



Research article

Occurrence and geochemical significance of fluorene and alkylfluorenes in crude oils and source rock extracts from Niger Delta basin, Nigeria

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ABSTRACT

The crude oils and their source rocks from Niger Delta basin, Nigeria were investigated by optical microscopy for the maceral compositions and by gas chromatography - mass spectrometry (GC-MS) for the composition, distribution and abundances of saturated and aromatic biomarkers. The data obtained showed that the rock samples and crude oils were formed from the mixed input of terrestrial and marine organic matter, and deposited under oxic to sub-oxic conditions in a lacustrine-fluvial/deltaic environment. The aliphatic maturity parameters calculated for the source rocks and oil samples showed that they have immature to early mature; and early oil window maturity respectively, whereas aromatic maturity ratios indicated that they were within immature to peak of oil generation and beyond; and peak to late oil generative window, respectively. The crude oils and source rocks were characterized by the dominance of C₂-fluorenes over other alkylated homologues. The predominance of C₂ fluorenes over other alkylated homologues might have been influenced by source facies and depositional environments. The relative percentages of fluorenes (FLs %), dibenzofurans (DBFs %) and dibenzothiophenes (DBTs %) values for the rock samples range from 9.36 to 38.04 %, 35.82–71.60 % and 10.02–42.52 %, respectively, while the crude oils have ranges of values from 18.91 to 56.38 %, 24.90–72.34 % and 5.99–19.02 %, respectively. These values showed that the crude oils and source rocks originated from the mixture of organic matter (terrestrial and marine) with higher contribution from terrestrial organic matter and deposited in a marine/brackish-saline lacustrine/swampy environments. The abundance and distribution of fluorenes and its derivatives were found to be effective in determining the origin and depositional environments of crude oils and source rocks in the Niger Delta Basin, Nigeria.

1. Introduction

With an estimated reserve of about 37 billion barrels of crude oil and 180 trillion cubic feet of natural gas [1], the Niger Delta Basin is recognized as one of the most important oil regions in the world.

The crude oils in the Niger Delta Basin are produced mostly in the Agbada Formation [1]. Nevertheless, some authors have reported that several directional paths form a “oil-rich sheet,” with the largest field and the lowest gas: the ratio of oil in the basin [2, 3, 4]. This layer stretches from the northwest offshore area to the southeast offshore sector, and over a variety of trends in north-south. It corresponds roughly to the transition from continental to oceanic crust, and is within a maximum sedimentary thickness zone. This hydrocarbon distribution was initially related to the timing of trap formation in relation to the petroleum migration. According to [5], petroleum was found at various viable horizons, at different depths apart, within the Niger Delta Basin. While

several authors have worked on crude oil and source rock samples from the Niger Delta Basin in order to determine the location and potential of the source rocks of the basin [5, 6, 7, 8, 9, 10], there is still no consensus on the true identity of the petroleum system(s) that led to the greater Niger Delta oil fields [11].

Fluorene and alkylfluorenes are important components of crude oils, coals and sedimentary extracts [12, 13, 14, 15]. Although little research was done on the sources of fluorene and its derivatives, it was widely believed that they were derived from pyrolysis or incomplete combustion of different organic materials [12]. Alkylfluorenes can be produced from cyclisation reactions of ortho-substituted biphenyls according to [16]. Similarly [17], stated that under non-catalytic conditions in laboratory experiments, the cyclization reaction of 2,3-dimethylbiphenyl could form 1-methylfluorene [13]. also proposed that biphenyl reactions on carbon surfaces with methylene species could yield fluorene. Fluorenes may thus be derived from biphenyls in crude oils and

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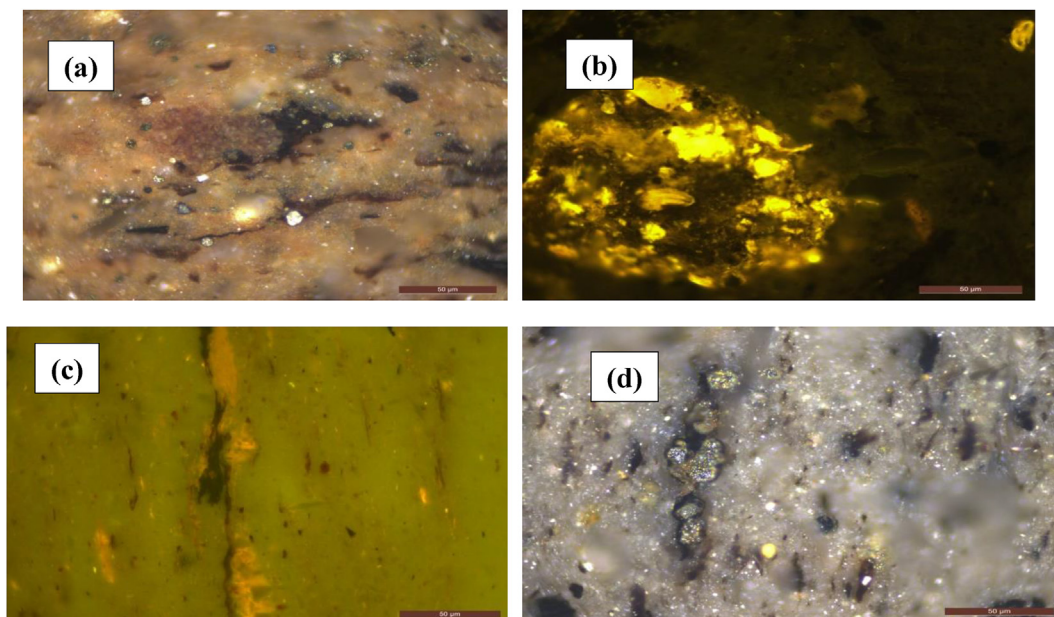


Figure 1. Images showing (a) Vitrinite, (b) exinite, (c) alginite and (d) inertinite maceral groups found in Niger Delta Source Rocks.

Table 1. Geological information, maceral compositions and related parameters in Niger Delta source rocks.

