

GEOCHEMICAL CHARACTERIZATION OF THE COASTAL AND OFFSHORE NIGER DELTA CRUDE OILS, NIGERIA

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Abstract

A suit of ten crude oils from oilfields in the Coastal and Offshore Niger Delta were analyzed for n-alkanes, isoprenoids and biomarker fingerprints using gas chromatography-mass spectrometry (GC-MS). The study was carried out to investigate the source organic matter input, palaeoenvironmental conditions, genetic relationships and relative thermal maturity. The results indicate that Pristane/phytane (Pr/Ph) ratio in the range 1.01 to 1.57 and 0.62 to 4.61 for the coastal and offshore oils respectively, suggest oxic- suboxic paleoenvironmental conditions of deposition. Cross plotting Pr/n-C₁₇ against Ph/n-C₁₈ shows mixed marine - terrestrial organic matter of Type II/III kerogen for the shallow offshore samples and marine algal organic matter (Type II Kerogen) for samples from the coastal swamp. Ternary plot of %C₂₇, %C₂₈ and %C₂₉ regular steranes relationship indicates that crude oils from the Coastal swamp were sourced mainly from planktonic/bacterial organic matters while those from Shallow offshore had their source input mainly from planktonic/land plants organic matters. The C₂₉: 20S/ (20S+20R), Ts/ (Ts+Tm), C₃₂H: 22S/(22S+22R), CPI and the oleanane index for the entire suit of oils indicate thermal maturity. The biomarker fingerprints of the studied crude oils show close genetic relationships, the observed compositional differences are linked with biodegradation, thermal maturity and possible compartmentalization of the oils in the reservoirs.

Keywords: Biomarkers; Thermal Maturity; Organic Matter; Coastal Swamp; Shallow Offshore; Niger Delta.

1. Introduction

The Niger Delta is ranked among the most prolific hydrocarbon producing provinces in the world, with an estimated recovery of about forty billion barrels of crude oil and more than forty trillion cubic feet of natural gas (Adegoke et al., 2017). Situated in the Gulf of Guinea tropical West Africa, the delta covers an estimated area of about 75,000 km² with siliciclastic deposits of about 9000 – 12,000m thickness (Adegoke et al., 2017). In terms of stratigraphy, the Niger Delta is composed of an upper delta top lithofacies of continental sands and gravels, delta front paralic facies of mostly sands and pro-delta marine shales (Avbovbo 1978; Short and Stauble 1967; Evamy et al., 1978). The Niger Delta is subdivided into a series of independent depositional centers known as depobelts, which represent successive stages of the delta development (Stacher, 1995; Knox and Omatsola, 1989; Reijers et al., 1997).

Previous studies indicated that the Niger Delta hydrocarbons belong to one family of oils derived from flowering plants of terrestrial origin, mostly Type III Kerogen of outer neritic – bathyal zone deposits (Bustin 1988; Onyia et al., 2005) and mixed Type II/III (Akinlua et al., 2005). However, there is need to investigate the genetic relationship among crude oils from coastal and offshore depobelts of the Niger Delta in order to ascertain if there are subtle differences or similarities among oils from different parts of the delta. Akinlua and Ajayi (2009) reported that crude oils from Central Niger Delta originated from organic materials of both terrestrial and marine sources, deposited in an oxidized environment. Similarly, Ekpo et al. (2018) showed that the crude oils from some parts of the Offshore Niger Delta are genetically related. This study utilizes the standard oil geochemical methods to investigate the geochemical fingerprints of selected crude oil samples from the Coastal and Offshore depobelts of the Niger Delta. The purpose of this study is to determine source organic matter input, palaeoenvironmental conditions of source rocks deposition, genetic relationship and relative thermal maturation.

2. Materials and methods

A suit of ten crude oils from five oilfields located in the Coastal (COS-1 to COS-5) and Offshore (SOD-1 to SOD-5) depobelts of the Niger Delta (Fig. 1) were analyzed for this study. Fractionation of the crude oils into saturated, aromatic hydrocarbons, and NSO compounds followed standard methods (Schoell et al 1981; Wehner and Teschner, 1981; Ekpo et al., 2013), where n-hexane was used to elute the saturated fraction, dichloromethane (50 ml) was used to elute the aromatic fractions, and the mixture, (1:2) methanol-dichloromethane (50 ml) was used to remove the heterocyclic fractions (NSO). GC-MS analysis was carried out on the saturated fractions using the Agilent technologies 7890 GC series, equipped with an Agilent HP-5 ms column. Sample injection was made using the splitless injection mode (temperature of 290 °C), the carrier gas was Helium at constant flow and the oven programed at 55°C/minute. The Acquisition was done using the EI Scan mode. Data processing was done using Chem Station G1701BA software and the peaks were integrated using the RTE integrator. Peak identification was based on retention times and comparison with set standards, literatures and mass chromatographic patterns interpretation. The cumulated peak area of individual compounds for each oil was transferred to an Excel spreadsheet for calculation of ratios, preparation of tables and plotting charts. Geochemical analyses were carried out in the laboratories of Matosaab Integrated Services Limited (Environmental & Laboratory Services) Port Harcourt Nigeria.

