518.27^{ab}±5.30	5.67^{b}±0.41	230.53^{b}±2.15	1.56^{c}±0.05	2.76^{ab}±0.10	5.72^{b}±0.28	102.85^{b}±7.57	302.83^{ab}±7.120	118.54^{a}±4.530	3.6^{ab}±0.50x10^{3}
W2	6.98^{ab}±0.01	27.88^{ab}±0.14	13110.80^{b}±6.35	6555.40^{b}±5.83	4.37^{b}±0.71	23.62^{b}±1.60	1823.88^{ab}±7.11	3.82^{ab}±0.33	272.16^{b}±2.40	1.26^{ab}±0.02	1.88^{a}±0.08	3.56^{ab}±0.14	98.34^{b}±5.30	420.76^{b}±11.815	158.550^{ab}±3.851	2.8^{ab}±0.31x10^{4}
W3	6.91^{ab}±0.03	29.30^{b}±0.09	8680.30^{ab}±4.51	4340.15^{ab}±2.85	2.89^{ab}±0.30	19.11^{ab}±1.22	1461.62^{a}±3.89	2.97^{a}±0.25	214.82^{ab}±1.74	0.97^{ab}±0.02	2.78^{ab}±0.12	4.67^{b}±0.22	76.21^{ab}±3.88	370.671^{ab}±9.630	134.882^{ab}±3.764	2.2^{a} ±0.28x10^{2}
W4	7.37^{b}±0.02	28.54^{ab}±0.07	15090.80^{c}±7.30	7545.40^{c}±6.22	5.03^{c}±1.10	26.81^{bc}±2.43	2742.68^{b}±3.52	6.36^{b}±0.53	330.48^{c}±2.28	0.36^{a}±0.01	3.56^{b}±0.15	2.24^{a}±0.17	90.25^{b}±4.10	481.560^{b}±14.380	176.310^{b}±5.310	1.8^{b} ±0.43x10^{6}
W5	6.95^{ab}±0.05	26.87^{a}±0.25	16170.50^{c}±9.30	8085.25^{c}±8.11	5.39^{c}±1.52	29.20^{c}±2.30	2932.90^{c}±5.34	8.42^{c}±0.71	360.30^{c}±3.10	1.52^{c}±0.03	4.10^{b}±0.20	3.89^{ab}±0.12	68.31^{a}±3.75	512.670^{c}±10.310	202.871^{b}±4.306	3.2^{ab} ±0.71x10^{4}
W6	6.88^{ab}±0.02	28.10^{ab}±0.08	15160.30^{c}±8.50	7580.15^{c}±7.63	5.05^{c}±0.90	34.95^{d}±2.75	2608.22^{b}±2.85	5.88^{b}±0.52	192.62^{ab}±1.30	0.88^{ab}±0.02	3.75^{b}±0.18	5.78^{b}±0.30	82.62^{b}±4.10	473.980^{b}±8.621	165.650±2.840	2.0^{a} ±0.22x10^{2}
W7	6.93^{ab}±0.02	28.36^{ab}±0.15	15920.70^{c}±8.12	7960.34^{c}±5.30	5.31^{c}±1.60	23.67^{b}±1.88	2884.71^{c}±6.41	5.21^{b}±0.48	223.78^{ab}±2.41	0.52^{a}±0.03	2.52^{ab}±0.12	7.32^{c}±0.35	110.43^{c}±8.24	478.520^{b}±11.330	170.431^{b}±4.211	3.6^{b} ±0.64x10^{5}
W8	6.95^{ab}±0.04	27.86^{ab}±0.31	13950.20^{b}±7.30	6975.11^{b}±4.80	4.65^{b}±0.83	19.28^{ab}±1.75	2362.93^{b}±3.92	4.27^{ab}±0.35	210.82^{ab}±1.88	1.36^{b}±0.04	1.93^{a}±0.06	4.80^{b}±0.28	73.71^{ab}±2.90	423.882^{b}±9.530	134.621^{ab}±2.870	4.3^{a} ±0.32x10^{2}