Field	Depth(m)	Reservoir Formation	Geological Age	Depobelt	Maceral compositions (%)				% Ro	%EqRo
					vit.	ex.	iner.	sap.		
MJI	2079–2098	Agbada	Eocene to Recent	Offshore	73	11	6	10	0.29	0.51
MJI	2299–2308	Agbada	Eocene to Recent	Offshore						0.58
MJI	2637–2655	Agbada	Eocene to Recent	Offshore	71	12	5	12	0.41	0.53
MJI	2857–2875	Agbada	Eocene to Recent	Offshore						0.58
MJI	2994–3012	Agbada	Eocene to Recent	Offshore	75	13	3	8	0.43	0.63
MJI	3085–3104	Agbada	Eocene to Recent	Offshore						0.62
MJI	3232–3250	Agbada	Eocene to Recent	Offshore	72	14	7	7	0.37	0.69
MJI	3323–3332	Agbada	Eocene to Recent	Offshore						0.65
MJI	3405–3424	Agbada	Eocene to Recent	Offshore	75	11	5	9	0.5	0.81
MJO	1616–1707	Agbada	Eocene to Recent	Offshore	78	13	4	5	0.3	0.49
MJO	1771–1872	Agbada	Eocene to Recent	Offshore						0.42
MJO	2091–2101	Agbada	Eocene to Recent	Offshore	80	11	3	6	0.38	0.38
MJO	2293–2366	Agbada	Eocene to Recent	Offshore	77	12	6	5	0.43	0.47
MJO	2570–2588	Agbada	Eocene to Recent	Offshore	58	26	6	9	0.4	0.44
MJO	2808–2817	Agbada	Eocene to Recent	Offshore	75	12	3	10	0.35	0.72
OKN	1537–1555	Agbada	Eocene to Recent	Offshore	59	32	4	5	0.23	-0.07
OKN	1729–1747	Agbada	Eocene to Recent	Offshore	61	30	3	6	0.23	0.20
OKN	2625–2643	Agbada	Eocene to Recent	Offshore						0.04
OKN	2780–2799	Agbada	Eocene to Recent	Offshore	60	26	4	10	0.29	0.09
OKN	2863–2881	Agbada	Eocene to Recent	Offshore	61	29	3	7	0.31	-0.27
OKN	2909–2927	Agbada	Eocene to Recent	Offshore	48	39	5	9	0.27	0.06

Vit.: vitrinite; ex.: exinite; iner.: inertinite; sap.: sapropelinite; Ro: vitrinite reflectance; EqRo: equivalent vitrinite reflectance ($0.018 \cdot T_{\max} - 7.16$) [33].

sediment extracts. Nevertheless, no clear correlation has been found in sediments, between the reduction of 2,3-dimethylbiphenyl and the increase of 1-methylfluorene [17]. The authors proposed that 2,3-dimethylbiphenyl depletion is not based on matrix impact, but on sediment maturity.

Fluorenes along with dibenzothiophenes and dibenzofurans can provide valuable information about sedimentary environments and the source sources of crude oils and extracts from sediments. For example, the high abundance of dibenzothiophenes indicates marine carbonate source rocks while the abundance of fluorenes and dibenzofurans is lower in freshwater source rocks [13, 18, 19, 20, 21]. This is why these

compounds were successfully used in oil-oil correlation [18, 19, 22] and oil-source rock correlation studies [20, 21].

Since fluorenes (FLs), dibenzothiophenes (DBTs) and dibenzofurans (DBFs) share a common chemical structure and may have genetic relationships, their relative abundance, such as ternary diagram, has been applied in the study of depositional environments, oil-to-oil and oil-to-source correlations as effective molecular indicators [23, 24, 25]. Nonetheless [14], were the first group of authors to systematically apply the entire ternary diagram of FLs, DBTs, and DBFs to differentiate various source rock depositional environments/lithologies. However, despite the enormous geochemical significance of fluorene and its alkylated

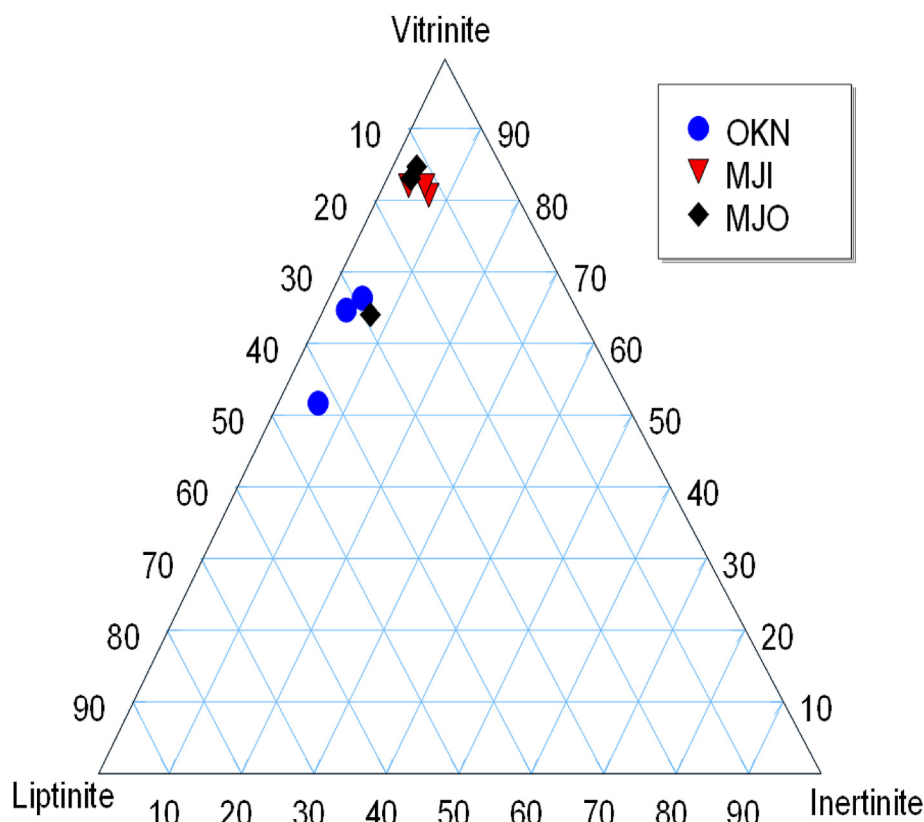


Figure 2. Triplot of the maceral groups found in the Niger Delta source rocks.

homologues in the petroleum geochemistry, they have not been studied or reported in Niger Delta source rocks and crude oils. This work is designed to investigate the occurrence and geochemical significance of fluorene and alkylfluorenes in source rocks and crude oils from Niger Delta basin, Nigeria for the first time and to re-assess the origin, depositional environment and thermal maturity status of the crude oils and source rocks from the basin based on the saturated and aromatic parameters that have not been explored in the Basin.