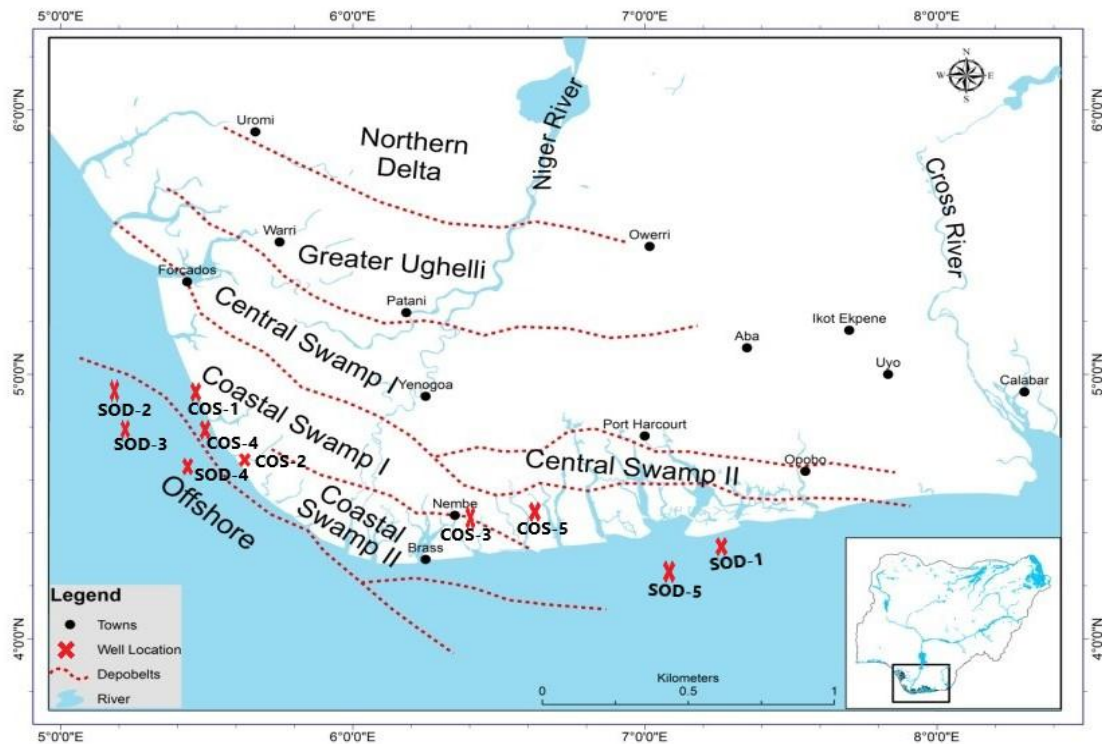


Fig 1 Outline map showing locations of the studied wells in the Coastal and Offshore Niger Delta (the inset box shows location map of Nigeria) (modified from Ukpogon et al., 2017).

3. Results and discussion

3.1. Crude oil composition

The saturated hydrocarbon fractions were the major fractions in the crude oils (Table 1). Crude oil fractionation is useful for classification. Crude oils containing high percentage of saturated hydrocarbons are classified as normal crude, and those with high composition of the aromatic fractions are usually placed in the class of aromatic intermediate crude oils (Tissot and Welte 1984). The studied crude oils contain high percentage of saturated hydrocarbons and are therefore classified as normal crudes. Significant composition of hetero compounds is used to indicate biodegraded crude oils because NSO compounds are more resistant to biodegradation than the fractions of hydrocarbon (Pampanin and Sydens 2013).

Table 1 Composition of crude oil samples in the coastal and offshore Niger Delta oils.

Samples	Saturates (%)	Aromatics (%)	NSO (%)
Coastal Swamp Depobelt			
COS-1	80.26	14.47	5.26
COS-2	55.39	38.46	6.15
COS-3	86.25	2.26	11.49
COS-4	25.49	43.14	31.37
COS-5	84.21	7.89	7.89
Shallow Offshore Depobelt			
SOD-1	83.08	7.69	9.23
SOD-2	69.35	6.45	24.19
SOD-3	77.45	18.63	3.92
SOD-4	32.87	66.67	0.46
SOD-5	24.55	47.27	28.18

3.2 Source and depositional conditions

The organic geochemical parameters for the analyzed crude oils are presented in Table 2. The n-alkanes and isoprenoids distribution were monitored on m/z 71 of the GC-MS chromatograms (Fig. 2). The n-alkanes distribution showed predominance of middle chain n-alkanes (n-C₂₁ and n-C₂₅), presence of waxy n-alkanes (+ n-C₂₅) and short chain alkanes ($\leq$ n-C₂₀). The degree of waxiness expressed as Σ (n-C₂₁- n-C₃₁)/ Σ (n-C₁₅ - n-C₂₀) (El-Diasty and Moldowan, 2012), indicated that the crude oils are waxy (waxiness >1) (Table 2). The presence of high molecular weight n-alkanes is an indication of input from higher plants terrestrial organic materials (Hedberg 1968; El-Diasty and Moldowan, 2012; Younes et al., 2017). The chromatograms on m/z 71 (Fig. 2) show evidence of mild biodegradation. This is demonstrated by the prominent chromatographic baseline hump, representing the unresolved complex mixture (Peters et al., 2005). The relative distribution of pristane (Pr) and phytane (Ph) in a crude oil have been used to indicate source depositional environment and precursor organism relationship. Low values (Pr/Ph <1.0) are usually used to indicate anoxic environments or hypersaline conditions, while high values (Pr/Ph >3.0) are used to indicate oxidizing terrestrial conditions (Peters et al., 2005). Values for the Pr/Ph are in the range of 1.01 to 1.57, for the coastal crude oils and 0.62 to 4.61 for the shallow offshore oils (Table 2).

Table 2 Diagnostic biomarker ratios of the studied crude oil samples in the coastal and offshore Niger Delta oils.

Parameters	Samples									
	Coastal Swamp					Shallow Offshore				
	COS-1	COS-2	COS-3	COS-4	COS-5	SOD-1	SOD-2	SOD-3	SOD-4	SOD-5
Pr/Ph	1.21	1.01	1.23	1.57	1.35	0.62	2.85	1.63	4.61	0.63
Pr/n- ₁₇	0.83	0.54	0.80	0.66	0.82	0.27	0.63	3.51	2.53	0.48
Ph/n-C ₁₈	1.32	0.60	1.29	0.73	1.33	0.34	0.25	1.85	0.17	0.26
CPI	0.99	0.68	1.01	0.93	0.98	1.21	1.24	0.87	0.87	1.22
Wax. Index	3.09	1.31	2.90	1.42	3.10	1.79	1.78	5.43	0.09	1.80
C ₂₉ /C ₂₇ Ster.	0.99	1.13	0.46	1.69	1.02	1.06	0.95	1.84	1.60	1.08
%C ₂₉ Ster.	38.64	41.29	23.29	49.03	40.74	33.20	27.98	48.23	50.24	40.10
%C ₂₈ Star	22.38	22.29	26.58	21.94	20.38	35.57	42.69	25.49	22.48	28.67
%C ₂₇ Star	38.97	36.42	50.13	29.03	38.87	31.23	29.33	26.27	27.27	31.33
C ₂₉ :20S/(20S+20R)	0.49	0.28	0.79	0.07	0.50	0.43	0.56	0.72	0.70	0.42
Ster./Hop	0.21	0.16	0.51	0.31	0.22	0.09	0.28	0.07	0.09	0.10
Hop/Ster.	4.79	6.12	1.94	3.18	4.76	11.55	3.57	14.15	15.01	7.01
Ster. Index	0.20	0.23	0.07	0.11	0.21	0.20	0.15	0.43	0.45	0.21
Ts/(Ts+Tm)	0.52	0.43	0.61	0.50	0.51	0.60	0.52	0.51	0.53	0.55
Olea. Index	0.90	0.90	0.70	0.39	1.01	0.43	0.99	4.67	4.76	0.42
C ₃₁ HH/C ₃₀ H	0.35	0.34	0.23	0.33	0.33	0.29	0.29	0.27	0.30	0.30
C ₂₉ H/C ₃₀ H	0.65	0.58	0.62	0.65	0.67	0.62	0.68	0.33	0.36	0.65
C ₃₂ H: 22S/(22S + 22R)	0.55	0.58	0.61	0.59	0.56	0.60	0.59	0.58	0.56	0.60

