

BIOLOGICAL MARKER FINGERPRINTS OF CRUDE OILS FROM THREE OILFIELDS IN THE CENTRAL NIGER DELTA: IMPLICATION TO SOURCE INPUT, CONDITIONS OF DEPOSITION, AND THERMAL MATURATION

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ABSTRACT

Crude oil samples recovered from three oilfields distributed within the central Niger Delta were used to investigate biological marker fingerprints, sources of organic matter, conditions of deposition, and thermal maturation. This was achieved by the application of gas chromatography-mass spectrometric (GC-MS) analyses on the saturated components of the crude oils. The biological marker ratios show low sterane/hopane (steranes/hopane < 1) in the scope of 0.29 to 0.61 indicating that the crude oils initiated from rocks containing high terrigenous biota (mainly land plants). The n-alkanes distribution and the pristane/phytane ratios (0.63 to 2.08) suggested source deposition under oxic to suboxic environmental conditions. The percentage composition of C₂₇, C₂₈, and C₂₉ steranes and oleanane index (18 α (H)-oleanane/ C₃₀ 17 α (H)-hopane) also indicated major contributions from terrigenous organic biota with minor marine source input. The studied crude oils have C₃₂:22S/ (22S+22R) ratios in the scope of 0.55 to 0.64, and these values suggested high maturation level. This agrees with the oleanane index (0.64 to 0.95), CPI (0.92 to 1.06), C₂₉: 20S/ (20S + 20R) sterane ratios (0.29 to 0.61), Ts/(Ts+Tm) ratio (0.45 to 0.83) and moretane/C₃₀ hopane proportion (0.16 to 0.24).

Keywords: Biological marker; Depositional conditions; Niger Delta; Organic matter; Thermal maturation.

1 INTRODUCTION

The Niger Delta Province is characterized by synsedimentary fault systems, which subdivided the Delta into five distinct sedimentation cycles of fluviomarine systems referred to as depobelts (Fig. 1). These depobelts (depocenters) represent successive growth stages and are self-contained, as regards to their structural framework and hydrocarbon distribution [1–3]. The stratigraphy of the Niger Delta is made up of an upper delta top lithofacies known as the Benin Formation, which is composed of continental sands and gravels of about 2000m thickness [4]. Benin Formation is underlain in a gradational fashion by the delta front paralic facies of the Agbada Formation (Fig. 2). The Agbada Formation is comprised of mostly sands with little shales in the topmost parts, and a succession of equal proportions of sands and shale in the lower units [5, 6]. This Formation is regarded as the true deltaic portion that bears the major petroleum horizons in the Niger Delta. The Pro-delta marine shales of the Akata Formation are found occurring at the base of the delta and are made up of thick sequences of shale referred to as the potential source rocks (Fig. 2) [5, 6].

Biological markers are complex organic molecules found in crude oils, sediments, and rocks [7–9]. They are molecular remnants of primitive life forms, having the same structural arrangement as their precursor organisms [9]. Biological markers are commonly referred to as biomarkers and may exist as remains of proteins, lipids, carbohydrates, nucleic acids, and other molecules. They are very useful because their complex structures are not usually different from their similar organic molecules present in living organisms [9]. Most biological markers are restricted to particular sources, easily analyzed from environmental and geologic samples, and are not compliant to geochemical alteration. Therefore, biomarkers can be used as proxies in recent environments and as chemical guide fossils.

The occurrences and distribution patterns of biological markers such as the hopanes and steranes in crude oils can be used to investigate generic relationships among crude oils, oil source rock relationship, depositional environments, and thermal maturity which are useful exploration indices [9]. The geochemical attributes of the Niger Delta crude oils and source rocks have been discussed in previous studies [10–12]. Bustin [11] concluded that the Niger Delta hydrocarbons belong to one family, originating from land plants (terrestrial organic materials) and other organic matters of undetermined structure. A study carried out by Ekpo et al. [13] recognized that crude oils from oilfields in the western offshore Niger Delta were source related and deposited under oxidizing conditions. Onojake et al. [14] indicated that oil samples from two oilfields located in the Niger Delta were sourced from terrestrial biotas deposited under an oxic environment. Similarly, Oforika et al. [15] opined that crude oil samples from the southwest Niger Delta had derived from terrestrial organic materials and deposited under oxic paleoenvironmental conditions. Akinlua and Ajayi [16] recognized that oil samples from some fields in the central part of the Niger Delta are thermally matured having source organic matter contributions from a mixture of terrigenous and marine, deposited in oxidizing environments. Sonibare et al. [17] indicated mixed organic matter input (both marine and terrestrial kerogen) for crude oil samples from onshore and offshore Niger Delta. Abrakasa and Muhammad [18] recognized the existence of a close geochemical relationship and thermal maturity gradient trend in the Southwest-Northeast direction for crude oils from an oilfield in the Niger Delta. Manilla and Eking [19] concluded that the Nigerian crude oils are of two different families of terrestrial and mixed (terrestrial and marine) petroleum systems. Anyanwu et al. [20] identified subtle geochemical dissimilarities among oil samples from the coastal and offshore Niger Delta. Onojake and Abrakasa [21] applied the presence of 18α (H)-oleanane skeletons and oleanane indices to indicate terrestrial source and Tertiary age for some crude oils from the Niger Delta. Anyanwu et al. [22] used biomarker fingerprints from the five depocentres of the Niger Delta to identify a single family of oil originating from source rocks with major input from terrestrial biotas deposited in a prevailing condition of oxic to sub-oxic environment.

Knowledge of the source input, conditions of deposition, and thermal maturation of oils and source rocks in a hydrocarbon producing basin are very useful in reservoir engineering and petroleum exploration. Most of the geochemical studies carried out in the Niger Delta suggested one petroleum system [10, 22, 23, 24, 25], with organic materials originating mostly from terrigenous land plants and other organic matters of undetermined structure [11, 21, 22]. A study of the geochemical characters of oil from the different segments of the Niger Delta is very important in order to ascertain if there are slight differences in the petroleum systems within the different units of the delta. This work attempts to investigate the organic geochemical fingerprints of crude oil samples recovered from three oil fields within the Central Niger Delta in order to characterize the crude oils and determine the organic matter source (s), depositional conditions, and thermal maturation. The study area (Niger Delta) is a major hydrocarbon zone in Africa located in the Gulf of Guinea, West Africa in-between latitude 3°N to 6°N and longitude 5°E to 8°E (Fig. 1).

