



Assessment of Total Petroleum Hydrocarbon Concentrations in Water and Sediments at Drainage Discharge Points into the New Calabar River, Port Harcourt, Nigeria

***Ikuromo, A.S., & Kpee, F.**

Department of Chemistry, Ignatius Ajuru University of Education, Port Harcourt, Nigeria

*Corresponding author email: aikuromo@gmail.com

Abstract

This research on the assessment of total petroleum hydrocarbon concentration in water and sediment at a drainage discharge point in New Calabar River. The study used four designated sample points where water and sediments were collected within the river at drainage discharge points while one of the stations was the control which does not have drainage system. After appropriate laboratory methods have been applied on the samples, extraction for TPH was performed using solvent extraction with dichloromethane then followed by column chromatography clean up. Agilent 5890 Gas Chromatography-Flame Ionization Detector (GC-FID) was used to detect TPH levels at the designated stations. The mean levels of TPH during the period in surface water ranged from 8.819 ± 2.033 to 11.149 ± 1.875 mg/L while that from the control was 5.856 ± 0.543 mg/L. In the sediments mean concentrations of TPH samples ranged from 25.592 ± 4.613 to 28.075 ± 5.671 mg/Kg while that of the control station was 17.590 ± 3.316 . The mean concentrations of TPH in water were slightly above the DPR and WHO requirements for drinking water while that of sediments were below the required limit by DPR and FME. The results indicated that the drainage discharge points contributed to the concentration of total petroleum hydrocarbons in the New Calabar River. Profiling and fingerprinting of TPH fractions identified sources from natural, biogenic and anthropogenic origin. The government and other relevant agencies should bring out measures that can cushion the effects posed by the drainages into the river.

Keywords: Concentration, Water, Sediment, Drainage, Discharge

Introduction

Water bodies are among the most important natural resources that sustain ecological balance, economic development, and human survival. Rivers, estuaries, wetlands, and coastal environments provide water for domestic, industrial, agricultural, transportation, and recreational purposes. However, rapid industrialization, urbanization, and anthropogenic activities have significantly degraded aquatic ecosystems globally through the discharge of untreated wastes, petroleum products, sewage, and industrial effluents into water bodies (Omokpariola et al., 2022). Among the numerous contaminants released into aquatic environments, petroleum hydrocarbons are recognized as one of the most persistent and hazardous pollutants because of their toxic, carcinogenic, mutagenic, and bioaccumulative properties.

Total Petroleum Hydrocarbons (TPHs) represent a broad class of compounds derived from crude oil, including aliphatic hydrocarbons, aromatic hydrocarbons, resins, and asphaltene. These compounds enter aquatic ecosystems through oil exploration and production activities, pipeline leakages, illegal refining, industrial effluents, urban runoff, and accidental spills. Once introduced into the environment, petroleum hydrocarbons tend to persist due to their hydrophobic nature and resistance to degradation, with sediments acting as long-term reservoirs of contamination (Zabbe et al., 1994). The Niger Delta region of Nigeria, one of the world's most important oil-producing regions,

has experienced severe environmental degradation due to decades of petroleum exploitation. Continuous oil-related activities have led to widespread contamination of rivers, creeks, and wetlands. Studies have shown that aquatic ecosystems in the region, including the New Calabar River, are increasingly impacted by petroleum hydrocarbon inputs from industrial, domestic, and municipal sources (Stanley et al., 2017). The New Calabar River is an important freshwater and estuarine ecosystem that supports fishing, transportation, domestic use, and biodiversity. However, the river is increasingly threatened by anthropogenic pressures such as industrial discharges, urban runoff, dredging, boat traffic, and drainage effluents from surrounding communities in Port Harcourt (Edori & Iyama, 2019). These drainage systems serve as major pathways through which petroleum-based pollutants are transported into the river, particularly during rainfall events when accumulated hydrocarbons on roads, mechanic workshops, fuel stations, and industrial areas are washed into receiving waters.

Petroleum hydrocarbons in aquatic environments pose serious ecological and human health risks. They reduce dissolved oxygen levels, impair photosynthesis, disrupt aquatic food chains, and cause toxicity to fish and benthic organisms. Some hydrocarbon fractions are also carcinogenic and may bioaccumulate in aquatic organisms, thereby entering the human food chain through consumption of contaminated seafood (Green et al., 2025). Chronic exposure to petroleum-contaminated water and sediment has been associated with adverse health outcomes in humans. Sediments are particularly important in hydrocarbon pollution studies because they serve as sinks and long-term storage compartments for pollutants. Unlike water, which reflects recent contamination, sediments provide historical records of pollution and can continuously release contaminants back into the water column under changing environmental conditions (Zabbey et al., 1994). Therefore, simultaneous assessment of TPHs in both water and sediment is essential for understanding the distribution, fate, and ecological impact of petroleum hydrocarbons in aquatic systems. Several studies have reported hydrocarbon contamination in the New Calabar River. Therefore, there is a need for continuous monitoring and site-specific assessment of TPH concentrations in water and sediments at drainage discharge points. Such studies are essential for identifying pollution hotspots, understanding spatial distribution patterns, and providing baseline data for environmental management and policy formulation. This study therefore aims to assess Total Petroleum Hydrocarbon concentrations in water and sediments at drainage discharge points into the New Calabar River, Port Harcourt, Nigeria.

Study Area

The study area is at three different point where effluents are discharged into the New Calabar River. These points were built by the Rivers State Government for drainage purposes, so that during the rainy seasons, water can easily be drained off from residential areas and the highways. The areas were at the Rumuolumeni axis of Port Harcourt, which houses many multinational and local industries that deal with petroleum and allied products. Effluents from these industries and homes are directly connected to the drainage system which runs into the New Calabar River. The point samples were taken include the Police Post area (4° 48' 52.1" N, 6° 56' 21.4" E), Minipiti (4° 41' 31.8" N, 6° 56' 8.4" E), both of which drains into the mangrove wetland of the river and the Iwofe Jetty area (4° 48' 32.4" N, 6° 55' 42.7" E) which drains directly into the river. The control station was collected at 4° 46' 34.6" N, 6° 48' 45.8" E. The geographic positions where samples were collected are shown in Table 1.1. The map of the area is shown in Figure 1.