2. Geological and stratigraphic setting

Niger Delta is a sedimentary basin located in the Gulf of Guinea, re-entrant to West Africa. The sub-aerial portion of the Niger Delta Basin contains about 75,000 km² and stretches from apex to mouth at approximately 200 km. The Niger Delta occupies an area of around 140,000 km², with a total sedimentary sequence of approximately 12,000 m [6]. Such sequences were classified into three main sedimentary units, namely the Akata, Agbada, and the Formations of Benin. The Eocene to Recent Akata Formation [26, 27], is the oldest of these three formations. The Akata Formation was formed in a marine setting, characterized by a persistent, uniform deposition of the shale. Characteristically, the Formation is composed of dark gray shale, often sandy or silty of prodelta origin [26, 28] (the shales of this formation are mostly under compacted, [28]).

The Eocene to Recent Agbada Formation is on top of the marine sequence. The Agbada Formation makes up the sequence's actual deltaic part. It is known to have accumulated in deltaic front, delta-topset and deltaic fluvial environments [29] and is composed mainly of alternating mudstone sandstone/sand bodies. According to Weber [30], the Agbada Formation is known to be composed of cyclic marine and fluvial deposit sequences. Capping the series is the primarily continental Benin formation, which was deposited during Oligocene to Recent [27]. Benin formation represents an almost continuous sequence of continental

deposits, ranging from medium to coarse-grained sands/sandstones (with very occasional short-lived marine incursions). Short and Stäuble [26] defined the Benin Formation sands/sandstones as generally coarse-grained, very granulated and pebbled, but also varying from grain to fine grain.

3. Materials and methods

3.1. Sampling

Thirty-nine crude oil and twenty-one rock samples were collected at depth ranging from 2602 m to 3036 m in five wells from five fields in the Northern and offshore, Agbada Formation, Niger Delta Basin, Nigeria.

3.2. Optical microscopy

The optical microscopic analysis was performed on Reichert Jung Polyvar photomicroscope fitted with halogen and HBO lamps, photomultiplier, and a computer unit. The shale samples were crushed to a maximum particle size of 2 mm, placed in epoxy resin and then ground and polished in the same way as coal samples are prepared for microscopy by incident light [31]. Maceral compositions were estimated in the rock samples using a semi-automated Swift Point Counter, with each maceral analysis based on at least forty counts in view of the sparse distribution of phytoclast in the shales. The program makes the setting of step-length from 0.05-2.00 mm for the study. The representatives of maceral groups found in the rock samples are shown in Figure 1.

3.3. Extraction and analysis

Rock samples were crushed into powder <100 mesh and then extracted in batches in a Soxhlet apparatus with 400ml dichloromethane and methanol (93:7, v:v) for 72 h. Silica gel/alumina column

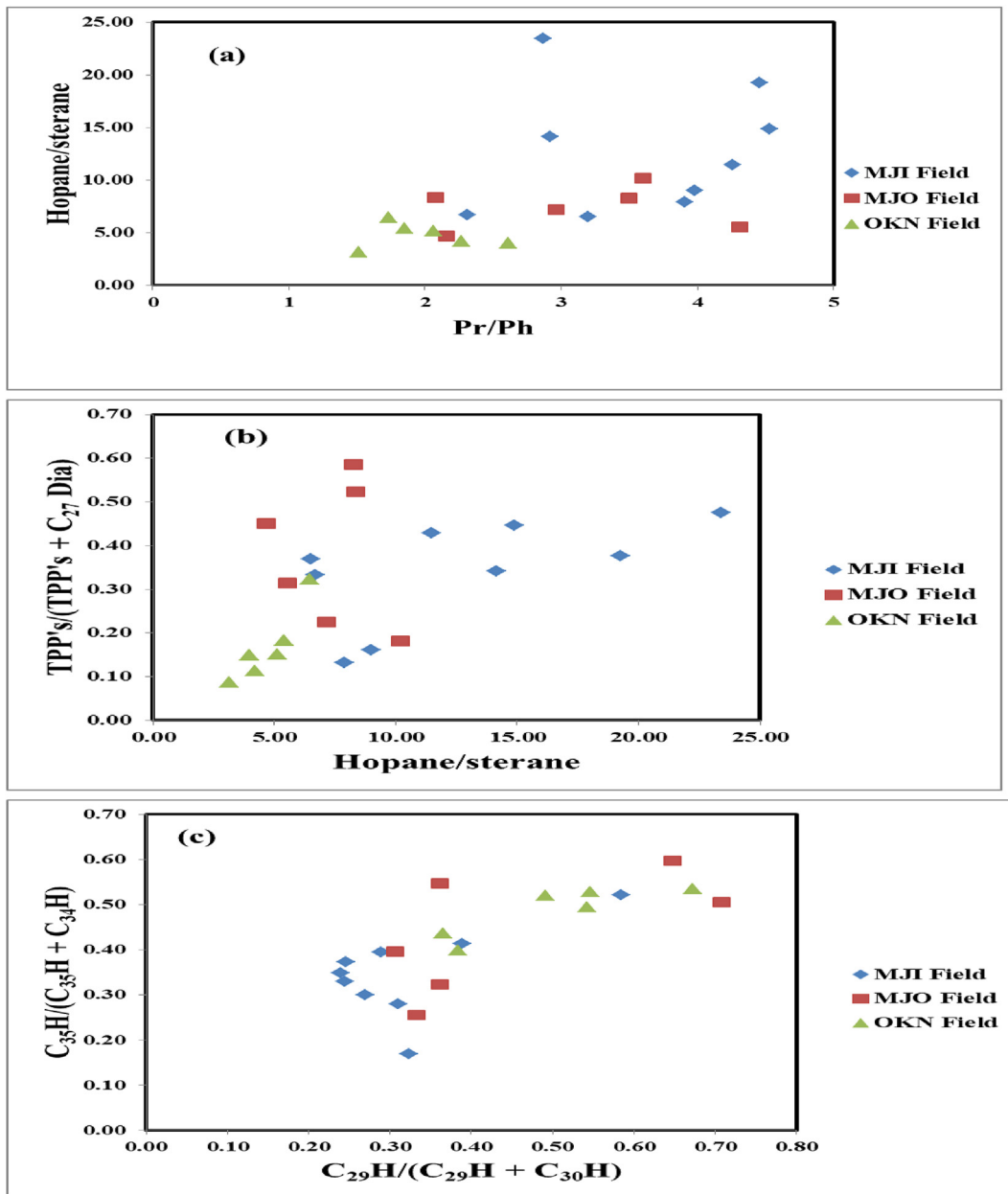


Figure 3. Cross plots of hopane/sterane versus (a) Pr/Ph, (b) TPP's/(TPP's + C₂₇ Dia), and (c) C₃₅H/(C₃₅H + C₃₄H) versus C₂₉H/(C₂₉H + C₃₀H) in Niger Delta source rocks. Note: Pr/Ph: pristane/phytane; TPP's/(TPP's + C₂₇ Dia) tetracyclic polyprenoids (a + b) and C₂₇ diasteranes; C₃₅H: C₃₅ homohopanes; C₃₄H: C₃₄ homohopanes; C₂₉H: 17 α (H),21 β (H)-30-norhopane; C₃₀H: 17 α (H),21 β (H)-30-hopane.