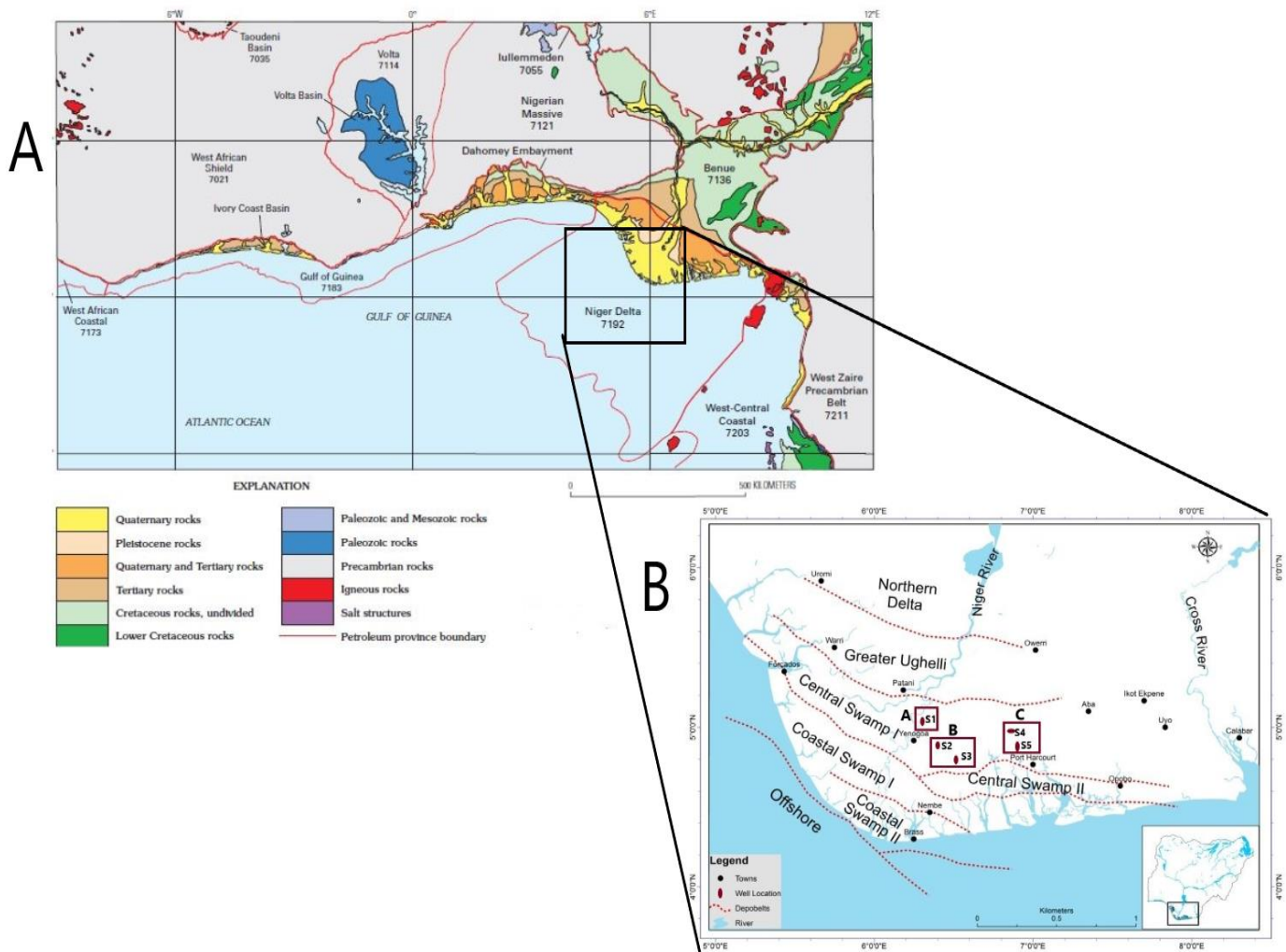


Figure 1. Location of the study area: **A.** A general geologic map of the Gulf of Guinea and surrounding areas [26]; **B.** Map of the Niger Delta showing the location of depobelts (location map of Nigeria in inset box); open squares show the locations of the three oilfields where the crude oil samples were collected [27]

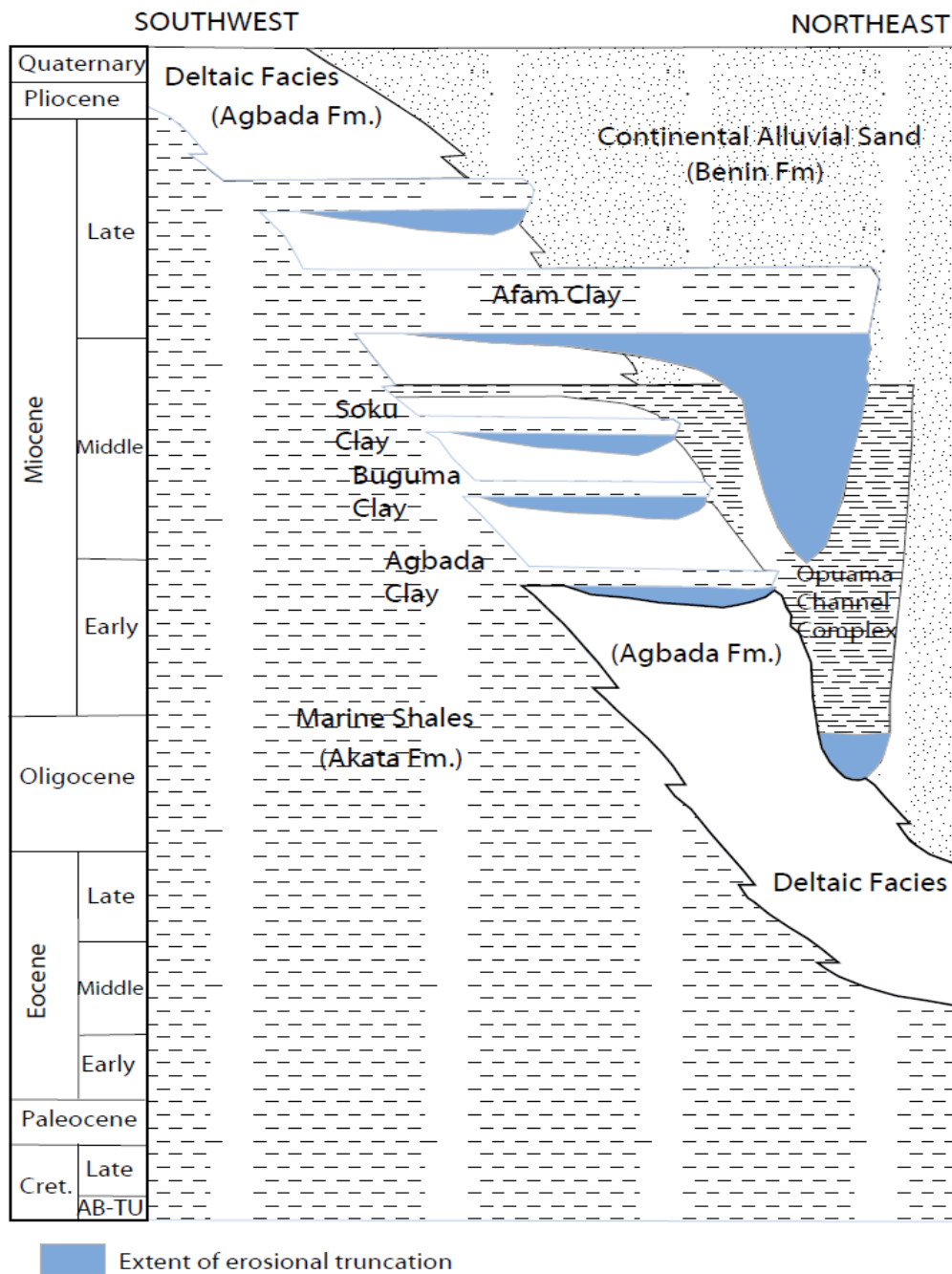


Figure 2. Stratigraphic column displaying the three formations of the Niger Delta; Fm = formation [6]

2 MATERIALS AND METHODS

Five crude oil samples (S1, S2, S3, S4, and S5) were collected from three oil producing fields (A, B, C) (Fig. 1). The crude oil samples are representatives from the Central Swamp depobelt comprising an alternation of equal proportions of sands and shale of the Eocene to Recent Agbada Formation, regarded as the true deltaic portion and

the major hydrocarbon horizon. The fractionation of the oil samples into saturates components, aromatic components, and hetero-compounds were done by liquid-chromatography using silica-gel promoted with alumina: n-hexane was used for elution of saturated hydrocarbons, aromatic fractions were eluted using dichloromethane and 1, 2 methanol-dichloromethane was used to elute the hetero-compounds.

