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Critical Evaluation of Crude Oil and Sediments from Selected Areas of the Niger Delta

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Abstract
Understanding the occurrence, composition, and distribution of aliphatic hydrocarbons (AHCs) is crucial for assessing anthropogenic contributions and identifying the sources of AHCs in the environment. Therefore, this study focused on analyzing the concentrations, distribution patterns, and compositional characteristics of AHCs present in crude oil and sediments from the Udu, Ethiope East, and Ughelli North Local Government Areas. A total of nine crude oil samples and ten sediment samples were gathered from the research area. The concentrations of AHCs in these samples were quantified using gas chromatography with a Flame Ionization Detector (GC-FID) following extraction with a hexane/dichloromethane mixture and subsequent purification using a silica gel/alumina packed column. Analysis of the molecular indices indicated that the AHCs present in the sediments originated from marine biogenic, terrestrial biogenic, and petrogenic sources, whereas the hydrocarbons in the crude oil were derived exclusively from marine and terrestrial biogenic sources.

Keywords
Aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, total petroleum hydrocarbons, pristane/phytane ratio, molecular weight

1. Introduction

The exploration and extraction of crude oil in Nigeria's Niger Delta have resulted in widespread environmental degradation. Sediments serve as major sinks for pollutants in this region. These sediments often have elevated Total Petroleum Hydrocarbons (TPHs) and Polycyclic Aromatic Hydrocarbons (PAHs). Levels frequently exceed recognized environmental standards and adversely affect ecosystems, especially mangrove habitats (Esi et al., 2025; Eyankware and Obasi, 2021). These pollutants mainly arise from oil spills, leaks, and operational discharges. The resulting ecological and socio-economic risks are severe and demand urgent remediation. Sediments are of particular concern because they function both as repositories and secondary sources of contamination. According to Wang et al. (2012), sediment-bound hydrocarbons and other toxicants can be released into overlying waters, where they impair aquatic organisms and degrade water quality. Consequently, sediments serve as sensitive indicators for monitoring pollutants in aquatic environments. In the Niger Delta, hydrocarbon-contaminated sediments manifest as polluted soils, tainted waters, and mangrove deposits, which collectively threaten environmental and human health (Eyankware et al., 2024).

The region's geology, characterized by dense sedimentary layers, not only facilitated the accumulation of petroleum deposits but also contributed to the persistence of contamination once spills occur. Nigeria's oil exploration history dates back to 1908, when the German-owned Nigerian Bitumen Corporation drilled exploratory wells in Lagos State. Although operations were interrupted by the First World War, oil exploration expanded significantly after independence, and today Nigeria hosts numerous onshore and offshore wells (Akinshola, 2006).

Petroleum remains a cornerstone of modern society, serving as a critical energy source and raw material for plastics, paints, fertilizers, insecticides, and medicines. Crude oil itself exists in liquid, solid, and gaseous states, comprising a complex mixture of hydrocarbon molecules whose properties vary by composition (Watt and Rousis, 2006; Carey, 2021).

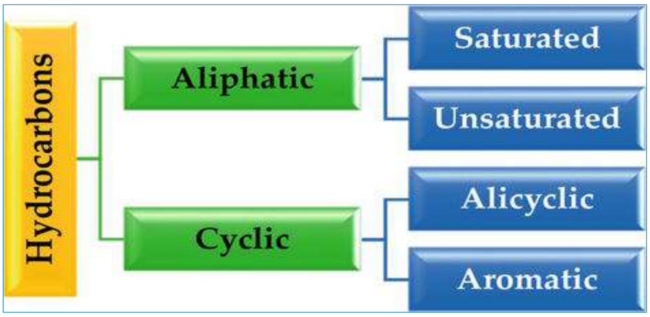

Fig. 1. Hydrocarbons classification (Muharrem and Olcay, 2019)

Hydrocarbons, while essential as energy resources, are highly flammable and release carbon dioxide, water, and heat upon combustion. They originate from kerogen through catagenesis and metagenesis, processes that ultimately determine the quantity and type of hydrocarbons produced (Wang et al., 2006a). The Niger Delta has long been plagued by oil spills that have devastated communities and ecosystems. Historical records highlight several large-scale spills, including the 570,000-barrel Forcados terminal spill in 1979, which contaminated swamp forests and coastal waters, and the 1980 Funiwa No. 5 Well blowout, which destroyed over 836 acres of mangrove forest (Tuttle et al., 2012).

Subsequent spills in the 1980s and 1990s continued to damage aquatic life, soil fertility, and food production systems. For example, vegetables exposed to oil contamination have been found to lose up to 36% of their ascorbic acid content, while cassava may exhibit a 40% increase in crude protein levels due to altered soil chemistry. Oil spill impacts extend beyond environmental damage to severe public health and socio-economic consequences. Studies indicate that crude oil contaminants—including PAHs, benzo[a]pyrene, trace metals, and naturally occurring radioactive materials—bioaccumulate in water, crops, and air, creating multiple pathways of human exposure. Contact with hydrocarbons can occur through inhalation, ingestion, or skin absorption, with evidence linking Nigerian crude oil exposure to hepatotoxicity, hemotoxicity, infertility, and increased cancer risk (Best and Seiyefa, 2023). These health challenges also undermine household food security, with estimates suggesting a potential 60% decline in food availability and a 24% rise in child malnutrition in affected areas.