Table 2. Source facies and depositional environment parameters calculated from the saturated biomarkers in Niger Delta source rocks.

Field	Depth(m)	Pr/Ph	TPP's/ (TPP's + C ₂₇ Dia)	C ₂₉ H/ (C ₂₉ H + C ₃₀ H)	C ₃₅ H/ (C ₃₅ H + C ₃₄ H)	Oleanane Index	Hopane/ Sterane	Sterane, %			αα 20R steranes		
								C ₂₇	C ₂₈	C ₂₉	C ₂₇ /C ₂₈	C ₂₉ /C ₂₈	C ₂₈ /C ₂₉
MJI	2079–2098	3.2	0.37	0.58	0.52	0.55	6.51	16.51	25.49	58	0.65	2.28	0.44
MJI	2299–2308	2.31	0.33	0.29	0.39	0.56	6.70	18.53	21.98	59.49	0.84	2.71	0.37
MJI	2637–2655	3.91	0.13	0.24	0.35	0.68	7.88	17.39	22.24	60.37	0.78	2.71	0.37
MJI	2857–2875	3.98	0.16	0.32	0.17	0.68	9.01	20.15	21.75	58.1	0.93	2.67	0.37
MJI	2994–3012	4.26	0.43	0.39	0.41	0.59	11.47	20.65	23.3	56.05	0.89	2.41	0.42
MJI	3085–3104	4.53	0.45	0.25	0.37	0.67	14.89	16.8	20.31	62.89	0.83	3.10	0.32
MJI	3232–3250	2.87	0.47	0.31	0.28	0.57	23.43	19.85	18.59	61.56	1.07	3.31	0.30
MJI	3323–3332	4.46	0.38	0.27	0.30	0.59	19.27	19.64	20.04	60.32	0.98	3.01	0.33
MJI	3405–3424	2.92	0.34	0.24	0.33	0.61	14.14	29.79	27.84	42.37	1.07	1.52	0.66
MJO	1616–1707	4.31	0.31	0.65	0.60	0.45	5.52	19.02	28.6	52.38	0.66	1.83	0.55
MJO	1771–1872	2.16	0.45	0.36	0.55	0.37	4.68	17.85	27.78	54.37	0.64	1.96	0.51
MJO	2091–2101	2.08	0.52	0.71	0.51	0.77	8.33	17.28	28.78	53.94	0.60	1.87	0.53
MJO	2293–2366	2.96	0.23	0.31	0.40	0.53	7.15	24.44	26.46	49.11	0.92	1.86	0.54
MJO	2570–2588	3.5	0.59	0.33	0.26	0.63	8.27	27.78	28.58	43.64	0.97	1.53	0.66
MJO	2808–2817	3.6	0.18	0.36	0.32	0.68	10.17	34.65	27.05	38.3	1.28	1.42	0.71
OKN	1537–1555	1.85	0.18	0.55	0.53	0.35	5.40	38.15	17.85	44	2.14	2.46	0.41
OKN	1729–1747	2.61	0.15	0.54	0.49	0.34	3.99	33.28	18.36	48.36	1.81	2.63	0.38
OKN	2625–2643	1.51	0.09	0.49	0.52	0.37	3.14	39.49	21.25	39.26	1.86	1.85	0.54
OKN	2780–2799	1.73	0.32	0.67	0.54	0.58	6.47	20.66	27.45	51.89	0.75	1.89	0.53
OKN	2863–2881	2.06	0.15	0.37	0.44	0.57	5.14	24.92	27.42	47.66	0.91	1.74	0.58
OKN	2909–2927	2.27	0.11	0.38	0.40	0.53	4.20	31.52	25.18	43.31	1.25	1.72	0.58

Pr/Ph: Pristane/phytane; Hopane/sterane: calculated using the peaks from hopanes (ion 191) and steranes (ion 217); C₃₀TPP's/(C₃₀TPP's + C₂₇diasteranes): tetracyclic polyprenoids (a + b) and C₂₇ βα(S + R) steranes from ion 259 of GC-MS of saturated hydrocarbons analysis. Oleanane index: Oleanane/(oleane + C₃₀hopane). % C₂₇–C₂₉steranes: 100% normalized from peak heights of steranes from GC-MS analysis of saturated hydrocarbons fractions.

chromatography eluted with n-hexane and dichloromethane: n-hexane (2:1, v: v), were used to fractionate the oil samples and rock extracts into saturated and aromatic hydrocarbon fractions, respectively.

An Agilent 5975i gas chromatograph (GC) fitted with an HP-5MS (5 % phenylmethylpolysiloxane) fused silica capillary column (60 m x 0.25 mm i.d., x 0.25 μm film thickness) coupled with an Agilent 5975i mass spectrometer (MS) was used for the analysis of the saturate and aromatic fractions of the crude oils and source rock extracts. The operating conditions of the GC are as follows: the temperature of the oven was held isothermally at 80 °C for 1 min, ramped to 310 °C at 3 °C/min, and kept isothermal for 16 min [32]. Helium was used with a steady flow rate of 1.2 mL min as the carrier gas. The MS was operated in 70eV electron impact (EI) mode, 250 °C ion source temperature and 285 °C injector temperature. In the corresponding mass chromatograms, the identification and elution order of fluorene and its derivatives was determined by comparing their mass spectra and relative retention times with those published in literature [12, 13, 14, 15, 17, 21]. The relative abundance in the respective ion chromatograms was determined from integrated peak areas.