Gas chromatographic-mass spectrometric (GC-MS) analyses were carried out with the aid of the Agilent's 7890 gas chromatography attached with an Agilent's HP-5 ms column. The oven operating conditions were held at 55 °C for 1 minute, programmed from 25 °C min⁻¹ to 320 °C, and held for 35 minutes. The carrying gas was helium (He), and placed at a continuous flow. The SI Scan monitoring mode was used, and GC operations were made at an electron ionization (EI) mode of 70 eV. Data processing was carried out using Chemstation G1701BA, peaks integration was by RTE integrator. Identifications of peaks were done by considering the retention time, comparing with set standards, mass fragmentation patterns, and literature. The cumulated peak area of each compound was used for the computation of ratios.

3 RESULTS AND DISCUSSION

3.1 Organic matter source(s) and depositional conditions

3.1.1 Normal-alkanes

Certain n-alkanes ratios are useful indicators of organic matter sources [9]. The n-alkanes distribution in the crude oil samples is shown on the (71m/z ion) mass chromatograms (Fig. 3). The mass chromatograms show an abundance of n-alkanes in the range of n-C₁₅ to n-C₂₀ with a low concentration of heavy n-alkanes for crude oils from the A and B oilfields and moderately to low concentration for oil samples from C oilfield. The n-alkanes distribution in the crude oil samples from A and B oilfields suggests input from marine organic matters of algal and planktonic origin whereas crude oil samples from C oilfield suggests mixed input from both marine and terrigenous organic materials [12, 28]. Low concentrations to the absence of normal alkanes in the range of n-C₆ to n-C₁₂ observed in the mass chromatograms as well as the non-uniformity in the distribution patterns suggests crude oil biodegradation and possible different genetic histories for the crude oils [9]. The degree of waxiness of oils was determined in this study using the ratio $\Sigma (n-C_{21} - n-C_{31}) / \Sigma (n-C_{15} - n-C_{20})$ [29] (Table 1). This idea is based on the proposition that terrestrial organic materials contribute the most to high molecular weight n-alkanes in crude oil [30]. It was used to describe the origin of organic materials in the source rock from where the studied crude oils were expelled. Crude oil samples from A (S1) and B (S2, S3) oilfields contains low waxy oil ratios (waxiness <1) while the crude oil samples from C oilfield (S4, S5) contain waxy oil ratios that are relatively high (waxiness >1) (Table 1). This suggested high concentrations of terrigenous organic materials derived from land plants for the crude oil samples from "C" oilfield and a relatively lower concentration for the crude oils from A (S1) and B (S2, S3) oilfields. The computed carbon preference index (CPI) for the analysed crude oil from A (S1) oilfield is 0.92 while those of B (S2, S3) and C (S4, S5) oilfields range from 1.01 to 1.06 (Table 1), this range of values showing no odd or even number carbon preference suggested matured crude oils [31].

3.1.2 Acyclic isoprenoids ratio (Pristane/phytane)

The Acyclic isoprenoids: pristane (Pr) and phytane (Ph) originates from the phytol which is a side chain of chlorophyll. Ph is derived during reducing conditions while the Pr is produced under oxidizing conditions [32]. The Pr/Ph ratio is among the most important indicators of environments of deposition [9], where Pr/Ph ratios less than one indicate crude oils sources from reducing environments. High Pr/Ph ratios (Pr/Ph > 3) normally indicate an oxic-terrestrial source rock depositional environment, while Pr/Ph ratios in the range of 1.00 to 3.00 reflects oxic environmental conditions of deposition [9, 33]. The crude oil samples from A (S1) and B (S2, S3) oilfields had Pr/Ph ratios of 2.08 and 0.98- 2.01 respectively, while crude oils from C (S4, S5) oilfield had Pr/Ph ratios of the range 0.63 to 0.65 (Table 1). This shows that the crude oils from A (S1) and B (S2, S3) oilfields were sourced from terrestrial organic matter or mixed organic matter sources, deposited under oxic conditions while those from C (S4, S5) oilfield were probably sourced from marine organic matter deposited in a suboxic environmental condition [9, 33, 34]. Moreover, the cross plot of CPI versus Pristane/Phytane shows that the crude oils from A

(S1) and B (S2, S3) oilfields fall within the field of more oxidizing environment while those of C (S4, S5) oilfield fall in the region of more reducing environment (Fig. 4).