*Pr - Pristane, Ph - Phytane

*C₂₉: 20S/(20S+20R) - C₂₉ α 20S stigmastane/(C₂₉ α 20S stigmastane + C₂₉ α 20R stigmastane)

*Oleanane index (Olea. Index) - α -oleanane/ C₃₀ 17 α (H)-hopane

*CPI- Carbon Preference Index = Odd number n-alkanes/even numbered n-alkanes (Bray and Evans, 1961).

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

*Ts/(Ts+Tm)- 18 α (H)-trisorhopane /(18 α (H)-trisorhopane +17 α (H)-trisorhopane)

*C₃₁H/C₃₀H- C₃₁-17 α (H), 21b(H)-30 homohopane (22S+22R)/2/ (C₃₀ 17 α (H)-hopane)

*C₂₉/C₃₀H- C₂₉ Tm 17 α (H)21b(H)-norhopane/C₃₀ 17 α (H)-hopane

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

* Ster : Steranes * Hop: Hopane *%C₂₈ Steranes *%C₂₇ Steranes *%C₂₉ Steranes

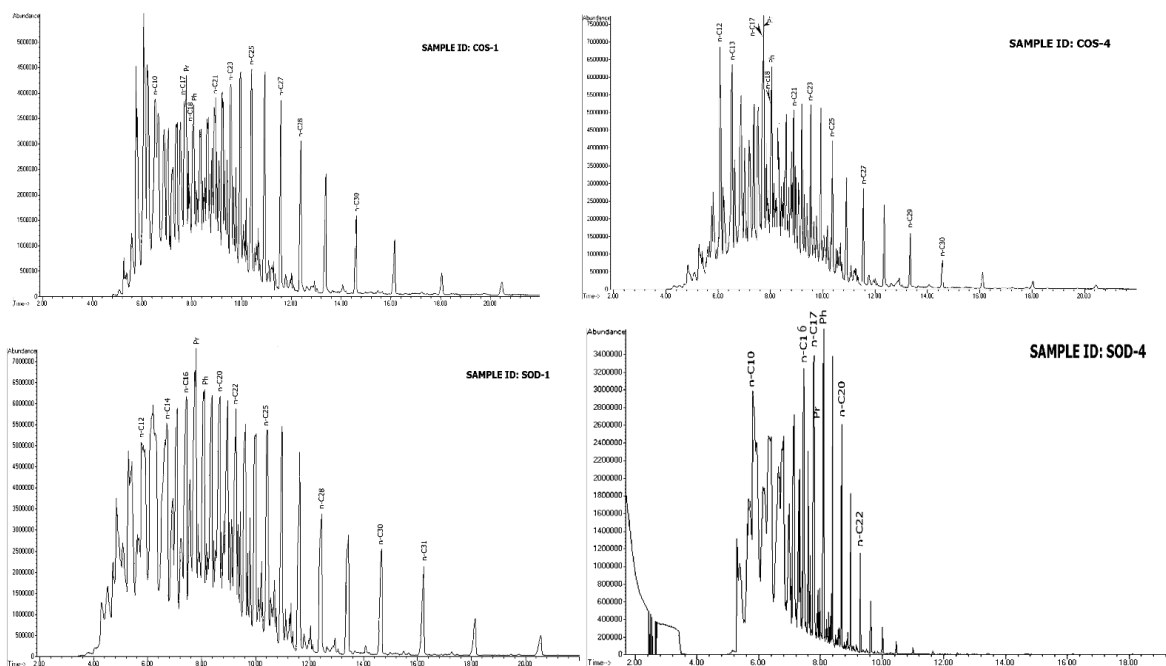


Fig. 2 Representative chromatograms ion (m/z 71) showing n-alkane and acyclic isoprenoid distribution in the coastal and offshore Niger Delta oils.

These values suggest oxic- suboxic paleoenvironmental conditions of deposition of a characteristic mixed terrestrial and marine organic matter input (Peters et al., 2005). The Pr/nC_{17} and Ph/nC_{18} values for the coastal swamp ranged from 0.54 to 0.83 and 0.60 to 1.33 respectively, while those from the shallow offshore ranged from 0.25-3.51 (Table 2). These values suggest mixed terrestrial and marine inputs (El-Diasty and Moldowan, 2012). Moreover, cross plotting of $Pr/n-C_{17}$ against $Ph/n-C_{18}$ indicates mixed marine- terrestrial organic matter of Type II/III kerogen for the crude oil samples from the shallow offshore and marine algal organic matter of Type II Kerogen for the coastal swamp (Fig. 3) (Peters et al., 2005). The odd numbered n-alkanes relationship with the even numbered n-alkanes are useful crude oil maturity indicators (Bray and Evans, 1961). Carbon preference index (CPI) values of 1.0 indicate crude oil maturity, values below 1.0 indicate immature crude oils (Peters et al., 2005). The CPI values for oil samples from the coastal swamp ranged from 0.68-1.01 while those from the shallow offshore ranged from 0.87 -1.24 (Table 2). A plot of Pr/Ph versus CPI shows that most oils from the coastal swamp and shallow offshore are sourced from thermally matured rocks, with a more oxidizing condition of deposition than a reducing condition (Fig. 4).