Table 1: Geographic positions

Sample Identity	Geographic Position (Coordinates)	Location
1	4° 48' 52.1" N, 6° 56' 21.4" E	Police Post
2	4° 41' 31.8" N, 6° 56' 8.4" E	Minipiti
3	4° 48' 32.4" N, 6° 55' 42.7" E	Iwofe Jetty
4	4° 46' 34.6" N, 6° 48' 45.8" E	Control

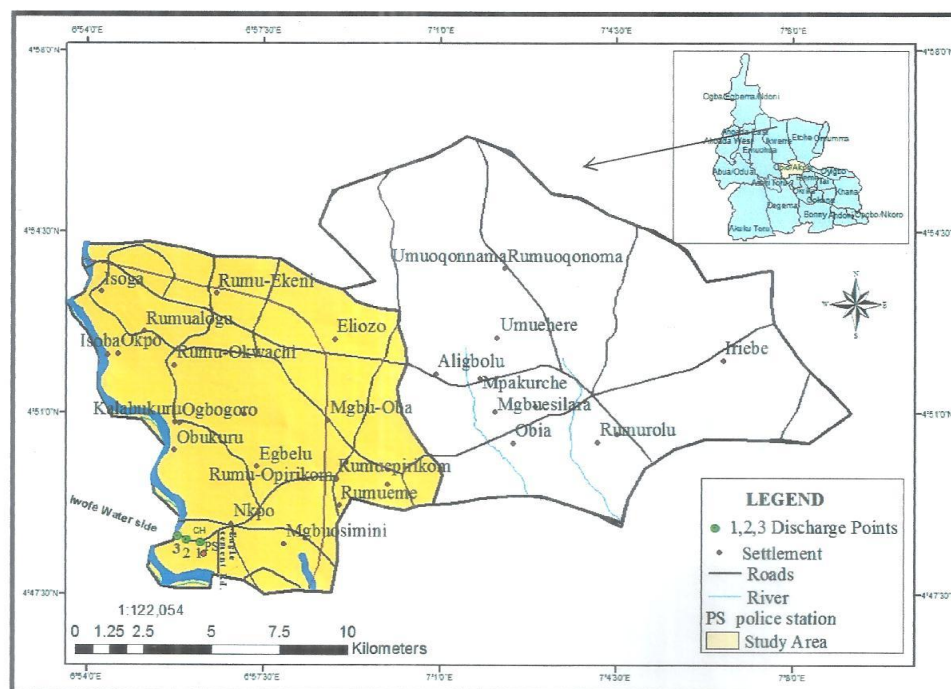


Figure 1: Rumuolumini South West showing Drainage Discharge Points.

Methods and Materials

Collection of Water Samples

Water samples were collected from three different stations at drainage discharge points into the New Calabar River and a control point two kilometres away from the discharge point. Glass bottles were used for the water collection. The glass bottles were previously washed with dichloromethane to ensure no contamination with the water sample. Three different points were collected in each station at a depth of 40cm and mixed together to form a representative sample. Preservation of the water sample was done by adding 2ml of 0.2M H_2SO_4 to bring the pH to about 2. In order to prevent any harm or contamination, the bottles were covered with sterile pieces of aluminium foil, after which the bottles were tightly covered with plastic screw. The bottles were then kept in an ice packed container maintained at 4°C and then transported to the laboratory for sample pre-treatment and analysis (Ikpe et al., 2016).

Collection of sediment samples

Sediment samples were collected at the three stations where the drainage empties into the New Calabar River and a control. Sediment samples were collected from the surface to 5 cm depth. Composite representative samples were formed by mixing sediments from three points within a collection sphere and thoroughly mixed together. The samples were collected using a hand held, van veen grab and transferred to glass bottles. The samples were then transported to the laboratory and allowed to dry under controlled conditions.

Extraction of total petroleum hydrocarbon from water samples

Water samples were filtered and then subjected to extraction procedures by the use of separatory funnel. Water samples collected from different stations were put into a two liters' (2L) glass separatory funnel and covered with a glass stopper. Then 30ml dichloromethane as solvent was added to the water samples in the funnel for extraction. The separatory funnel was shaken for at least 5-10 minutes. This allowed for a separation of the organic layer and the aqueous layer. A mass of 5g anhydrous sodium sulphate was mixed with the extract (lower layer) in order to remove water. The sample was then collected into a beaker with the aid of filter paper. The filtrate was allowed to evaporate at room temperature in a fume cupboard. The filtrate was allowed to be concentrated to 3ml. The process or extraction was repeated three times for each sample collected (LAWI, 2011).

Extraction of total petroleum hydrocarbon from sediment samples

An analytical weighing balance was used to weigh 10g of weighed sediment sample and was transferred into an amber bottle. Then 5g of anhydrous sodium sulphate (Na_2SO_4) was measured and put into the amber glass bottle which contained the sediment sample, and then the sediment sample was shaken vigorously for effective mixing of particles. The purpose of adding anhydrous sodium sulphate is to reduce moisture from the sediment sample. After thorough mixing of the sample, 30ml dichloromethane was added to the sediment sample as the extracting solvent. After the addition of dichloromethane, the amber bottle was then very tightly closed and then transferred to a mechanical shaker and was agitated at room temperature. The sample was allowed to settle for 1hr. Then using a 110mm filter paper the sediment sample is filtered into a clean beaker. The filtrate from the sediment sample is allowed to concentrate to 1ml by evaporation (LAWI, 2011).