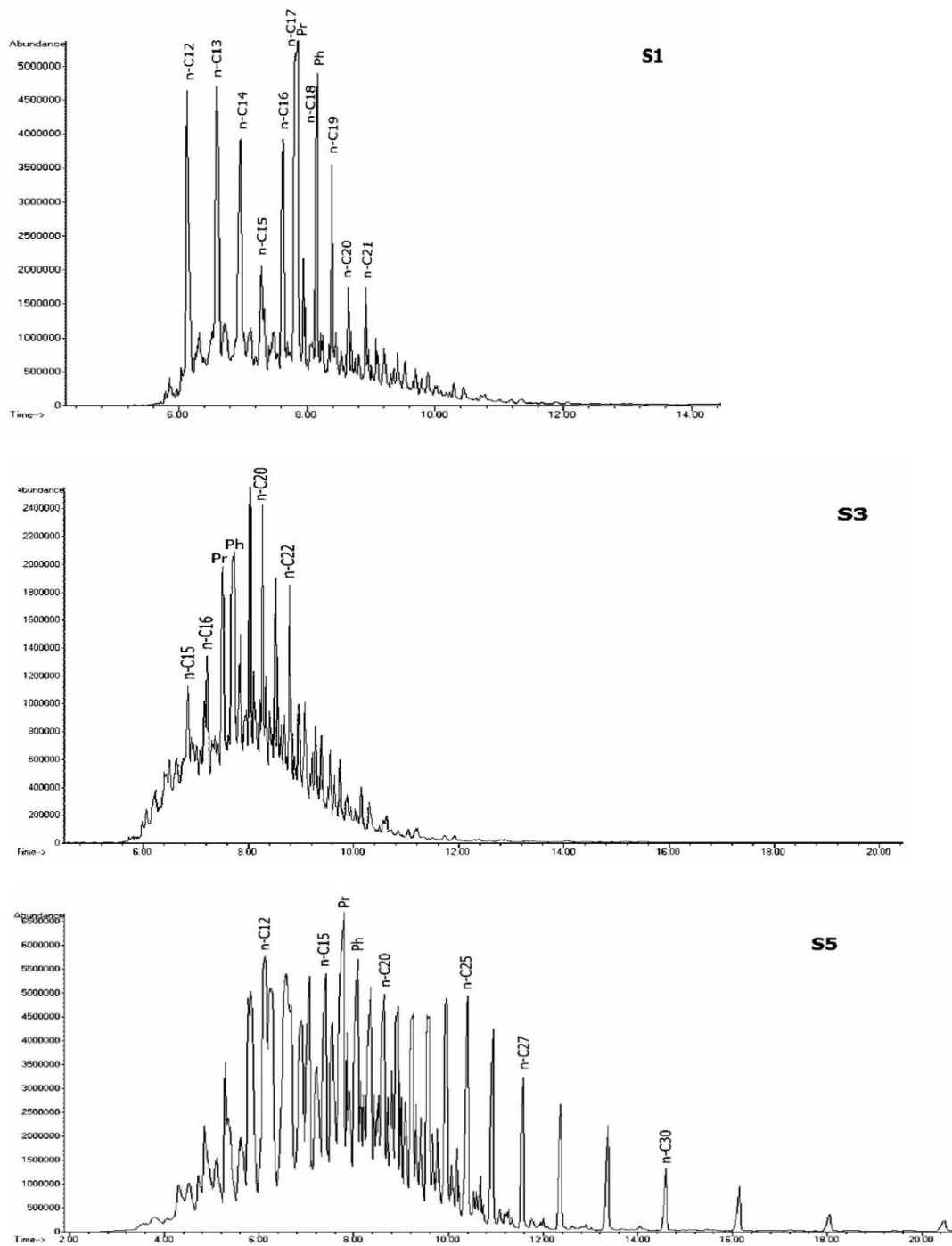


Figure 3. Typical mass chromatograms (71 m/z ion) of the saturated hydrocarbons of crude oils from the Central Niger Delta: Pr = pristane and Ph = phytane

Table 1. Biological marker parameters derived from GC–MS analyses of the saturated hydrocarbon fractions of crude oils from the central Niger Delta, Nigeria

| Parameters | A-Oilfield | | B-Oilfield | | C-Oilfield | |
|---|------------|-------|------------|-------|------------|--|
| | S1 | S2 | S3 | S4 | S5 | |
| Pr/Ph | 2.08 | 0.98 | 2.01 | 0.65 | 0.63 | |
| Pr/n-C ₁₇ | 0.90 | 1.08 | 0.89 | 0.51 | 0.50 | |
| Ph/n-C ₁₈ | 1.20 | 0.41 | 1.22 | 2.60 | 2.59 | |
| CPI | 0.92 | 1.06 | 1.03 | 1.02 | 1.01 | |
| Wax. Index | 0.05 | 0.37 | 0.09 | 1.40 | 1.41 | |
| 2 ₈ /C ₂₉ Ster. | 0.52 | 0.56 | 0.53 | 0.62 | 0.76 | |
| C ₂₉ /C ₂₇ Ster. | 1.01 | 3.78 | 1.03 | 1.00 | 1.19 | |
| %C ₂₉ Ster. | 39.90 | 54.81 | 40.11 | 38.16 | 38.40 | |
| %C ₂₈ Star | 20.71 | 30.68 | 19.61 | 23.73 | 29.22 | |
| %C ₂₇ Star | 39.38 | 14.51 | 39.37 | 38.11 | 32.39 | |
| C ₂₉ : 20S/(20S+20R) | 0.29 | 0.44 | 0.41 | 0.61 | 0.46 | |
| Ster./Hop | 0.16 | 0.15 | 0.19 | 0.20 | 0.36 | |
| Ts/(Ts+Tm) | 0.45 | 0.47 | 0.48 | 0.83 | 0.50 | |
| Ts/Tm | 0.81 | 0.88 | 0.82 | 4.78 | 0.99 | |
| Olea. Index | 0.91 | 0.89 | 0.93 | 0.95 | 0.64 | |
| C ₃₁ HH/C ₃₀ H | 0.32 | 0.33 | 0.35 | 0.34 | 0.39 | |
| Mor./C ₃₀ Hop | 0.16 | 0.17 | 0.16 | 0.19 | 0.24 | |
| C ₂₉ H/C ₃₀ H | 0.08 | 0.56 | 0.12 | 0.61 | 0.50 | |
| C ₂₉ Ts/[C ₂₉ Hop + C ₂₉ Ts] | 0.90 | 0.10 | 0.89 | 0.12 | 0.10 | |
| C ₃₂ H: 22S/(22S + 22R) | 0.57 | 0.64 | 0.55 | 0.57 | 0.57 | |

*Pr – Pristanes,

*Ph – Phytanes

*Pr / (Pr + Ph) – Pristines / (Pristines + Phytanes)

*C₂₉: 20S/ (20S+20R) - C₂₉ αα 20S/ (C₂₉ αα 20S + C₂₉ αα 20R)

*Oleananes index (Olea. Index) - α-oleananes/ C₃₀ 17α (H)-hopanes

*CPI – Carbon Preferences Indices = Odd number n-alkanes/even number n-alkanes [35].

*Waxiness Index (Wax. Index) – Σ (n-C₂₁- n-C₃₁)/ Σ (n-C₁₅ - n-C₂₀)

Ts/(Ts+Tm): 18α(H)-trisorhopanes / (18α(H)-trisorhopanes + 17α(H)-trisorhopanes)

Ts/Tm: 18α (H)-trisorhopanes/17α (H)-trisorhopanes

C₃₁H/C₃₀H- C₃₁-17a (H), 21b (H)-30 homohopanes (22S+22R)/2/ (C₃₀ 17α (H)-hopanes)

Mor. / C₃₀Hop- C₃₀-17b (H), 21a (H)-moretanes / C₃₀ 17α (H)-hopanes

C₂₉/C₃₀H- C₂₉ Tm 17a (H) 21b (H)-norhopanes / C₃₀ 17α (H)-hopanes

C₂₉Ts/ [C₂₉Hop + C₂₉Ts] – C₂₉-18a (H) norneohopanes (29Ts) / (C₂₉ Tm 17a (H) 21b (H)-norhopanes + C₂₉-18a (H) norneohopanes (29Ts))

*C₃₂H: 22S/ (22S + 22R) – C₃₂-17a (H), 21b (H)-30 bishomohopanes (22S)/ (C₃₂-17a (H), 21b (H)-30 bishomohopanes (22S) + C₃₂-17a (H), 21b (H)-30 bishomohopanes (22R))

*Ster. / Hop. – Regular Steranes /17α-hopanes

*Ster: Steranes

*Hop: Hopanes

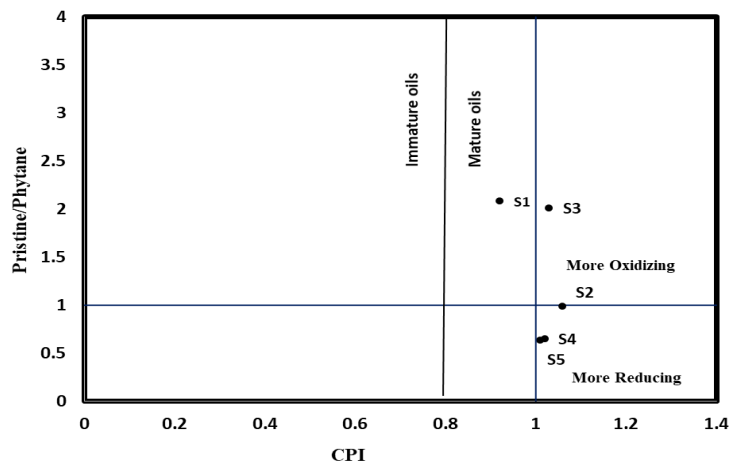


Figure 4. Plot of CPI versus Pristine/Phytane of the studied crude oils from the Central Niger Delta indicating a more oxidizing environment for A (S1) and B (S2, S3) oilfields and more reducing environment for C (S4, S5) oilfield

