



Oil-Derived Polycyclic Aromatic Hydrocarbons and Total Petroleum Hydrocarbons in Surface Water of Okpare Olomu River, Niger Delta: Contamination Levels and Risk Evaluation.

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Abstract. This study investigates the contamination of surface water in the Okpare Olomu River, an oil-producing region in the Niger Delta, Nigeria, focusing on polycyclic aromatic hydrocarbons (PAHs) and total petroleum hydrocarbons (TPHs). Surface water samples from four stations were analyzed using gas chromatography. Sixteen priority PAHs were detected, with total concentrations ranging from 1006.19 µg/L at Station 1 to 2022.26 µg/L at Station 3, indicating a predominantly petrogenic origin. Twenty-eight TPH compounds were identified, with total concentrations ranging from 1914.31 to 5621.50 µg/L. Station 4 exhibited the highest TPH levels, followed by Stations 2, 1, and 3. Concentrations exceeded Nigerian and international guideline limits by several orders of magnitude, with WHO's 10 µg/L guideline for drinking water surpassed by over 500-fold at some stations. Diagnostic ratios and the presence of low molecular weight hydrocarbons suggested crude oil-related inputs alongside evidence of weathering and partial biodegradation. Statistical analyses, including ANOVA and multivariate methods, confirmed significant spatial variation and a strong positive association between PAHs and TPHs, reflecting common pollutant sources. The contamination levels pose serious ecological risks to aquatic biota and potential human health hazards through water and food chain exposure. These findings align with earlier reports of petroleum hydrocarbon pollution in the Niger Delta but highlight even higher contamination levels in this locality. The study underscores the urgent need for remediation, continuous monitoring, and stricter enforcement of environmental regulations to protect the ecosystem and dependent communities

Keywords: Total Petroleum Hydrocarbons (TPH), Polycyclic Aromatic Hydrocarbons (PAHs), Oil

Pollution, Okpare Olomu River, Ecological Risk Assessment, Niger Delta

1. Introduction

Rivers and streams are essential natural resources that support domestic, agricultural, and industrial activities. However, they are increasingly exposed to pressures from both natural processes and human activities. When contaminant levels surpass the natural self-purification capacity of aquatic systems, the quality of water deteriorates, threatening aquatic organisms and human health (Boyd, 2020). In regions where crude oil production dominates, hydrocarbon pollution is a major concern because of its persistence, toxicity, and long-term ecological impacts.

Among petroleum-related pollutants, polycyclic aromatic hydrocarbons (PAHs) and total petroleum hydrocarbons (TPHs) are of particular interest due to their widespread occurrence and health significance. PAHs are a group of hydrophobic organic molecules that enter aquatic environments primarily through oil spills, petroleum discharges, atmospheric fallout, and incomplete combustion of fossil fuels. They are resistant to degradation, tend to accumulate in sediments and living organisms, and several congeners are classified as carcinogenic and mutagenic, making them priority pollutants under USEPA regulations (Nasr *et al.*, 2012; Leon *et al.*, 2014; Dong *et al.*, 2021). TPHs, on the other hand, represent a complex mixture of aliphatic and aromatic hydrocarbons and are often measured collectively as an indicator of petroleum contamination. Elevated concentrations of TPHs in aquatic systems can lower dissolved oxygen, disrupt aquatic balance, and pose chronic health threats when humans consume contaminated water or

aquatic species (ATSDR, 1999; Pampanin and Sydnes, 2010; Inyang *et al.*, 2018).

The sources of hydrocarbon contamination in surface waters are diverse, ranging from crude oil extraction and pipeline failures to artisanal refining, industrial effluents, and surface runoff (Chikere *et al.*, 2009; Anyanwu *et al.*, 2021). In the Niger Delta, decades of intensive petroleum exploitation have resulted in extensive environmental degradation. Numerous studies have linked these activities to the contamination of rivers, creeks, and wetlands, with serious implications for biodiversity, fisheries, and human well-being (Egubbe *et al.*, 2015; Anyanwu *et al.*, 2021). Hydrocarbon presence in water alters chemical and physical properties, reduces water quality, and adversely affects aquatic biodiversity and ecological services (Boyd, 2020; Tundu *et al.*, 2018; Wen *et al.*, 2007). The Okpare Olomu River, located in Ughelli South, Delta State, is a water body of both ecological and socio-economic significance. It provides drinking water, supports fishing and farming, and sustains numerous domestic uses for local communities. Despite this importance, comprehensive investigations of hydrocarbon levels in the river remain scarce. Preliminary reports indicate the occurrence of petroleum hydrocarbons and related ecological risks (Diejomaoh and Okoro, 2024). However, detailed assessments are lacking, and this knowledge gap limits the effectiveness of monitoring and management efforts. In view of this, the present study examines the concentrations and patterns of PAHs and TPHs in the Okpare Olomu River and evaluates their potential ecological and human health implications.

2.1 Sampling Design and Locations

Surface water samples were collected from four monitoring stations along the Okpare Olomu River to capture spatial variations in hydrocarbon contamination. The GPS coordinates for each location are:

Station 1 / Ejeba Okpare	N 05° 27. 795'	E 005° 54. 409'
Station 2 / Uhrovwodo Okpare	N 05° 27. 600'	E 005° 53. 980'
Station 3 / Ogbe Okpare	N 05° 27. 115'	E 005° 53. 742'
Station 4 / Arovie Okpare	N 05° 25. 859'	E 005° 53. 569'

Sampling campaigns were conducted monthly over a 12-month period (January–December 2020) to encompass both wet and dry seasonal dynamics. A map illustrating the study area and sampling sites is presented in Figure 1.

1.1 Climatic Conditions

The climate of the region is typically equatorial, with two dominant seasons a humid rainy season and a relatively dry season. Annual rainfall is heavy, averaging around 3,000 mm, and is most intense between April and September, while a shorter dry season occurs between November and March (Agbaire and Emoyan, 2012; Okumagba and Ozabor, 2014). Humidity levels are generally high in the wet months, while the dry season is marked by increased temperatures. Mean annual temperature is approximately 30°C, with average daily maximum values between 28°C and 33°C and minimum values between 22°C and 26°C ([19] Okumagba and Ozabor, 2014).

2. Materials and Methods: Study Area

This investigation was carried out in Okpare Olomu, situated within Ughelli South Local Government Area of Delta State, Nigeria, at approximately Latitude 5°30'N and Longitude 6°00'E. The sampling points were carefully selected based on the level of human activity in the vicinity and documented cases of oil spill incidents. Delta State occupies a landmass of about 16,842 km² (Ebewore, 2020) and lies in the tropical rainforest ecological zone of southern Nigeria. The area is ecologically diverse, supporting numerous terrestrial and aquatic organisms, but is also highly vulnerable to oil exploration–related disturbances (NDES, 1997; Uyigwe and Agho, 2007; Ekpo *et al.*, 2018).

