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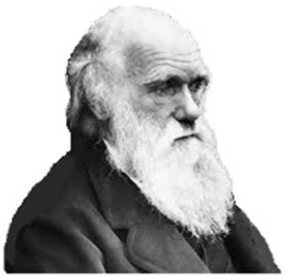

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Distribution and Source Fingerprinting of Total Petroleum Hydrocarbons in Sediments of the River Niger at Okpu and Iyiowa-Odekpe Axes in South-Eastern, Nigeria

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ABSTRACT

The assessment of total petroleum hydrocarbons (TPH) status as well as the aliphatic profiles of sediments from the Okpu and Iyiowa-Odekpe segments of the River Niger in South-Eastern Nigeria was conducted during the year 2021 – 2022. Composites samples taken from sediments at five (5) different locations (ST-A, ST-B, ST-C, ST-D, & ST-E) for the months of June, September, December, and February, were extracted with dichloromethane (DCM) using soxhlet extractor followed by a silica gel clean up and fractionation into aliphatic and aromatic fractions. Analysis of aliphatic fraction (Total Aliphatic Hydrocarbons –TAH - and aliphatic components) were done with gas chromatography-flame ionization detector (GC-FID); while the polycyclic aromatic hydrocarbons (PAHs) were determined with gas chromatography-mass spectrometry (GC-MS). The summations of TAHs and PAHs gave the TPHs concentrations that ranged from 108.04 – 1091.46mg/Kg with a mean of 440.0234 ± 54.78mg/Kg. The mean value for the raining season (515.10±281.73 mg/Kg) was significantly higher than that of the dry season (364.94 ± 205.54 mg/Kg). The range of values were also much higher than the Nigerian Department of Petroleum Resources (DPR) target value of 50mg/Kg but considerably much lower than the intervention value (5,000mg/Kg) set by the same body. Source diagnostic indices of aliphatic hydrocarbons gave range of: even to odd numbered n-alkane ratio (0.7183 – 1.7184), carbon preference index – CPI (0.65041 – 1.4520), sum of low molecular weight to high molecular weight n-alkane (1.0559 – 8.8077), nC31/nC19 (0.16867 – 1.1461), sum of long chain hydrocarbons to short chain hydrocarbons (0.1686 – 1.1470), and pristane/phytane ratio (0.6523 – 2.5284); suggesting that the TPHs in sediments were from mixed origin – anthropogenic and biogenic. Inputs from biogenic sources were however, dominated by marine sources. Developmental plans and actions that will reduce these anthropogenic inputs are necessary to protect the aquatic lives and sustain public health.

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***Keywords*:** Total petroleum hydrocarbons, River Niger, Sediments, Source diagnostic index, Anthropogenic, Biogenic, Contamination

1. INTRODUCTION

The coastal water of the Niger Delta has been most hit with pollution resulting from oil related activities. The discovering and exploration of oil in Nigeria is not without its attendant woos as oil spillage arising from inappropriate handling of sites facilities as well as deliberate bunkering activities have often presented great damage to the environment. As there are several hundreds of chemical compounds in crude oil and its refined products, it is difficult to measure each compound separately in the environment.

Therefore, Total Petroleum Hydrocarbons (TPHs) measure is used to give a definitive picture of the whole. TPH is frequently used gross parameter for the quantification of environmental contaminants originating from crude oil and its products such as fuels, oils, lubricants, waxes etc, and is majorly composed of hydrogen and carbon, thus, the name petroleum hydrocarbon (ESD, 1993; Schwartz, 2012). TPHs is available in the range of C8 – C40 as mixtures composing hundreds to thousands of hydrocarbons including aliphatic (straight carbon chain, branched chains and cycloalkanes), and aromatics (carbon ring) compounds. Priority pollutants such as volatile organic compounds (VOCs), semi-volatile compounds (SVOCs), and metals may also be present in such mixture (Inyang et al., 2018) Hydrocarbons though present naturally in the environment, larger portion of it in contaminated environment which gets into water bodies comes from the activities of man such as: oil exploration and exploitation, pipelines leakages and vandalization, runoff from petroleum contaminated soils, leakages from farm tanks, tankers, trucks, vessels and ships, oil spills, and indiscriminate dumping of petroleum products on water ways (Nia, 2020; Joshua, 2020).

Sewage, municipal and industrial discharges, automobile wastes and vehicular emission arising from incomplete combustion carried by runoff and brought down to water bodies constitute other anthropogenic sources of TPH (Chokor, 2021). Flocculation, coagulation, and sedimentation processes serve to scavenged the TPH from water column onto sediments such that their concentrations in sediments may be several order magnitude higher than in water column (Oliver, 2008; Adeniji et al., 2017a). The accumulation of petroleum hydrocarbons in sediments represent a potential health risk to benthic fauna and may results to developmental malformations, loss of reproductive capacity and several diseases in sediment dwelling organisms and fishes. The lipophilic, low-biodegradability, and persistence nature of some petroleum hydrocarbons enhance their biological magnification along the food chain and accumulation in higher organisms and man (Suresh, 2019; Muhammad, 2015).