The scale of oil production in the Niger Delta underscores the complexity of managing pollution. Oil Mining Lease (OML) 30, one of the largest onshore concessions in the Ughelli depobelt, spans over 1,095 km² and includes 11 producing fields. Despite its economic importance, crude oil spills in the Niger Delta continue to average 240,000 barrels annually, caused by pipeline failures, sabotage, and mechanical malfunctions (Best and Seiyefa, 2023).

The persistence of such spills highlights the urgent need to monitor, assess, and mitigate the hydrocarbon contamination of sediments, which remain critical reservoirs and indicators of environmental quality in this region. Hence, this study is aimed at analyzing the concentrations, distribution patterns, and compositional characteristics (Fig. 1) of AHCs present in crude oil and sediments from the Udu, Ethiope East, and Ughelli North Local Government Area.

2. Study Area

The Delta Central Senatorial Districts in Delta State include eight Local Government Areas (LGAs): Ethiope East, Ethiope West, Sapele, Okpe, Ughelli North, Ughelli South, Udu, and Uvwie. This study focuses on Ethiope East, Udu, and Ughelli North (Fig. 2). A selection of oil wells and flow stations from OML 30 and 34 were analyzed. The nine flow stations constituting OML 30 include Eriemu, Evwreni, Oweh, Oroni, Osioka, Kokori, Afiesere, Uzere, and Olomoro-Oleh (Figs. 3a, 3b, 3c, 3d and 3e).

3. Materials and Methods

3.1. Materials/Reagents

The apparatus used in this study included an Agilent 6890 Gas Chromatograph with a Flame Ionization Detector (GC-FID), a weighing balance (S-Mettler FA210A model, USA), and a rotary evaporator (Searchtech instrument RE52-2 model, USA). Other items included Teflon screw-cap vials, glass wool, a glass fractionating column, a 2mL glass pipette, a 100mL conical flask, a 100mL beaker, a 100mL measuring cylinder, and a Soxhlet extractor.

3.1.1. Reagents

The chemical reagents employed for the analysis of the samples were of analytical quality.

i. Dichloromethane, DCM (99% reagent grade) from Fisher Scientific (Loughborough, UK).
ii. Anhydrous Sodium Sulphate (BDH grade)
iii. Silica gel (60-120 mesh)
iv. Acetone (Analar grade)
v. n-Hexane (HPLC grade)

3.1.2. Sample Extraction

The extraction of n-alkanes from sediment was performed utilizing a Soxhlet extractor. A solvent mixture comprising hexane and dichloromethane in a 1:1 ratio was prepared. Ten grams of finely ground sediment, which had been sieved through a 0.4µm mesh, were measured and placed into extractable thimbles. To eliminate any residual moisture, 5 grams of anhydrous sodium sulfate were added to each sample. Two hundred milliliters of the prepared solvent mix was transferred into the round-bottom flask connected to the Soxhlet extractor, allowing it to reflux sufficiently for a complete extraction. Following this process, the extract was concentrated to 3 mL using a Rotary Evaporator before being transferred into a Teflon screw-cap vial and labeled clearly.

3.1.3. Preparation of Packed Fractionating Column

The extraction of n-alkanes from sediment was performed utilizing a Soxhlet extractor. A solvent mixture comprising hexane and dichloromethane in a 1:1 ratio was prepared. Ten grams of finely ground sediment, which had been sieved through a 0.4 µm mesh, were measured and placed into extractable thimbles. To eliminate any residual moisture, 5 grams of anhydrous sodium sulfate were added to each sample. Two hundred milliliters of the prepared solvent mix was transferred into the round-bottom flask connected to the Soxhlet extractor, allowing it to reflux sufficiently for a complete extraction. Following this process, the extract was concentrated to 3 mL using a rotary evaporator before being transferred into a Teflon screw-cap vial and labeled clearly.