W9	7.26^{b}±0.02	27.28^{ab}±0.18	15010.50^{c}±8.30	7505.26^{c}±7.22	5.00^{c}±1.17	26.70^{bc}±2.30	2551.41^{b}±4.20	7.18^{c}±0.61	315.95^{c}±2.94	1.22^{ab}±0.03	5.30^{c}±0.24	7.41^{c}±0.33	88.35^{b}±5.10	501.726^{b}±12.514	197.268^{c}±4.426	2.8^{ab} ±0.56x10^{4}
W10	6.92^{ab}±0.07	26.97^{a}±0.22	15760.80^{c}±7.55	7880.42^{c}±5.28	5.25^{c}±1.34	30.42^{c}±2.15	2716.88^{b}±7.96	4.93^{b}±0.30	294.82^{c}±2.60	0.89^{ab}±0.03	2.86^{ab}±0.15	5.70^{b}±0.26	65.48^{a}±2.70	454.128^{b}±10.130	153.672^{ab}±2.832	3.2^{a} ±0.35x10^{2}
W11	6.95^{ab}±0.03	28.47^{ab}±0.13	10220.80^{ab}±5.40	5110.39^{ab}±3.35	3.41^{ab}±0.48	27.89^{bc}±2.80	1640.67^{ab}±4.34	2.75^{a}±0.18	183.62^{a}±1.73	0.37^{a}±0.02	1.67^{a}±0.05	3.35^{ab}±0.12	112.52^{c}±8.72	382.880^{ab}±7.226	137.635^{ab}±3.355	1.7^{b} ±0.21x10^{5}
W12	7.31^{b}±0.02	27.87^{ab}±0.12	14610.60^{b}±6.87	7305.29^{b}±5.23	4.87^{b}±0.91	18.43^{ab}±1.30	2303.78^{b}±5.60	8.22^{c}±0.90	221.88^{ab}±1.50	1.20^{ab}±0.03	2.10^{a}±0.09	6.36^{c}±0.38	82.66^{b}±5.22	462.631^{b}±9.643	150.434^{ab}±2.370	2.3^{ab}±0.48x10^{4}
W13	6.85^{ab}±0.04	26.98^{a}±0.30	16490.80^{c}±9.41	8245.38^{c}±7.58	5.50^{c}±1.80	21.56^{b}±1.76	2925.21^{c}±8.51	5.95^{b}±0.43	195.32^{ab}±1.45	1.18^{ab}±0.02	3.42^{b}±0.13	2.88^{a}±0.09	56.74^{a}±2.36	532.755^{c}±13.735	221.532^{c}±4.225	1.5^{b} ±0.17x10^{5}
W14	6.85^{ab}±0.02	28.12^{ab}±0.07	7240.40^{a}±5.30	3620.18^{a}±3.57	2.41^{a}±0.23	13.29^{a}±0.97	1379.54^{a}±4.30	3.40^{ab}±0.26	173.56^{a}±1.20	0.88^{ab}±0.03	2.73^{ab}±0.11	4.52^{b}±0.23	60.28^{a}±3.12	289.452^{a}±5.820	97.264^{a}±1.936	2.6^{a} ±0.25x10^{2}
W15	7.64^{b}±0.05	27.53^{ab}±0.18	5850.73^{a}±3.70	2925^{a}.37±1.65	1.95^{a}±0.08	10.63^{a}±0.50	1287.33^{a}±3.85	2.67^{a}±0.20	156.30^{a}±0.80	0.97^{ab}±0.02	1.88^{a}±0.04	3.65^{ab}±0.18	72.72^{ab}±0.34	220.530^{a}±3.753	88.351^{a}±1.705	3.1^{a} ±0.69x10^{2}
P- Value	P<0.05	P<0.05	P<0.05	P<0.05	P<0.05	P<0.05	P<0.05	P<0.05	P<0.05	P<0.05	P<0.05	P<0.05	P<0.05	P<0.05	P<0.05	P<0.05
NSDWQ Limits	6.5-8.5	Ambient	1000	500	-	-	250	50	100	-	-	-	-	-	0.20	-
WHO Limits	6.5-8.5	28	1000	500	-	5	250	10	500	-	0.4	4	10	-	-	-