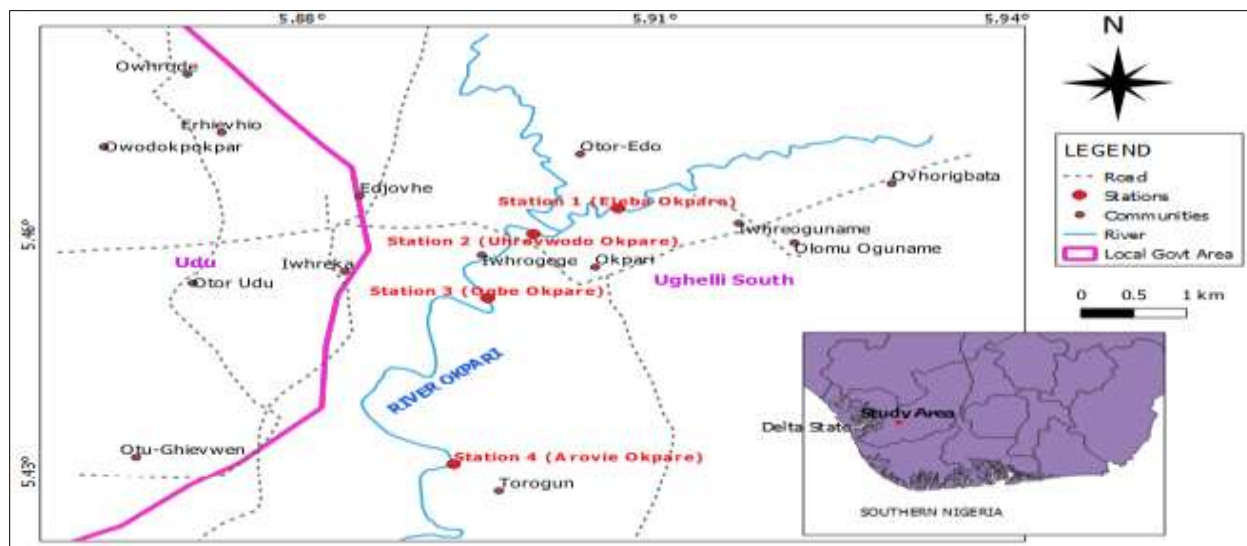


Figure 1: Map of Ughelli South showing water and sediment sampling stations
Source: ArcGIS Map

2.2 Sampling Periodicity

The four sampling stations were monitored quarterly over a one-year period, resulting in five separate field campaigns. During each campaign, five replicate samples were collected from each station to ensure reliability and representativeness of the data. Field sampling activities were typically carried out between 07:00 and 11:00 hours (Nigerian time) to minimize diurnal variations in water quality parameters. Sampling commenced at Station 1 (upstream) and proceeded sequentially to Station 4 (downstream). At each location, surface water samples were collected simultaneously for the analysis of all targeted parameters, including hydrocarbons. Prior to each field trip, all sampling equipment and analytical devices were inspected and calibrated according to the manufacturer's specifications to ensure accuracy and data integrity.

2.3 Methods for Polycyclic Aromatic Hydrocarbons (PAHs) and Total Petroleum Hydrocarbons (TPHs) Analysis:

2.3.1 Sample Extraction and Cleanup

The determination of PAHs and TPHs in water samples was performed using a modified USEPA ([2002] method for the gas chromatographic analysis of diesel-range organics (DRO). Soxhlet extraction was employed for hydrocarbon recovery. A 10 mL aliquot of each water sample was digested using an aluminum block digester (BD 110) after adding 4 mL perchloric acid, 20 mL concentrated nitric acid, and 2 mL concentrated sulfuric acid. The mixture was

heated until the appearance of white fumes and a clear solution was obtained. The extract was evaporated to near dryness using a rotary vacuum evaporator maintained at 40 °C.

For sample cleanup, the residue was reconstituted with n-hexane and transferred onto a 5 mL Florisil column. Florisil (magnesium silicate, 60–100 mesh) was pre-activated by oven-heating at 130 °C for 15 h and stored in a desiccator until use. A mixture of 1 g Florisil and 0.5 g anhydrous sodium sulfate (Na_2SO_4) was packed into an 8 mL glass column plugged with glass wool. The column was conditioned with 5 mL n-hexane before loading the extract. After sample loading with a disposable Pasteur pipette, each evaporating flask was rinsed twice with 1 mL n-hexane and added to the column. The eluate was collected, rotary-evaporated to dryness, and finally re-dissolved in 1 mL n-hexane for subsequent chromatographic analysis.

2.3.2 Polycyclic aromatic hydrocarbon analysis

Polycyclic aromatic hydrocarbons (PAHs) were quantified using an HP 5890 PLUS II gas chromatograph (Hewlett-Packard, USA) equipped with a Flame Ionization Detector (FID) and an HP 7353 auto-sampler. The system was fitted with an HP-5 capillary column (30 m × 0.32 mm internal diameter × 0.5 μm film thickness). Nitrogen served as the carrier gas, and the injection port was operated at a temperature of 250 °C. The detector temperature was maintained at 350 °C to prevent analyte condensation. One microlitre of each sample extract was injected into the column in split mode. The oven temperature was initially set at 100 °C and held for one minute,

then ramped at a rate of 4 °C per minute to 200 °C, held for one minute, and subsequently increased at 5 °C per minute to 320 °C, giving a total run time of approximately 51 minutes. Data acquisition and processing were carried out using Agilent ChemStation software.

2.3.4 Total Petroleum Hydrocarbon Analysis

Similarly, total petroleum hydrocarbons (TPHs) were analyzed using the same HP 5890 PLUS II GC-FID system with identical column and auto-sampler specifications. The carrier gas was nitrogen, while hydrogen and compressed air served as auxiliary gases. The injection port and detector were maintained at 250 °C and 350 °C, respectively, and an injection volume of 1 µL was used. The oven temperature program for TPH analysis differed slightly, with an initial setting of 50 °C, followed by a ramp of 5 °C per minute to 280 °C, which was held for six minutes, resulting in a total run time of approximately 52 minutes. All gas flows, split ratios, injection and detector temperatures were optimized and verified prior to analysis, and the GC system was calibrated with appropriate hydrocarbon standards to ensure accurate and reliable quantification.

2.4 Instrument Calibration and Quality Control

All gas flow rates, split ratios, injection, and detector temperatures were optimized and verified before analysis to ensure data reliability. The GC system was checked for leaks and calibrated using appropriate hydrocarbon standards prior to sample runs. Detector temperatures were maintained at the upper end of the oven range to minimize analyte condensation or precipitation.

2.5 Statistical Analysis

Statistical analyses were performed using Microsoft Excel, SPSS version 20.0 and PAST4. Descriptive statistics summarized the data, while one-way ANOVA assessed differences in PAH and TPH concentrations among stations; significant results ($p < 0.05$) were further examined using Duncan's Multiple Range test. Multivariate analyses, including cluster analysis (PAST4) and principal component analysis with varimax rotation (R), were applied to explore patterns among variables, and Pearson correlation was used to evaluate relationships between parameters.