Sample clean-up/purification

To prepare a column, 10g - 100g of activated silica gel was weighed into a beaker, Hexane/Methylene chloride was added to form slurry that was poured into the chromatographic column with a based glass wool, rinsing all the silica gel into the column with the solvent used. Then 10mL of hexane was used to condition the column, while 20mL of methylene chloride used for elution at a rate of 1 drop/sec. The elution was stopped when the solvent reaches the top of the column after which the eluate was concentrated to 2ml using rotary evaporator, and 1g of Sodium sulphate was added to remove any remaining water in the extract which was stored in a 2 ml GC vial below 4°C prior to GC analysis.

Sample separation and detection of total petroleum hydrocarbons

Agilent 5890N gas chromatography-flame ionization detector (GC-FID) was used for the detection of total petroleum hydrocarbons in sediment and water samples from different stations of drainage discharge points (Corte et al., 2012). A volume of 3ml concentrated sample was injected into the gas chromatography vial for cleaning of syringe, the blank dichloromethane was injected into micro-syringe of gas chromatography. Before the analysis of the sample, the cleaning of the syringe was done thrice. The micro-syringe was rinsed later with the sample after which the sample was then injected into the total separation of the different compound of component of the sample. After separation of compounds in the sample. The amount of total hydrocarbon content resolved at a particular chromatogram was then measured in ml/Kg for the sediment sample and ml/l for water sample.

Fingerprinting, profiling and source identification of pollution markers for total petroleum hydrocarbons

The evaluation of the origin and source of total petroleum hydrocarbons pollution in the water and sediment columns at the discharge point into the New Calabar River was performed using some indices. These indices were used to profile and fingerprint the nature of the pollution due to total petroleum hydrocarbons. The indices used include; low molecular weight to high molecular weight (L/H) ratio, Long Chain Hydrocarbons/ Short Chain Hydrocarbons (LHC/SHC) ratio, Carbon Preference Index (CPI), $\text{C}_{31}/\text{C}_{19}$ hydrocarbon ratio and Average Carbon Length (ACL), to identify the source and origin of total petroleum hydrocarbons (Duan et al., 2010) in any river, water and sediment systems.

L/ H ratio: Total petroleum hydrocarbons (n-alkanes) of Low Molecular Weight (L) originated from aquatic biogenic sources, while total petroleum hydrocarbons (n-alkanes) of High Molecular Weight (H) originate basically from terrestrial vascular plants (Fagbote & Olanipekun, 2013). L gives the total sum of the level of the aliphatic hydrocarbons present in the system between C_{15} to C_{20} while H gives the total sum of the level of aliphatic hydrocarbons present in the system between C_{21} to C_{40} . When the ratio is below one it signifies contamination from natural sources and terrestrial biogenic origin, and values above one indicates natural sources of biogenic origin.

LHC/SHC ratio: Long Chain Hydrocarbons/ Short Chain Hydrocarbons ratio is useful in calculating the abundance of phytoplankton and vascular plants in the marine/aquatic environment (Fagbote & Olanipekun, 2013). The addition of C_{15} , C_{17} and C_{19} hydrocarbons gives SHC while addition of C_{27} , C_{29} and C_{31} hydrocarbons gives LHC.

Carbon preference index (CPI): The index gives the ratio of odd numbered hydrocarbons to that of even numbered hydrocarbons in the sediment columns of the aquatic environment. When CPI value is equal to 1, implies hydrocarbons that have origin from petrogenic source, while CPI values less 1 might possibly have originated from bitumen and oils that have their origin from pyrogenic (evaporate rocks) origin or from carbonate sources (Fagbote & Olanipekun,

2013). When CPI values are higher than 1 it shows that the n-alkanes (total petroleum hydrocarbons) are from biogenic input. The CPI index was calculated by applying the mathematical expression;

$$\text{CPI} = 0.5 [(C_{25}-C_{33})/(C_{25}-C_{32})] + [(C_{25}-C_{33})/(C_{26}-C_{34})] \quad (1)$$

Determination of C_{31}/C_{19} : This ratio evaluates the origin and sources of petroleum hydrocarbons (n-alkanes) input in the aquatic/marine environment. The detection of the incidence of C_{31} hydrocarbons disclosed hydrocarbons of terrestrial biogenic sources while the presence of C_{19} hydrocarbons indicated hydrocarbons origin of marine biogenic inputs.

Average carbon length (ACL): The mathematical equation used by Kiran et al. (2015) and Wang et al. (2015) was adopted in the determination of this index. The index is important in the estimation of odd hydrocarbons in a molecule existing in a sample in order for a link to institute a relationship with higher plants linked with petroleum hydrocarbons (n-alkanes). The mathematical formula for calculating ACL value is given as;

$$\text{ACL}_{\text{value}} = \frac{25(nC_{25}) + 27(nC_{27}) + 29(nC_{29}) + 31(nC_{31}) + 33(nC_{33})}{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}} \quad (2)$$

Partition coefficient for total petroleum hydrocarbons at effluent discharge points of the New Calabar River

The bio availability of TPH in sediments at the drainage points into the river rest exclusively on the distribution of the concentrations between the sediments and the surface water columns. The distribution or spread between the water and sediment phases of the contaminants is measured by partition coefficient. The partition coefficient is expressed mathematically as;

$$K_d = \frac{\text{concentration of pollutant in Sediment}}{\text{concentration of pollutant in water}} \quad (3)$$

The partition coefficient ascertains the most stable phase of the contaminants or the phase of preference of the contaminants.