3.1.3 Isoprenoids/n-alkanes

The isoprenoids/n-alkanes relationships ($Pr/n-C_{17}$ and $Ph/n-C_{18}$) are used to obtain information on depositional environmental conditions, thermal maturation, organic matter sources, diagenetic conditions, and crude oil biodegradation [33]. An increase in thermal maturation leads to an increased rate of n-alkanes generation and a reduction in isoprenoids, the reverse occurs during biodegradation [36]. The $Pr/n-C_{17}$ and $Ph/n-C_{18}$ ratios for A (S1) oilfield are 0.90 and 1.20 respectively; $Pr/n-C_{17}$ and $Ph/n-C_{18}$ ratios for B oilfield are 1.08 and 0.41 (S2), 0.89 and 1.22 (S3) respectively; $Pr/n-C_{17}$ and $Ph/n-C_{18}$ ratios for C (S4, S5) oilfield are 0.51 and 2.60 (S4), 0.50 and 2.59 (S5) respectively (Table 1). These ratios suggest mixed source input from both marine terrestrial organic matter of mainly algae and land plants [9]. Moreover, the cross plot of $Pr/n-C_{17}$ versus $Ph/n-C_{18}$ indicates Terrigenous “Type III kerogen” and Marine algal “Type II kerogen” source deposition under oxygenated to sub-oxygenated and reducing environmental conditions with an increasing thermal maturation level [37] (Fig. 5).

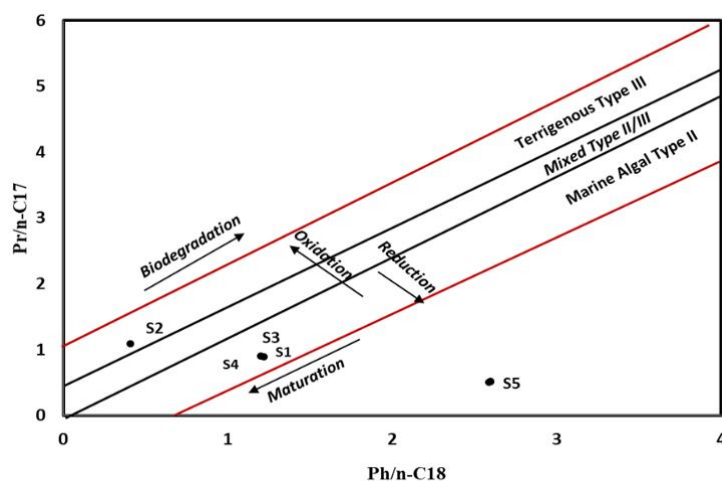


Figure 5. Plot of $Pr/n-C_{17}$ vs. $Ph/n-C_{18}$ indicating terrigenous “Type III kerogen” and marine algal “Type II kerogen” and source deposition under oxic, suboxic to reducing environments with an increasing thermal maturation level [37]

3.1.4 Sterane biomarkers

The sterane biomarker fingerprints were recognized on m/z 217+218 fragmentograms of the studied crude oils (Fig 6). Table 2 shows the identification of chromatographic peaks on m/z 217+218 ions (steranes) and m/z 191 ions (hopanes). The comparative distribution of C_{27} – C_{29} steranes is indicative of the differences in source biogenic input [38]. The percentage abundances of C_{27} , C_{28} and C_{29} regular steranes show that the studied crude oil from A-oilfield (S1) had nearly equal proportion of C_{29} (39.90%) and C_{27} (39.38%) compared to C_{28} (20.71%) regular steranes; similarly, crude oil samples from B-oilfield (S2, S3) had a high proportion of C_{29} (40.11%–54.81%) compared to C_{27} (14.51%–39.37%) and C_{28} (19.61%–30.68%) regular steranes while crude oils from C-oilfield (S4, S5) had a nearly equal proportion of C_{29} (38.16%–38.40%) and C_{27} (32.39%–38.11%) and lower C_{28} (23.73%–29.22%) regular steranes (Table 1). The C_{27} to C_{29} steranes distribution is demonstrated using the ternary plot of Huang and Meinschein [39]. According to Huang and Meinschein's [39] classification, higher abundances of C_{27} regular steranes indicate a strong marine algal input, while higher C_{29} regular steranes indicate a strong terrestrial influence and organic matter input from land plants. Inferences from this ternary diagram classification (Fig. 7), show that the studied crude oil samples were deposited in a mixed environment of both marine and land influences, with major organic materials from marine planktonic and flowering land plants.