Organisms and individuals exposed to petroleum hydrocarbons exhibits a number of health complications such as: disruption in the activities of various body organs, severe damage to the pancreas, kidney, liver, blood circulatory system, and ultimately death (Abha and Singh, 2012; Oyinbo et al., 2018). humans health complications like skin rashes and irritation, genotoxicity, deoxyribonucleic acid (DNA) damage, birth defects, childhood leukaemia, infertility and miscarriages in women, respiratory system disorders, and cancers of different parts (organs) of the body, have also been linked to petroleum hydrocarbons contamination (Hurtig and Sabastian, 2002; Sudakin et al., 2011; Olawoyin et al., 2012; Ordinioha and Brisibe,

2013; Gudzenko et al., 2015; Ezekwe and Edoghotu, 2015; Kponee et al., 2015; Asghar et al, 2016, Briggs and Briggs, 2018; Ite et al., 2018; Chokor, 2021).

Factors that could determined the impact of petroleum hydrocarbon on aquatic system and human health in general include: the bioavailability of specific hydrocarbon and its degradability, organisms capability to metabolize and accumulate such hydrocarbons, the fate of the metabolized products, and the interference of specific hydrocarbons with normal metabolic processes (Lamardo et al., 2013; Lee et al., 2015). However, impairment of feeding mechanisms, growth rates, development rates, and increased susceptibility to diseases and other histopathological disorders are some of the general subtle acute effects that may crop up due to petroleum hydrocarbons exposure (Al-Shwafi 2008; Enuneku et al., 2015). Shorten survival rate, reduced reproductive success, and impaired physiology are possible chronic low-level exposure effects (Enuneku et al., 2015; Lee et al., 2015; Chokor, 2021).

Various diagnostic indices have been used to determine the source of hydrocarbons in water and sediments environment by various authors (Riccardia et al., 2008; Kanzari et al., 2012; Fagbote and Olanipekun, 2013; Farid et al., 2014; Ahmed et al., 2015; Adeniji et al., 2017a; Chokor,2021). Among them are: ratio of even to odd numbered alkanes, carbon preference index (CPI), ratio of low molecular weight to high molecular weight hydrocarbons (∑LMH/∑HMH), nC31/nC19 ratio, long chain to short chain hydrocarbon ratio (LHC/SHC), pristane to phytane (Pr/Ph) ratio, average carbon length (ACL), etc. Proper applications of these indices have helped to delineates whether hydrocarbons in an environmental medium are from anthropogenic petroleum source or from biogenic (natural) sources; and if biogenic the index also tells if source is terrestrial or marine. Previous pollution study in the Okpu and Iyiowa-Odekpe segments of the River Niger by Chokor (2021), dealt with the surface water. This study however, focus on the distribution of Total Petroleum Hydrocarbons (TPH) content in the sediments as well source(s) identification of the same using suitable diagnostics ratios of aliphatic hydrocarbons profiles.

2. MATERIALS AND METHODS

2. 1. Study area

The Niger River originates from the Guinea Highlands in South-Eastern Guinea goes through almost every climatic zone in West Africa. It is the third longest river in Africa, exceeded only by the Nile and Congo River (also called the Zaire River), encompassing about 4,180 Km (2,600 mi) with a drainage basin of about 2,117,700 Km^2 (817,600 sqmi) in area. It meanders through Mali, Niger on the border with Benin and then enters into Nigeria where it's eventually discharge through a massive delta known as the Niger Delta into the Guinea Gulf of Atlantic Ocean. Sediment samples were taken from the bottom surface (5 –10 cm) using a Van Veen grab sampler at the vicinity of the popular Niger Bridge which connects Okpu, Delta State (South-Southern Nigeria) and Iyiowa-Odekpe in Ogbaru local Government Area, Anambra State (South-Eastern Nigeria). Five composite samples were collected at five different locations at some kilometres apart in the River and their coordinates were properly recorded viz: ST-A (N06°07'00.78" E06°45'11.95"), ST-B (N06°06'00.22" E06°43'38.13"), ST-C (N06°05'25.98" E06°45'16.35"), ST-D (N06°04'37.50" E06°44'43.84") and ST-E (N06°02'11.03" E06°44'07.12"). The area is characterized by the presence of: petroleum and allied products companies (such as Cychris Petroleum Ltd, Edga Petroleum Ltd, and Filling

Stations), food processing and packaging factories (e.g. Pax Christi integrated food and beverage Ltd, MUR foods and restaurant) and a naval base (Navy outpost, Odekpe), etc. The major activities taking place at the river side's include: commercial marketing (Ogbo Agbada Market), sand dredging, commercial shipping, and regular vehicular transportation including movement of trucks (Tippers). Also evident in the area is the indiscriminate dumping of waste on the River.

2. 2. Sample collection

Composited samples of sediments were taken the different locations of the river and placed in a pre-cleaned wide-mouth amber bottle. They were kept in an ice-parked cooler at temperature below 4 °C for onward transportation to laboratory for analysis (Ikpe et al., 2016). Collections of samples were done in the months of June, September, December and February.

2. 3. Extraction of TPH

Sediment samples were air dried at room temperature for a period of five (5) days. The samples were sieved and homogenized. The aliquot of the air dried samples (10g) was mixed with sufficient quantity of anhydrous sodium sulphate (Na_2SO_4) (about 5g) to remove moisture, spiked with surrogate standard (10 µg/mL of 1-chlorooctadecane), wrapped in a filter paper, placed in a thimble and then loaded into the main chamber of the soxhlet extractor. Extraction was done with dichloromethane for 24 hr. Extracts were dried by passing through column of anhydrous sodium sulphate; and reduced to about 2mL with a rotator evaporator (Adeniji et al, 2017a; Iyang et al., 2018).