Results

Table 1: Mean concentrations (mg/L) of total petroleum hydrocarbons in surface water samples at drainage discharge points into the New Calabar River

Carbon Length (mg/L)	Stations			
	1	2	3	Control
C8	0.278±0.035	0.232±0.012	ND	ND
C9	0.195±0.017	0.061±0.007	ND	ND
C10	0.084±0.006	0.002±0.000	0.042±0.002	0.063±0.009
C11	0.634±0.143	0.109±0.014	0.029±0.006	0.018±0.004
C12	0.893±0.208	0.016±0.001	0.153±0.005	ND
C13	0.563±0.035	0.021±0.001	0.425±0.012	0.159±0.007
C14	0.482±0.079	0.522±0.134	ND	0.024±0.005
C15	0.161±0.007	0.394±0.083	0.155±0.009	0.132±0.011
C16	0.404±0.035	0.541±0.163	0.029±0.002	0.089±0.003
C17	0.953±0.223	0.822±0.269	0.427±0.058	0.409±0.055
C18	0.454±0.038	0.423±0.108	0.198±0.009	0.164±0.004
C19	1.050±0.093	1.253±0.248	1.518±0.199	0.647±0.054
C20	1.254±0.368	0.421±0.108	1.415±0.237	0.503±0.036
C21	0.108±0.012	1.758±0.586	1.056±0.237	0.372±0.017
C22	0.387±0.028	0.553±0.111	1.974±0.398	1.248±0.019
C23	0.034±0.006	0.130±0.006	0.997±0.182	0.259±0.023
C24	0.976±0.149	0.546±0.070	1.232±0.284	0.367±0.018
C25	0.234±0.025	0.014±0.001	0.209±0.008	0.145±0.023
C26	0.603±0.099	0.347±0.068	0.350±0.021	0.249±0.018
C27	0.017±0.001	0.002±0.000	0.053±0.001	0.216±0.088
C28	0.605±0.160	0.065±0.008	0.188±0.010	0.180±0.014
C29	0.087±0.004	0.212±0.023	0.006±0.003	0.016±0.008

Carbon Length (mg/L)	Stations			
	1	2	3	Control
C30	0.075±0.027	0.130±0.005	0.129±0.014	0.059±0.005
C31	0.158±0.041	0.007±0.001	0.047±0.011	0.037±0.013
C32	0.258±0.024	0.141±0.004	0.178±0.010	0.242±0.016
C33	0.016±0.001	ND	0.010±0.002	ND
C34	0.186±0.011	ND	ND	0.006±0.001
C35	ND	0.097±0.002	ND	0.252±0.092
C36	ND	ND	0.008±0.001	ND
C37	ND	ND	ND	ND
C38	ND	ND	ND	ND
C39	ND	ND	ND	ND
C40	ND	ND	ND	ND
Total	11.149±1.875	8.819±2.033	10.828±1.721	5.856±0.543

Table 2: Mean concentrations (mg/Kg) of total petroleum hydrocarbons in sediment samples at drainage discharge points into the New Calabar River

Carbon Length (mg/L)	Stations			
	1	2	3	Control
C8	0.060±0.008	0.392±0.025	0.711±0.130	0.468±0.135
C9	0.139±0.005	0.554±0.177	0.560±0.024	0.021±0.005
C10	0.825±0.167	0.818±0.209	0.314±0.032	ND
C11	0.838±0.248	0.540±0.130	0.230±0.029	0.582±0.082
C12	0.877±0.084	1.298±0.382	1.185±0.298	0.612±0.059
C13	0.581±0.057	0.650±0.035	0.426±0.015	0.231±0.027
C14	0.740±0.100	0.880±0.185	0.932±0.108	0.199±0.016
C15	0.695±0.096	1.352±0.252	1.019±0.041	0.843±0.126
C16	3.609±0.853	0.583±0.041	1.385±0.277	1.401±0.121
C17	1.597±0.336	1.235±0.132	2.767±0.540	1.826±0.095
C18	0.702±0.112	1.072±0.208	1.034±0.033	0.602±0.048
C19	4.378±1.130	1.611±0.398	2.388±0.616	2.212±0.883
C20	0.903±0.125	2.175±0.499	0.860±0.230	1.452±0.255
C21	1.223±0.449	1.254±0.330	0.500±0.030	ND
C22	0.538±0.033	0.816±0.105	0.623±0.166	1.047±0.206
C23	0.725±0.259	2.704±0.694	1.097±0.157	ND
C24	0.775±0.242	1.572±0.468	1.161±0.197	1.113±0.310
C25	3.218±0.514	1.789±0.635	1.266±0.349	ND
C26	1.073±0.142	1.888±0.344	1.457±0.262	2.700±0.701
C27	0.239±0.009	0.586±0.133	0.290±0.012	0.056±0.013
C28	1.215±0.194	1.045±0.309	1.783±0.342	0.447±0.059
C29	0.933±0.204	0.745±0.027	0.498±0.166	ND
C30	0.364±0.027	0.616±0.229	1.153±0.268	0.735±0.054
C31	0.802±0.155	0.618±0.037	0.377±0.103	0.285±0.035
C32	0.543±0.108	0.364±0.035	0.374±0.026	0.119±0.017
C33	ND	0.237±0.031	0.191±0.022	0.113±0.004
C34	0.182±0.011	0.089±0.003	0.388±0.100	ND
C35	0.152±0.002	0.004±0.001	0.156±0.004	0.526±0.065
C36	0.149±0.001	0.113±0.005	0.238±0.013	ND
C37	ND	ND	ND	ND
C38	ND	ND	ND	ND
C39	ND	0.038±0.01	0.229±0.023	ND
C40	ND	ND	ND	ND
Total	28.075±5.671	27.680±6.069	25.592±4.613	17.590±3.316

Table 3: Source diagnostic ratio and profiling of total petroleum hydrocarbons of the surface water at the drainage discharge points

Parameters	Stations			Mean
	1	2	3	
TPH	11.149	8.819	10.828	10.265
C ₁₅ - C ₁₉ (odd number TPH)	2.164	2.469	2.100	2.244
C ₁₈ - C ₂₂ (even number TPH)	2.095	1.397	3.587	2.360
C ₂₅ - C ₃₅	2.239	1.015	1.170	1.475
L/H (C ₁₅ -C ₂₀)/ C ₂₁ -C ₄₀)	1.142	0.963	0.581	0.895
C ₃₁ /C ₁₉	0.150	0.006	0.031	0.062

Table 4: Source diagnostic ratio and profiling of total petroleum hydrocarbons of the sediments at the drainage discharge points