3. Results

The concentrations of polycyclic aromatic hydrocarbons (PAHs) detected in water samples from the Okpare Olomu River are summarized in Table 1. Of the sixteen (16) PAH compounds regulated by the United States Environmental Protection Agency (USEPA[20]) due to their potential human and ecological health effects, twelve (12) were detected across the sampling stations. These included naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene and benzo(g,h,i)perylene. The detected PAHs were classified into low molecular weight (LMW) PAHs (2–4 fused aromatic rings) and high molecular weight (HMW) PAHs (5–6 fused aromatic rings). The LMW PAHs comprised naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, and fluoranthene, whereas the HMW PAHs included pyrene, chrysene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene, and benzo(g,h,i)perylene. Four PAHs fluoranthene, benzo(a)anthracene, benzo(b)fluoranthene and benzo(k)fluoranthene were not detected in any of the water samples. Statistical analysis revealed no significant variation ($p > 0.05$) in PAH concentrations among the four sampling stations.

Table 1: Polycyclic Aromatic Hydrocarbons (PAHs) content of surface water samples at four sampled stations

$\bar{x} \pm SD$ = average mean generated from values across the months per station, \pm standard deviation; min-max = minimum and

	Station 1 $\bar{x} \pm SD$ (Min-Max)	Station 2 $\bar{x} \pm SD$ (Min-Max)	Station 3 $\bar{x} \pm SD$ (Min-Max)	Station 4 $\bar{x} \pm SD$ (Min-Max)	p-Value
Naphthalene	44.311±88.602 (0.010-177.213) 0.010±0.000	71.043±142.067 (0.010-284.143) 0.010±0.000	602.133±1204.247 (0.010-2408.503) 0.010±0.000	208.197±416.374 (0.010-832.757) 0.010±0.000	p>0.05
Acenaphthylene	(0.010-0.010) 735.376±864.687 (0.010-1670.741)	(0.010-0.010) 1004.250±1159.741 (0.010-2030.989)	(0.010-0.010) 1071.176±1239.568 (0.010-2242.342)	(0.010-0.010) 965.824±1121.931 (0.010-2081.638)	p>0.05
Acenaphthene	36.207±72.393 (0.010-144.797) 0.010±0.000	3.793±7.565 (0.010-15.140) 0.010±0.000	11.552±23.084 (0.010-46.178) 41.724±83.428	14.155±28.290 (0.010-56.590) 26.259±52.497	p>0.05
Fluorene	(0.010-0.010) 0.010±0.000	(0.010-0.010) 0.010±0.000	(0.010-166.867) 24.365±48.710	(0.010-105.004) 29.920±59.821	p>0.05
Phenanthrene	(0.010-0.010) 0.010±0.000	(0.010-0.010) 0.010±0.000	(0.010-97.429) 0.010±0.000	(0.010-119.652) 0.010±0.000	p>0.05
Anthracene	10.495±20.970 (0.010-41.951)	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	p>0.05
Fluoranthene	171.908±202.645 (0.010-393.805)	238.021±319.686 (0.010-676.032)	271.343±285.748 (0.010-607.166)	297.151±352.690 (0.010-694.291)	p>0.05
Pyrene	7.940±15.860 (0.010-31.730)	9.309±18.598 (0.010-37.206)	0.010±0.000 (0.010-0.010)	5.397±10.774 (0.010-21.557)	p>0.05
Chrysene	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	p>0.05
Benzo(a)anthracene	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	p>0.05
Benzo(b)fluoranthene	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	p>0.05
Benzo(k)fluoranthene	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	p>0.05
Benzo(a)pyrene	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	12.609±14.548 (0.010-25.209)	P>0.05
Indeno(1,2,3-cd) pyrene	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	255.250±294.754 (0.010-515.490)	P>0.05
Dibenz(a,h)anthracene	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	0.010±0.000 (0.010-0.010)	13.244±15.368 (0.010-28.478)	P>0.05
Benzo(g,h,i)perylene	1006.198±969.018 (0.010-2064.546)	1326.385±1356.556 (0.010-2707.021)	2022.258±1359.636 (0.010-2849.508)	1862.221±1578.934 (0.010-3413.662)	p>0.05
ΣPAH					

maximum values for each parameter per station; post hoc = values with different superscripts (a > b > c > d) are significantly different (p < 0.05 or 0.01) while values with same superscript are not significantly different (p > 0.05).

*p < 0.05 (significant difference)

**p < 0.01 (highly significant difference)

Across the study area, LMW PAHs accounted for a higher proportion of the detected compounds compared to HMW PAHs. The distribution of LMW PAHs followed the order: Station 3 (1750.95 µg/L) > Station 4 (1244.36 µg/L) > Station 2 (1079.09 µg/L) > Station 1 (826.39 µg/L). In contrast, HMW PAHs were detected at lower concentrations and followed the trend: Station 4 (617.93 µg/L) > Station 3 (271.34 µg/L) > Station 2 (247.33 µg/L) > Station 1 (179.85 µg/L). The total PAH concentrations across the river showed contamination at varying levels, with the overall distribution pattern: Station 3 (2022.26 µg/L) > Station 4 (1862.29 µg/L) > Station 2 (1326.42 µg/L) > Station 1 (1006.24 µg/L). These findings are consistent with previous studies reporting PAHs in aquatic ecosystems at levels that raise concerns regarding persistence and potential bioaccumulation.

At the individual station level, notable variations were observed in the composition of PAHs across the study area. In Station 1, six compounds accounted for the highest contributions, with acenaphthene (735.38 µg/L) being most abundant, followed by pyrene (171.91 µg/L), naphthalene (44.31 µg/L), fluorene (36.21 µg/L), fluoranthene (10.50 µg/L), and chrysene (7.94 µg/L). The distribution pattern in this station varied considerably across sampling months, reflecting uneven temporal occurrence. In Station 2, five dominant PAHs were recorded, led by acenaphthene (1004.25 µg/L), then pyrene (238.02 µg/L), naphthalene (71.04 µg/L), chrysene (9.31 µg/L), and fluorene (3.79 µg/L); their concentrations fluctuated monthly, further indicating temporal variation. Station 3 similarly exhibited six key PAHs, where acenaphthene (1071.18 µg/L) had the highest concentration, followed by naphthalene (602.13 µg/L), pyrene (271.34 µg/L), phenanthrene (41.72 µg/L), anthracene (24.37 µg/L), and fluorene (11.52 µg/L); unlike Stations 1 and 2, PAH concentrations at this site were more evenly distributed throughout the sampling period. In Station 4, eleven

PAHs were detected, with acenaphthene (965.82 µg/L) dominating, followed by pyrene (297.15 µg/L), dibenz(a,h)anthracene (255.25 µg/L), naphthalene (208.20 µg/L), benzo(a)pyrene (34.28 µg/L), anthracene (29.92 µg/L), phenanthrene (26.26 µg/L), fluorene (14.16 µg/L), benzo(g,h,i)perylene (13.24 µg/L), indeno(1,2,3-cd)pyrene (12.61 µg/L), and chrysene (5.40 µg/L); compared to the other stations, monthly concentrations here showed relatively even distribution. Overall, these spatial trends confirm that PAH contamination was widespread throughout the Okpare Olomu River, with the lower molecular weight fractions dominating the overall profile. Figure 2 shows the spatial and temporal variation in PAH compounds in at the sampled stations during sampling months.