The distribution of steranes biomarkers were monitored in ion (m/z 217+218) mass chromatograms (Fig. 5). The peaks assignments (m/z 191 and m/z 217+218) are presented on Table 3. Sterols are the main biological precursors of steranes found in eukaryotic organisms (algae and flowering plants) alone (Peters et al., 2005). The relative distribution of C_{27} , C_{28} , and C_{29} -sterol homologs could be useful in differentiating depositional environment. Huang and Meinschein (1979) proposed that dominance of C_{27} steranes could be used to indicate organic matter source from marine algae while the dominance of C_{29} sterols could indicate sources from higher plants. The regular steranes ($\%C_{29}$, $\%C_{27}$ and $\%C_{28}$) were found in relative abundance in all the analysed crude oil samples (Table 2). The proportion of C_{27} regular steranes (29.03- 50.13%) was relatively higher in the Coastal swamp depobelt, followed by the C_{29} steranes (23.29%-49.03%), and the C_{28} (20.38% – 26.58%) (Table 2). This pattern of distribution indicated mixed marine and terrestrial source, contributed majorly by land plants, planktonic diatoms/bryophytes source organic matter (Huang and Meinschein, 1979; Peters et al., 2005). Results from the Shallow Offshore depobelt also showed higher percentage of C_{29} regular steranes (27.98%- 50.24%), with a slightly lower C_{28} steranes (22.48% – 42.69%) and C_{27} steranes (26.27 – 31.33%) (Table 2) suggesting source input from marine planktonic/bacterial for the Coastal swamp oils and terrestrial-land plant organic matters for the shallow Offshore (Fig. 6). The C_{29}/C_{27} steranes ratio are useful indicators of type of organic matter in source rocks, values greater than one ($C_{29}/C_{27} > 1.0$) are used to indicate higher land plants sources while lower values ($C_{29}/C_{27} < 1.0$) indicate marine sourced planktonic/bacterial organic matter input (Peters and Moldowan, 1993; Mohammed et al., 2021). The C_{29}/C_{27} regular steranes ratio ranged from 0.46 – 1.69 for the coastal swamp and 0.95 – 1.84 for the shallow offshore crude oils (Table 2). These values strongly indicate a mixed source from both terrestrial land plants and Marine planktonic/bacterial or algal organic matter (Peters and Moldowan, 1993).

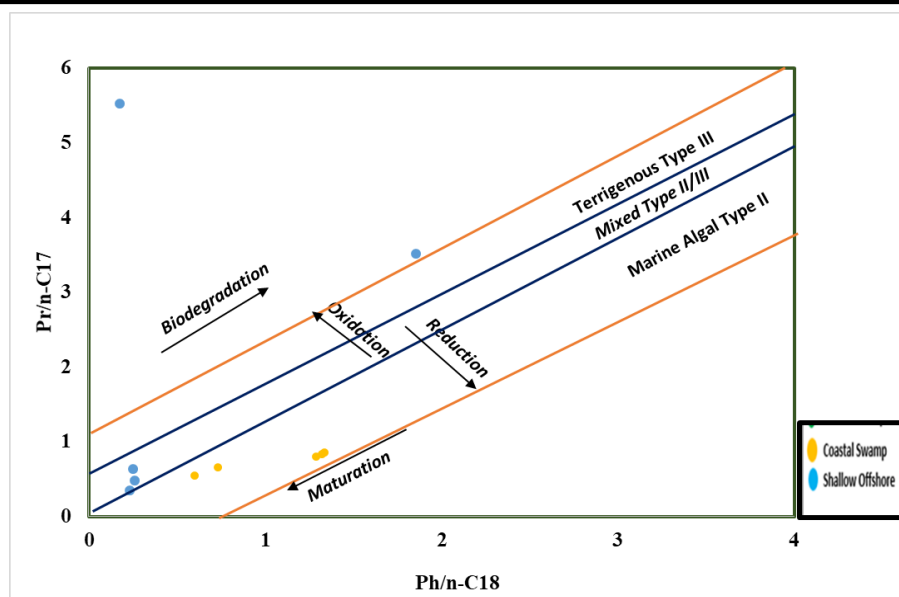


Fig. 3 Cross plot of Pr/n-C17 vs. Ph/n-C18 in the coastal and offshore Niger Delta oils (Peters et al., 2005).

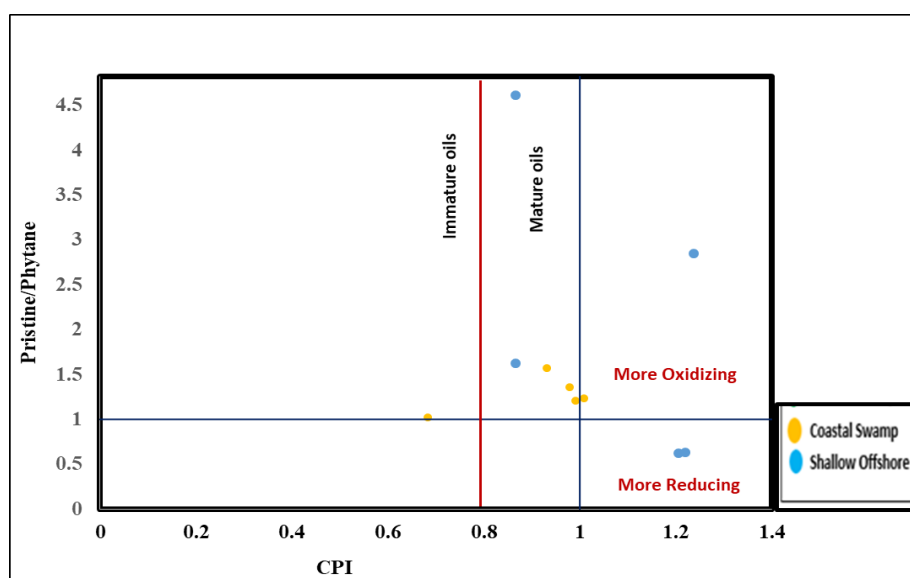


Fig. 4 Cross-plot of Pristine/Phytane versus CPI in the coastal and offshore Niger Delta oils (Peters et al., 2005).