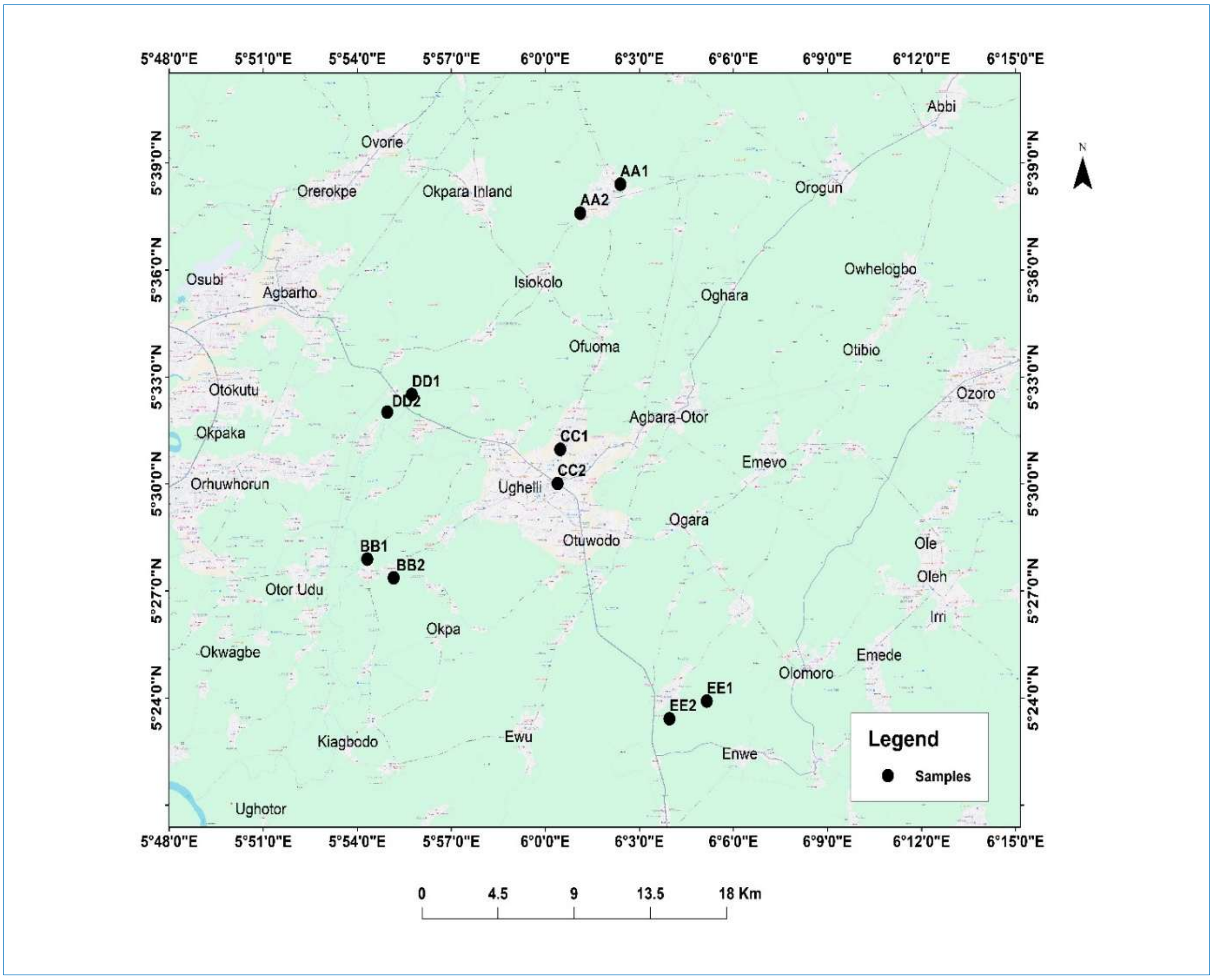

Fig. 2. Location map of the study area showing the sample points

The glass column was filled with glass wool, while 10 g of silica gel with a mesh size of 60–120 was activated overnight at 105 °C. This activated silica gel was then dissolved in dichloromethane (DCM) to form a slurry, which was subsequently packed into the column. Prior to the extraction process, the fractionating glass column was conditioned with 10 mL of DCM, following the addition of 5 g of anhydrous sodium sulfate to facilitate water absorption (US EPA, 1996). The extracts underwent desasphalting by being precipitated in a 1:30 dichloromethane-petroleum ether solution (boiling point 40-60 °C) for 20 minutes at a speed of 3000 rpm, as detailed by Schoelle et al. (1981), Wehner and Teschner (1981), and Ekpo et al. (2013). The deasphalted extracts underwent separation into three categories: saturated compounds, aromatic compounds, and heterocompounds (which include resins or NSO).

This process utilized liquid chromatography alongside silica gel (70/230 mesh, pre-activated for 6 hours at 400 °C), enhanced with neutral alumina that had been activated for 2 hours at 700 °C. The fraction containing saturated aliphatic hydrocarbons was eluted using 50 mL of n-hexane, while both the monoaromatic and polycyclic aromatic hydrocarbons were separated with 50 mL of dichloromethane. Subsequently, the heterocyclic fractions (resin or NSO) were removed by employing a 50 mL mixture of methanol and dichloromethane in a 1:2 ratio. Following this, the solvents were evaporated using a nitrogen stream.

3.1.4. Sample Analysis Using Gas Chromatography (GC)

An Agilent 6890 chromatograph, equipped with a 30 m x 0.25 mm x 0.25 µm film thickness (DB-5MS) capillary column and a flame ionization detector (FID), was employed for the GC analysis of complete oil samples. The operational temperature of the oven was programmed to rise from 60 ºC to 295 ºC at a rate of 3 ºC/min, utilizing helium as the carrier gas at a flow rate of 300 mL/s. Initial and final temperature holds were set for five minutes and twenty minutes, respectively. The detection of peak positions was achieved through electronic integration, retention time measurements, and comparisons with standards at 300 ºC. Additionally, the identification of specific compounds was facilitated by analyzing mass spectra against established standards and GC retention times (Ekpo et al., 2013; Simoneite et al., 2017).

4. Results and Discussion

4.1. Sources of AHCS in the Crude Oil and Sediment Samples

Identifying the origins of AHCs across various environmental matrices can be challenging, owing to the intricate and diverse sources stemming from the post-deposition and environmental alterations of parent chemicals. Nevertheless, compositional evaluation stands out as an essential technique for source signature analysis.

The results of source apportionment from this study are presented in Table 1.