NB: $p < 0.05$ – Significant; $p > 0.05$ – Not Significant;. Similar superscript indicates no significant difference, Unsimilar superscript indicates significant difference

Table 3.2: Summary of the Results for Physicochemical Parameters of Surface Water.

	Range		
Parameters	**Minimum**	**Maximum**	**Mean**
pH	6.09	7.64	6.87±0.06
Temperature(°C)	26.87	29.3	28.09±0.17
EC (µ∫/cm)	5850.73	16490.76	11170.75±6.56
TDS (mg/L)	2925.365	8245.38	5585.37±4.62
Salinity (PSU)	1.950	5.50	3.72±0.94
TSS (mg/L)	10.63	34.95	22.79±1.63
Chloride (mg/L)	1287.33	2932.9	2110.12±4.60
Nitrate (mg/L)	2.67	8.42	5.55±0.46
Sulphate (mg/L)	156.3	360.3	258.30±1.95
Ammonia (mg/L)	0.36	1.56	0.96±0.03
Phosphate (mg/L)	1.67	5.30	3.49±0.15
BOD_5 (mg/L)	2.24	7.41	4.83±0.25
COD (mg/L)	56.74	112.52	84.63±5.54
Ca (mg/L)	220.53	532.755	376.64±8.74
Mg (mg/L)	88.351	221.532	154.94±2.97
Microbial Count (cfu/mL)	2.0×10^2	1.8×10^6	$9.0 \pm 0.33 \times 10^5$

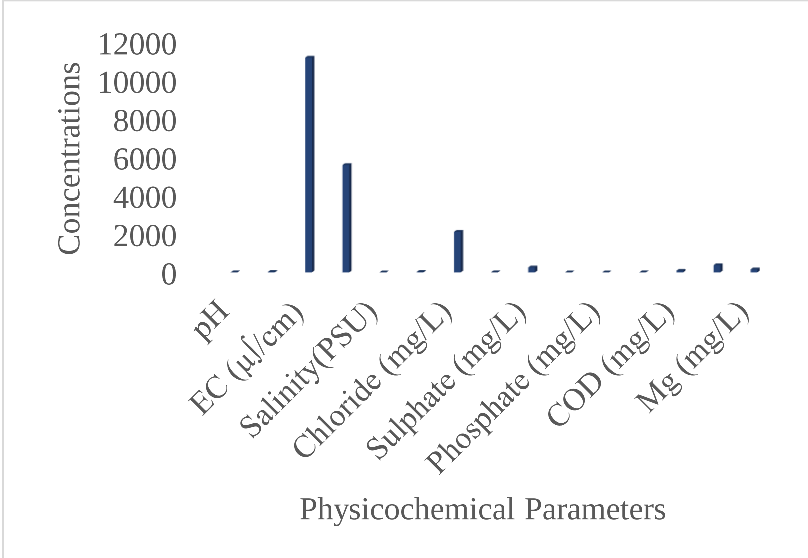

Figure 3.1: Mean Concentrations of Physicochemical Parameters in the Surface Water of the different Stations of the Bonny River

