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Characterization and Correlation of Aliphatic Hydrocarbons in Oil Polluted Waters of Bonny Local Government Area, Rivers State

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Authors' contributions

This work was carried out in collaboration among all authors. Author IC designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors IC, OL and OM managed the analyses of the study and the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Forensic chemical analyses was used to characterize, determine the source and correlate aliphatic hydrocarbons (AHCs) in water samples collected from Bonny L.G.A, Rivers State. AHCs were extracted from the water samples with *n*-hexane in a separatory funnel, clean-up achieved by column chromatography using *n*-hexane and analysis by Gas Chromatography Flame Ionization Detector (GC-FID). The GC chromatogram showed well resolved AHC peaks which distributed from $n\text{C}_9$ –$n\text{C}_{40}$. The GC chromatograms of AHCs, with a wide range of low molecular weight hydrocarbons, indicate minimal biodegradation of the oil hydrocarbons in the samples. CPI values from 0.68 to 0.78 for BY-A1, BY-A3, BY-A4 and 0.97 for BY-A2 suggest two sources of oil hydrocarbons. Calculated Pr/Ph ratios showed BY-A1 (2.08), BY-A3 (2.00) and BY-A4 (2.20) were derived from mixed marine and terrestrial source deposited in suboxic environment, while BY-A2 (3.70) was mainly terrigenous source in an oxic environment. A cross-plot of Pr/n-C_{17} and Ph/n-C_{18}

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ratios also showed a tight cluster for samples BY-A1, BY-A3 and BY-A4 which were degraded with sample BY-A2 separate and slightly degraded. Results from this study revealed that the spilled oil was derived from mixed organic sources deposited in an oxic environment with different oil input from external sources showing more terrestrial contribution.

Keywords: Aliphatic; pristane; phytane; depositional environment; oxic.

1. INTRODUCTION

A major form of pollution and contamination of the environment is the spillage of crude oil and petroleum derived products. Crude oil pollution has become a matter of serious environmental concern all over the world because of its adverse effects on the ecosystem [1]. Oil spillage could result from inadequate maintenance of infrastructure, burst of oil pipeline, spills during processing, as well as leaks that occur during transportation of petroleum and petroleum products. It can also occur as a consequence of intentional damage to oil facilities or oil theft. Crude oil consists of complex mixtures of hydrocarbons and non-hydrocarbons that can be classified in bulk groups of saturates, aromatics, resin and asphaltenes [2]. Saturates include straight chain and branched chain (also called aliphatics) and cycloalkanes (also called naphthenes). Analyzing the composition of the aliphatic hydrocarbons in polluted water samples can provide much information about the crude oil source, its diagenetic processes and also provide information on the extent of degradation [3-5]. Recent studies have determined the aliphatic hydrocarbon fingerprints of oil polluted water and sediment samples [6] as well as oil polluted waters receiving input from other sources and the implication of its aliphatic hydrocarbon fingerprint on source-rock correlation.

Bonny is an island town and a local government area (LGA) in Rivers State located between longitude 7°10’ East and latitude 4°26’ North. The region produces the crude oil type referred to as Bonny light oil. It plays host to multinational oil companies such as Shell Petroleum Development Company (SPDC), Mobil Producing Unlimited, Chevron Nigeria Limited and Nigeria Liquefied Natural Gas (NLNG) Limited which are all involved in the production of oil and gas. The oil and gas pipeline system in the region include the Trans Niger Pipeline (TNP), which transports crude oil to the Bonny Export Terminal and the Nembe Creek Trunk Line (NCTL), which evacuates crude from the Niger Delta to the Atlantic coast for export. Presence of these oil and gas facilities in Bonny renders the area prone to oil spills. Also sabotage of oil facilities and artisanal refining activities (also called KPO FIRE) take place in the area.

The current study focuses on the characterization of aliphatic hydrocarbons in oil contaminated waters from Bonny L.G.A, Rivers State and correlation of the results of the different oil contaminated waters from different locations. This will aid us to know the distribution and sources of aliphatic hydrocarbons in the contaminated waters.

2. MATERIALS AND METHODS

2.1 Sampling

Water samples were collected from Igoni polo waterfront located in Bonny local government area of Rivers State between longitude 7°10’8 East and latitude 4°27’7 North of the equator. Dark bottles were used to collect water samples randomly at four different locations. One (1) liter each of the water samples was collected, sealed and labeled accordingly (BY-A1, BY-A2, BY-A3 and BY-A4). Sealed bottles were placed in a box containing ice packs, taken to the laboratory and stored at a temperature of about 4°C prior to analysis.