Parameters	Stations			Mean
	1	2	3	
TPH	28.075	27.680	25.592	27.116
C ₁₅ -C ₁₉ (odd number TPH)	6.670	4.198	6.174	5.681
C ₁₈ -C ₂₂ (even number TPH)	2.143	4.063	2.517	2.908
C ₂₅ -C ₃₅	8.721	7.981	7.933	8.212
LHC/SHC	0.296	0.464	0.189	0.316
L/H (C ₁₅ -C ₂₀)/(C ₂₁ -C ₄₀)	0.980	0.553	0.802	0.778
C ₃₁ /C ₁₉	0.183	0.384	0.158	0.242
CPI	2.191	1.355	0.730	1.425
ACL	26.738	27.454	27.912	27.368

Table 5: Partition coefficient of total petroleum hydrocarbons between sediment and water phases at effluent discharge points of the New Calabar River

Carbon Length (mg/L)	Stations		
	1	2	3
C8	0.216	1.690	-
C9	0.713	1.690	-
C10	9.821	409.000	7.476
C11	1.322	4.954	7.931
C12	0.982	61.610	7.745
C13	1.032	30.952	1.002
C14	1.535	1.686	-
C15	4.317	3.431	6.574
C16	8.933	1.077	47.759
C17	1.676	1.502	6.480
C18	1.546	2.534	5.222
C19	4.170	1.286	12.061
C20	0.720	5.166	0.608
C21	11.324	0.713	0.473
C22	1.390	1.476	0.316
C23	21.324	20.800	1.000
C24	0.861	2.879	0.942
C25	13.752	127.786	6.057
C26	1.779	5.441	4.163
C27	14.059	293.000	5.472

Carbon Length (mg/L)	Stations		
	1	2	3
C28	0.915	16.077	9.484
C29	10.724	3.514	83.000
C30	4.853	4.738	8.938
C31	5.076	88.286	8.021
C32	2.105	2.582	2.101
C33	-	-	19.100
C34	0.978	-	-
C35	-	0.041	-
C36	-	-	29.750
C37	-	-	-
C38	-	-	-
C39	-	-	-
C40	-	-	-

Discussion

Concentration of total petroleum hydrocarbon in surface water and sediment at drainage discharge points into the New Calabar River

The mean concentrations of total petroleum hydrocarbon as contaminants or pollutants at the drainage discharge points of the New Calabar River within the stations of the surface water during the study were Station 1; 11.149 ± 1.875 mg/L, Station 2; 8.819 ± 2.033 mg/L and Station 3; 10.828 ± 1.721 mg/L and control 5.856 ± 0.543 mg/L. The general observation recorded in the concentration of total petroleum hydrocarbons at the drainage discharge points of the New Calabar River was that the level of concentration of hydrocarbon pollutants was higher at the drainage discharge points of the river when compared to that of the control which was taken at another point within the river where drainage does not discharge effluents. This was due to the much runoff from drainages, which add to the other sources of total petroleum hydrocarbons such as aerial deposition, transportation activities and possibly from illegal oil transactions (oil bunkering) that is associated with the river under investigation. The slight variations recorded in the concentrations of total petroleum hydrocarbons within the stations of the drainage discharge points within the river could primarily be due to the difference in the degree of petroleum hydrocarbons business that took place within the area the drainages are situated (Kpee & Bekee, 2021). The mean concentration obtained for total petroleum hydrocarbons in this research in the stations of the drainage discharge points of the New Calabar River were slightly above or below the national tolerable or acceptable requirement of 10.00 mg/L in both surface and groundwater established by DPR and FEPA (FEPA, 2003; DPR, 2011) for potable water and that for other domestic usages. However, the mean concentrations at the control station within the river was observed to be lower than the required target acceptable by DPR and FEPA (FEPA, 2003; DPR, 2011).

The mean concentrations of total petroleum hydrocarbon as contaminants or pollutants at the drainage discharge points of the New Calabar River within the stations of the sediments during the study were Station 1; 28.075 ± 5.671 mg/Kg, Station 2; 27.680 ± 6.069 mg/Kg and Station 3; 25.592 ± 4.613 mg/Kg and control 17.590 ± 3.316 mg/Kg. The general observation recorded in the concentration of total petroleum hydrocarbons at the drainage discharge points into the New Calabar River was higher than the control due to the influence of the effluents that come from the drainage points. The variations recorded in the concentrations of total petroleum hydrocarbons within the stations used at the drainage discharge points of the river was primarily due to the difference in the level of petroleum hydrocarbons business that take place within the area that has to do with that particular drainage into the river investigated (Edori & Marcus, 2021). The level of contamination of total petroleum hydrocarbons was higher at the drainage discharge points of the New Calabar River than the control point within the same river where drainage do not discharge effluents. This was basically true due to the fact that additional total petroleum hydrocarbons were being added into the river through the drainages. Total petroleum hydrocarbons from exhaust of vehicles, generators and spills from sources that use hydrocarbon-based fuel. The mean concentrations of total petroleum hydrocarbons recorded for the stations at drainage discharge points into the New Calabar River were all lower or slightly lower than the tolerable range established by the Federal Ministry of Environment, which is 30 mg/Kg in water (FME, 1991) and also lower than that which is obligatory by the Directorate of petroleum Resources satisfactory target of 50 mg/Kg and far lower than the 5000 mg/Kg maximum level of intervention required by the same body (DPR, 2002).