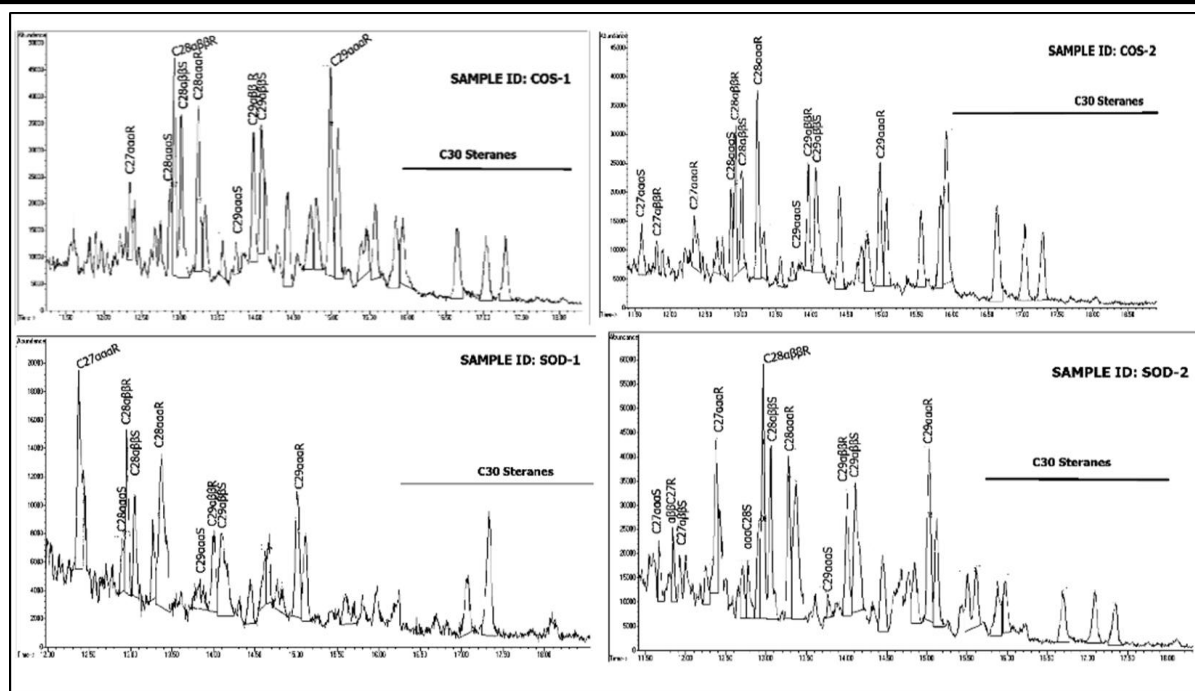


Fig. 5 Representative mass chromatograms of m/z 217+218(steranes) for the analyzed crude oils from coastal and offshore Niger Delta.

Table 3: Peaks identification on m/z 191 (hopanes) and m/z 217+218 (steranes) mass chromatograms

Peak	Compound name
Ts	18α(H)- trisnorhopane
Tm	17α(H)-trisnorhopane
αβC ₂₉ Hop	C ₂₉ Tm 17a(H)21b(H)-norhopane
C ₂₉ Ts	C ₂₉ -18a(H) norneohopane (29Ts)
βαC ₂₉ Diahop	C ₂₉ -17a(H), 21b(H)-25-dinorhopane
α-ole	18α (H) -oleanane
αβC ₃₀ Hop	C ₃₀ 17α (H)-hopane
βαC ₃₀ Mor	C ₃₀ -17b(H), 21a(H)-moretane
αβC ₃₁ SHop	C ₃₁ -17a(H), 21b(H)-30 homohopane (22S)
αβC ₃₁ RHop	C ₃₁ -17a(H), 21b(H)-30 homohopane (22R)
αβC ₃₂ SHop	C ₃₂ -17a(H), 21b(H)-30 bishomohopane (22S)
αβC ₃₂ RHop	C ₃₂ -17a(H), 21b(H)-30 bishomohopane (22R)
C ₂₇ αααS	C ₂₇ 5a(H) 14a(H) 17a(H) cholestane (20S)
C ₂₇ αββR	C ₂₇ 13b(H) 17a(H) Diacholestane (20R)
C ₂₇ αββS	C ₂₇ 5a(H) 14b(H) 17b(H) cholestane (20S)
C ₂₇ αααR	C ₂₇ 5a(H) 14a(H) 17a(H) cholestane (20R)
C ₂₈ αααS	C ₂₈ 5a(H) 14a(H) 17a(H) ergostane (20S)
C ₂₈ αββR	C ₂₈ 5a(H) 14b(H) 17b(H) cholestane (20R)
C ₂₈ αββS	C ₂₈ 5a(H) 14b(H) 17b(H) cholestane (20S)
C ₂₈ αααR	C ₂₈ 5a(H) 14a(H) 17a(H) ergostane (20R)
C ₂₉ αααS	C ₂₉ 5a(H) 14a(H) 17a(H) stigmastane (20S)
C ₂₉ αββR	C ₂₉ 5a(H) 14b(H) 17b(H) stigmastane (20R)
C ₂₉ αββS	C ₂₉ 5a(H) 14b(H) 17b(H) stigmastane (20S)
C ₂₉ αααR	C ₂₉ 5a(H) 14a(H) 17a(H) stigmastane (20R)