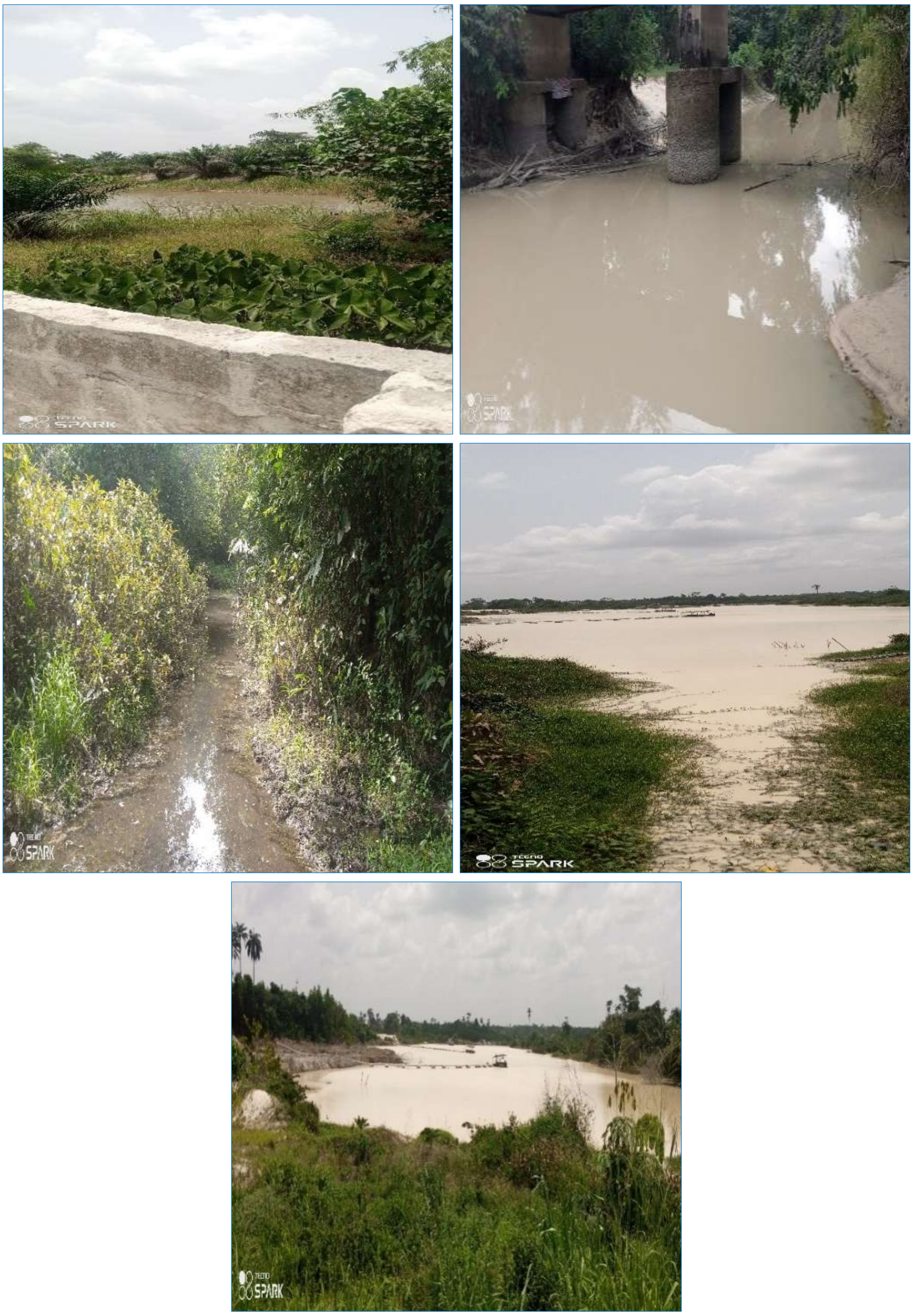

Fig. 3. Photos of some flow stations: a) Kokori, b) Eruemukowharien River, c) Ewvreni River, d) Utorogu River and e) Afiersere River

Table 1. Total aliphatic hydrocarbons present in the sediments examined in this study have been compared with those reported in existing literature

Location (Country)	Concentration (mg/Kg)	References
Udu, Ughelli North and Ethiope East, Niger Delta (Nigeria)	10.8-470	This study
Egboko, Ifie and Ubeji creeks (Nigeria)	0.03–287	Eguvbe et al. (2015)
Forcados River (Nigeria)	0.02–0.60	Iwegbue et al. (2016)
Escravos Estuary (Nigeria)	95-3430	Iwegbue et al. (2021)
Qua Iboe Estuary (Nigeria)	5.0–232	Essien et al. (2012)
Qua-Iboe River (Nigeria)	270–830	Iyang et al. (2018)
Coastal areas of the Bonny River (Nigeria)	1.65–12.7	Ekpo et al. (2012)
Jiaozhou Bay, Qingdao (China)	0.50-8.20	Wang et al. (2006b)
Arabian Gulf (Bahrain)	0.67-4.30	Tolosa et al. (2005)
Black Sea (Turkey, Russia and Ukraine)	0.10-3.40	Readman et al. (2002)
Nuequen River (Argentina)	0.41-125	Monza et al. (2013)
Prai Strait (Penang, Malaysia)	421-3135	Sakari et al. (2008)
South China Sea off Kuching division (Sarawak)	35.6-1466	Yusoff et al. (2012)
Fraser River basin (Canada)	1.60-20.6	Yunkerand Macdonald (2003)
Sao Sebastiao (Brazil)	0.03-4.77	Medeiros and Bicego (2004)
Kaohsiung harbor (Taiwan)	0.46-22.6	Lee et al. (2005)
Sfax coastal zone (Tunisia)	2.18-430	Zaghden et al. (2007)
Khniss coast (Tunisia)	9.69-36.08	Zrafi et al. (2013)
Itajai-Acu estuary (Brazil)	0.50-69.7	Frena et al. (2017)
Shatt Al-Arab, River (Iraq)	0.08-42.58	Farid (2017)
Guanabara Bay	7.66-57.22	Wagener et al. (2012)
Marmugoaharbor (India)	1.60-10.7	Harji et al. (2008)
Gulf of Fos (France)	7.80-180	Mille et al. (2007)
Yellow River (China)	22.1-81.15	Wang et al. (2011)