2. 4. Sample clean-up and separation

Concentrated extracts were transferred into a chromatographic column (10 mm i.d. X 30 cm) parked with 10g activated silica gel slurry about 2cm anhydrous Na_2SO_4 layer on top. The sample was first eluted with 30 mL of n-hexane to obtain the hydrocarbon fraction followed by 30 mL of DCM to obtain the aromatic fraction. The eluates were concentrated to approximately 2 mL with rotator evaporator at 30 °C; 1.5mL of it was transferred into chromatographic vial and stored at 4 °C awaiting gas chromatographic analysis. A blank sample was processed the same way for quality assurance (Maioli et al., 2011; Adeniji et al., 2017a; Iyang et al., 2018).

2. 5. Gas chromatography analysis

The TAHs (Aliphatic hydrocarbons) analyses were done with gas chromatography coupled to a flame ionization detector (GC-FID); Agilent 6890N system equipped with DB-5 capillary column with dimension of 30 m X 0.32 mm X 0.25 µm. The volume of sample injected was 1 µL while the carrier gas was helium at a flow rate of 1mL/min. Samples injection was in split less mode. The column temperature was programmed with initial temperature of 50 °C for 5 minutes then increased to 150 °C at rate of 10 °C /min. for 15 minutes; after which it was ramped at 16 °C/min to 280 °C and held for 5 minutes. The injector and detector temperatures were set at 200 and 300 °C respectively.

The sum of the sixteen priority polycyclic aromatic hydrocarbons (∑16PAHs) were determined in the aromatic fractions by the same version of gas chromatography (Agilent 6890N) above but couple to a mass spectrometer as detector The gas chromatographic column had an initial temperature of 70 °C, which was held for 20 min, and was then increased at 25

°C min^{-1} to 150 °C; it was further raised to 200 °C at 3 °C min^{-1}, and finally increased to 300 °C at 2 °C min^{-1}. The temperature of the injection port, ion source, quadrupole and transfer line were 250, 230, 150 and 280 °C respectively. The sample was injected into the GC via a pulsed spit-less mode with an injection volume of 1µL. The sum of all aliphatic and aromatic hydrocarbons measured by the GC provides a measure of total petroleum hydrocarbons (TPH) concentration.

2. 6. Determination of Physicochemical Parameters

The physicochemical properties of the sediments: pH, organic matter, and particle size analyses were determined using Standard methods (Folson et al., 1981; Nelson and Sommer, 1982; Gee and Or, 2002).

3. RESULTS AND DISCUSSION

3. 1. Concentrations of TPH in sediments

Table 1 and Fig. 1 express the levels of total petroleum hydrocarbons (TPH) for the months of June, September, December, and February at the different sampled stations alongside with the calculated mean for the months and stations (ST- A, B, C, D, & E). The pollution statuses of TPHs in the stations did not follow any regular fashion down or upstream; an indication that pollutants TPHs were from diverse sources rather than originating from a point source.

The average TPH values for the months of June, September, December, and February for all locations were: 489.41 ±289.19, 504.80 ±309.18, 372.90 ±229.24, and 356.98 ±205.77 mg/Kg respectively. The mean concentrations for each station in all the sampled months were: 487.33 ±163.24, 214.92 ±110.14, 310.64 ±87.51, 842.06 ±182.39, and 345.17 ±48.55 mg/Kg for stations A, B, C, D, and E respectively. The mean for all samples at all stations for all the months was 440.0234±54.78 mg/Kg.

Station D had the highest mean (842.06 ±182.39 mg/Kg) for the months' sampled while; the least was in station B (214.92 ±110.14 mg/Kg). The values in other stations were: A (487.33 ±163.24mg/Kg), C (310.64 ±87.51 mg/Kg), and E (345.17 ±48.55 mg/Kg). The highest concentration (1,091.46 mg/Kg) was recorded in September at station D while the lowest (108.04 mg/Kg) was observed in the month of February at station B. Temporal distribution of TPH in the sediments follows the order previously reported by Chokor (2021) for surface water of the same River viz: September > June > December > February. The mean for the samples taken during the raining season (June and September) was 515.10±281.73 mg/Kg with a range of 238.40 – 1,091.46 mg/Kg, while that for the dry season (December and February) was 364.94 ± 205.54 mg/Kg with a range of 108.04 – 752.46 mg/Kg. Generally, the values for the raining season were more than that for the dry season.

This could be adduced to: washing of TPH into the river from land and road surface during the rains, increased volatilization and degradation of TPHs due to increased temperature during the dry season (Chokor, 2021). Higher temperature also increase the photochemical decomposition of hydrocarbon in the atmosphere, a factor that could aid the reduction of contaminants recorded in the season. The re-suspension of TPH from sediments due to increased water current arising from increase discharged during the raining season perhaps is not enough to counteract the above effects.

Table 1. Concentrations (mg/Kg) of TPH in sediments at different locations in different months.