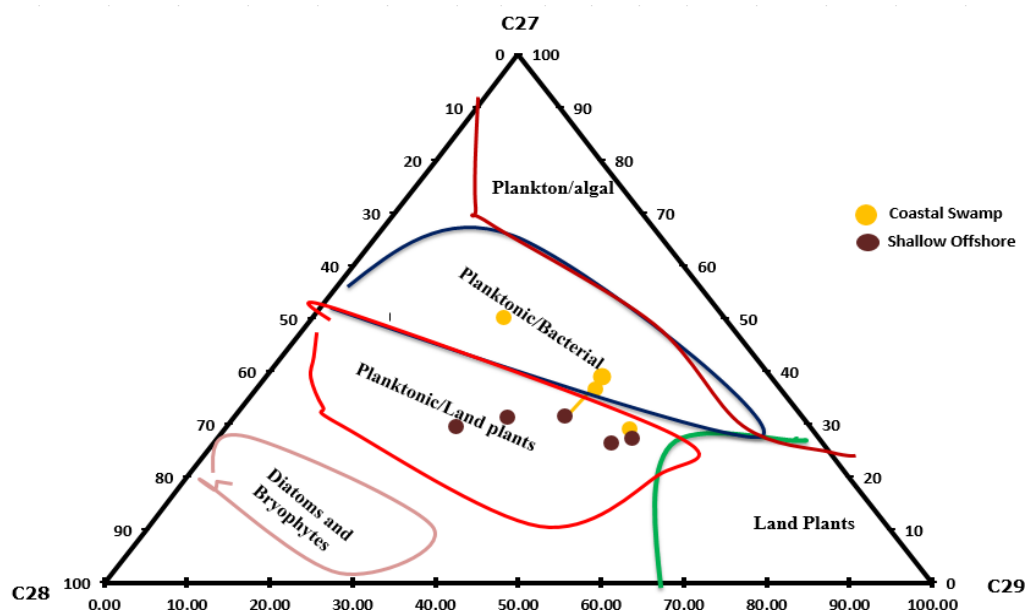


Fig. 6 Ternary diagram of %C₂₇, %C₂₈, and %C₂₉ regular steranes showing that the crude oils from the coastal swamp were sourced mainly from planktonic /bacterial organic matters while those from shallow offshore had their source input mainly from planktonic /land plants organic matters (Huang and Meinshein, 1979).

The hopanes and 18 α (H)-oleanane skeletons in the crude oil samples were monitored on m/z 191 GC-MS chromatograms (Fig. 7). The biological precursors of hopanes are the bacteriohopanetetrol, and the polyfunctional C₃₅ hopanoids in prokaryotes (Ourisson et al., 1984; Rohmer, 1987; Peters et al., 2005). The hopanes are useful indicators of redox conditions of sediments deposition (Peters et al., 2005). The relative concentration of C₂₉ 17 α (H)-30-norhopane relative to the C₃₀ 17a (H)-hopane are used to indicate carbonate source rocks organic matter deposited in an anoxic conditions (Peters et al., 2005). The C₂₉/C₃₀H ratio is normally greater than one (>1) for anoxic carbonate/marl source rocks but less than one (C₂₉/C₃₀H <1) for clastic/shale source rocks deposited in an oxic condition (Peters et al., 2005). The C₂₉/C₃₀H ratios were observed to be less than one (C₂₉/C₃₀H <1) (Table 2) for all the analysed crude oils suggesting clastic/shale source rocks deposited in an oxic environmental condition. The presence of 18 α (H)-oleanane in crude oils is an indication of higher-plant source organic matters of Cretaceous and younger ages (Ekweozor et al, 1979). The (m/z 191) GC-MS chromatograms (Fig. 7), shows the preponderance of 18 α (H)-oleanane in all the analysed crude oils. The oleanane index, expressed as 18 α (H)-oleanane/ C₃₀ 17a (H)-hopane is a maturity indicator, it increases from immature oils and maximizes at the peak of the oil-generation (Peters and Moldowan, 1993). Crude oils from the shallow offshore had the highest oleanane index (0.42-4.76) while that of the coastal swamp ranged from 0.39- 1.01 (Table 2). It has been established that crude oils from the Niger Delta have 18 α (H)-oleanane in abundance (Ekweozor et al., 1979) owing to their high plant macerals (vitrinite and resinite) and high oleanane index values (Udo and Ekweozor, 1990). The 18 α (H)-oleanane are sourced from betulins (Grantham et al., 1983; El-Sabagh et al., 2018), the taraxerene (ten Haven and Rullkotter 1988), and other pentacyclic triterpenoids of higher plants (Whitehead, 1974).

The ratio of regular steranes/17 α -hopanes is normally useful in recognizing sources from eukaryotic and prokaryotic organisms in petroleum and source rocks (Peters et al., 2005); where high steranes/hopanes ratio (≥ 1) indicates marine planktons/bacterial or marine

algal (Peters et al., 2005), and lower values of steranes/hopanes ratio (≤ 1) indicates land plants sources or microbially reworked organic matter materials (Tissot and Welte, 1984; Moldowan et al., 1985). The ratio for the regular steranes/ 17α -hopanes ranged from 0.16 – 0.51 for the Coastal Swamp crude oils and 0.07-0.28 for the shallow offshore oils (Table 2). These results indicate main sources from terrigenous land plants and/or microbially reworked organic matter (Tissot and Welte, 1984; Moldowan et al., 1985; Peters et al., 2005; Ekpo et al., 2013).