Total petroleum hydrocarbons distribution pattern at drainage discharge points into the New Calabar River

The level of contamination by total petroleum hydrocarbons in the surface water and sediments at drainage discharge points into the New Calabar River indicated that there were variations of the hydrocarbon fractions which actually displayed that many sources could be probably responsible for the petroleum origin at drainage discharge points into the New Calabar River. The occurrence of C₂₅-C₃₅, with a mean level of 1.475 mg/L in surface water and 8.212 mg/Kg in sediment at drainage discharge points into the New Calabar River is a suggestion of both biogenic input, which originated from vascular and terrestrial plants and anthropogenic sources. The results also indicated a slight predominance of C₁₅, C₁₇ and C₁₉ hydrocarbons fractions which also specifies to contributions from algae and phytoplankton sources credited to biogenic origin. The incidence of petroleum hydrocarbons components of C₁₆, C₁₈ and C₂₀ in both the surface water and sediments at drainage discharge points into the New Calabar River is also an indication of anthropogenic origin or source of pollution. Also, in the same way the incidence of hydrocarbon components of C₁₂ and C₁₄ in the aquatic environment shows sources originating from microbial biogenic activities (Gao & Chen, 2008; Al-Baldawi et al., 2015). The study revealed that petroleum hydrocarbons fractions of C₈-C₁₄ were present in varying quantities in both surface water and sediment samples at the drainage discharge points into the New Calabar River. The presence of C₁₅ to C₃₉ hydrocarbon fractions were also identified in both the surface water and sediments of the creek, although C₃₂ to C₄₀ components were either found in very little quantity or completely absent in the surface water or sediments drainage discharge points into the New Calabar River during the time of the study. There was a slight dominance of odd hydrocarbons fractions as against even hydrocarbons fractions in both surface water and sediments at the drainage discharge points. In both surface water and sediments heavier components were observed to be more than the lighter components. Odd hydrocarbons component of C₂₁ and above were detected in both the surface water and sediments at the drainage discharge points of the river. This observation is in consonance with that recorded by Ahmed et al. (2015). Petroleum hydrocarbon fractions that do not contain aliphatic (aromatic) compounds, which occur in the aquatic environments originate completely from biogenic sources. The presence of total petroleum hydrocarbons (n-alkanes) in the sediments at the drainage discharge points of the river were basically from both biogenic and anthropogenic sources that could be due to runoffs from homes, illegal refining sites, industries, direct discharge, transportation and from aerial deposition.

Low molecular weight petroleum hydrocarbons/high molecular weight petroleum hydrocarbons (L/H)

The low molecular weight of total petroleum hydrocarbons ranges from C₁₅ - C₂₀, while the high molecular weight hydrocarbons range from C₂₁ - C₄₀. The sum total of the low molecular weight/the sum total of the high molecular weight gave a certain ratio, which is a useful instrument in identifying sources and origin of the petroleum hydrocarbons in the environment (Fagbote & Olanipekun, 2013; Ahmed et al., 2015). The ratio (L/H) varied from 0.581 to 1.142 in the surface water of the diverse stations at drainage discharge points into the New Calabar River with a mean value of 0.895. In the sediment samples at drainage discharge points into the New Calabar River, the ratio varied from ratio varied from 0.553 to 0.980 with a mean value of 0.778. When the ratio of low molecular weight hydrocarbon to that of high molecular weight hydrocarbon is less than one, it shows total dominance of hydrocarbons from marine animals, higher plants and water bacteria, but when the values are close to one, it gives an insight that the total petroleum hydrocarbon components is from plankton and petroleum origin. When the ratio obtained is more than two, it is an indication that the pollution probably originated from fresh hydrocarbon oil in the water body (Edori & Edori, 2021). From the results recorded at drainage discharge points into the New Calabar River, it reveals that multiples sources must have been responsible for the occurrence of total petroleum hydrocarbons in the at the drainage discharge points of the river. This is true to the fact that calculated ratios of the low molecular weight to that of high molecular weight hydrocarbons vary from station to station in the creek at the time of study.

Long chain hydrocarbons/short chain hydrocarbons

The total petroleum hydrocarbons components that are below or equal to C₂₆ are classified to as short chain hydrocarbons (SHC), while those petroleum hydrocarbons components whose chain length are higher than C₂₆ are known as long chain hydrocarbons (LHC). Short chain hydrocarbons originate from plankton and benthic algae, while long chain hydrocarbons originate from vascular plants. The ratio LHC/SHC is used in calculating the abundance of phytoplankton and vascular plants present in the marine environment (Fagbote & Olanipekun, 2013). When the estimated ratio lies within 0.21 to 0.80, it shows that phytoplankton is dominant, but when the ratio estimated lies within 2.38 to 4.33 it shows hydrocarbons of mixed origin. But when the calculated ratio is higher than 4 the source is possibly from terrestrial plant waxes (Bianchi, 2007). At the drainage discharge points into the New Calabar River,

the ratios obtained were from 0.189 to 0.464 with an average value of 0.316. The results obtained in this work showed that the total petroleum hydrocarbons originated from phytoplankton.

Carbon preference index (CPI)

The source and origin of total petroleum hydrocarbons in the aquatic ecosystem could also be understood by using the CPI ratio measurement. This gives the ratio of odd hydrocarbons components to those of even numbered hydrocarbons components of the total petroleum hydrocarbons in the aquatic sediments. The CPI index has the ability in providing information on the predominance of natural occurring hydrocarbons as against anthropogenic hydrocarbons (Wu et al., 2001; Maioli et al., 2011). The recorded values of CPI in this work were in the range of 0.730 to 2.191 with a mean value of 1.425 drainage discharge points into the New Calabar River. The values obtained from the drainage discharge points into the New Calabar River indicated that aliphatic hydrocarbons might have originated from mixed sources (petrogenic, pyrogenic and biogenic inputs). When the CPI value recorded is higher than one, (that is between 3 to 10 range), it classifies that the petroleum hydrocarbons components originated from biogenic sources (e.g. waxes of terrestrial vascular plants and algae) and largely predominated by odd numbered hydrocarbons. When there is a clear predominance of odd carbon hydrocarbon fractions of C_{15} - C_{21} range, it is naturally from algae or microbial source and those that fall between C_{23} - C_{31} groups are chiefly from vascular plants. The occurrence of total petroleum hydrocarbons components from petrochemical origin give CPI values close to 1 (Luan & Szelewski, 2008; Michelle et al., 2014). This observation in this work showed that part of the hydrocarbon components could have originated from petrochemical sources.