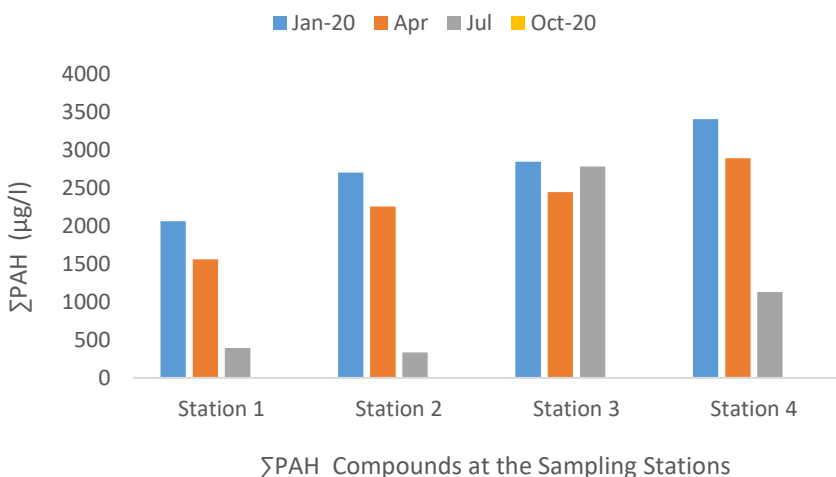


Figure 2 shows the spatio-temporal variation in ΣPAH compounds at the sampled stations during sampling months.

Cluster Analysis for PAHs in Surface Water from Okpare Olomu River

The Euclidean similarity and distance indices for polycyclic aromatic hydrocarbons (PAHs) in surface water from the Okpare Olomu River are presented in Table 2, while Figure 3 illustrates the dendrogram generated from the cluster analysis. The analysis was based on the total PAH concentrations obtained from the four sampling stations: Station 1 (Ejeba Okpare), Station 2 (Uhrovwodo Okpare), Station 3 (Ogbe Okpare), and Station 4 (Arovie Okpare). The Euclidean dissimilarity and distance indices revealed distinct variations among the stations, with values of 0.000 between identical stations, 425.513 between Stations 1 and 2, 1212.150 between Stations 1 and 3, and 947.243 between Stations 1 and 4. Additional dissimilarities were observed between Stations 2 and 3 (879.980), Stations 2 and 4 (615.846), and Stations 3 and 4 (509.435) (Table 2).

The dendrogram indicated that the prevailing conditions at Station 1 during sampling were markedly different from those at Stations 3 and 4, though closely related to Station 2. Similarly, the conditions observed at Station 3 differed from those at Stations 1 and 2, but were more similar to Station 4. Overall, the cluster analysis demonstrated that PAH profiles varied across all stations, with no two sites showing identical conditions at the time of sampling. This variation was defined by Euclidean distance metrics and cluster grouping using Ward’s method. These findings suggest that the total PAH concentrations in surface water from Okpare Olomu River exhibit spatially distinct patterns influenced by localized factors.

Table 2: Similarity or Distance Index (Euclidean)

	Station 1	Station 2	Station 3	Station 4
Station 1	0.000			
Station 2	425.513	0.000		
Station 3	1212.150	879.980	0.000	
Station 4	947.243	615.846	509.435	0.000

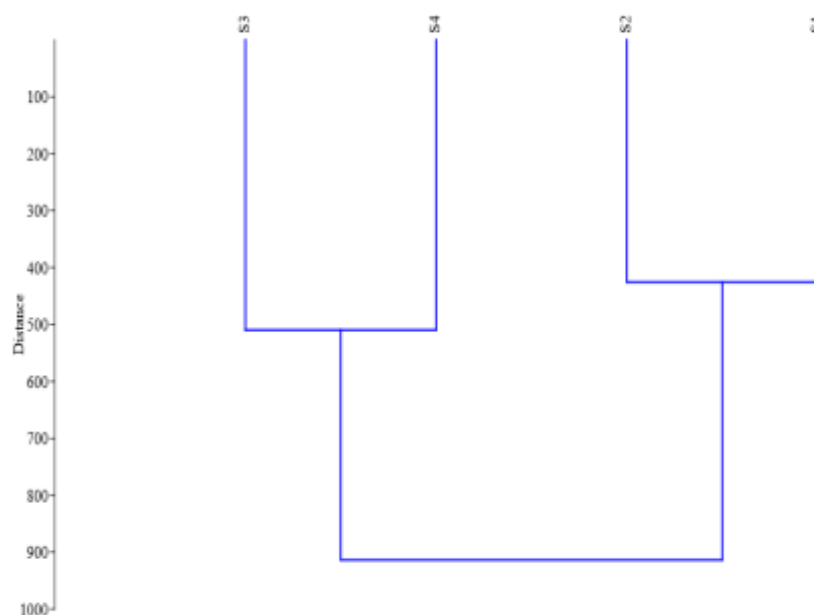


Figure 3: Dendrogram showing cluster analysis of PAH concentrations in surface water from Okpare Olomu River. Dissimilarity was determined using Euclidean distance and Ward's method.

Total Petroleum Hydrocarbon (TPH) in Surface Water from Okpare Olomu River

The results of TPHs in water samples from Okpare Olomu River are presented in Table 3. A total of twenty-eight (28) TPH compounds were analyzed in water samples from the four sampled stations, and all twenty-eight compounds were detected across the study area with varying concentrations. The TPH compounds detected include n-octane, n-nonane, n-decane, n-undecane, n-dodecane, n-tridecane, n-tetradecane, n-pentadecane, n-hexadecane, n-heptadecane, pristane, n-octadecane, phytane, n-nonadecane, n-eicosane, n-heneicosane, n-docasane, n-tricosane, n-tetracosane, n-pentacosane, n-hexacosane, n-heptacosane, n-octacosane, n-nonacosane, n-tricontane, n-hentriacontane, n-dotriacontane, and n-tritriacontane.