Stations Concentrations (mg/Kg)	Raining season		Dry season			
	Jun.	Sep.	Dec.	Feb.	Range	Mean
ST-A	731.6989	417.9525	392.5007	407.1526	392.50 – 731.70	487.3262 ±163.2487
ST-B	238.4044	358.9581	154.2773	108.0437	108.04 – 358.96	214.9209 ±110.1493
ST-C	249.8353	437.0276	253.8138	301.8942	253.81 – 437.03	310.6427 ±87.5152
ST-D	853.7953	1091.4635	752.4647	670.5063	670.51-1,091.46	842.0575 ±182.3895
ST-E	373.3390	398.5761	311.4319	297.3317	297.33 – 398.58	345.1697 ±48.5539
Mean	489.4146 ±285.1986	540.7956 ±309.1813	372.8977 ±229.2429	356.9857 ±205.7776	356.99 – 540.80	440.0234 ±54.78

*ST: station

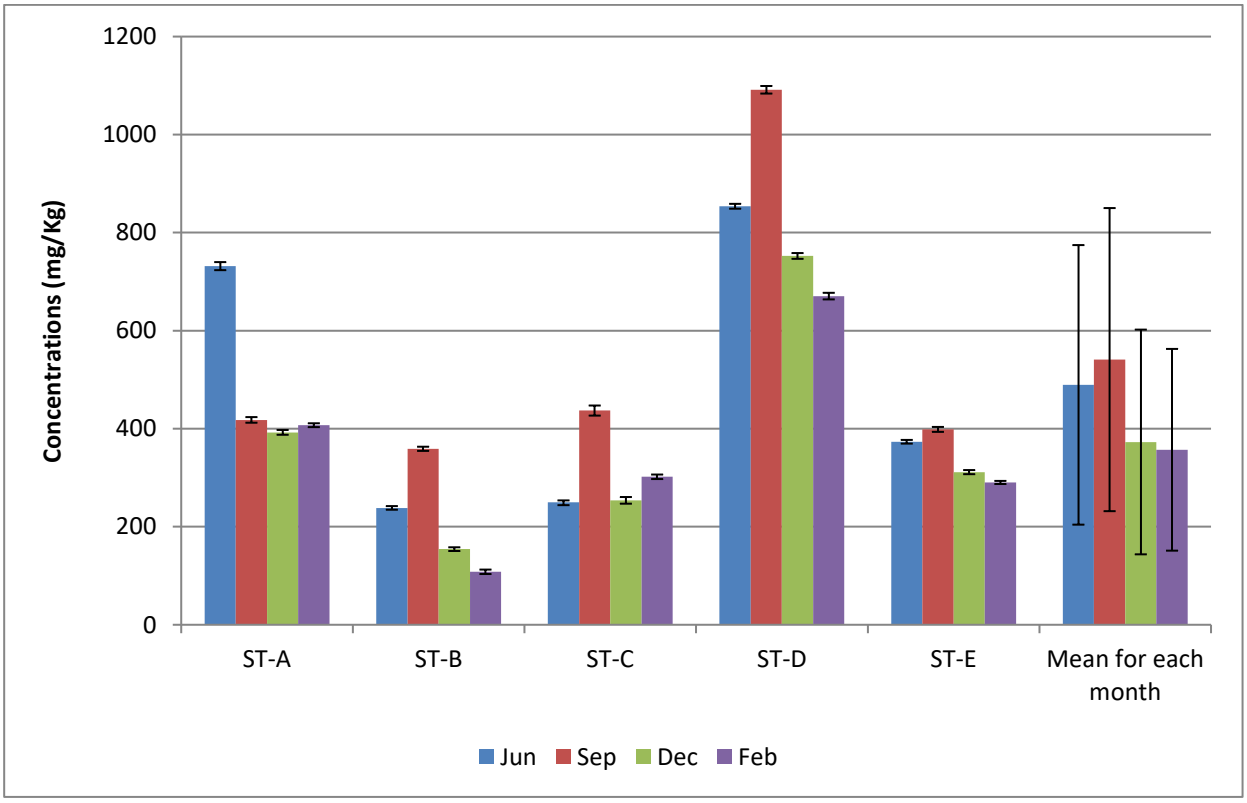

Fig. 1. Levels of TPHs (mg/Kg) in sediments at different stations in the different months

Four levels of hydrocarbon pollution have been proposed by Massoud et al (1996) for the assessment of marine sediments viz: unpolluted (10 – 15 mg/Kg), slightly polluted (15 – 50 mg/Kg), moderately polluted (50 – 200 mg/Kg), and heavily polluted (> 2000 mg/Kg). The Nigerian Department of Petroleum Resources (DPR) however, set target and intervention values of 50 mg/Kg and 5,000 mg/Kg respectively as environmental guidelines for soil and sediment's TPH. The range of values obtained in this report tends to suggest heavily polluted status. However, the values were much below the DPR intervention value.