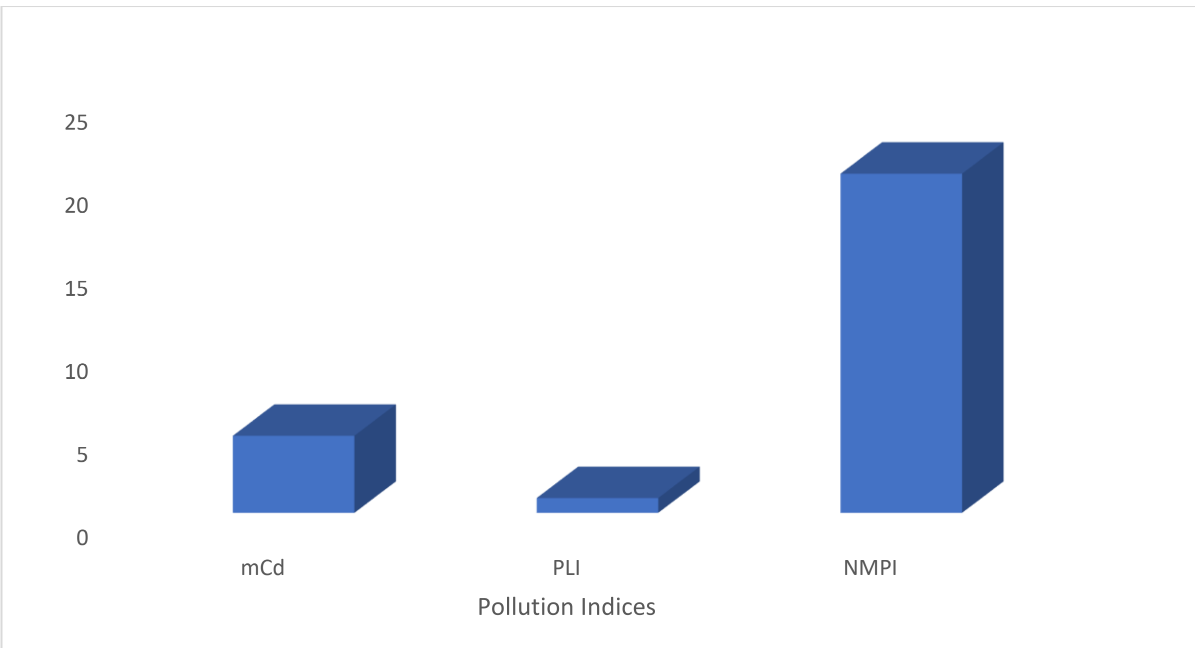

Figure 3.2: Pollution Indices of heavy metals contaminations in water samples
*mCd (Modified contamination degree), PLI (Pollution Load Index), NMPI (Nemerow Multi pollution index)

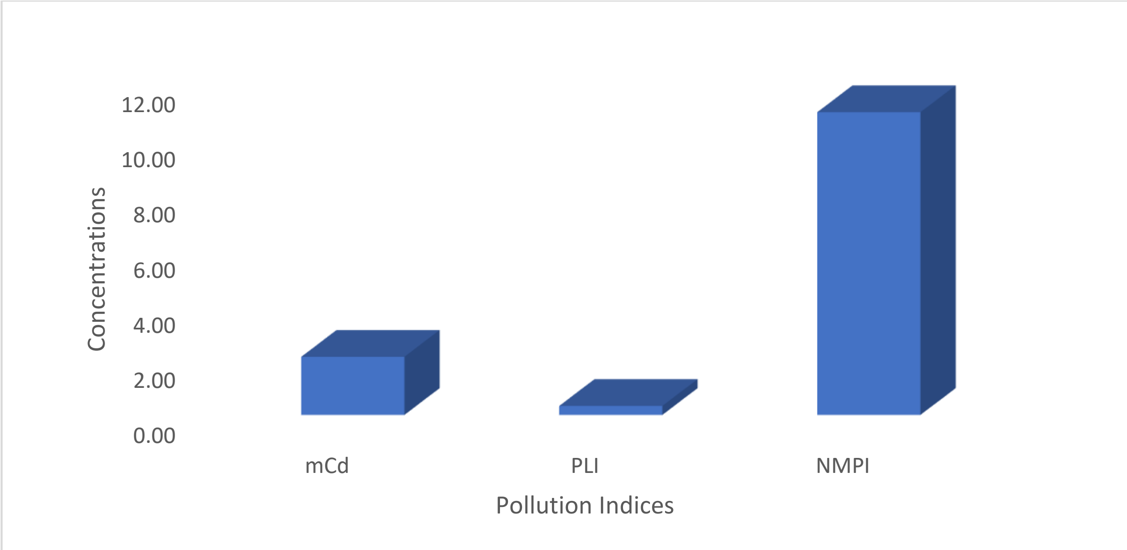

Figure 3.3: Pollution Indices of heavy metals contaminations in sediment samples
*mCd (Modified contamination degree), PLI (Pollution Load Index), NMPI (Nemerow Multi pollution index)