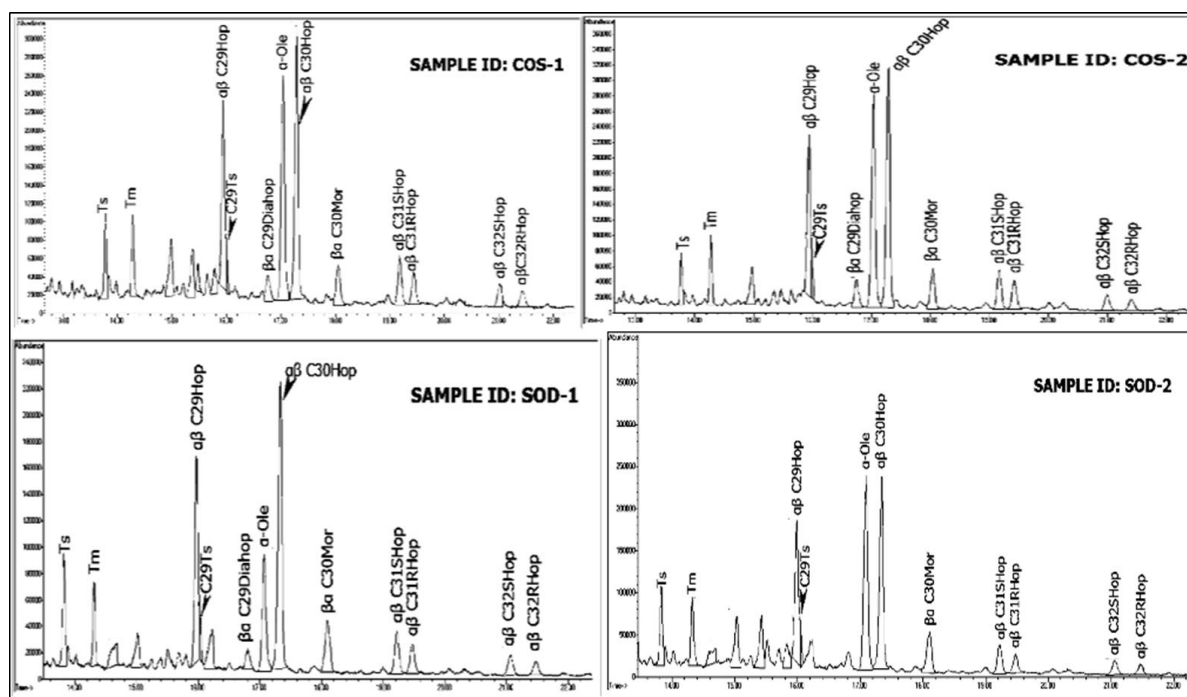


Fig. 7 Representative mass chromatogram of m/z 191 ion (hopanes) of crude oils from the coastal swamp depobelt and shallow offshore depobelt, Niger Delta.

3.3. Genetic relationships

Oil to oil correlations were carried out to determine geochemical relations among the crude oils and establish possible genetic linkages. Crude oil correlation using their biomarker fingerprints is very important in the assessment of reservoir connectivity, petroleum migration and plays evaluation (Peters and Moldowan, 1993; Peters et al., 2005). Source diagnostic biomarker parameters (Peters et al., 2000; Peters et al., 2005), were used for plotting of star diagrams (Fig. 8). The similarities in the biomarker patterns indicate possible genetic relationships among the studied oils (Fig. 8). However, the major deviations exhibited by the $Pr/n-17$, $Ph/n-18$, Ts/Tm , C_{29}/C_{27} Steranes ratio, C_{29} Steranes, waxiness index and oleanane index is possibly linked to slight compositional differences among the crude oils due to reservoir compartmentalization (Peters et al., 2005; Ekpo et al., 2018).

3.4. Thermal maturity

The $Ts/(Tm+Ts)$ is significantly influenced by maturity, the Ts has greater thermal stability than the Tm . The $C_{29}:20S/(20S + 20R)$ steranes ratio increases with maturity (Seifert and Moldowan 1980), from 0 to 0.5 (0.52-0.55 = attaining equilibrium) with continuous maturity increase (Dahi et al., 1999; Peters et al., 2005). The $C_{29}: 20S/(20S+20R)$ reaches equilibrium at/or near the peak of oil generation and maintain a stable

equilibrium afterwards (Peters and Moldowan, 1993). The $C_{29}:20S/(20S+20R)$ ratio for the crude oil samples from Coastal Swamp are in the range of 0.07 - 0.79 and those from Shallow Offshore have values in the range of 0.42-0.72 (Table 2). These values show that most of the crude oils had already approached thermal equilibrium for $C_{29}: 20S/(20S+20R)$ maturity while others are just about attaining equilibrium. The $Ts/(Ts+Tm)$ ratio approaches its endpoint close to the end of the oil generative window (Peters and Moldowan, 1993), and increases with maturity, exceeding the peak of the oil generation. For the $C_{29}: 20S/(20S+20R)$, the values will maintain stability when equilibrium is attained (Peters and Moldowan, 1993). The values for $Ts/Ts+Tm$ ranged from 0.42-0.61 for the Coastal Swamp and 0.51-0.60 for the Shallow Offshore oils. The $Ts/(Ts + Tm)$ and $C_{29} 20S/(20S + 20R)$ values of the analysed crude oils show that most of the crude oils had already approached thermal equilibrium while others are within the equilibrium or just about attaining equilibrium point for crude oil generation (Fig. 9) (Hunt, 1996). The $C_{32} 22S/(22S+22R)$ values for the crude oil samples from the coastal swamp (0.55-0.61) and shallow offshore (0.56-0.60) are within the thermal maturation equilibrium range (Table 2) (El- Sabagh et al., 2017). The CPI values for the coastal swamp ranged from 0.68-1.01 while those from the shallow offshore ranged from 0.87 -1.24 (Table 2), both indicated marginally matured oils (Peters et al., 2005). The Oleanane index is known to increase from lower values in immature rocks to high values at the peak of oil generation (Ekweozor and Telnaes, 1990). The studied crude oils have significant values for the oleanane index, with values from 0.42 to 4.76 and 0.39 to 1.01 for the shallow offshore and coastal oils respectively (Table 2), indicating oil generation from a marginally matured to matured source rocks (Peters et al., 2005).