Determination of C_{31}/C_{19}

The C_{31}/C_{19} ratio is useful in differentiating the sources and origin of petroleum hydrocarbons (n-alkanes) in the aquatic environment. The incidence of C_{31} hydrocarbon component showed hydrocarbons of terrestrial (land-dwelling) biogenic origin. In contrast, the incidence of C_{19} hydrocarbons indicates input from aquatic biogenic sources (Fagbote & Olanipekun, 2013). This ratio is important in measuring the predominance from any of the sources. In this study, the C_{31}/C_{19} ratio obtained fell between 0.006 to 0.150 with an average value of 0.062 in the surface water at drainage discharge points into the New Calabar River and in the sediments the values were from 0.158 to 0.384 with an average value of 0.242. This observation showed a predominance of the C_{19} hydrocarbon components over the C_{31} hydrocarbon components at drainage discharge points into the New Calabar River. The domination of the C_{19} hydrocarbon component revealed that the petroleum hydrocarbons present at drainage discharge points into the New Calabar River are from aquatic biogenic sources. This ratio gives the differences between petroleum hydrocarbons of marine origin and that from terrestrial sources. The range of values of the ratio obtained in this work were lower than 0.4 range which revealed that the hydrocarbons at drainage discharge points into the New Calabar River were from marine biogenic sources. This observation agreed with Ahmed et al. (2015). The recorded values for the C_{31}/C_{19} ratio at drainage discharge points into the New Calabar River further showed that the incidence of hydrocarbon components of terrestrial origin in the river was low.

Average carbon length (ACL)

The ACL index estimates the odd hydrocarbons in a molecule that exist in sediment samples in order to establish a link with higher plants associated with n-alkanes (petroleum hydrocarbons). In non-polluted sites the value always remains constant while in polluted sites the values of total petroleum hydrocarbons vary within the studied locations (Jeng, 2006). The ACL value in the sediments at drainage discharge points into the New Calabar River ranged from 26.738 to 27.912 with an average value of 27.368. The values of ACL obtained in this study indicated that the drainage discharge points into the New Calabar River was contaminated or polluted with total petroleum hydrocarbons that had origin from both natural and anthropogenic sources. The relationship between CPI and ACL is that CPI values increases when ACL values are increasing (Fagbote & Olanipekun, 2013). This agreed with the findings in this present investigation.

Partition coefficient of total petroleum hydrocarbons at effluent discharge points of the New Calabar River

The partition coefficient of total petroleum hydrocarbons is a function of how stable total petroleum hydrocarbons as a pollutant exist in the water and sediment columns at the drainage discharge points of the New Calabar River. Partition coefficient is useful in explaining and showing the phase preference of aquatic pollutants such as total petroleum hydrocarbons in the water and sediment columns of any water body such as rivers, creek and estuaries. From the recorded results, values lower than one showed that the pollutant is more in the water phase or prefers the water phase

while values higher than one showed that the pollutant is more in the sediment phase or sediment loving. Table 5 above indicate partition coefficient of total petroleum hydrocarbons concentrations between sediment and water phases in order to know which phase is more acceptable. The result obtained showed that the sediment phase was higher than the water phase. This could be as a result of the hydrophobic nature of total petroleum hydrocarbon components. Results recorded revealed that the studied contaminant, total petroleum hydrocarbons have preference for the sediments phase. The results obtained from the drainage discharge points of the New Calabar River showed that certain hydrocarbon components were more in the water phase, (that is being more) in the surface water than the sediment. This could be as a result of the prevalent conditions at the stations during the time the samples were collected. This recorded observation might have been due to the mode of flow at the drainage discharge, fresh oil being released into the river at the points of discharge, and disturbances linked with that station where such occur. Also it may be due to the affinity the pollutant have for the water phase. Moreover, leakages and accidental release of hydrocarbon oils that contains TPH components could be floating on the water surface for a short while, thereafter biodegradation by microorganisms or the sun alters them and then mix them up with particulate/suspended matter floating on the water surface that originated from runoffs and then gradually fall to the bottom and sedimented through the force of gravity (Okoro, 2008). In general, there is the tendency for total petroleum hydrocarbons to have increased levels in the sediments when compared to the surface water. This is as a result of complex components of the hydrocarbon remains found in the sediments due to sinking and settling down to be an integral part of the sediments (Ololade, et al., 2009). This observation confirms the fact that heavy metals and heavier components of petroleum residue are solids, therefore prefer the sediment phase of the water bodies.

Conclusion

This research work studied assessment of total petroleum hydrocarbons concentrations in water and sediments at drainage discharge points into the New Calabar River, Port Harcourt, Nigeria. This research work revealed that total petroleum hydrocarbons were present in the water and sediment from the samples collected at the different stations of New Calabar River where there is drainage discharge more than places where there were no drainage discharges. The contamination of the river at those points used in the investigation by total petroleum hydrocarbons were basically due to the effects of the drainage that bring into the river land-based hydrocarbon components which could have been due to anthropogenic activities such as oil bunkering, transportation, gas flaring and effluents from industries, homes and public places which find their way through runoffs from drainages into the river.

Recommendations

1. The concentration of total petroleum hydrocarbons (TPH) in surface water at the drainage discharge points into the New Calabar River exceeded acceptable limits, indicating significant contamination. Therefore, the water should not be used for domestic activities such as bathing and washing.
2. Local residents should avoid consuming aquatic plants and animals from the affected areas of the river to minimize the risk of TPH accumulation in human tissues and the associated health hazards.
3. Government agencies should implement effective monitoring and control measures to prevent further hydrocarbon contamination of the New Calabar River, particularly by regulating materials discharged through drainage systems into the river.