The range of TPH in sediments (108.0437 – 1,091.4635 mg/Kg) obtained in this study, is comparable to the values of: 270 – 830 mg/Kg reported for the Qua-Iboe River, Akwa-Ibom State, Nigeria (Inyang et al., 2018), the 112.30 – 657.30mg/Kg observed for the New Calabar River, South-Southern Nigeria (Ibigoni et al., 2009), and the 54.72 – 2,002 mg/Kg recorded for River Oluwa, western Nigeria (Fagbote and Olanipekun, 2013). Elsewhere, around the world, the range of values is comparable to the 12.59 – 1,100 mg/Kg range reported for the sediment of the Buffalo River Estuary, Eastern Cape Province, South Africa (Adeniji et al., 2017b), the 50 – 1,122 mg/Kg range recorded by Massoud et al (1996) for Arabian Gulf sediments in Kuwait, and the 35.6 – 1,466.1 mg/Kg range reported for surface sediments from South China Sea of Kuching Division (Yusoff et al., 2012).

The range of values were however, much lower than the 400 – 6,205 mg/Kg reported for sediments from the Upper Reaches of the Sombreiro River, Niger Delta, Nigeria (Howard et al., 2012), the 1,403 – 3,755 mg/Kg reported by Wokoma (2014) for sediments of polluted tidal creek in Bonny River, Nigeria, and the 1,242 – 5,200 mg/Kg reported for soils in communities of Niger Delta region, Nigeria (Alinnor et al., 2014). The range of values were also less significant than the 496 – 8,972 mg/Kg observed by Guerra-Gracia et al (2005) for sediment of Ceuta harbour, North Africa, Spain, as well as the 1,116.3 – 2,137.4 mg/Kg reported by Farid et al (2014) for sediments along discharged Basin of Suez oil Refinery Company, South West of the Suez Gulf.

The ranges of values however, were larger than those reported from Onyima Creek, Niger Delta, Nigeria (25.46 – 69.35 mg/Kg) (Edori and Edori, 2021), Woji Creek, Niger Delta Estuary of Rivers State, Nigeria (3.162 – 8.758 mg/Kg) (Ihunwo et al., 2021), Algoa Bay, Eastern Cape, South Africa (0.72 – 27.03 mg/Kg) (Adeniji et al., 2017a), Bizerte Lagoon, Tunisia (0.05 – 20 mg/Kg) (Mzoughi et al., 2005), Candarli Gulf, Turkey (3.88 – 24.7 mg/Kg) (Filiz et al., 2012), Mediterranean Sea, Dameltal harbour (0.16 – 4.16 mg/Kg) (Shereet, 2009) and the Black Sea, Monaco (2.1 – 310 mg/Kg) (Readman et al., 2002). The value range was also higher than the 0.52 – 4.59 mg/Kg and 0.26 – 1.64 mg/Kg respectively reported for the coaster areas of Papar and Putatan, both in Sabah, Malaysia (Siti Aishah et al., 2013).

The mean of this study (440.023 ±54.78 mg/Kg) is much higher than the 0.131 mg/Kg reported for Ugbo water ways, South Western Nigeria (Ashiru and Ogundare, 2019), the 41.214 mg/Kg of Onyima Creek, Niger Delta reported by Edori and Edori (2021). It was also greater than the 184.89 mg/Kg reported by Horsefall (Jr) et al (1994) for sediments of New Calabar River, South Southern Nigeria; the 339.2 mg/Kg observed for sediment of oil polluted coastal areas of South Eastern Nigeria (Eja et al., 2003), and the 219 ±229 mg/Kg reported for six different streams and rivers sediments of Ibadan, Western Nigeria (Onianwu and Essien, 1999). Elsewhere around the globe, the value is greater than the 209.81 mg/Kg recorded for sediments of Buffalo River Estuary, Eastern Cape Province in South-Africa (Adeniji et al., 2017b), the 8.695 mg/Kg reported for Candarli Gulf, Turkey (Filiz et al., 2012), the 59.656 mg/Kg observed

for the Black Sea, Monaco (Readman et al., 2002), and the 10.46 ±6.83 mg/Kg reported for the coastal sediments of Askar, East of Bahrain (Al-Khatlan et al., 2019).

The mean was however lower than those reported for sediments of some Nigerian Rivers viz: 606.83±229.48 mg/Kg for the Qua-Iboe River (Inyang et al., 2018), 528.25 mg/Kg in the Upper Bonny River (Ideriah et al., 2006), 1,602.4±8.9 mg/Kg for the Ubeji River (Adewuyi et al., 2011), 41,900 mg/Kg for the Benin River adjacent to a Lubricating oil production Factory (Akporido and Ipeaiyeda, 2014), and the 215,730±81 and 215,700±77 mg/Kg for the Odidi and Egwa Rivers(both in Warri) respectively (Ogeleka et al., 2016). Elsewhere around the world, the value is comparably lower than the 1820mg/Kg observed for the Baku Bay, Azerbaijan (Tolosa et al., 2004), the 779 mg/Kg in Bapco Oil Coastline – around a refinery in Bahrain (Tolosa et al., 2005), and the 1,638.683 mg/Kg along discharged Basin of Suez Oil Refinery Company, South west of the Suez Gulf (Farid et al., 2014).

3. 2. TPH relationship with physicochemical properties of the sediments

Some basic physicochemical properties of the sediments are as shown in Table 2 while their relationships with TPH are shown in Table 3.