Table 2. Molecular indices for source apportionment of AHCs in the crude oil and sediments

	Sample	MH	LMW/HMW	CPI	C31/C19	Pr/Ph	n-C17/Pr	C18/Ph	n-C29/n-C17	TAR	NAR	Paq	ACL
Crude Oil	A	C16	2.42	1.06	0.68	1.53	1.12	1.86	0.74	0.89	0.05	0.58	28.2
	B1	C16	3.27	1.09	0.29	1.69	0.94	1.59	0.48	0.54	0.07	0.57	28.3
	B2	C18	2.14	1.27	1.04	1.49	1.19	2.03	0.81	0.88	0.12	0.40	28.8
	C1	C31	0.48	1.56	3.39	1.83	0.18	0.69	8.02	2.71	0.24	0.01	30.3
	C2	C8	0.86	1.30	3.07	1.58	0.32	0.58	3.98	1.78	0.18	0.26	29.5
	D1	C31	1.41	1.12	1.71	1.66	1.10	2.33	1.19	1.34	0.05	0.34	29.1
	D2	C32	0.31	0.78	12.76	0.82	0.95	1.53	2.85	2.12	-0.17	0.12	30.7
	E1	Pr	1.66	0.92	0.54	3.18	0.59	1.76	1.16	0.72	0.00	0.41	28.8
	E2	C32	1.06	0.37	0.68	1.37	1.27	2.74	0.89	1.21	-0.28	0.48	28.0
Sediment	AA1	C36	3.39	2.62	0.00	0.78	1.28	1.67	0.00	1.00	0.22	1.00	25.7
	AA2	C36	2.36	1.24	0.00	1.92	0.46	0.97	0.00	0.86	-0.03	1.00	26.0
	BB1	C38	11.19	2.44	0.00	1.05	0.73	1.73	0.00	1.10	0.21	1.00	25.7
	BB2	C38	3.07	0.44	0.00	0.79	1.31	1.85	0.00	1.00	-0.20	1.00	27.0
	CC1	C24	0.00	0.59	0.00	1.81	0.49	0.99	0.00	0.36	-0.11	1.00	25.0
	CC2	C38	12.18	2.50	0.00	1.08	0.75	1.86	0.00	1.10	0.16	1.00	25.7
	DD1	C37	1.91	1.29	0.00	0.86	1.27	2.24	1.57	0.97	0.09	0.73	26.5
	DD2	C37	1.95	1.40	0.00	0.80	1.27	2.29	1.57	0.98	0.10	0.76	26.4
	EE1	C25	1.01	1.42	21.03	1.28	0.46	0.58	2.68	2.00	0.09	0.60	28.4
	EE2	C34	0.18	1.60	18.70	2.53	0.44	2.49	2.94	11.47	0.09	0.41	30.7

The API gravity of crude oils generally ranges from 10 to 50, with the majority of crude oils situated between 20 and 45. Based on API gravity, conventional crude oils are typically categorized as light (API > 30), medium (30 > API > 22), and heavy (API < 22). According to Table 2, B1, B2, and C2 are classified as light crude oils, whereas A is classified as medium, and C1, D1, D2, E1, and E2 are deemed slightly heavy. The specific gravity for the samples varied from 0.8576 in sample B2 to 0.9485 in sample E2, and the API gravity exhibited a range from 33.50 in sample B2 to 17.68 in sample E2.

4.1.1. Major Hydrocarbon

Major hydrocarbons (MH) refer to the AHCs with the highest carbon numbers, which play a crucial role in the overall concentration of AHCs (Colombo et al., 1989). This index can serve as a means to verify the hydrocarbon load's direction, as it exhibits variability across different sites. In the crude oil and sediment samples analyzed during this study, the predominant hydrocarbons (MH) were those with even carbon numbers, including C8, C16, C18, C32, C34, C36, and C38, with the exceptions being samples C1, D1, and E1 for crude oil, along with DD1 and DD2 for sediments.

4.1.2. Low Molecular Weight/High Molecular Weight (LMW/HMW AHCs ratio)

The estimation of the LMW/HMW aliphatic hydrocarbon ratio was conducted to ascertain the origins of these hydrocarbons and to differentiate between terrestrial and macrophyte sources. This ratio is determined by calculating the quotient of low-molecular-weight aliphatic hydrocarbons against high-molecular-weight aliphatic hydrocarbons.

Specifically, LMW-AHCs comprise n-alkanes with carbon chain lengths from C16 to C26, while HMW-AHCs encompass n-alkanes that range from C27 to C36. As noted by Fagbote and Olanipekun (2013), high molecular weight n-alkanes are associated with terrestrial vascular plants, in contrast to low molecular weight n-alkanes, which are linked to marine biogenic sources. n-Alkanes indicative of higher plants, marine organisms, and sedimentary bacteria exhibit an LMW/HMW alkane ratio of 1. In contrast, n-alkanes derived from petroleum and plankton show an LMW/HMW alkane ratio that is approximately equal to 1. Fresh oil contamination is characterized by an LMW/HMW ratio exceeding 2 (Iwegbue et al., 2021; Gao et al., 2007).