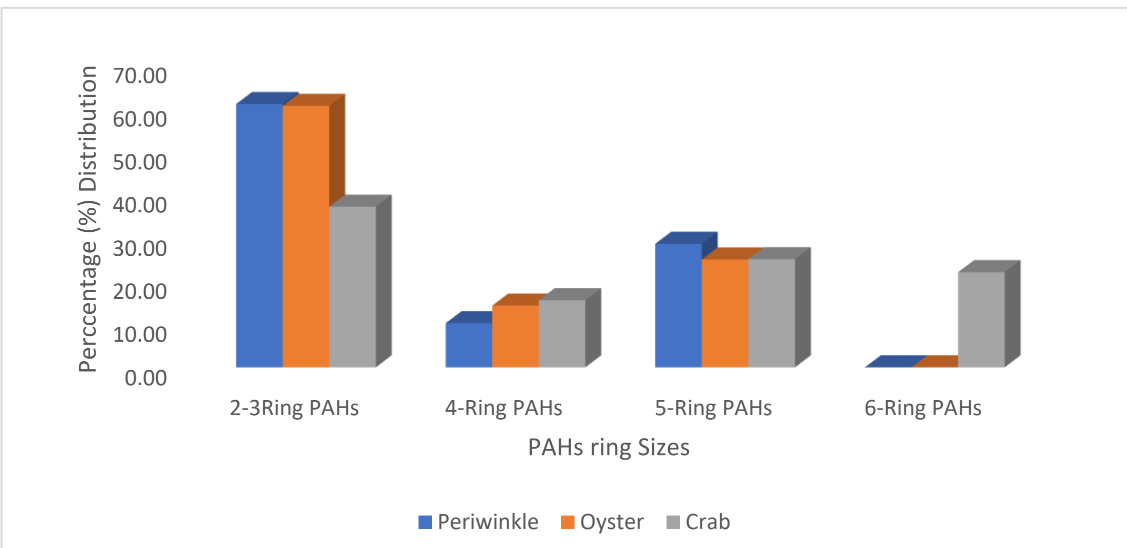

Figure 3.4: The percentage distribution of PAHs ring-size in seafoods

The heavy metal concentrations in Bonny River surface water exhibited significant spatial variability ($p < 0.05$) across sampling points. Arsenic (As) levels ranged from non-detectable to 0.016 mg/L, with a mean of 0.006 mg/L, falling below both WHO (0.05 mg/L) and NSDWQ (0.01 mg/L) limits. Copper (Cu) concentrations varied between 0.022 and 0.045 mg/L, with a mean of 0.035 mg/L, below the WHO (0.5 mg/L) and NSDWQ (1.0 mg/L) limits. Cadmium (Cd) levels ranged from non-detectable to 0.025 mg/L, with a mean of 0.013 mg/L, exceeding the WHO and NSDWQ limit of 0.003 mg/L. Chromium (Cr) concentrations ranged from non-detectable to 0.251 mg/L, with a mean of 0.044 mg/L, below the WHO and NSDWQ limits. Cobalt (Co) ranged from 0.017 to 0.083 mg/L, with a mean of 0.041 mg/L, below the WHO limit of 0.05 mg/L. Lead (Pb) concentrations ranged from 0.168 to 0.335 mg/L, with a mean of 0.285 mg/L, exceeding both WHO and NSDWQ limits (0.01 mg/L). Iron (Fe) concentrations ranged from 0.873 to 3.518 mg/L, with a mean of 1.894 mg/L, exceeding the WHO and NSDWQ limits of 0.3 mg/L. Manganese (Mn) concentrations ranged from 0.033 to 0.152 mg/L, with a mean of 0.064 mg/L, below both WHO and NSDWQ limits. Zinc (Zn) levels ranged from 0.159 to 0.546 mg/L, with a mean of 0.358 mg/L, well below the WHO and NSDWQ limit of 3 mg/L. Iron had the highest concentration, while arsenic had the lowest among the metals analyzed.

Table 3.3: Summary of Heavy Metal Concentrations in Surface Water Samples Compared with Standard Regulatory Limits.