Table 2. Some physicochemical properties of the sediments

Stations Properties	pH	% OM	% Sand	% Clay	% Silt
ST-A	6.19	2.57	17.71	71.95	10.34
ST-B	5.89	3.24	23.57	72.10	4.33
ST-C	5.94	3.76	16.46	70.35	6.19
ST-D	6.08	7.00	15.15	81.11	3.74
ST-E	6.16	1.27	25.38	66.97	7.65
Mean	6.05±0.13	3.57±2.13	19.65±4.53	72.50±5.24	6.45±2.67

Table 3. Correlation coefficient between TPH and some physicochemical Properties of the Sediments.

	pH	% OM	% Sand	% Clay	% Silt
TPH	-0.5132*	0.7647**	-0.6550*	0.8427**	-0.1944

** Significant at 1% level, *Significant at 5% level

The pH range was from 5.89 – 6.19, while that organic matter was from 1.27 – 7.00%. Particle size analysis reveals the sediments to be largely dominated by clay size particles. Very

significant positive correlations between TPH and Sediments' physicochemical properties (Table 3) were observed only for organic matter and clay content. Clay sized particles and organic matter (OM) can serve as a useful media for sorption of contaminants thus, playing active roles in the accumulation and release of contaminants in sediments. The relative high percent of organic matter (OM) and clay sized particles in these sediments encourage the much sorption of petroleum hydrocarbons in the sediments. This fact is revealing by the strong correlation between organic matters, clay sized particles and TPH in the sediments. The slight negative correlation between percent sand and TPH reveals that the more the sand fractions in sediments, the less the TPHs accumulated in it. Likewise, the slight negative correlation between pH and TPH might have resulted from the ability of TPHs pollutants to contribute to sediments' acidity. Thus, the more the TPH in sediments, the more acidic (decreasing pH) the sediments becomes. Chemical pollutants are known to effect change in pH levels, and impact toxicity of the medium.

3. 3. Distributions of aliphatic hydrocarbons and source identification

Table 4, shows the average distributions of aliphatic hydrocarbons for the months in the different stations in the sediments of Okpu and Iyiowa-Odekpe sections of the Niger River. Its reveal that the most visible hydrocarbons range was the $C_{15} – C_{24}$. This was followed by the hydrocarbon range of $C_{30} – C_{35}$ with station A (ST-A) having more contributions to this range of hydrocarbons. The isoprenoid hydrocarbons – pristane and phytane were also present in all sampled sites. TPH has been grouped based on fate and transport in the environment into Gasoline Range Organic (GRO), Diesel Range Organic (DRO), and Oil Range Organic (ORO) with hydrocarbons ranges fallen within, $C_6 –C_{10}$, $C_{10} – C_{28}$, and above C_{28} respectively (TPHCWG, 1997). It can therefore be said, that the hydrocarbons contaminants in these sediments were majorly in the Diesel and Oil range organics. However, the lack of strong presence of Gasoline range organic and lower fractions of hydrocarbons (up to C_{14}) in the sediment could be adduced to: their high volatility, higher solubility in water column (relative to heavier fractions), and probably the sample preparative stages that allow some of the lower fractions to be removed during drying and concentration processes. The strong presence of Diesel and Oil range hydrocarbons could have come from spills from heavy truck engines, diesel-engine generators, and tanks, fuel from ships engines as well as hydrocarbons washed down the drain by the rains. Relatively high concentrations of THP in surface water of this area due large presence of heavy trucks and vehicles in the vicinity of the overhead bridge as well as the prevalence of commercial shipping activities have been reported by Chokor (2021). Petroleum hydrocarbons in surface water are finally scavenged from the water column unto bottom sediment through processes of flocculation, sedimentation and coagulation resulting concentrations in sediments several orders of magnitude greater than in the water column. The large presence of low molecular weight hydrocarbons particularly, $C_{15} – C_{21}$ tended to suggest a recent contamination of these sediments (Ekpo et al., 2012). Anthropogenic inputs from transportation activities, spills from petroleum products, outboard and inboard boats engines, and run-off from domestic waste, sewage out-falls and industrial discharge are the likely culpable sources of these contaminants. The TPH in the bottom sediments were largely due to aliphatic hydrocarbons, as PAHs (Polycyclic Aromatic Hydrocarbons) constituted less than 1% of the total petroleum hydrocarbon (TPH) content (Table 4). The sum of sixteen priority PAHs ($\sum$16PAHs) in the sampled stations ranges from 0.5065 – 4.1629 mg/Kg corresponding to 0.23 – 0.85% of the TPH.

Table 4. Mean aliphatic profiles of hydrocarbons in sediments at the different stations.