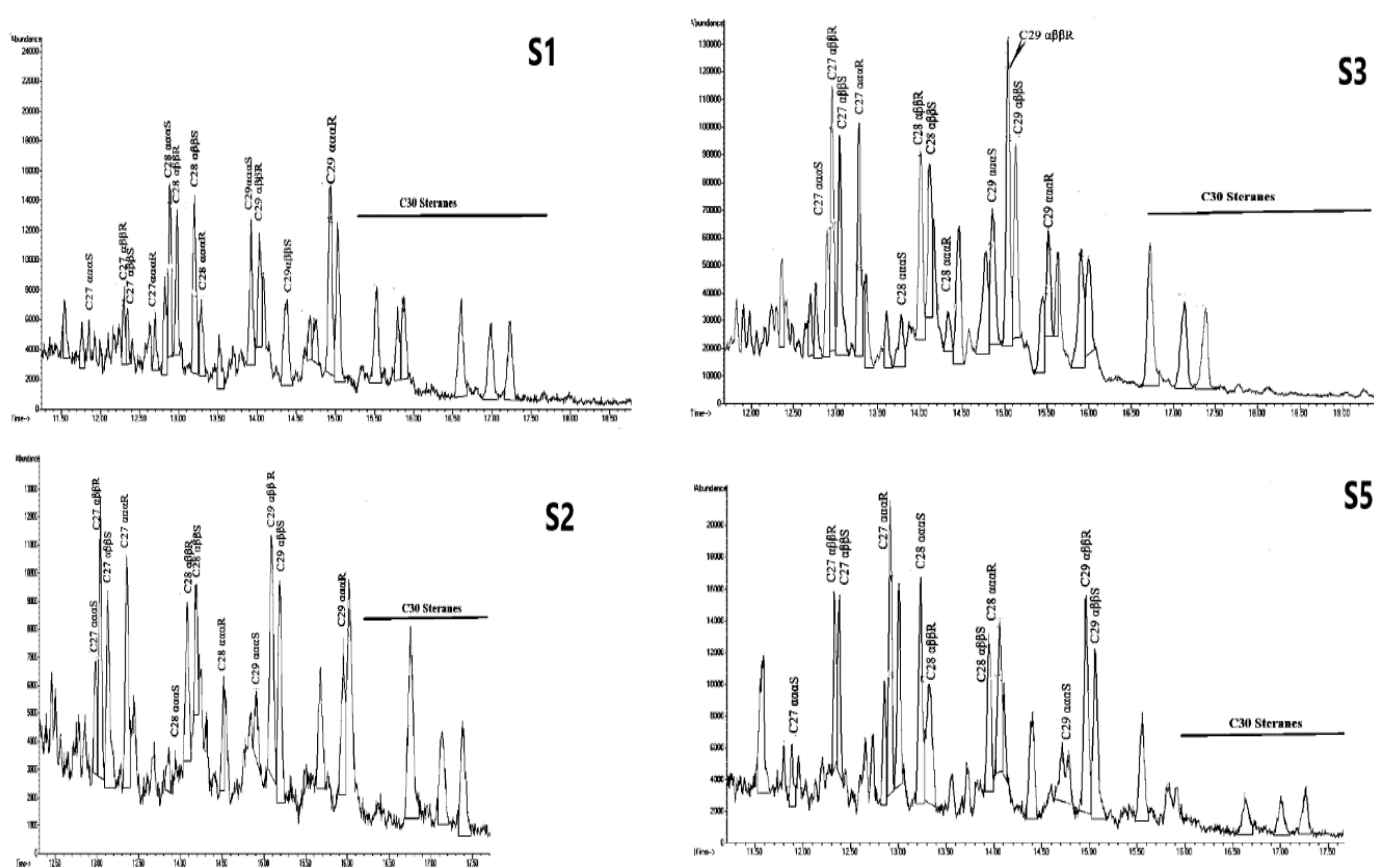
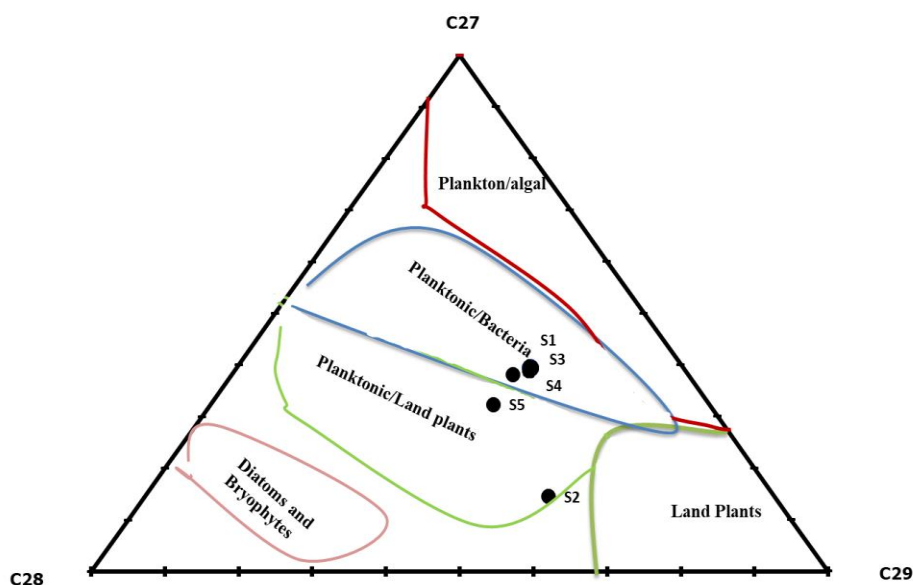


Figure 6. Typical mass chromatograms (217+218 m/z ion) showing steranes distribution in the crude oil samples from the Central Niger Delta

Table 2. Identification of chromatographic peaks on m/z 217+218 ions (steranes) and m/z 191 ions (hopanes)

| Peak | Compound name |
|--|---|
| Ts | 18 α (H) – trisnorneohopanes |
| Tm | 17 α (H) – trisnorhopanes |
| $\alpha\beta$ C ₂₉ Hop | C ₂₉ Tm 17a (H) 21 β (H) norhopanes |
| C ₂₉ Ts | C ₂₉ -18 α (H) norneohopanes (₂₉ Ts) |
| $\beta\alpha$ C ₂₉ Diahop | C ₂₉ -17 α (H), 21 β (H)-25-dinorhopanes |
| α -ole | 18 α (H) – oleananes |
| $\alpha\beta$ C ₃₀ Hop | C ₃₀ 17 α (H) – hopanes |
| $\beta\alpha$ C ₃₀ Mor | C ₃₀ -17 β (H), 21 α (H) – moretanes |
| $\alpha\beta$ C ₃₁ SHop | C ₃₁ -17 α (H), 21 β (H) – 30 (22S) homohopanes |
| $\alpha\beta$ C ₃₁ RHop | C ₃₁ -17 α (H), 21 β (H) – 30 (22R) homohopanes |
| $\alpha\beta$ C ₃₂ SHop | C ₃₂ -17 α (H), 21 β (H) – 30 (22S) bishomohopanes |
| $\alpha\beta$ C ₃₂ RHop | C ₃₂ -17 a (H), 21 β (H) – 30 (22R) bishomohopanes |
| C ₂₇ $\alpha\alpha\alpha$ S | C ₂₇ 5 α (H) 14 α (H) 17 α H (20S) cholestanes |
| C ₂₇ $\alpha\beta\beta$ R | C ₂₇ 13 β (H) 17 α (H) (20 R) diacholestanes |
| C ₂₇ $\alpha\beta\beta$ S | C ₂₇ 5 α (H) 14 β (H) 17 β H (20S) cholestanes |
| C ₂₇ $\alpha\alpha\alpha$ R | C ₂₇ 5 α (H) 14 α (H) 17 α H (20R) cholestanes |
| C ₂₈ $\alpha\alpha\alpha$ S | C ₂₈ 5 α (H) 14 α (H) 17 α H (20S) ergostanes |
| C ₂₈ $\alpha\beta\beta$ R | C ₂₈ 5 α (H) 14 β (H) 17 β H (20R) cholestanes |
| C ₂₈ $\alpha\beta\beta$ S | C ₂₈ 5 α (H) 14 β (H) 17 β H (20S) cholestanes |
| C ₂₈ $\alpha\alpha\alpha$ R | C ₂₈ 5 α (H) 14 α (H) 17 α H (20R) ergostanes |
| C ₂₉ $\alpha\alpha\alpha$ S | C ₂₉ 5 α (H) 14 α (H) 17 α H (20S) stigmastanes |
| C ₂₉ $\alpha\beta\beta$ R | C ₂₉ 5 α (H) 14 β (H) 17 β H (20R) stigmastanes |
| C ₂₉ $\alpha\beta\beta$ S | C ₂₉ 5 α (H) 14 β (H) 17 β H (20S) stigmastanes |
| C ₂₉ $\alpha\alpha\alpha$ R | C ₂₉ 5 α (H) 14 α (H) 17 α H (20R) stigmastanes |

**Figure 7.** Ternary plot of (C_{27} , C_{28} and C_{29}) regular steranes showing sterane compositions in relationship to source organic matter input and environments of deposition for the studied crude oils [39]

The C_{29}/C_{27} , C_{28}/C_{29} , and $C_{29}: 20S/ (20S + 20R)$ sterane proportions were additionally determined and the outcomes were presented in Table 1. The C_{29}/C_{27} normal steranes proportion have been used as markers of the kind of biotas present in source rocks, $C_{29}/C_{27} > 1.0$ demonstrates input from higher land plants (terrestrial), and $C_{29}/C_{27} < 1.0$ are utilized to show marine source biotic information (planktonic/bacterial) [40]. The crude oil samples from A (S1) and B (S2, S3) oilfields had C_{29}/C_{27} normal steranes proportions of 1.01 and 1.03 to 3.78 respectively, while crude oils from C (S4, S5) oilfield had C_{29}/C_{27} regular steranes proportions going from 1.00 to 1.19 (Table 1). This value demonstrates a significant contribution from higher land plants (terrestrial) [40].