2.2 Extraction and Fractionation

The separatory funnel liquid-liquid extraction method [7] was adopted to extract the petroleum hydrocarbons from the water samples. One hundred milliliters (100 ml) of the water sample was measured into a separatory funnel and fifty milliliters (50 ml) of hexane added. The separatory funnel was agitated for 30 minutes to allow for maximum extraction of the petroleum hydrocarbons. The mixture was left to stand for an hour to maximize separation into layers. After separation into two layers, the contents were eluted through the funnel tap into separate beakers. The eluted water sample (aqueous phase) was subjected to two more extractions following the above mentioned procedure. The hexane extracts were collected in a beaker and anhydrous magnesium sulphate ($MgSO_4$) added into it to remove moisture. The extract was filtered and concentrated by evaporating hexane under a stream of nitrogen at 40°C. Fractionation of the extract was achieved by transferring it onto the top of a 30 cm x 1 cm glass chromatographic column packed with activated silica gel and plugged with glass wool at the base. The saturate hydrocarbon (containing the aliphatic hydrocarbons) was eluted by pouring *n*-hexane into the column and thereafter concentrated by evaporating the solvent at room temperature. The aliphatics were subjected to a compositional analysis via Gas Chromatography (GC).

2.3 Gas Chromatography

Analysis of the aliphatic fraction of each sample for the *n*-alkane distribution was achieved using an Agilent7890B Gas Chromatograph (GC) equipped with a 50 m x 0.25 µm capillary column, G4513A automatic liquid sampler (ALS) and also a flame ionization detector (FID). With the aid of the automatic liquid sampler, 1 µL each of the concentrated saturates dissolved in hexane, was injected into the GC capillary column using the splitless injection mode. Hydrogen at a linear velocity of 30 mL/min was used as carrier gas. GC oven temperature was programmed from 40°C to 260°C at 10°C/min with a 5 mins hold at 40°C and a 20 mins hold at 260°C. Compound peaks revealed through the read out device were identified by their relative retention times and by comparison with spectra reported in literature.

3. RESULTS AND DISCUSSION

The GC-FID chromatogram of the analyzed saturate fraction of the water samples revealed well resolved *n*-alkane peaks which ranged from C_9-C_{40} and includes the acyclic isoprenoids, pristane (Pr) and phytane (Ph) (Fig. 1). This *n*-alkane distribution pattern is similar to that of crude oil [8] suggesting that the water samples were contaminated with crude oil and not refined petroleum product. Furthermore, the gas chromatogram which shows a range of low and high molecular weight *n*-alkanes from C_9-C_{40} indicates a bimodal *n*-alkane distribution consisting of low and high molecular weight *n*-alkanes. The low molecular weight *n*-alkanes were dominated by C_{14} to C_{19} while C_{30} to C_{35} dominated the high molecular weight *n*-alkanes. This suggests that the crude oil was derived from mixed marine and terrestrial organic matter. Marine organisms synthesize paraffins up to about C_{19} while land plants synthesize hydrocarbons to C_{37} hence the dominance of C_{13}-C_{20} *n*-alkanes on a GC chromatogram reflect marine sources for crude oils while dominance of C_{25}-C_{35} *n*-alkanes indicate terrestrial sources [9,10].

The carbon preference index (CPI) of Bray and Evans [11] is used to determine the oil source. Carbon preference index is the ratio of odd carbon-numbered alkanes to even carbon-numbered alkanes in a specific molecular weight range of C_{23} to C_{34}. CPI is used in identification of source; crude oils have CPI values close to 1 while values below unity suggest degraded crude oils [12,13]. For this study, calculated CPI values range from 0.68 to 0.97 (Table 1). Sample BY-A2 has the highest value of 0.97 which indicate mature crude oil. The CPI values for BY-A1 (0.73), BY-A3 (0.78) and BY-A4 (0.68) were close suggesting oils from a similar source. Furthermore, these CPI values less than 1 indicates that the oils are degraded. Observed unresolved complex mixture (UCM) in the chromatograms suggest oil degradation in the order: BY-A4> BY-A1> BY-A3 >BY-A2.