4. Results and discussion

4.1. Organic petrological characteristics of source rocks from Niger delta basin based on maceral compositions and vitrinite reflectance

Macerals are individual components in the kerogenes which have distinct petrographic and geochemical properties [33] and that consist of individual organic or phytoclastic particles [33]. Maceral compositions in sedimentary rocks can provide useful information on the type and origin of organic matter [34, 35], making it a potential tool for source rock evaluation. The main macerals in coals and sedimentary rocks were classified into three groups, namely liptinites (alginites and exinites), vitrinites, and inertinites [33, 36, 37]. The representative maceral groups found in the rock samples studied are shown in Figure 1. In the rock

samples, the values of vitrinite, exinite, inertinite and sapropelinite range from 48% to 80%, 11%–39%, 3%–7% and 5%–12% respectively (Table 1). The data obtained from maceral analysis in the rock samples from MJI and MJO oilfields indicate a predominant terrestrial origin (Type III kerogen) organic matter (Table 1). The dominant component of all the study samples is vitrinite (58–80 %) (Table 1, Figure 2), which suggests type III kerogen for MJI and MJO oilfield source rocks [31, 38] (Figure 2). MJI and MJO oilfield rock samples are distinguished by very low liptinite (11–26 %) and inertinite (3–7 %) abundances. The low liptinite values indicate low marine contribution to the organic matter that formed the source rocks [31, 38]. A triplot of the three major maceral groups found in the rock samples (Figure 2) reveals a strong similarity in the maceral distribution, indicating similar rank [39].

The values of maceral compositions recorded in OKN rock samples indicate type II kerogen (Table 1) which are consistent with the Type II kerogen source rocks and this agreed with the recent study on the same set of rock samples using rock-eval pyrolysis [40]. Figure 2 shows that the dominant component of the samples in OKN field is vitrinite (48–61%). However, the rock samples have significant values of liptinite (26–39%) and lowest amount of inertinite (3–5%). The values of liptinite suggest a major marine contribution to the organic matter of the source rocks [31, 38]. A triplot of the three major maceral groups in the source rocks (Figure 2) shows that the maceral have similar rank [39]. The vitrinite reflectance (Ro) values of the samples range from 0.23 to 0.50 %Ro [16, 17, 41]. According to Peters et al. [33], Ro values <0.50, 0.50 to 0.60 and 0.60 to 0.90 indicate immature, early mature and peak of oil generation respectively. Therefore, the Ro values obtained in the rock samples indicate immature to early mature stage. This finding is in agreement with the recent report on the source rocks from the same fields using rock-eval pyrolysis [40]. The equivalent vitrinite reflectance (0.018 * T_{max} - 7.16) calculated for the rock samples are in the range of -0.27 to 0.81 % (Table 1), supporting immature to early maturity range already inferred from the measured vitrinite reflectance (Ro %) in the source rocks [33].

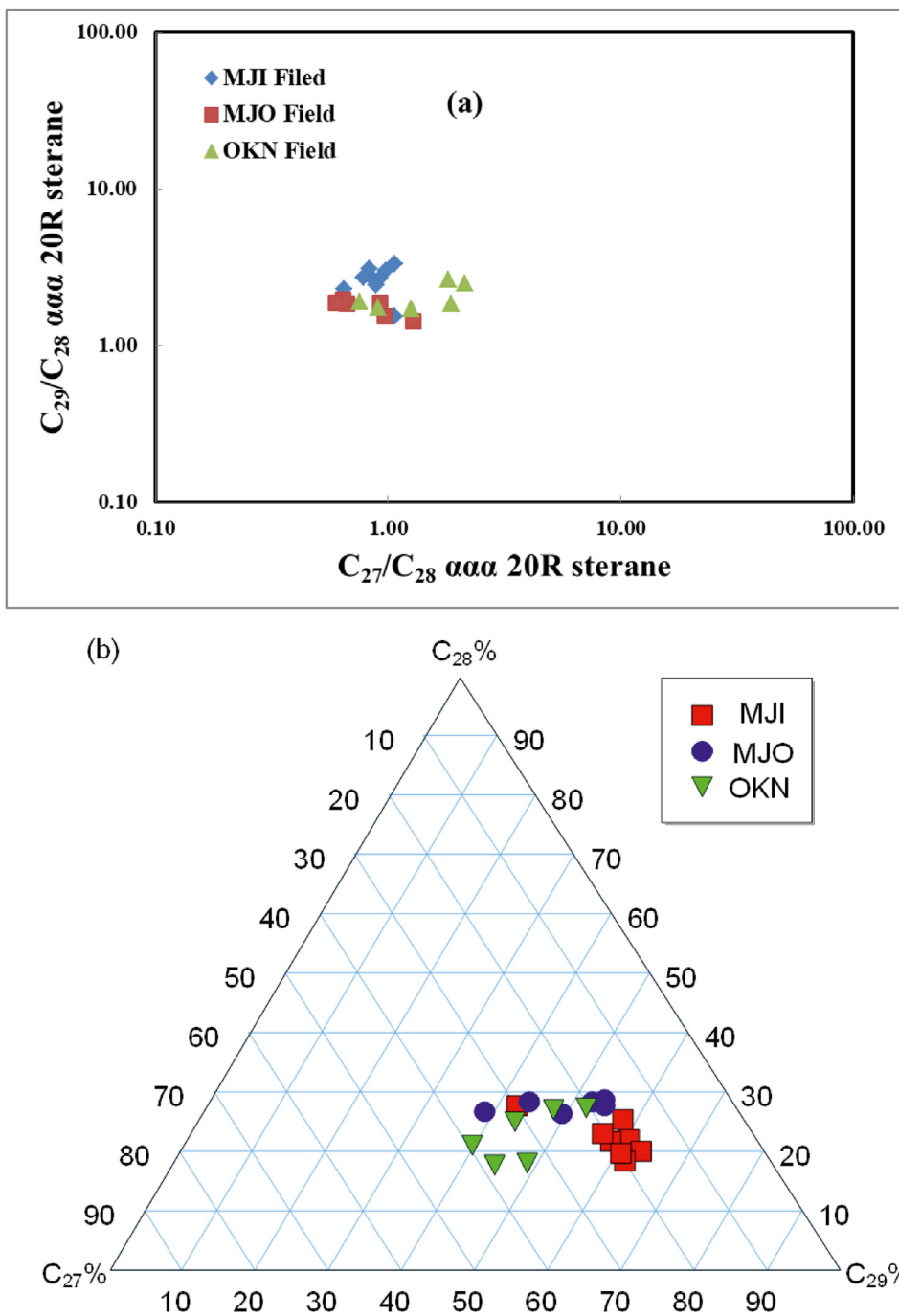


Figure 4. (a) Cross plots of C_{29}/C_{28} $\alpha\alpha$ 20R steranes versus C_{27}/C_{28} $\alpha\alpha$ 20R steranes and (b) Triplots of C_{27} to C_{29} regular steranes in Niger Delta source rocks. Note: C_{27} to C_{29} regular steranes = Relative abundances of C_{27} , C_{28} and C_{29} regular steranes.