Various investigations have detailed an increasing concentration of C_{28} regular steranes with a related decline in C_{29} regular steranes in marine source rocks and petroleum through geologic time [41, 42]. The high composition of C_{28} normal steranes has been connected to the enhancement and overflow of marine phytoplankton (diatoms, dinoflagellates coccolithophores, in the Jurassic to Cretaceous periods [9]. The C_{28}/C_{29} normal steranes proportion < 0.5 is utilized to show Lower Paleozoic and older crude oils from marine source rocks, proportions in the scope of 0.4 to 0.7 demonstrate Upper Paleozoic to Lower Jurassic crude oils, while values > 0.7 are utilized to demonstrate Upper Jurassic to Miocene oils [42]. The crude oil samples from A (S1) and B (S2, S3) oilfields had C_{28}/C_{29} steranes proportions of 0.52 and 0.53 to 0.56 respectively, while crude oils from C (S4, S5) oilfield had C_{28}/C_{29} steranes proportions going from 0.62 to 0.76 (Table 1). These values show Upper Paleozoic to Lower Jurassic and Upper Jurassic to Miocene ages for the crude oils [42].

3.1.5 Steranes/hopanes

The proportion of regular steranes and hopanes are indicatives of contribution from eukaryotic biotas (algae and flowering plants) and prokaryotic biotas (fundamentally bacteria) to sediments and source rocks [9]. Relative high Steranes/hopane (Steranes/hopane ≥ 1) proportion is utilized to demonstrate input from marine biogenic source though low steranes values and moderately low sterane/hopane (Steranes/hopane < 1) proportions recommend terrigenous input or microbially reworked organic materials [9]. The studied crude oils had low sterane/hopane (steranes/hopane < 1) proportions, in the scope of 0.29 to 0.61 (Table 1). This recommends that the crude oils under study originated from a high terrigenous biogenic source [9].

3.2 Thermal maturation

3.2.1 $C_{29}: 20S/ (20S + 20R)$ regular sterane ratio

It has been established that the degree of maturation of crude oils rises with increasing $C_{29}: 20S/ (20S + 20R)$ steranes ratio. The $C_{29}: 20S/ (20S + 20R)$ sterane proportions increments with the ascent in thermal maturation from 0 to 0.5 and achieves equilibrium at/or near the pinnacle of the oil-generative window (0.52 to 0.55) where it keeps up with stability [22, 43, 44]. The crude oils from A (S1) and B (S2, S3) oilfields had $C_{29}: 20S/ (20S + 20R)$ sterane proportions of 0.29 and 0.41 to 0.44 respectively, while crude oils from C (S4, S5) oilfield had $C_{29}: 20S/ (20S + 20R)$ sterane proportions going from 0.46 to 0.61 (Table 1). These proportions propose that the crude oils from A (S1) and B (S2, S3) oilfields, and sample "S5" (C oilfield) have not accomplished thermal equilibrium for $C_{29}: 20S/ (20S + 20R)$ sterane proportions, only crude oil "S4" (0.61) in C oilfield is thermally mature for $C_{29}: 20S/ (20S + 20R)$ sterane proportions and has attained the oil generative window.

3.2.2 Hopane biomarkers

The hopane biomarkers are vital on the grounds they retain the original signatures of the parent biological compounds. Hopanes, homohopanes, and 18α (H) - oleanane fingerprints were observed on mass chromatogram ($m/z = 191$) (Fig. 8). The chromatographic peaks are distinguished in Table 2 for hopanes (m/z 191 particles) and steranes (m/z 217+218 particles). The hopanes are significant biomarkers ordinarily used to unravel the depositional conditions of crude oils and source rocks [33]. The homohopanes originated from bacteriopolyhopanol of the prokaryotic cell layer found in the C_{35} homohopane, and are generally connected to a significant degree of bacterial activity during deposition [45, 9, 28]. The $C_{32}: 22S/ (22S+22R)$ homohopane proportion is a significant biomarker maturation parameter. The proportion is known to increments from 0 during

maturation, achieving equilibrium at 0.6, from 0.50 to 0.54 is known as the peak of oil generative window [44]. The sampled crude oils had $C_{32}:22S/(22S+22R)$ proportions in the range of 0.55 to 0.64, these qualities propose that the crude oils from the central Niger Delta have accomplished equilibrium and had high thermal maturity (Fig. 9) [44].

Oleanane skeletons in crude oils and source rocks are indicative of contribution from higher-plant biota with source ages going from Cretaceous to Tertiary [21, 42]. The 18α (H) - oleanane originated from betulins [46], taraxerenes, and other pentacyclic triterpenoids of land plants [47, 48]. By and large, it is realized that the Niger Delta crude oils are rich in 18α (H) - oleanane [10, 49], with a relatively high concentration of plant macerals and oleanane index values [49, 21]. The 18α (H)- oleanane dispersion and oleanane index for crude oils from the Central Niger Delta are indicative of Tertiary matured source rocks with exceptionally high contribution of terrigenous materials [21, 22]. The oleanane index (18α (H) – oleanane/ $C_{30} 17\alpha$ (H) – hopane) is additionally a maturation indicator as it increases from minimum during maturation, approaching its maximum point at the peak of oil-generation [40]. Oil samples from the Central Niger Delta show a high proportion for the oleanane index (0.64 to 0.95), recommending Tertiary matured source rocks with extremely high contribution of terrigenous materials, and a fulfillment of the equilibrium point of oil generation (Table 1). Ogbesejana et al. [50] reported a matured to immature and early maturation status for the Niger Delta crude oils and source rocks respectively.