Total petroleum hydrocarbon (TPH) refers to a family of chemical compounds that originate from crude oil. Because crude oil and other petroleum products contain numerous chemicals, it is impractical to measure each separately. Instead, measuring the total amount of TPH provides useful insight into overall hydrocarbon contamination in the study area. Anthropogenic activities occurring around the sampled stations exerted similar influences on TPH concentrations in the Okpare Olomu River. TPHs are hydrocarbons because they consist of hydrogen and carbon (ATSDR[5]). As presented in Table 3, the following TPH compounds—n-octane, n-nonane, n-decane, n-undecane, n-dodecane, n-tetradecane, n-pentadecane, n-hexadecane, n-heptadecane, pristane, n-octadecane, phytane, n-nonadecane, n-eicosane, n-tricosane, n-heptacosane, n-hentriacontane, and n-tritriacontane—showed no significant difference ($p > 0.05$) among the sampled stations. However, n-tridecane, n-heneicosane, n-docasane, n-tetracosane, n-pentacosane, n-hexacosane, n-octacosane, n-nonacosane, n-tricontane, and n-dotriacontane exhibited significant differences ($p < 0.05$) between intraspecific variations among the sampled stations. It is evident that the water samples from all four stations were contaminated with TPHs at varying concentrations, with the distribution following the order: Station 4 (5621.503 $\mu\text{g/L}$) > Station 2 (2516.052 $\mu\text{g/L}$) > Station 1 (2297.733 $\mu\text{g/L}$) > Station 3 (1914.306 $\mu\text{g/L}$). For Station 1, ten (10) TPH compounds contributed to the largest group of chemical compounds (values greater than 15 $\mu\text{g/L}$ were used as the benchmark). The distribution order was: n-dotriacontane (953.553 $\mu\text{g/L}$) > n-pentadecane (729.526 $\mu\text{g/L}$) > n-hentriacontane (206.975 $\mu\text{g/L}$) > n-nonane (109.800 $\mu\text{g/L}$) > pristane (59.091 $\mu\text{g/L}$) > n-undecane (50.567 $\mu\text{g/L}$) > n-decane (40.240 $\mu\text{g/L}$) > n-octadecane (24.368 $\mu\text{g/L}$) > n-hexadecane (20.605 $\mu\text{g/L}$) > phytane (18.906 $\mu\text{g/L}$).

Table 3: TPH content of surface water samples at different sample stations

	Station 1 x̄±SD (Min-Max)	Station 2 x̄±SD (Min-Max)	Station 3 x̄±SD (Min-Max)	Station 4 x̄±SD (Min-Max)	p-Value-
n-octane (µg/L)	0.010±0.000 (0.010-0.010) 109.800±160.317	0.010±0.000 (0.010-0.010) 3.214±6.408	4.490±8.961 (0.010-17.932) 42.155±32.600	0.197±0.374 (0.010-0.758) 143.139±171.558	p>0.05
n-nonane (µg/L)	(10.603-349.400) 40.240±23.640	(0.010-12.827) 69.961±102.949	(11.132-70.314) 92.538±109.911	(8.072-394.676) 46.290±20.937	p>0.05
n-decane (µg/L)	(6.656-62.162) 50.567±43.578	(8.330-223.998) 50.227±40.949	(0.469-252.169) 84.962±47.758	(16.735-66.155) 63.896±35.580	p>0.05
n-undecane (µg/L)	(0.480-87.062) 13.762±13.484	(0.630-100.922) 22.930±23.319	(16.455-127.547) 28.030±20.468	(16.699-91.373) 36.570±14.614	p>0.05
n-dodecane (µg/L)	(1.738-25.437) 4.662 ^c ±2.846	(2.281-43.122) 6.705 ^b ±4.432	(1.970-44.368) 6.004 ^b ±3.988	(14.967-45.525) 15.589 ^a ±10.258	p>0.05
n-tridecane (µg/L)	(1.772-7.106) 7.333±2.841	(0.234-9.580) 2.445±2.606	(0.121-8.476) 11.620±10.630	(0.205-21.017) 5.457±3.867	P<0.05
n-tetradecane (µg/L)	(3.456-10.293) 729.526±149.506	(0.044-4.699) 752.913±495.466	(5.575-27.484) 710.148±450.748	(0.234-9.576) 638.672±106.800	p>0.05
n-pentadecane (µg/L)	(654.035-953.780) 20.605±8.826	(9.942-1017.888) 101.165±89.525	(40.442-977.189) 88.244±79.114	(528.635-730.237) 81.051±73.464	p>0.05
n-hexadecane (µg/L)	(13.573-31.873) 14.186±6.907	(5.728-177.512) 31.374±23.246	(13.141-156.592) 27.504±9.203	(7.500-144.249) 23.778±10.207	p>0.05
n-heptadecane (µg/L)	(10.039-24.429) 59.091±22.369	(1.679-49.889) 82.690±55.714	(17.839-35.373) 68.022±42.222	(14.647-32.615) 69.583±37.379	p>0.05
Pristine (µg/L)	(34.792-78.098) 24.368±13.206	(10.406-126.557) 51.654±50.356	(30.178-104.577) 61.223±22.635	(36.678-101.952) 29.364±10.402	p>0.05
n-octadecane (µg/L)	(10.379-35.643) 18.906±5.267	(0.695-94.923) 29.340±20.953	(33.028-79.538) 23.517±17.490	(14.018-37.140) 11.757±8.160	p>0.05
Phytane (µg/L)	(12.719-23.284) 5.749±6.068	(4.327-46.649) 5.164±3.488	(5.451-38.506) 12.627±7.048	(2.497-22.389) 7.665±1.235	p>0.05
n-nonadecane (µg/L)	(1.024-13.726) 2.891±1.768	(0.264-8.526) 7.268±9.186	(2.279-18.113) 8.681±10.890	(6.287-9.291) 17.594±15.548	p>0.05
n-eicosane (µg/L)	(0.958-4.392) 1.857 ^b ±0.384	(1.029-20.932) 0.368 ^b ±0.250	(2.546-24.946) 2.082 ^b ±1.399	(0.850-30.829) 21.075 ^a ±20.170	p>0.05
n-heneicosane (µg/L)	(1.451-2.185)- 3.084 ^c ±2.466	(0.215-0.738)- 0.662 ^d ±0.415	(1.342-4.179)- 7.237 ^b ±6.441	(0.586-38.399) 77.176 ^a ±83.468	p<0.05
n-docasane (µg/L)	(0.010-5.078) 5.853±3.867	(0.067-1.033) 8.393±4.666	(2.799-16.453) 18.740±18.804	(0.054-149.377) 10.691±5.664	P<0.05
n-tricosane (µg/L)	(0.129-8.201) 4.868 ^c ±3.137	(1.929-13.076) 5.106 ^c ±1.928	(5.275-46.595) 15.095 ^b ±5.940	(3.509-15.224) 218.608 ^a ±249.904	p>0.05
n – tetracosane (µg/L)	(1.439-7.530) 0.124 ^b ±0.105	(2.214-6.074) 0.067 ^c ±0.054	(6.447-19.998) 0.103 ^b ±0.084	(1.859-435.031) 0.418 ^a ±0.399	P<0.05
n-pentacosane (µg/L)	(0.010-0.213) 0.138 ^b ±0.135	(0.010-0.113) 0.055 ^c ±0.038	(0.010-0.174) 0.140 ^b ±0.123	(0.049-0.763) 0.628 ^a ±0.640	P<0.05
n-hexacosane (µg/L)	(0.010-0.255) 1.267±1.988	(0.015-0.107) 1.319±0.900	(0.025-0.314) 2.105±3.504	(0.010-1.180) 1.096±0.909	P<0.05
n-heptacosane (µg/L)	(0.188-4.247) 0.165 ^b ±0.178	(0.010-1.911) 0.010 ^c ±0.000	(0.251-7.356) 2.413 ^a ±2.138	(0.010-1.846) 2.539 ^a ±1.720	p>0.05
n-octacosane (µg/L)	(0.010-0.319) 7.481 ^b ±8.627	(0.010-0.010) 0.010 ^c ±0.000	(0.010-5.217) 9.709 ^b ±6.779	(0.010-3.860) 198.267 ^a ±228.392	P<0.05
n-nonacosane (µg/L)	(0.010-14.953) 2.351 ^b ±2.604	(0.010-0.010) 0.010 ^c ±0.000	(0.010-14.382) 4.302 ^b ±2.862	(0.010-396.060) 320.829 ^a ±370.450	P<0.05
n-tricontane (µg/L)	(0.010-4.605) 206.975 ±211.968	(0.010-0.010) 0.010±0.000	(0.010-5.796) 110.326±125.944	(0.010-641.648) 130.059±225.554	P<0.05
n-hentriacontane (µg/L)	(0.010-503.529) 953.553 ^b ±508.444	(0.010-0.010) 1276.449 ^b ±288.253	(0.010-219.393) 427.261 ^c ±728.679	(0.010-467.884) ±2531.855 ^a	p>0.05
n-dotriacontane (µg/L)	(196.431-1292.468) 8.976±11.142	(1064.727-1675.207) 7.859±4.386	(21.794-1516.579) 44.790±83.024	(331.624-5134.249) 124.002±133.764	P<0.05
n-tritriacontane (µg/L)	(3.386-25.689) 2297.733 ^b ±138.037	(4.797-14.099) 2516.052 ^b ±569.432	(0.010-169.125) 1914.306 ^b ±911.332	(7.982-239.845) 5261.503 ^a ±3709.631	p>0.05
ΣTPH (µg/L)	(2115.899-2405.031)	(1678.700-2954.085)	(726.348-2947.955)	(2023.669-8474.088)	P<0.05