In this research, the LMW/HMW ratios for crude oil varied from 0.31 to 3.27, while sediment ratios ranged from 0.18 to 12.18 (Table 2). The findings revealed that n-alkanes found in crude oil samples from sites C1, C2, and D2, along with those in sediment from site EE2, are linked to higher plants, marine life, and sedimentary microorganisms. This reinforces the idea that aliphatic hydrocarbons originate from a combination of petroleum and terrestrial biogenic sources, while also acknowledging significant input from marine biogenic sources (Fig. 4).

4.1.3. Carbon Preference Index (CPI)

CPI values play a significant role in distinguishing between anthropogenic and biogenic inputs of aliphatic hydrocarbons present in the environment, as shown in *Equation 1*. A CPI value exceeding 1 indicates a contribution from odd-numbered aliphatic hydrocarbons that are of biogenic nature (Li et al., 2010).

As noted by Colombo et al. (1989), CPI values ranging from 3 to 6 typically reflect the influence of vascular plants on the environment. In samples exhibiting high maturity, where there is a substantial presence of both even and odd aliphatic hydrocarbons, it is common to find that even-numbered hydrocarbons have CPI values below 1, indicating a petroleum origin. The assessment of CPI was based on the n-C25 to n-C33 range. Notably, the CPI ratios were found to be above 1 for all samples except for D2, E1, and E2 from crude oil, as well as BB2 and CC1 from sediments, as shown in Table 2 and Fig. 5. This indicates that the aliphatic hydrocarbons originate from biogenic sources, specifically terrestrial higher plant waxes, as well as from petroleum.

$$CPI = 0.5 \times \left[\frac{C25+C27+C29+C31+C33}{C24+C26+C28+C30+C32}\right] + \left[\frac{C25+C27+C29+C31+C33}{C26+C28+C30+C32+C34}\right] \quad (1)$$

4.1.4. n-C31/n-C19 Ratio

A carbon chain length of C31 serves as an indicator of terrestrial biogenic hydrocarbons, whereas C19 is associated with marine biogenic sources (Yusoff et al., 2012). The ratio of n-C31/n-C19 is a marker of the predominance of hydrocarbon input from the land or sea. The value of n-C31/n-C19< 0.4 and > 0.4 shows the predominance of marine biogenic sources and land-derived hydrocarbons respectively (Yusoff et al., 2012). The ratios of n-C31 to n-C19 in both the crude oil and sediment samples EE1 and EE2 exceeded 0.4 as shown in Table 2. This indicates that the hydrocarbons were mainly delivered to research locations through human activities and are largely derived from terrestrial sources. This observation aligns with the conclusions drawn by Commendatore and Esteves (2004).

4.1.5. Pristane/Phytane Ratio

While phytol and other isoprenoidyl compounds are not critical elements of most terrestrial biota, they do undergo diagenetic changes to transform into phytone and pristane hydrocarbons (Peters et al., 2005). These compounds are indeed found in living organisms as well as in petroleum. It is suggested that pristane and phytane are naturally occurring hydrocarbons formed during post-depositional processes, which may involve the catalytic hydrogenation of phytadiene or oxidation reactions of the phytol side chain. Their presence in zooplankton and various marine organisms, along with their occurrence in crude oils, supports this theory (Gomez-Belinchone et al., 1988).

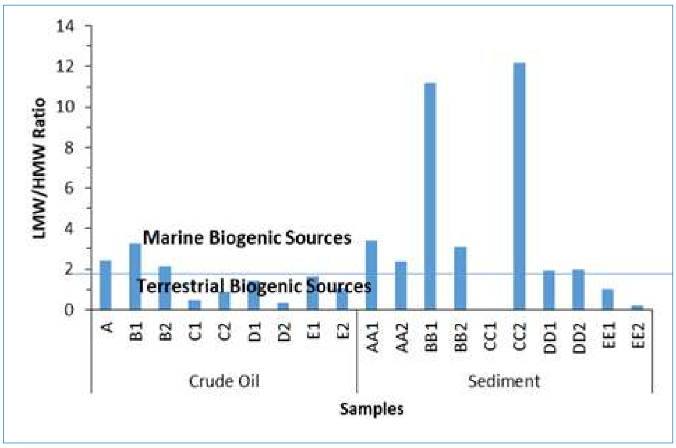

Fig. 4. Plot of LMW/HMW n-alkanes in the crude oil against sediment samples

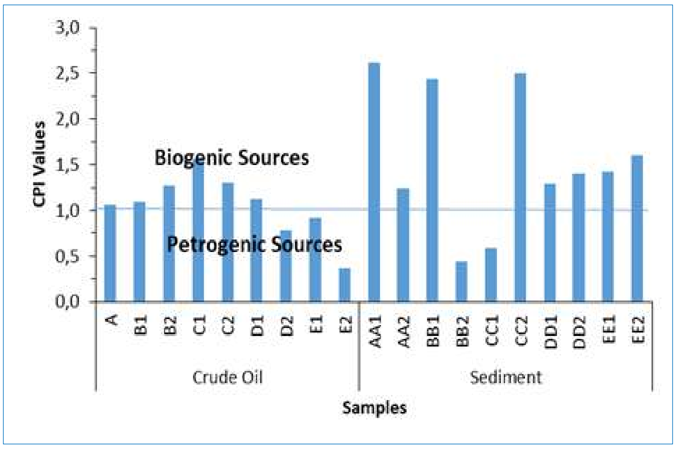

Fig. 5. CPI values of aliphatic hydrocarbons in crude oil and sediment samples

Furthermore, the ratio of Pristane to Phytane typically tends to be greater in biogenic samples than in oil (UNEP, 1992; Volkman et al., 1992). In sediments that lack hydrocarbon input, the Pr/Ph ratio typically falls within the range of 3 to 5, whereas a Pr/Ph value of ≤ 1 is indicative of petroleum contamination. The observed Pr/Ph ratio range in the sediments, which spans from 0.78 to 2.53 (Table 2), suggests a combination of biogenic and petrogenic sources. Furthermore, Pr/Ph ratio for the crude oil varied from 0.82 to 3.18, signifying the presence of biogenic input (Fig. 6).