References

- Ahmed, O. E., Mahmoud, S. A., & El-Nemr, A. (2015). Distribution and sources of n-alkanes in aquatic sediments. *Egyptian Journal of Aquatic Research*, 41(3), 209–217.
- Al-Baldawi, I. A., Abdullah, S. R. S., Suja, F., & Anuar, N. (2015). Phytodegradation of total petroleum hydrocarbons in diesel-contaminated water using aquatic plants. *Ecological Engineering*, 74, 463–473.
- Bianchi, T. S. (2007). *Biogeochemistry of estuaries*. Oxford University Press.
- Corte, C., Ferrari, B., & Piazzalunga, A. (2012). Gas chromatographic determination of petroleum hydrocarbons in environmental samples. *Journal of Chromatographic Science*, 50(9), 803–810.
- Directorate of Petroleum Resources (DPR). (2002). *Environmental guidelines and standards for the petroleum industry in Nigeria (EGASPIN)*. Department of Petroleum Resources.
- Directorate of Petroleum Resources (DPR). (2011). *Guidelines and standards for environmental pollution control in Nigeria*. Department of Petroleum Resources.
- Duan, F., He, K., & Liu, X. (2010). Characteristics and source identification of fine particulate n-alkanes in Beijing, China. *Journal of Environmental Sciences*, 22(7), 998–1005.

- Edori, O. S., & Edori, E. S. (2021). Ecological implications of petroleum hydrocarbon contamination in aquatic ecosystems. *World News of Natural Sciences*, 37, 75–89.
- Edori, O. S., & Iyama, W. A. (2019). Source identification of polycyclic aromatic hydrocarbons in water at point of effluent discharge into the New Calabar River, Port Harcourt, Rivers State, Nigeria. *International Journal of Environment and Climate Change*, 9(6), 343–349.
- Edori, O. S., & Marcus, A. C. (2021). Hydrocarbon pollution and sediment quality assessment in aquatic ecosystems. *International Journal of Environment and Pollution Research*, 9(1), 45–59.
- Fagbote, E. O., & Olanipekun, E. O. (2013). Characterization and sources of aliphatic hydrocarbons of the sediments of River Oluwa at Agbabu Bitumen area, Western Nigeria. *Journal of Scientific Research and Reports*, 2(1), 228–248.
- Federal Environmental Protection Agency (FEPA). (2003). *Guidelines and standards for environmental pollution control in Nigeria*. Federal Environmental Protection Agency.
- Federal Ministry of Environment (FME). (1991). *National environmental protection regulations*. Federal Ministry of Environment.
- Gao, X., & Chen, S. (2008). Sources and distribution of hydrocarbons in surface sediments from the Bohai Sea, China. *Marine Pollution Bulletin*, 56(5), 1000–1005.
- Green, A. F., Owoh, A. A., Timothy, C. F., Ofuru, R. O., & Samuel, C. (2025). Investigating total petroleum hydrocarbon (TPH) level in aquatic organisms in the New Calabar River, Nigeria. *Asian Journal of Fisheries and Aquatic Research*, 27(5), 106–112.
- Ikpe, F. N., Owate, I. O., & Menkiti, M. C. (2016). Evaluation of total petroleum hydrocarbon contamination in Ethiopie River, Nigeria. *International Journal of Scientific and Engineering Research*, 7(5), 136–143.
- Jeng, W. L. (2006). Higher plant n-alkane average chain length as an indicator of petrogenic hydrocarbon contamination in marine sediments. *Marine Chemistry*, 102(3–4), 242–251.
- Kiran, R., Prasad, M. B. K., & Rao, G. D. (2015). Assessment of petroleum hydrocarbon contamination using average carbon length indices. *Environmental Monitoring and Assessment*, 187(8), 510.
- Kpee, F., & Bekee, B. A. (2021). Ecological consequences of petroleum hydrocarbon contamination in aquatic ecosystems. *Journal of Environmental Science and Public Health*, 5(4), 356–369.
- LAWI. (2011). *Laboratory analytical work instructions for hydrocarbon extraction methods*. Laboratory Analytical Work Institute.
- Luan, T., & Szelewski, M. (2008). Carbon preference index as an indicator of petroleum contamination. *Environmental Forensics*, 9(4), 340–347.
- Maioli, O. L. G., Rodrigues, K. C., & Knoppers, B. A. (2011). Distribution and sources of hydrocarbons in sediments. *Marine Pollution Bulletin*, 62(9), 1919–1929.
- Michelle, A., Brown, T., & Evans, R. (2014). Application of carbon preference index in environmental hydrocarbon studies. *Environmental Monitoring and Assessment*, 186(12), 8451–8460.
- Okoro, D. (2008). Fate of petroleum hydrocarbons in aquatic environments. *Nigerian Journal of Environmental Sciences*, 2(1), 40–49.
- Ololade, I. A., Lajide, L., & Amoo, I. A. (2009). Petroleum hydrocarbon contamination in sediments and surface water. *Research Journal of Environmental Sciences*, 3(4), 394–402.
- Omokpariola, D. O., Nduka, J. K., Kelle, H. I., Mgbemena, N. M., & Iduseri, E. O. (2022). Chemometrics, health risk assessment and probable sources of soluble total petroleum hydrocarbons in atmospheric rainwater, Rivers State, Nigeria. *Scientific Reports*, 12, 118–129.
- Stanley, H. O., Immanuel, O. M., & Nwagboso, A. (2017). Water quality assessment of the New Calabar River. *Journal of Applied Life Sciences International*, 15(2), 1–5.
- Wang, Z., Stout, S. A., & Fingas, M. (2015). Forensic fingerprinting of petroleum hydrocarbons in environmental matrices. *Journal of Chromatography*, 843(1), 369–411.
- Wu, Y., Zhang, J., & Mi, T. (2001). Sources and distribution of hydrocarbons in sediments from Chinese estuaries. *Marine Chemistry*, 76(2), 1–16.
- Zabbey, N., Hart, A. I., & Wolf, H. D. (1994). Petroleum hydrocarbon pollution: Distribution in sediment and water of the New Calabar River, Port Harcourt, Nigeria. *Science of the Total Environment*, 141(1–3), 217–221.