Table 3. Thermal maturity parameters calculated from the saturated biomarkers in Niger Delta source rocks.

Field	Depth(m)	Ts/(Tm + Ts)	$\alpha\beta/(\alpha\beta + \beta\alpha)$ C ₂₉	$\alpha\beta/(\alpha\beta + \beta\alpha)$ C ₃₀	22S/22S + 22R C ₃₁	22S/22S + 22R C ₃₂	20S/20S + 20R C ₂₉	$\beta\beta/(\beta\beta + \alpha\alpha)$ C ₂₉
MJI	2079–2098	0.24	0.73	0.47	0.24	0.23	0.15	0.35
MJI	2299–2308	0.19	0.54	0.54	0.36	0.30	0.15	0.32
MJI	2637–2655	0.19	0.54	0.48	0.46	0.38	0.21	0.40
MJI	2857–2875	0.27	0.67	0.65	0.52	0.50	0.29	0.35
MJI	2994–3012	0.34	0.79	0.74	0.53	0.53	0.30	0.38
MJI	3085–3104	0.35	0.73	0.81	0.58	0.57	0.40	0.37
MJI	3232–3250	0.34	0.84	0.84	0.59	0.58	0.46	0.42
MJI	3323–3332	0.37	0.86	0.85	0.59	0.58	0.52	0.48
MJI	3405–3424	0.57	0.85	0.87	0.58	0.57	0.48	0.55
MJO	1616–1707	0.24	0.70	0.71	0.25	0.34	0.16	0.33
MJO	1771–1872	0.29	0.54	0.58	0.35	0.46	0.41	0.25
MJO	2091–2101	0.17	0.67	0.29	0.30	0.25	0.21	0.31
MJO	2293–2366	0.18	0.60	0.61	0.42	0.33	0.13	0.32
MJO	2570–2588	0.32	0.76	0.71	0.54	0.49	0.19	0.30
MJO	2808–2817	0.57	0.85	0.84	0.57	0.57	0.38	0.35
OKN	1537–1555	0.59	0.73	0.52	0.29	0.54	0.18	0.35
OKN	1729–1747	0.55	0.67	0.58	0.35	0.51	0.14	0.30
OKN	2625–2643	0.48	0.62	0.61	0.35	0.54	0.30	0.41
OKN	2780–2799	0.25	0.74	0.48	0.35	0.39	0.24	0.34
OKN	2863–2881	0.31	0.51	0.47	0.37	0.43	0.34	0.38
OKN	2909–2927	0.34	0.56	0.53	0.35	0.39	0.28	0.38

Ts/(Ts + Tm), 18a(H)-22,29,30-trisnorneohopane/(18a(H)-22,29,30-trisnorneohopane + 17a(H)-22,29,30-trisnorhopane). $\alpha\beta/(\alpha\beta + \beta\alpha)$ C₂₉Hop: 17a(H),21b(H)-30-norhopane/(17a(H),21b(H)-30-norhopane + 17b(H),21a(H)-30-norhopane); $\alpha\beta/(\alpha\beta + \beta\alpha)$ C₃₀Hop: 17a(H),21b(H)-hopane/(17a(H),21b(H)-hopane + 17b(H),21a(H)-hopane); 22S/(22S + 22R), C₃₁ Hop:17a(H)-homohopane; 22S/(22S + 22R) C₃₂ Hop: 17a(H)-bishomohopane; $\beta\beta/(\beta\beta + \alpha\alpha)$ C₂₉-Steranes: 14b(H),21b(H)/[14b(H),21b(H) + 14a(H),21a(H)] 20R ethylcholestane; 20S/(20S + 20R) C₂₉sterane: 14a(H),21a(H)-ethylcholestane.

4.2. Geochemical characteristics of Niger delta source rocks based on biomarker distribution

Biomarkers have been widely used in geochemical studies of petroleum, such as rock source evaluation and oil-oil or oil-source rock correlations [33]. For instance, the pristane/phytane (Pr/Ph) ratio is commonly used as an indicator for redox conditions in depositional environment studies [42, 43, 44]. The pristane/phytane (Pr/Ph) ratios in the present study range from 1.51 to 4.53 [16,45] (Table 2). These values indicate source rocks formed from the mixed origin of terrestrial and marine organic matter and deposited in a lacustrine-fluvial/deltaic environments under oxic to sub-oxic conditions [42, 43, 44]. However, the high Pr/Ph values reported in some of the samples indicate a major terrestrial organic matter contribution to the source rock [42, 46]. In freshwater lacustrine oils, the tetracyclic polyprenoids (TPP's) commonly identified in m/z 259 have been recorded in relatively high abundance [13, 47]. The relative abundance of the TPP versus C₂₇ $\beta\alpha$ -diasteranes was interpreted as indicating the input of lacustrine organic matter [13], while the high hopane/sterane ratio suggest the predominance of terrigenous organic matter input in petroleum [13]. Recent study, for example, showed that TPP's/(TPP's + C₂₇ diasteranes) values ranging between 0.34 to 0.55, 0.09 to 0.81, 0.07 to 0.55, 0.48 to 0.91 and 0.21 to 0.57 suggest marine carbonate, marine shale, marine-terrigenous organic matter, lacustrine and coaly shale, respectively [13] while hopane/sterane values that range from 0.79 to 10.51, 0.40 to 10.20, 4.70 to 29.00, 5.77 to 46.30 and 3.90 to 42.30 indicate marine carbonate, marine shale, marine-terrigenous organic matter, lacustrine and coaly shale, respectively [13, 33]. In the present study, the values of TPP's/(TPP's + C₂₇ dia) and hopane/sterane in the rock samples differ from 0.09 to 0.59 and 3.14 to 23.43, respectively (Table 2). Such values indicate source rocks formed from the mixed input of marine and terrigenous organic matter [13, 33]. This interpretation agree with what was observed in the rock samples from the maceral compositions (type II/III kerogen). The diagnostic ratios C₂₉H/(C₂₉H + C₃₀H) and C₃₅H/(C₃₅H + C₃₄H) can be used to