4.1.6. n-Alkane/Isoprenoid Ratio

Due to their lower susceptibility to biodegradation, n-alkanes act as significant indicators that can provide essential insights into the origins, fate, and relative importance of both aquatic and terrestrial organic materials (Liu et al., 2012; Eyankware, et al., 2025b). Consequently, the ratios of n-C17/Pr and n-C18/Ph prove to be valuable instruments for assessing the source and degree of degradation in petroleum 2 (Companioni et al., 2009). As microorganisms tend to preferentially utilize n-alkanes over isoprenoids for energy during the biodegradation process, a ratio below 1 typically signifies biodegraded petroleum, whereas more recent inputs are likely to result in values exceeding 1 (Tarozo et al., 2010). The ratios of n-C17/Pr and n-C18/Ph for crude oil varied from 0.32 to 1.27 and 0.58 to 2.74 respectively (Table 2), while for sediment, they ranged from 0.44 to 1.31 and 0.58 to 2.49 respectively. These n-C17/Pr and n-C18/Ph ratios observed in both crude oil and sediment imply the presence of a combination of extensively degraded hydrocarbons alongside more recent inputs.

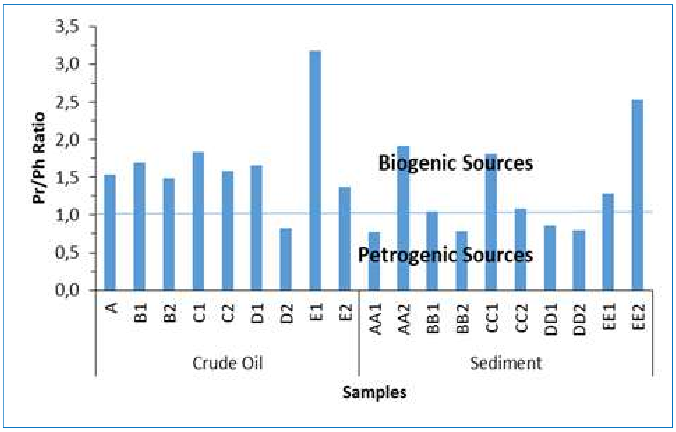

Fig. 6. Pr/Ph ratio of aliphatic hydrocarbons in the crude oil and sediment samples

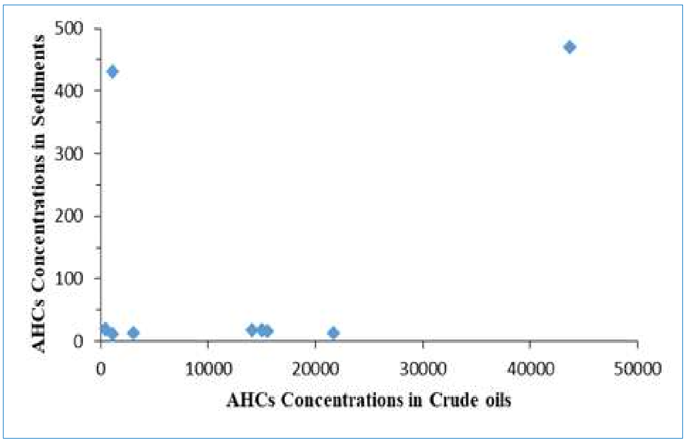

Fig. 7. Plot of AHCs concentrations in crude oil against AHCs in sediment

4.1.7. n-C29/n-C17 Ratio

The ratio of n-C29 to n-C17 offers valuable insights into the relative contributions of allochthonous and autochthonous hydrocarbons in environmental samples, given that n-C29 is linked to terrestrial plants, whereas n-C17 is related to marine life (Rouidi et al., 2013). In the analyzed samples, the n-C29/n-C17 ratios varied from 0.48 to 8.02 for crude oil and from 1.57 to 2.94 for sediment as shown in Table 2. Notably, values exceeding 1 were observed in 55% of the crude oil samples and 40% of the sediment samples, indicating dominance of allochthonous hydrocarbons. Conversely, 45% of the crude oil exhibited n-C29/n-C17 ratios below 1, which implies a predominance of autochthonous contributions.