Pr/Ph, Pr/*n*-C_{17} and Ph/*n*-C_{18} ratios are commonly used for oil correlation studies to indicate source, depositional environment, redox condition and extent of degradation [14,15]. Low Pr/Ph values (<1.0) indicate anoxic conditions, values ranging between 1.0 and 3.0 reflect oxidizing depositional environment while Pr/Ph values above 3.0 indicates terrigenous plant input deposited under oxic to suboxic conditions [14,16]. The calculated ratios are presented in Table 1. Pr/Ph ratios which ranged from 2.00 – 3.70 suggest the oil was derived from source rock containing mixed marine and terrestrial organic matter deposited under oxic conditions. Sample BY-A2 having the highest Pr/Ph ratio of 3.70 indicates an increased terrigenous organic matter input. The ratios of isoprenoids to *n*-paraffin (Pr/*n*C_{17} and Ph/*n*C_{18}) provide valuable information on biodegradation and maturation [17]. According to Table 1, ratio values of Pr/*n*-C_{17} from 1.44 – 1.92 and Ph/*n*-C_{18} from 0.39 – 1.05 suggests the spilled oil was degraded with sample BY-A2 being slightly degraded having Pr/*n*-C_{17} and Ph/*n*-C_{18} values of 1.44 and 0.39 respectively.

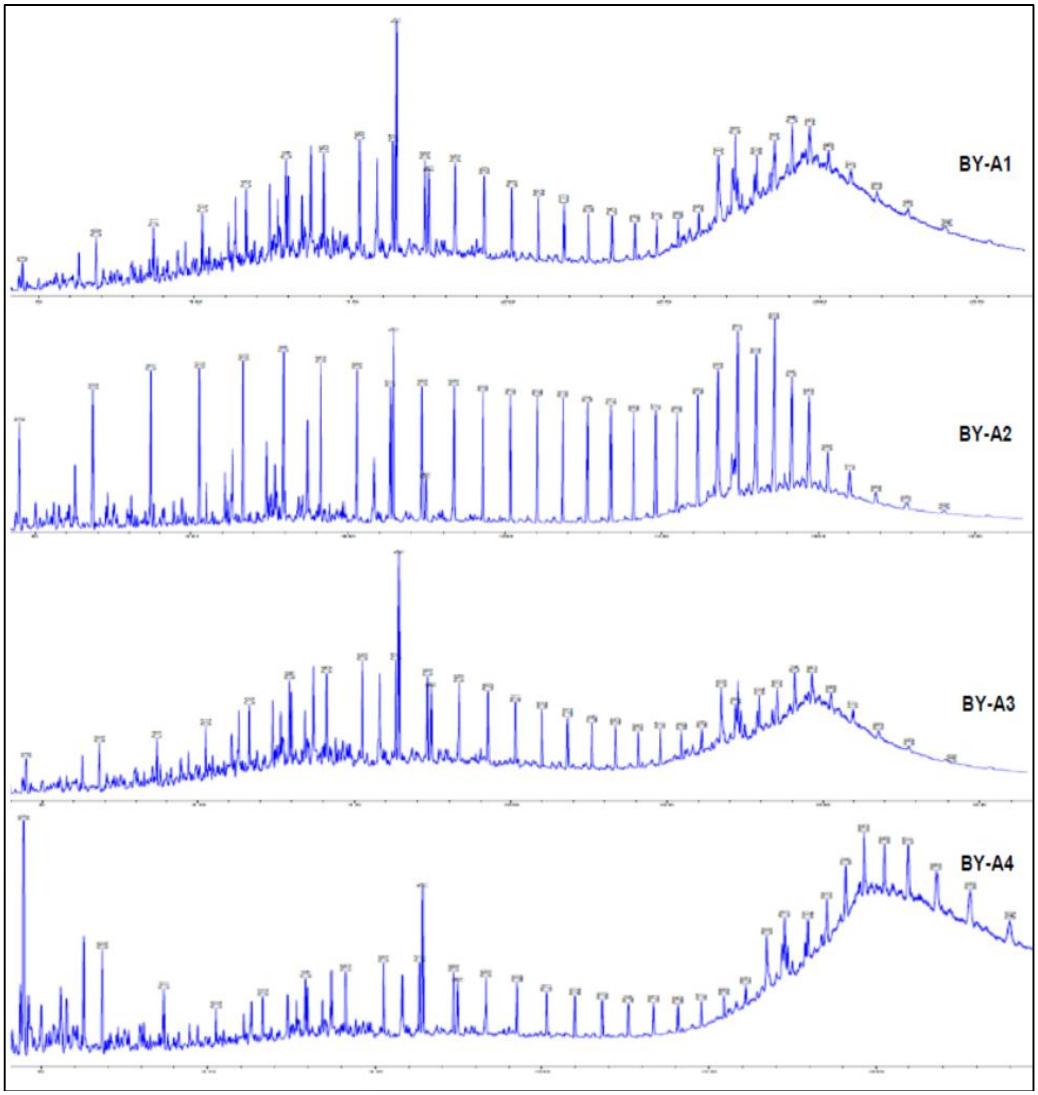

Fig. 1. Gas chromatograms of aliphatic hydrocarbons in the analyzed water samples