Components Concentrations (mg/Kg)	ST-A	ST-B	ST-C	ST-D	ST-E
C_8	5.2105	0.1576	3.0685	4.7129	2.0585
C_9	0.0155	0.0445	0.0432	0.0119	0.0115
C_{10}	0.2967	0.0167	0.1849	0.2854	0.1600
C_{11}	0.1324	0.1558	0.0551	0.0578	0.0353
C_{12}	0.1864	0.1653	0.0898	0.1359	0.0536
C_{13}	0.8771	0.8290	0.5168	2.6520	1.1536
C_{14}	5.3736	1.6478	3.3002	8.4929	2.0848
C_{15}	8.9014	7.6004	5.7016	18.8026	4.7574
C_{16}	21.1479	5.4726	12.2657	44.7555	20.4515
C_{17}	50.4599	10.1641	32.5459	131.4696	62.4834
Pristane	35.9160	17.6057	22.5557	97.4467	42.7447
C_{18}	28.5439	25.1270	17.0250	74.0641	34.6780
Phytane	34.1437	26.9830	19.9366	118.6376	16.9058
C_{19}	16.8949	27.5148	28.2062	64.3092	26.6586
C_{20}	81.3473	17.0397	18.4462	41.5176	22.1243
C_{21}	29.1385	3.2187	17.6916	84.4604	17.7657
C_{22}	9.2404	7.6389	6.4537	20.3358	6.6213
C_{23}	3.4781	1.1594	10.9151	10.5881	14.4535
C_{24}	5.9091	2.2392	3.0537	30.7265	16.6268
C_{25}	0.6666	0.2168	0.8859	1.9452	5.0963
C_{26}	2.9910	1.2180	1.3641	2.5950	1.0159
C_{27}	1.1029	3.0672	1.0940	2.7976	1.1119
C_{28}	2.9354	1.2811	4.5078	1.9763	1.0862
C_{29}	2.1718	1.8311	6.0019	6.0270	2.8731

C_{30}	12.5062	10.2083	7.0202	7.0839	3.0699
C_{31}	19.3770	14.4170	14.4298	10.8474	5.9966
C_{32}	15.4183	6.6911	4.0233	14.2037	4.4205
C_{33}	22.6400	2.7975	14.1151	3.8479	5.9006
C_{34}	30.7548	3.8437	16.5864	2.9488	1.5515
C_{35}	13.5185	3.4066	24.9965	27.6110	12.9695
C_{36}	3.9537	5.2212	4.8111	0.8104	2.6243
C_{37}	9.4389	1.4353	2.7585	3.5412	0.9906
C_{38}	4.3002	1.2603	1.7500	1.5018	0.5795
C_{39}	6.3720	1.6653	1.3744	0.7278	0.5266
C_{40}	0.8605	1.0736	1.8279	0.9668	0.5694
TAH	486.2212	214.4144	309.6024	842.8946	342.2105
∑16PAH	1.1050	0.5065	1.0403	4.1629	2.9592
TPH	487.3262	214.9209	310.6427	842.0575	345.1697

*ST: Station, TAH: Total Aliphatic Hydrocarbons, ∑16PAH: Total Poly Aromatic Hydrocarbons, TPH: Total Petroleum Hydrocarbons.

Table 5. Calculated aliphatic hydrocarbon source diagnostic ratios in the different stations.

Diagnostic indices	Stations						
	ST-A	ST-B	ST-C	ST-D	ST-E	Range	Average
∑LMH/∑HMH	1.3093	1.9663	1.0559	8.8077	3.8939	1.0559 – 8.8077	3.4066
E/O	1.7184	1.0521	0.7183	0.7629	0.8227	0.7183 – 1.7184	1.01488
LHC/SHC	1.14609	0.52397	0.51158	0.1686	0.22494	0.1686 – 1.14609	0.51519
nC31/nC19	1.14609	0.52397	0.51158	0.16867	0.2249	0.16867 – 1.14609	0.51504
CPI	0.93362	0.996353	1.45196	0.65041	1.341307	0.65041 – 1.45196	1.07473
Pr/Ph	1.0519	0.65247	1.13137	0.82138	2.5284	0.65247 – 2.5284	1.2371

*∑LMW/∑HMW: sum of low molecular weight hydrocarbon to sum of high molecular weight hydrocarbon, E/O: even to odd hydrocarbons ratio, LHC/SHC: long chain to short chain hydrocarbons, CPI: carbon preference index, Pr/Ph: pristane over phytane ratio

Table 5 gives some source diagnostic ratio of hydrocarbons for the studied sampled sites. It reveals that the calculated ratio of sum of low molecular weight hydrocarbons to high molecular weight hydrocarbons (∑LMH/∑HMH) were all greater than one (1), an indication of petroleum source (Riccardia et al., 2008; Farid et al., 2014). The ratio of sum of low molecular weight hydrocarbons to the sum of high molecular weight hydrocarbons serves as a useful indicator of hydrocarbons sources.

Values of this ratio that are less than unity (1) typically indicates n-alkanes sourced from higher plants, marine animals, and sedimentary bacterial, whereas, ratios closed to or greater than unity implicates hydrocarbons mainly from petroleum and plankton origin (Riccardia et al., 2008; Kanzari et al., 2014; Farid et al., 2014). The high ratio recorded in stations D and E typified recent contamination. Low molecular weight hydrocarbons usually dominate in fresh oil release, with the resultant ∑LMH/∑HMH ratio been much higher than one (1) (Chokor, 2021).