x ± SD = average mean generated from values across the months per station, ± standard deviation; min-max = minimum and maximum values for each parameter per station; post hoc = values with different superscripts (a > b > c > d) are significantly different (p < 0.05 or 0.01) while values with same superscript are not significantly different (p > 0.05).

*p < 0.05 (significant difference)
 **p < 0.01 (highly significant difference)

For Station 2, ten (10) TPH compounds also contributed to the largest group. The distribution order was: n-dotriacontane (1276.449 µg/L) > n-pentadecane (752.913 µg/L) > n-hexadecane (101.165 µg/L) > pristane (82.690 µg/L) > n-decane (69.961 µg/L) > n-octadecane (51.654 µg/L) > n-undecane (50.227 µg/L) > n-heptadecane (31.374 µg/L) > phytane (29.340 µg/L) > n-dodecane (22.930 µg/L). Figure 4 shows the spatial and temporal variation in ΣTPH compounds at the sampled stations during sampling months.

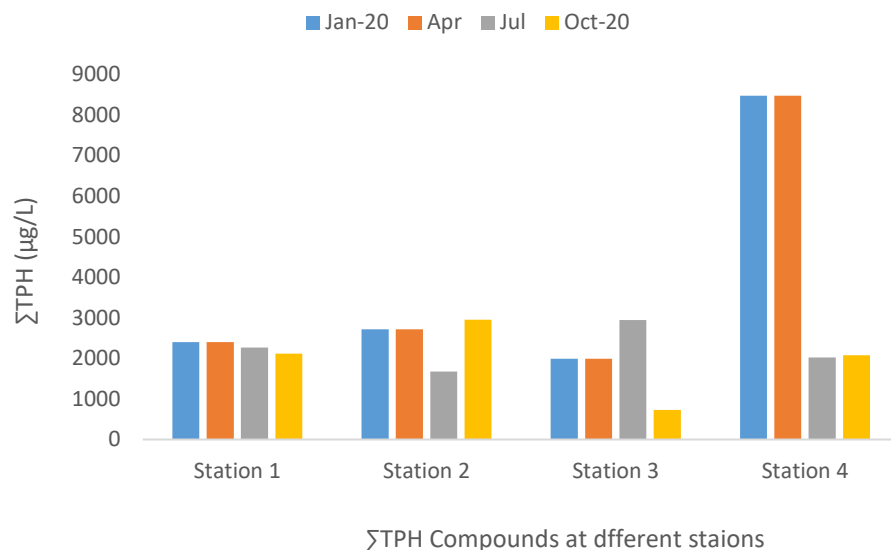


Figure 4 shows the spatial and temporal variation in ΣTPH compounds at the sampled stations during sampling months.

The TPH compounds contributing to the largest group in Station 2 were evenly distributed throughout the sampling months. For Station 3, fifteen (15) TPH compounds contributed to the largest group. The distribution order was: n-pentadecane (710.148 µg/L) > n-dotriacontane (427.261 µg/L) > n-hentriacontane (110.326 µg/L) > n-decane (92.538 µg/L) > n-hexadecane (88.244 µg/L) > n-undecane (84.962 µg/L) > pristane (68.022 µg/L) > n-octadecane (61.223 µg/L) > n-tritriacontane (44.790 µg/L) > n-nonane (42.155 µg/L) > n-dodecane (28.030 µg/L) > n-heptadecane (27.504 µg/L) > phytane (23.517 µg/L) > n-tricosane (18.740 µg/L) > n-tetracosane (15.095 µg/L). For Station 4, seventeen (17) TPH compounds contributed to the largest group. The distribution order was: n-dotriacontane (2966.654 µg/L) > n-pentadecane (638.672 µg/L) > n-tricontane (320.829 µg/L) > n-tetracosane (218.608 µg/L) > n-nonacosane (198.267 µg/L) > n-nonane (143.139 µg/L) > n-hentriacontane (130.059 µg/L) > n-tritriacontane (124.002 µg/L) > n-hexadecane (81.051 µg/L) > n-docasane (77.176 µg/L) > pristane (69.583 µg/L) > n-undecane (63.896 µg/L) > n-decane (46.290 µg/L) > n-dodecane (36.570 µg/L) > n-octadecane (29.364 µg/L) > n-heptadecane (23.778 µg/L) > n-heneicosane (21.075 µg/L) > n-eicosane (17.594 µg/L). The TPH compounds contributing to the largest group in Station 4 were also evenly distributed across the sampling months.