	Range		
Heavy metals (mg/L)	**Minimum**	**Maximum**	**Mean±SD**
As (mg/L)	0.000±0.000	0.016±0.005	0.006±0.002
Cu (mg/L)	0.022±0.005	0.045±0.011	0.035±0.007
Cd (mg/L)	0.000±0.000	0.025±0.008	0.013±0.004
Cr (mg/L)	0.000±0.000	0.251±0.005	0.044±0.005
Co (mg/L)	0.017±0.002	0.083±0.018	0.041±0.009
Pb (mg/L)	0.168±0.014	0.335±0.033	0.285±0.019
Fe (mg/L)	0.873±0.037	3.518±0.560	1.894±0.196
Mn (mg/L)	0.033±0.008	0.152±0.017	0.064±0.010

Zn (mg/L)	0.159±0.012	0.546±0.034	0.358±0.018

Table 3.4: Pearson's Correlation Coefficients Analysis of Water Samples

	As	Cu	Cd	Cr	Co	Pb	Fe	Mn	Zn
As	1								
Cu	0.544	1							
Cd	0.641	0.870	1						
Cr	0.356	0.555	0.576	1					
Co	0.361	0.551	0.557	-0.020	1				
Pb	0.582	0.888	0.908	0.458	0.601	1			
Fe	-0.006	0.017	-0.205	-0.074	-0.263	-0.066	1		
Mn	-0.456	-0.139	-0.451	-0.253	0.061	-0.295	-0.102	1	
Zn	0.144	0.300	0.389	0.295	0.446	0.417	-0.618	0.207	1

Table 4.5: PCA Analysis of Water Samples

	Components		
Heavy Metals	PC1	PC2	PC3
As	0.357	0.006	-0.246
Cu	0.902	0.059	0.046
Cd	0.813	-0.168	-0.318
Cr	0.339	-0.037	-0.111
Co	0.430	-0.145	0.070
Pb	0.886	0.007	-0.157
Fe	-0.001	0.963	-0.031
Mn	-0.144	-0.045	0.956
Zn	0.221	-0.400	0.147
Eigen value	4.287	1.793	1.028

% of Variance	47.64	19.92	11.42
Cumulative %	47.64	67.55	78.98

3.1 Discussion

The physicochemical assessment of the Bonny River highlights concerning pollution levels, with several parameters exceeding WHO and NSDWQ standards. While the pH (6.09–7.64) remained within acceptable limits, suggesting limited acidity or alkalinity alterations, elevated electrical conductivity (up to 16,490.76 µS/cm), total dissolved solids, and salinity indicate substantial seawater intrusion and anthropogenic contributions from industrial and urban runoff (Aghoghovwia et al., 2021; Ajibola et al., 2022). High phosphate levels (1.67–5.30 mg/L) and elevated biochemical oxygen demand (BOD5: 4.83 mg/L) point to eutrophication and organic pollution, which exacerbate oxygen depletion and harm aquatic life (Onwuchekwa et al., 2023). Furthermore, increased chemical oxygen demand (COD: 84.63 mg/L) and microbial counts signify significant contamination from untreated sewage and industrial discharges, posing severe health risks to water users and the ecosystem (Chukwuocha et al., 2021; Ubah et al., 2023). These findings emphasize the urgent need for robust pollution control policies, improved waste management systems, and consistent water quality monitoring efforts.

The Bonny River in Nigeria is an essential water body supporting human and ecological functions but faces heavy metal contamination posing environmental and health challenges. For arsenic (As), concentrations ranged from non-detectable to 0.016 mg/L, with a mean of 0.006 ± 0.002 mg/L, below WHO and NSDWQ limits, suggesting minimal health risk (Joebolosho et al., 2023; Nubi et al., 2020). Copper (Cu) levels ranged from 0.022 to 0.045 mg/L, with a mean of 0.035 ± 0.007 mg/L, also below regulatory limits, reflecting minimal contamination (Jolaosho et al., 2023). However, cadmium (Cd) concentrations exceeded permissible levels with a mean of 0.013 ± 0.004 mg/L, highlighting contamination from industrial and anthropogenic activities (Obianefo et al., 2018; Mahdi et al., 2021). Chromium (Cr) levels, averaging 0.044 ± 0.005 mg/L, were below thresholds but demonstrated local industrial influences (Akan et al., 2010). Lead (Pb) concentrations significantly exceeded safe limits, with a mean of 0.285 ± 0.019 mg/L, linked to industrial discharges and oil spills (Nduka & Orisakwe, 2010). Similarly, iron (Fe) and manganese (Mn) levels indicated notable contamination, especially Fe with a mean of 1.894 ± 0.196 mg/L, surpassing WHO limits (Edori & Iyama, 2020). Zinc (Zn) levels remained within acceptable ranges, reflecting moderate impact (Essien et al., 2009). These findings underline the urgent need for stringent pollution control and effective water management strategies to mitigate health and ecological risks.

The assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in water, sediments, and biota from 15 sampling stations along the Bonny River highlighted the significant contamination of these environmental compartments by both pyrogenic and petrogenic sources. Water samples showed high concentrations of carcinogenic PAHs, such as Benzo(a)pyrene, while sediment samples revealed a mixture of PAH sources, indicating contamination from oil spills and industrial activities (Akinmoladun et al., 2021; Oluwaseun et al., 2023). The bioaccumulation of these toxic compounds in biota, particularly in species near pollution sources, suggests a potential risk to the aquatic food chain and human health. These findings align with recent studies in the Niger Delta, confirming both combustion and petroleum-related sources as significant contributors to PAH pollution in aquatic environments (Abah et al., 2023). The persistence and toxicity of PAHs in these ecosystems underscore the need for effective pollution control measures to mitigate health risks associated with long-term exposure (Olajire et al., 2022).

5 Conclusion

This study assessed the levels of polycyclic aromatic hydrocarbons (PAHs) and heavy metals in water, sediment, and biota from fifteen strategically chosen stations along the Bonny River, including 15 sampling points such as Jetty to Mguodeya, Eagle Island opposite Emenike waterfront, and 107 Emenike Street waterfront by Slaughter. Other stations included locations like the Abonnema Wharf Rd, Oil Terminal, Wait and Bush Jetty, Nembe Jetty, Old PH Tourist Beach 1, Port Harcourt Tourist Beach 2, and Borokiri Sandfill 1. These stations were selected to represent various potential sources of pollution, ranging from urban runoff to industrial and oil-related activities. The study revealed that contaminants in water and sediment, such as electrical conductivity, chloride, and chemical oxygen demand, exceeded national and WHO standards, indicating significant pollution. Heavy metals in water samples posed substantial health risks, and sediment analysis showed high levels of cadmium and lead. Biota, including oysters, crabs, and periwinkles, exhibited alarming bioaccumulation of these metals, signaling a serious environmental and public health concern. PAH sources were identified as a mix of pyrogenic (combustion-related) and petrogenic (oil-related) activities, with diagnostic ratios and correlations indicating complex contamination sources. PAH analysis in biota demonstrated elevated carcinogenic potential, especially in oysters and crabs, highlighting the need for stronger pollution control measures and monitoring efforts across the river.

6. Recommendations

Based on the findings, we propose the following actions:

i. Strengthen Pollution Control: Industrial discharges and urban runoff were identified as major sources of PAHs and heavy metals. Tighter regulations on industrial waste and urban runoff are needed to reduce contamination levels, especially in sediments and seafood.

ii. Enhance Public Awareness: The carcinogenic and non-carcinogenic risks associated with seafood consumption, including high B(a)Pteq levels in oysters and crabs, indicate a need for increased community education on the health risks of consuming contaminated seafood.

iii. Adopt Bioremediation: Given the high levels of BOD, COD, and heavy metals, bioremediation strategies should be implemented to restore water and sediment quality and mitigate contamination.

iv. Implement Monitoring Programs: Continuous monitoring is essential to track contamination trends, as identified by PCA and PAH diagnostic ratios, to ensure the effectiveness of pollution control measures and sustain environmental health.

v. Incorporate Health Risk Assessments: The elevated carcinogenic risks from seafood, which exceed safety thresholds, should be integrated into policy frameworks to establish stricter safety measures and provide alternative protein sources for affected communities.

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