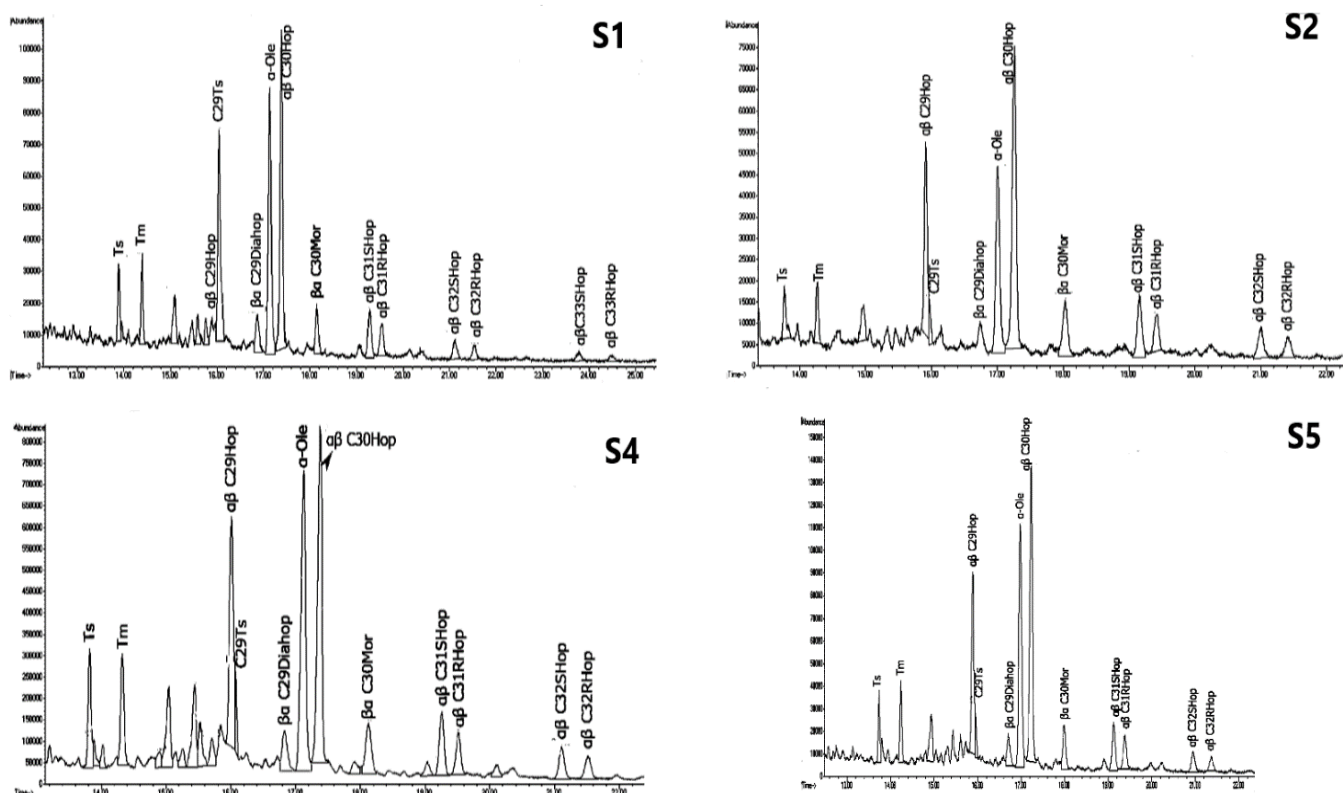


Figure 8. Typical mass chromatograms ($m/z = 191$) showing hopanes distribution in the saturated fractions of the crude oil samples from Central Niger Delta

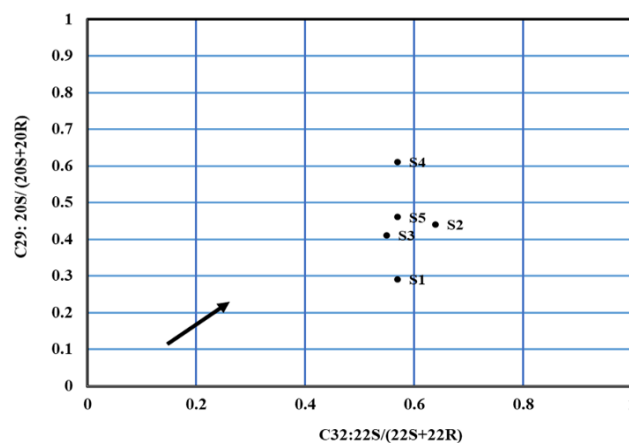


Figure 9. Cross plot of $C_{32}:22S/(22S+22R)$ versus $C_{29} 20S/(20S+20R)$ [37]. The arrow shows direction of thermal maturation

The C_{31}/C_{30} hopane proportion has been utilized to separate marine and terrestrial source organic matter. Crude oils from marine shale, marl, or carbonate source rocks for the most part show high C_{31} homohopane/ C_{30} hopane ($C_{31}/C_{30}H > 0.25$) proportion [9]. The studied crude oils had C_{31}/C_{30} hopane proportion in the scope of 0.32 to 0.39 which recommends marine shale source rocks (Table 1). Also, the convergence of $C_{29} 17\alpha (H) - 30$ -norhopane comparative with $C_{30} 17a (H) -$ hopane are helpful signs of anoxic circumstances and carbonate source rocks [9]. The $C_{29}/C_{30}H > 1$ is utilized to show anoxic carbonate/marl sources while $C_{29}/C_{30}H < 1$ recommends oxygenated states of clastic/shale source rocks deposition [9]. The $C_{29}/C_{30}H$ proportions for the studied crude oils went from 0.08 to 0.61 proposing oxygenated conditions of clastic/shale source rocks deposition (Table 1). The T_s/T_m and $T_s/(T_s+T_m)$ are diagnostic of depositional conditions and thermal maturation. T_m has less stability than the T_s . The $T_s/(T_s+T_m)$ proportion increments from least quantities in less mature oils to 1.0 at the pinnacle of oil generation [51]. The $T_s/(T_s+T_m)$ proportions for the studied oils are in the scope of 0.45 to 0.83 which recommends that the crude oils have not achieved the pinnacle of oil generation for $T_s/(T_s+T_m)$ (Table 1).

Moretane/Hopane ($Mor/C_{30}Hop$) is often utilized as indicators of thermal maturation. The $17b, 21a (H) -$ moretane are known to be less stable when contrasted with $17a, 21b (H)$ hopane. Increasing thermal maturation will result into a change of Moretane to C_{30} hopane [33], resulting in a low concentration of moretane as maturity increments [33, 52]. The Moretane/Hopane proportion declines with maturity development from a base proportion of around 0.8 in immature source rocks and within the scope of 0.05 to 0.15 in mature source organic matter [52]. The studied crude oils had moretane/hopane proportion in the scope of 0.16 to 0.24 recommending matured source rocks (Table 1).

4 CONCLUSIONS

Crude oils collected from three oilfields (A, B, C) in the Central Niger Delta were examined for their biological marker fingerprints using the gas chromatographic-mass spectrometric (GC-MS) technique on the saturated fractions of the crude oils. The study was done to determine source organic matter information, paleoenvironmental conditions of deposition, and thermal maturation. The results demonstrated that the crude oils originated from source rocks containing terrigenous organic matter (essentially land plants) with minor marine organic matter (planktonic/bacterial) source deposition under the pervasiveness of oxic to suboxic conditions. The n-alkanes distribution proposed high terrigenous organic matter from land plants, and isoprenoids proportions (0.63 to 2.08) showed a source input from organic materials, deposited under oxic and suboxic environmental conditions. The low sterane values, low sterane/hopane (steranes/hopane < 1) proportions in the scope of 0.29 to 0.61 showed major terrigenous organic matter input (flowering plants), the distribution of C_{27} , C_{28} , and C_{29} normal steranes demonstrated source input from both marine and terrestrial, with significant organic materials from marine planktonic and flowering land plants. The oleanane indices ($18\alpha (H) -$ oleanane/ $C_{30} 17a (H) -$ hopane)

recommended Tertiary matured source rocks with an extremely high contribution of terrigenous materials and an achievement of the equilibrium point of oil generation. All the more thus, the studied crude oils have $C_{32}:22S/(22S+22R)$ proportions in the scope of 0.55 to 0.64, these qualities point at the fact that the crude oils have accomplished equilibrium and have high thermal maturation. This is in concurrence with the oleanane indices (0.64 to 0.95), CPI (0.92 to 1.06), $C_{29}:20S/(20S+20R)$ sterane proportions (0.29 to 0.61), $Ts/(Ts+Tm)$ proportion (0.45 to 0.83) and moretane/ C_{30} hopane proportion (0.16 to 0.24). The cross plotting of $Pr/n-C_{17}$ versus $Ph/n-C_{18}$ demonstrates Terrigenous "Type III kerogen" and Marine algal "Type II kerogen" source deposition under an oxic to suboxic conditions with increasing maturation level.

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