Cluster Analysis for TPH in Surface Water from Okpare Olomu River

Table 4 presents the Euclidean similarity and distance indices for total petroleum hydrocarbons (TPHs) in surface water samples obtained from the four sampled stations, while Figure 5 illustrates the dendrogram generated from the cluster analysis. The analysis was based on the TPH concentrations measured in water samples from Okpare Olomu River in Ughelli South, Delta State. The study locations include Station 1 (Ejeba Okpare), Station 2 (Uhrovwodo Okpare), Station 3 (Ogbe Okpare), and Station 4 (Arovie Okpare).

The Euclidean dissimilarity and distance indices showed varying degrees of differences among the sampled stations, with calculated values of 0.000, 253.039, 158.270, and 457.921, respectively. According to the dendrogram clustering, the prevailing conditions at Station 1 during sampling were distinct from those observed at Stations 2, 3, and 4. Similarly, the conditions at Station 2 were comparable to those at Station 3 but differed from those at Stations 1 and

4. The prevailing conditions at Station 3 were also similar to Station 2 but different from Stations 1 and 4. However, the combined conditions at Stations 2 and 3 were closer to those of Station 1 but still differed significantly from Station 4. Overall, the prevailing environmental conditions during sampling revealed dissimilarities across all stations. These differences were defined by Euclidean distance metrics and hierarchical cluster analysis using Ward’s method (PAST3, 2018). The clustering pattern clearly indicates variations in total petroleum hydrocarbon levels among the sampled stations of Okpare Olomu River.

Table 4: Similarity or Distance Index (Euclidean)

	S1	S2	S3	S4
S1	0.000			
S2	253.039	0.000		
S3	158.270	135.329	0.000	
S4	457.921	496.211	449.782	0.000

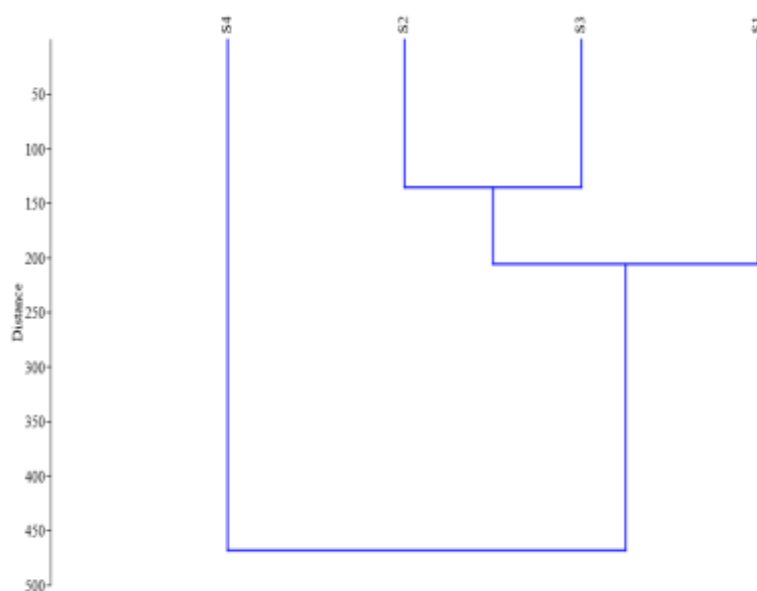


Figure 5: Dendrogram for cluster analysis based on TPH concentrations in surface water samples from Okpare Olomu River. Dissimilarity is defined by Euclidean distance, and clustering is based on Ward’s method.

4. Discussion

PAHs in Surface Water Samples from Okpare Olomu River

Surface water bodies in the Niger Delta region of Nigeria are exposed to significant anthropogenic pressures, largely driven by municipal effluents, transportation activities, and petroleum exploration (Bastami *et al.*, 2013). Findings from this study indicate that twelve (12) PAH compounds were detected in water samples from Okpare Olomu River. Among these, low molecular weight (LMW) PAHs constituted the predominant group compared to high molecular weight (HMW) PAHs across the sampled stations. Notably, fluoranthene, benzo(a)anthracene,

benzo(b)fluoranthene, and benzo(k)fluoranthene were not detected in any of the water samples analyzed. The total PAH concentrations revealed contamination at varying levels among the stations, following the order: station 3 (2022.258 µg/L) > station 4 (1862.288 µg/L) > station 2 (1326.416 µg/L) > station 1 (1006.237 µg/L). This spatial pattern indicates that PAH contamination is most pronounced downstream around station 3 and least at station 1. In terms of the number of compounds, station 1 contained three (3) detectable PAHs, station 2 contained five (5), station 3 contained six (6), and station 4 contained eleven (11). This variation suggests differences in the degree and possibly the sources of hydrocarbon inputs at each station.

The detection of these PAHs is consistent with other environmental studies where PAHs have been found in both aquatic and terrestrial ecosystems at levels sufficient to raise concerns about bioaccumulation and toxicity. Of particular importance are HMW PAHs, which are more persistent and recalcitrant in the environment and are associated with adverse effects such as carcinogenicity, genotoxicity, and mutagenicity (Xue and Warshawsky, 2005). In comparison, Bastami *et al.* (2013) reported lower concentrations of PAHs (3.12–5.88 µg/L) in coastal waters from the northern part of the Hormuz Strait (Persian Gulf), with 8 and 7 PAH compounds detected at their study locations. This highlights that PAH levels in Okpare Olomu River are relatively higher, reflecting greater hydrocarbon inputs in this oil-producing region.

When compared against the United States Environmental Protection Agency (USEPA) water quality standards for protection of human health (carcinogenic effects), none of the PAH concentrations measured in this study exceeded the recommended criteria ([USEPA, 1980). These standards specify threshold values such as: benzo(a)anthracene (100 µg/L); benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene (200 µg/L); chrysene and dibenzo(a,h)anthracene (300 µg/L); indeno(1,2,3-cd)pyrene (400 µg/L). Thus, although PAHs are present at varying levels across the stations, their concentrations remain below the carcinogenic risk thresholds set by USEPA.

TPH in Surface Water Samples from Okpare Olomu River

A total of twenty-eight total petroleum hydrocarbon (TPH) compounds were analyzed in the surface water samples collected from four stations along the Okpare Olomu River, and all twenty-eight compounds were detected with varying concentrations across the study area. The total TPH concentrations clearly indicate that the river is contaminated, and the distribution pattern followed the order: Station 4 (5621.503 µg/L) > Station 2 (2516.052 µg/L) > Station 1 (2297.733 µg/L) > Station 3 (1914.306 µg/L). Using a benchmark of values greater than 15 µg/L for selecting significant TPH compounds, the results showed that ten compounds in Station 1 and Station 2, fifteen compounds in Station 3, and seventeen compounds in Station 4 contributed to the largest group of TPHs detected in the study area. This distribution highlights that Station 4 recorded the highest contamination, whereas Station 3 had the lowest levels.