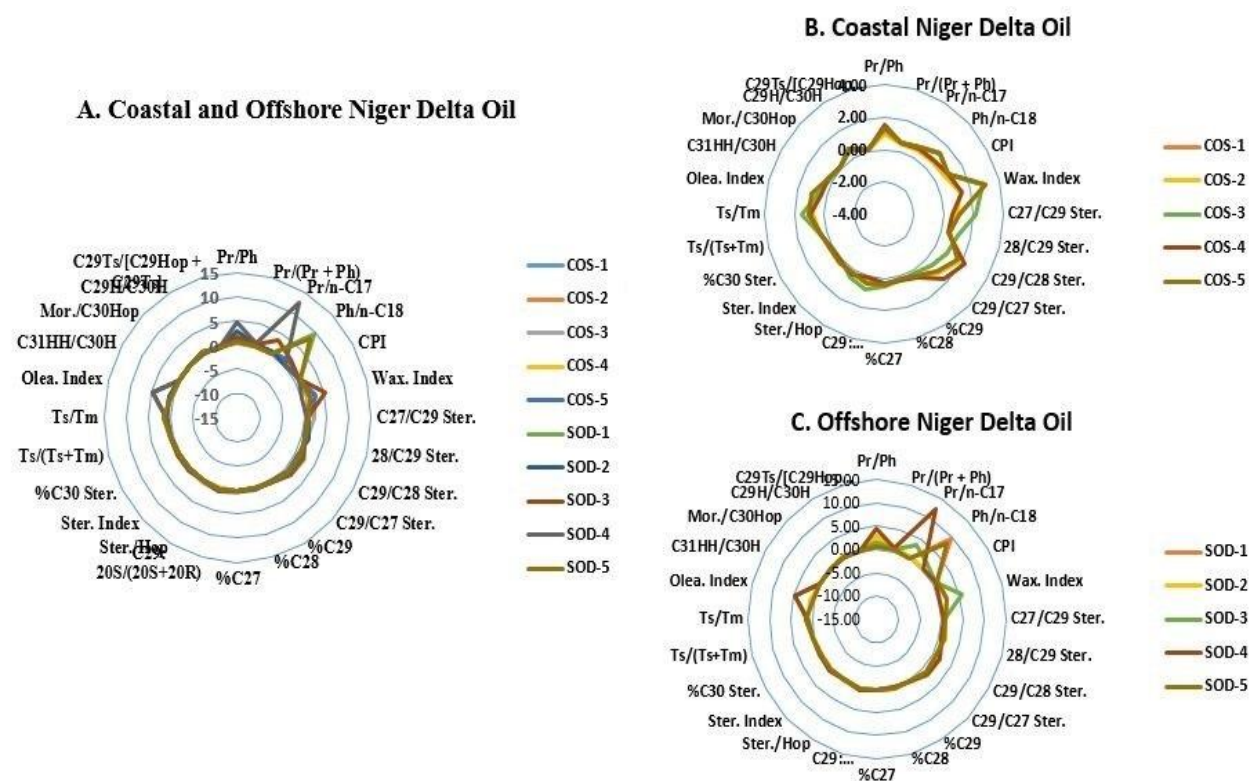


Fig. 8 Star plots of biomarker parameters of the Niger Delta oils: A-crude oils from both coastal and offshore; B- coastal alone; C- offshore alone.

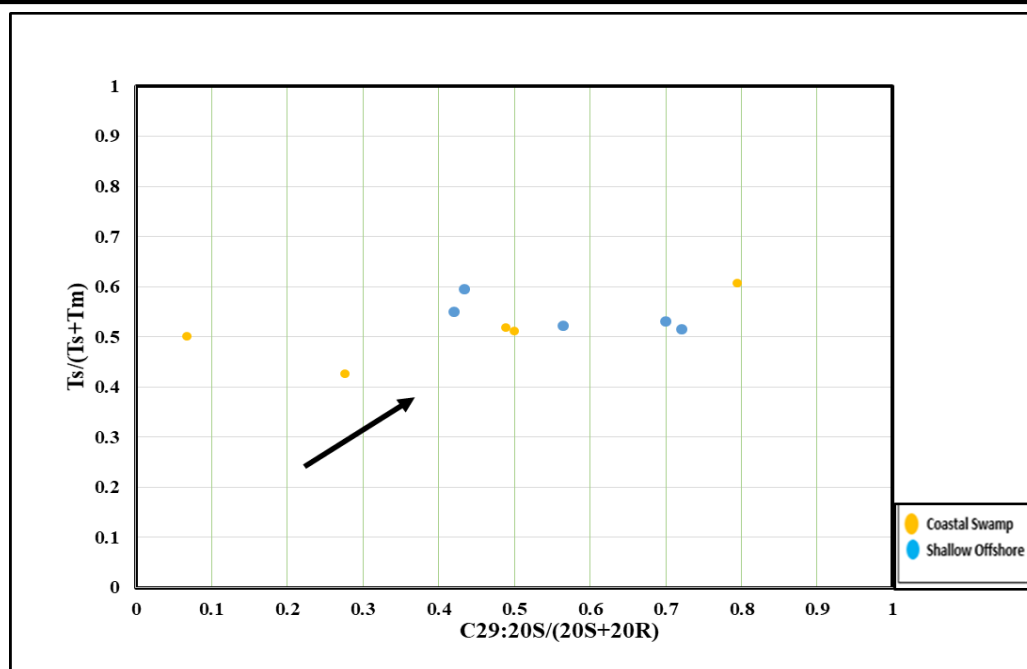


Fig. 9 A plot of $T_s/(T_s + T_m)$ versus $C_{29} 20S/(20S + 20R)$ values of the analysed crude oils shows that most of the crude oils had already approached thermal equilibrium while some are within the equilibrium or just about attaining equilibrium (Hunt, 1996). Thermal maturity direction is shown with the arrow.

4. Conclusions

Organic geochemical characterization of the coastal and offshore Niger Delta oils shows that the crude oils were derived from organic matters of both terrestrial and marine origin and deposited under oxic- suboxic paleoenvironmental conditions. A cross plot of $Pr/n-C_{17}$ versus $Ph/n-C_{18}$ indicated mixed marine- terrestrial organic matter of Type II/III kerogen for the crude oil samples from the shallow offshore and marine algal organic matter of Type II kerogen for the coastal swamp oils. Ternary diagram of $\%C_{27}$, $\%C_{28}$, and $\%C_{29}$ regular steranes indicated that crude oils from the coastal swamp were sourced mainly from planktonic /bacterial organic matters while those from shallow offshore had their source input mainly from planktonic /land plants organic matters. The C_{28}/C_{29} regular steranes ratios indicate Upper Jurassic to Miocene source rock ages for the analyzed crude oils. A cross plot of Pr/Ph versus 17α -hopanes /regular steranes ratio distinguishes the crude oils into two source families. Family A oils composed of mainly oils from the shallow offshore with source input from Marine bacterial organic matter while family B oils predominantly composed of crude oils from the coastal swamp and is characterized by more of marine algal inputs and plant derived organic matter. The $T_s/(T_s+T_m)$, $C_{29}: 20S/(20S+20R)$, $C_{32} 22S/(22S+22R)$, CPI and the oleanane index for the entire suit of oils indicate thermal maturity. The biomarker fingerprints of the coastal and offshore Niger Delta oils show close genetic relationships, the observed compositional differences are linked with biodegradation, thermal maturity and possible compartmentalization of the oils in the reservoirs.

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