distinguish marine carbonate source facies from marine shale or terrigenous-marine shale [13] while significant oleanane index (oleanane/oleanane + C₃₀ hopane) values suggest terrigenous organic matter [7, 13, 33]. For instance, the C₂₉H/(C₂₉H + C₃₀H) values that range from 0.44 to 0.80, 0.28 to 0.43, 0.30 to 0.50, 0.27 to 0.35 and 0.28 to 0.53 suggest marine carbonate, marine shale, marine-terrigenous organic matter, lacustrine and coaly shale, respectively [13] while (C₃₅H/(C₃₅H + C₃₄H) values ranging from 0.36 to 0.80, 0.34 to 0.48, 0.29 to 0.49, 0.28 to 0.45 and 0.26 to 0.42 indicate marine carbonate, marine shale, marine-terrigenous organic matter, lacustrine and coaly shale, respectively [13]. In our study, the C₂₉H/(C₂₉H + C₃₀H), C₃₅H/(C₃₅H + C₃₄H) and oleanane index in the rock samples range from 0.24 to 0.71, 0.17 to 0.60 and 0.34 to 0.77, respectively (Table 2), indicating mixed contribution of terrigenous and marine organic matter. The high values of oleanane index recorded in the rock samples reflect significant input of terrigenous organic matter into the source rocks [7, 13]. The cross plots of TPP's/(TPP's + C₂₇ diasteranes) and Pr/Ph versus hopane/sterane ratios (Figure 3a, 3b), and the plot of C₂₉H/(C₂₉H + C₃₀H) versus C₃₅H/(C₃₅H + C₃₄H) (Figure 3c) values have been successfully applied to distinguish source facies of oils on the basis of organic matter source and depositional environments [13]. In the present study, these plots clearly support mixed input of terrestrial and marine organic matter for the rocks samples (Figure 3a, 3b, 3c).

The distribution of C₂₇₋₂₉ steranes can provide information on the origin of the precursor organic matter [48]. For example, the abundance of C₂₉ steranes in geological materials suggests terrestrial organic matter [48, 49], whereas the elevated content of C₂₇ and C₂₈ steranes indicates the contribution of marine organic matter [49]. For this study, the rock samples are characterized by mixed sterane distribution with most samples having C₂₉ > C₂₇ < C₂₈ distributions, as shown in Figure 4a. The values of $\alpha\alpha$ -20R steranes C₂₇/C₂₈, C₂₉/C₂₈ and C₂₈/C₂₉ ratios are in the range of 0.60–2.14, 1.42 to 3.31, 0.30 to 0.71, respectively (Table 2). The relative percentages of C₂₇, C₂₈ and C₂₉ steranes are in the ranges of 16.80 to 39.49 %, 17.85–28.60 %, and 38.30–62.89 %, respectively