4.1.8. Terrigenous/Aquatic n-Alkane Ratio (TAR)

The proportion of terrigenous to aquatic n-alkanes was employed to determine the relative contributions of these two sources to the origins of AHCs, as illustrated in *Equation 2*. The TAR values for crude oil ranged from 0.54 to 2.71, while for sediment, they varied from 0.36 to 11.47, as detailed in Table 2. This elevated TAR ratio may be explained by the tendency of shorter-chain n-alkanes to degrade more readily than their longer-chain counterparts (Johnsen et al., 2005; Jeng and Huh, 2006). Nevertheless, the TAR values obtained in this study align with those previously reported for sediments from the Red Sea (Aly Salem et al., 2014).

$$TAR = \frac{C27+C29+C31}{C15+C17+C19} \tag{2}$$

4.1.9. Natural n-Alkane (NAR) Ratio

Aly Salem et al. (2014) note that an NAR value approaching 1 implies a higher presence of terrestrial or marine vegetation, such as posidonia, as referenced in *Equation 3*. The findings of this study revealed NAR values fluctuating between -0.17 and 0.18 for crude oil, and from -0.03 to 0.22 for sediments, as illustrated in Table 2. These results highlight a diverse range of terrestrial and marine contributions. The ratio presented below was employed to assess the NAR.

$$NAR = \sum n - alkanes\ (C19 - C32) - [2 \times \frac{\sum n - alkanes\ (C20 - C32)}{\sum n - alkanes\ (C19 - C32)} \tag{3}$$

4.1.10. n-Alkane Proxy (Paq)

Paq values ranging from 0.01 to 0.23 (Table 2), are indicative of terrestrial plant waxes, whereas values between 0.48 and 0.94, derived from *Equation 4*, are linked to submerged or floating macrophyte species (Ficken et al., 2000). As shown in Table 2, the Paq ratios for crude oil and sediment fluctuated from 0.01 to 0.58 and 0.41 to 1.0, respectively. This data suggests that aliphatic hydrocarbons result from a blend of terrestrial plant waxes and submerged or floating macrophytes.

$$P_{aq} = \frac{C23+C25}{C23+C25+C29+C31} \tag{4}$$

4.1.11. Average Carbon Chain Length (ACL)

This information is valuable for identifying environmental alterations that impact a specific ecosystem. The consistent value of ACL illustrates the infrequency of changes within an environment (El Nemret, et al., 2013), with ACL being calculated through *Equation 5*. The measured ACL ratios for sediments and crude oil ranged from 25.0 to 30.7, as shown in Table 2. For sediments and crude oil, the ACL revealed variances of 2.7 and 5.7 units, respectively. Due to substantial human activities and inputs that disturb the balance of ACL with petroleum hydrocarbons and their derivatives, the sediment may have experienced a significant range of transformations (Iwegbue, et al., 2021; Emoyaet al., 2020). This was evaluated using the subsequent ratio.

$$ACL = \frac{25\,(C25) + 27\,(C27) + 29\,(C29) + 31\,(C31) + 33\,(C33)}{C25 + C27 + C29 + 31 + C33} \quad (5)$$

4.2. Relationship between AHCs in Crude Oil and Sediments

Fig. 7 illustrates the regression relationship between the amounts of AHCs found in crude oils and sediments. According to the regression analysis, there is minimal to no correlation between the AHC levels in crude oil and those present in sediment. This lack of a significant relationship may be attributed to the influence of multiple sources and the continual input of fresh aliphatic hydrocarbons.

The API of crude oils varies typically between 10 and 50, with most crude oils falling in the range of 20 – 45. Using API gravity, the conventional crude oils can be generally considered as light (0API >30), medium (30 >0API > 22), and heavy (0API <22). From Table 3, B1, B2, and C2 are light crude oil, while A is medium, and C1, D1, D2, E1, and E2 are slightly heavy. The Specific gravity ranged from 0.8576 in sample B2 to 0.9485 in sample E2, while the APIO gravity ranged from 33.50 to 17.68, also in samples B2 and E2, respectively.

Table 3. Results for specific gravity and API^{O} for crude oil samples

Parameter	Sample Code								
	A	B1	B2	C1	C2	D1	D2	E1	E2
Specific Gravity	0.8895	0.8596	0.8576	0.9436	0.8785	0.9373	0.9437	0.9423	0.9485
API^{O}	27.58	33.11	33.50	18.46	29.57	19.47	18.44	18.66	17.68

The API gravity of crude oils generally ranges from 10 to 50, with the majority of crude oils typically categorized between 20 and 45. According to API gravity classifications, conventional crude oils can be classified as light (^{0}API > 30), medium (30 > ^{0}API > 22), or heavy (^{0}API < 22).

As indicated in Table 3, samples B1, B2, and C2 are classified as light crude oils, whereas sample A is categorized as medium, and samples C1, D1, D2, E1, and E2 are regarded as slightly heavy. The specific gravity values varied from 0.8576 in sample B2 to 0.9485 in sample E2, while the API gravity measurements ranged from 33.50 for sample B2 to 17.68 for sample E2.

5. Conclusion

This research conducted a geochemical analysis of crude oil and bottom sediments from water bodies in the Udu, Ethiope East, and Ughelli North Local Government Areas within the Niger Delta Basin. Findings from the study identified the concentration levels, compositional characteristics, and origins of AHCs present in both crude oil and bottom sediments in the region. The investigation determined the average concentrations of aliphatic hydrocarbons to be 102.74±2.85 mg/Kg in crude oil and 12859.11±7884.68 mg/Kg in bottom water sediments, respectively. The investigation indicated that the AHCs present in the sediments originated from petrogenic, terrestrial, and marine biogenic sources, in contrast to crude oil, which was sourced from both marine and terrestrial biogenic origins. Consequently, the study illustrated the concentrations of aliphatic hydrocarbons from these diverse sources.

6. Recommendations

In light of the results obtained from this research, it is advisable to implement the following recommendations:

1. An environmental clean-up and remediation process should be initiated in the study area.
2. Additional investigations should be conducted regarding the presence and distribution of other organic contaminants, including monoaromatic hydrocarbons (BTEX), polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls, among sediments, water, and biota within the study region.

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