The anthropogenic input of TPH is well supported by the even to odd number ratios in stations A and B (ST-A and ST-B) which were higher than one (1); Whereas, the slight dominance of odd numbered alkanes (nC_{15}, nC_{17}, nC_{19}) over even numbered ones (nC_{16}, nC_{18}, nC_{20}), as reflected in the even to odd numbered alkanes ratio (E/O) slightly less than unity (1) in stations C, D, and E, tend to give credence to biogenic inputs (Sakari et al., 2012; Adeniji et al., 2017a). This suggests that the sources of hydrocarbons in the sediments are not without biogenic contributions. The ratio of long chain hydrocarbons to short chain hydrocarbons (LHC/SHC) is normally evaluated by Eq. 1.

$$[\sum (nC_{27} + nC_{29} + nC_{31})/\sum (nC_{15} + nC_{17} + nC_{19})] \quad (1)$$

The ratio is useful for inferring whether a hydrocarbon source is from phytoplankton marine origin or terrestrial vascular plants. Higher ratio greater than 4 is implicative of terrestrial plant waxes, ratios within 0.21 – 0.80 suggests phytoplankton (marine) origins. A mixture of both source is implied when the ratio falls between 2.38 and 4.33 (Fagbote and Olanipekun, 2013; Adeniji et al., 2017a). The values obtained in this study viz: ST-A (1.147), ST-B (0.524), ST-C (0.512), ST-D (0.169), and ST-E (0.225) tend to suggest that the biogenic sources are majorly from phytoplankton marine inputs. The phytoplankton biogenic source was supported by the nC_{31}/nC_{19} ratios in sites D and E with corresponding ratios of 0.169 and 0.225 respectively. The values for the other stations viz: A (1.146), B (0.523), and C (0.512) however, suggest non-marine (terrestrial) inputs. The C_{31}/ C_{19} ratio has been used to index source of n-alkanes in sediments. The presence of nC_{31} is indicative of terrestrial biogenic inputs whereas, nC_{19} suggest marine biogenic sources. Therefore, the ratio is applied to indicate the dominance of either source. Ratio above 0.4 connote non-marine or terrestrial derived hydrocarbons whereas, values below it represent marine sources (Yussoff et al., 2012; Fagbote and Olanipekun, 2013; Adeniji et al., 2017b, Chokor, 2021; Edori and Edori, 2021,).

The carbon preference index (CPI) is measure of the ratio odd to even numbered carbon hydrocarbons calculated using different formula. Eq. 2 is an expression of the CPI.

$$CPI_{25\text{-}33} = 0.5 \times [(C_{25} – C_{33})/ (C_{24} – C_{32})] + [(C_{25} –C_{33})/ (C_{26} – C_{34})] \quad (2)$$

The ratio is useful in the evaluation of the predominance of natural hydrocarbons over anthropogenic ones (Omayma et al., 2015; Abdallal et al., 2015). The dominance of odd

numbered n-alkanes with resultant ratio greater than one (particularly in the range of 3 – 10) connotes biogenic sources such as those from marine algae or terrestrial vascular plants (Jeanneau et al., 2006; Iheonye et al., 2019. Large presence of odd numbered hydrocarbons in the range of nC_{15} – nC_{21} suggest the presence of n-alkanes from algae or microbial sources whereas, those in the range of nC_{23} – nC_{31} represents vascular plants source. The value of CPI close to one (1) however, suggests hydrocarbons from petroleum inputs while that below unity suggest degraded crude oil (Maioli et al., 2011; Onyema et al., 2013; Iheonye et al., 2019). The values of CPI for this studied locations viz: ST-A (0.9336), ST-B (0.9964), ST-C (1.4520), ST-D (0.650), and ST-E (1.3413), tend to suggest hydrocarbons whose contributory sources are largely anthropogenic and of petroleum origin (Sakari et al., 2008; Yusoff et al., 2012).

The pristane (Pr) to phytane (Ph) ratio is also an important diagnostic tool as high values clearly indicates a marine biological origin and reliably implicates the absence of petroleum. Biogenic hydrocarbons are characterized by abundance of pristane over phytane. Phytoplankton inputs will thus, result in abnormally high pristane/phytane ratio (Abdullah et al., 2015). The pristane/phytane (Pr/Ph) ratios of the different stations shown in Table 3, have values ranging from 0.65 – 2.53, with an average value of 1.24. Except for ST-E with value of 2.53, the others either have value close to one (1) or less than one. These suggest contaminations from petroleum origin (Chokor, 2021). The relatively high level of TPH in sediments with much of it diagnosed to have come from petroleum provides evidence of petroleum contamination which exposes the benthic community to a wide range of toxicological effects with its ultimate impacts on man. Human exposure to petroleum hydrocarbons is capable of resulting carcinogenic and non-carcinogenic health defects (Ordinioha and Brisibe, 2013).

4. CONCLUSIONS

The study evaluated the status and sources of petroleum hydrocarbons in the sediments of the River Niger at the Okpu and Iyiowa-Odekpe sections in South-Eastern Nigeria. The TPH range of 108.0437 – 1,091.4635 mg/Kg with a mean of 440.0234±54.78 mg/Kg observed for the sediments were much higher than the 50 mg/Kg target values established by the Nigerian Department of Petroleum Resources (DPR) but were much lower than the 5,000 mg/Kg intervention value established by same body. Aliphatic profiles and source fingerprinting show that the hydrocarbons content in sediments were from both biogenic and anthropogenic inputs; with biogenic inputs been less terrestrial than marine. The relatively high values of TPHs in the sediments represent potential health risk to benthic fauna and may ultimately impact public health due to possible biological magnification along the food chain to man. Therefore, concerted effort towards development of management plan that ensures protection of petroleum hydrocarbons contaminations should be put in place in order to sustain healthy aquatic life and protect public health.

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