Table 1. Calculated diagnostic ratios of aliphatic hydrocarbons for the samples

Sample code	CPI	Pr/ Ph	Pr/ n-C_{17}	Ph/ n-C_{18}
BY-A1	0.73	2.08	1.85	1.03
BY-A2	0.97	3.70	1.44	0.39
BY-A3	0.78	2.00	1.82	1.12
BY-A4	0.68	2.20	1.92	1.05

CPI = $(C_{23} + C_{25} + C_{27} + C_{29} + C_{31} + C_{33}) / (C_{24} + C_{26} + C_{28} + C_{30} + C_{32} + C_{34})$
Pr = Pristane
Ph = Phytane

A cross-plot of Pr/n-C_{17} and Ph/n-C_{18} ratios show a tight cluster for samples BY-A1, BY-A3 and BY-A4 with sample BY-A2 separate (Fig. 2). This suggests that samples BY-A1, BY-A3 and BY-A4 were derived from mixed marine and terrigenous sources deposited in a suboxic environment while sample BY-A2 has a higher terrigenous organic matter input deposited in an oxic environment. The cross plot also showed that BY-A1, BY-A3 and BY-A4 were more degraded than BY-A2 which was slightly degraded and was of a mature oil source.

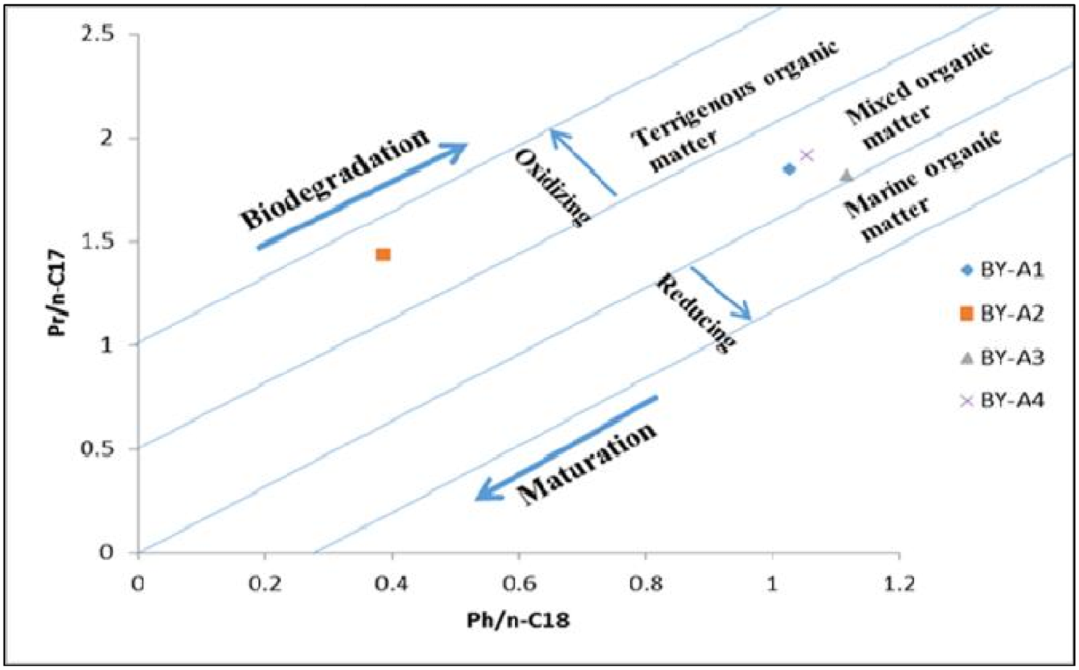

Fig. 2. Cross plot of Pr/*n*-C_{17} versus Ph/*n*-C_{18}

4. CONCLUSION

From the result of the analysis, Igoni Polo waterfront, Bonny LGA was contaminated with crude oil and not refined product. The results of this study were used to evaluate the source organic matter input, depositional environment and degradation of aliphatic hydrocarbons in the oil contaminated waters. The gas chromatography analyses coupled with diagnostic ratios of source-specific marker compounds revealed different sources for oil hydrocarbons in the contaminated waters: Mixed marine and terrigenous, and terrigenous source, which were deposited in suboxic to oxic environments respectively. It also revealed that the aliphatic hydrocarbons in the contaminated waters were slightly degraded.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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