The concentrations observed in this study are of significant environmental concern. According to the National Research Council (2003), TPH concentrations of several hundred micrograms per liter in rivers and creeks adversely affect sensitive aquatic organisms, while concentrations in the several thousand micrograms per liter range can eliminate even highly tolerant species. The findings of this study fall within this alarming range. Earlier reports have shown similar or lower TPH values in the Niger Delta and other regions. Moffat and Linden (1995) recorded comparable concentrations of dissolved petroleum hydrocarbons in Niger Delta surface waters in the 1990s, while Ibiebele (1986) reported much higher levels ranging from 53,000 to 62,700 µg/L in refinery wastewater. Adewuyi and Olowu (2012) reported lower TPH concentrations between 59.74 and 67.35 µg/L in surface waters, while Eitchie *et al.* (2011) documented 250–380 µg/L in the same environmental medium. The results of this present study are therefore several-fold higher, with values approximately ten times greater than those reported by Adewuyi and Olowu (2012).

When compared to other global regions, the Okpare Olomu River also reflects high levels of contamination. Alinnor *et al.* (2014) reported TPH concentrations of 1352–12,110 µg/L in groundwater from Niger Delta communities, while Adewuyi *et al.* (2011) documented even higher levels of 73,500 µg/L in surface water from Ubeji, Warri. In other regions, Suratman (2013) reported TPH concentrations of 25–2,795 µg/L in the Strait of Johor, Malaysia, and Sammarco *et al.* (2013) documented levels between 60,000 and 260,000 µg/L in the Gulf of Mexico following the Deepwater Horizon oil spill. In contrast, much lower TPH concentrations have been reported elsewhere, including 12–41 µg/L in the Dungun River Basin, Malaysia (Suratman, 2013) and 19–88 µg/L along the Levantine Basin of the Israeli coastline (SOGRLI, 2014). Inyang *et al.* (2018) also observed comparatively lower TPH values in the surface water and sediments of the Qua-Iboe River in Ibeno, Akwa Ibom State.

From a human health perspective, the observed TPH concentrations are alarming. Even low levels of propane, a component of TPH, can result in swelling, itching, and skin inflammation, while higher levels may lead to eczema and acute pulmonary edema (NRC, 2003; UNEP, 2011). The mean concentrations of TPH in this study far exceed internationally accepted standards. The European Union Environmental Protection Agency (EUEPA, 2009) and the Nigerian drinking water standard (DPR, 2002) specify 3 µg/L as the maximum acceptable limit for

petroleum hydrocarbons in river and basin water, while the World Health Organization (WHO, 2003) guideline for TPHs in drinking water is 10 µg/L. The results from this study are therefore several orders of magnitude higher, with concentrations approximately 521 times greater at Station 4, 251 times greater at Station 2, 229 times greater at Station 1, and 191 times greater at Station 3 when compared to the WHO guideline.

These findings demonstrate that the surface water of Okpare Olomu River is grossly contaminated with petroleum hydrocarbons, rendering it unfit for human consumption and posing serious ecological and public health risks. The elevated concentrations of known carcinogenic TPHs underscore the urgent need for effective environmental monitoring, remediation, and enforcement of pollution control measures in the region.

Degradation Indicators and Risk Evaluation

The detection of lighter hydrocarbon fractions such as n-octane and n-decane at comparatively lower concentrations suggests that some degree of weathering and biodegradation is occurring within the Okpare Olomu River system. This natural attenuation process may have partially reduced the levels of more volatile compounds; however, the overwhelming total petroleum hydrocarbon (TPH) burden recorded in the study area continues to pose substantial ecological and human health risks. According to the National Research Council (2003), TPH concentrations above 100 µg/L can impair sensitive aquatic organisms, while concentrations exceeding 1000 µg/L as observed in Station 4 and other sampling locations are likely to have severe toxic effects even on tolerant species.

The ecological risks are compounded by the potential for bioaccumulation and biomagnification through aquatic food chains, which increases the likelihood of human exposure through the consumption of contaminated fish and other aquatic organisms. Chronic exposure to elevated TPH levels has been associated with multiple adverse health effects, including liver dysfunction, immune system suppression, and an increased risk of cancer (ATSDR, 1999; Diejomaoh and Okoro, 2024). These findings underscore the urgent need for targeted remediation strategies and strict regulatory interventions to prevent further environmental degradation and reduce public health hazards in communities dependent on this river system.

Relationship between PAHs and TPH in this Study

The occurrence of both polycyclic aromatic hydrocarbons (PAHs) and total petroleum hydrocarbons (TPHs) in surface water samples from Okpare Olomu River reflects their common origin from petroleum-related activities, including oil exploration, transportation, and municipal discharges. Both contaminant groups were detected across all sampling stations, though at varying concentrations, indicating widespread hydrocarbon pollution within the study area. PAHs constitute the aromatic fraction of petroleum hydrocarbons, while TPHs represent the total mixture of aliphatic and aromatic hydrocarbons. The higher abundance of TPHs compared to PAHs in all stations suggests that the bulk of hydrocarbon contamination originates from crude oil and refined petroleum products rather than incomplete combustion alone. The presence of low molecular weight (LMW) PAHs and lighter TPH fractions also points to recent petroleum inputs, while the detection of some high molecular weight (HMW) PAHs suggests a contribution from more persistent and aged residues.

A positive association can be inferred between the distribution trends of TPH and PAH concentrations. Stations with elevated TPH levels (particularly Stations 4 and 2) also showed higher diversity and concentrations of PAHs. This pattern indicates that petroleum-derived hydrocarbons are likely the primary source of PAHs in the river, and both contaminants share similar transport and deposition mechanisms within the aquatic environment. The co-occurrence of PAHs and TPHs raises significant ecological and human health concerns due to their toxic, mutagenic, and carcinogenic properties. Their combined presence increases the risk of bioaccumulation and chronic exposure for aquatic organisms and nearby communities relying on the river for domestic and fishing activities. These findings underscore the need for integrated management strategies that simultaneously address both contaminant groups to mitigate environmental and public health risks.

5. Conclusion

The findings of this study demonstrate that surface waters of the Okpare Olomu River are heavily impacted by petroleum-derived hydrocarbons, with both PAHs and TPHs detected across all sampled stations. The contaminant profile indicates predominantly petrogenic inputs, reflecting ongoing oil exploration and related anthropogenic activities within the region. Importantly, the measured TPH concentrations exceeded national and international guideline values by several orders of magnitude, underscoring a significant risk to aquatic ecosystems

and human populations dependent on the river for domestic and subsistence activities. These results align with previous research conducted in oil-impacted ecosystems of the Niger Delta and comparable global regions, further highlighting the persistence and scale of hydrocarbon pollution in petroleum-producing areas. The documented contamination emphasizes the urgent need for comprehensive mitigation strategies, including strict enforcement of environmental regulations, remediation of affected sites, and sustained monitoring programs. Without these interventions, the ecological integrity of the river and public health of nearby communities will remain under severe threat.

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