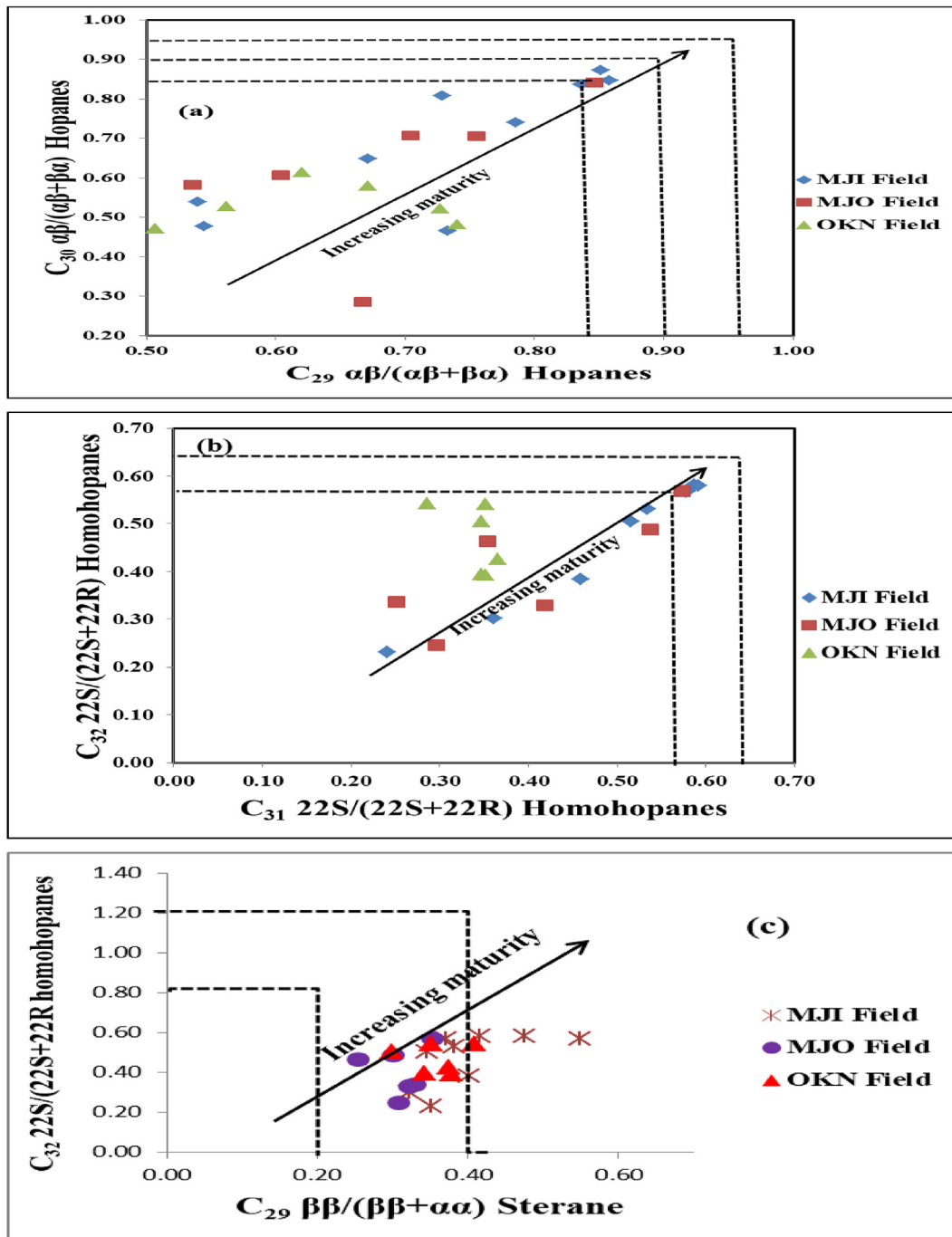


Figure 5. Cross plots of (a) $C_{30} \alpha\beta/(\alpha\beta+\beta\alpha)$ hopanes versus $C_{29} \alpha\beta/(\alpha\beta+\beta\alpha)$ hopanes, (b) $C_{32} 22S/(22S + 22R)$ homohopanes versus $C_{31} 22S/(22S + 22R)$ homohopanes, and (c) $C_{32} 22S/(22S + 22R)$ homohopanes versus $C_{29} \beta\beta/(\beta\beta+\alpha\alpha)$ steranes in Niger Delta source rocks. Note: $C_{30} \alpha\beta/(\alpha\beta+\beta\alpha)$ hopanes: $17\alpha(H), 21\beta(H)-30$ -hopane/ $(17\alpha(H), 21\beta(H)-30$ -hopane+ $17\beta(H), 21\alpha(H)-30$ -hopane); $C_{29} \alpha\beta/(\alpha\beta+\beta\alpha)$ hopanes: $17\alpha(H), 21\beta(H)-30$ -norhopane/ $(17\alpha(H), 21\beta(H)-30$ -norhopane+ $17\beta(H), 21\alpha(H)-30$ -norhopane); $C_{31} 22S/(22S + 22R)$: $17\alpha(H)$ -homohopane $C_{32} 22S/(22S + 22R)$: $17\alpha(H)$ -bishomohopane; $C_{29} \beta\beta/(\beta\beta+\alpha\alpha)$ steranes: $14\beta(H), 21\beta(H)/[14\alpha(H), 21\alpha(H) + 14\beta(H), 21\beta(H)]$ 20R-ethylcholestane.

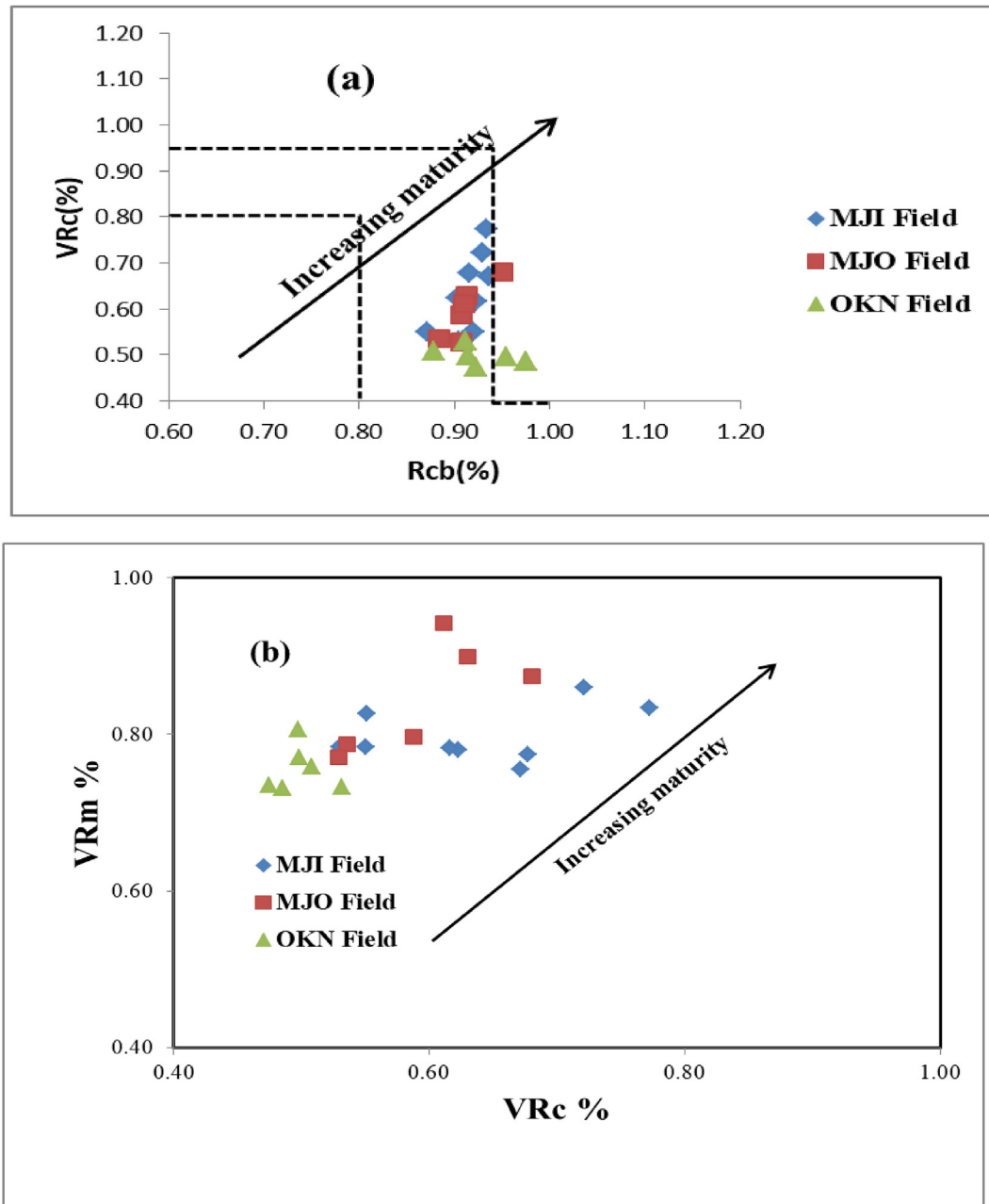


Figure 6. Cross plots of VRc versus (a) Rcb, and (b) VRm in Niger Delta source rocks. Note: VRc: calculated vitrinite reflectance ($0.6 \times \text{MPI-1} + 0.4$); Rcb: $0.40 + 0.6 \times (\text{TNR}-2)$; VRm: $0.073 \times \text{MDR} + 0.51$.

Table 4. Source facies and thermal maturity parameters calculated from the aromatic biomarkers in Niger Delta source rocks.

Field	MPI-1	MPI-2	VRc	TMNR-1	TMNR-2	Rcb	VRm	1,2,5-/1,2,7-TMN	1,2,6-/1,2,4-TMN	1,2,5,6-/1,2,5,7-TeMN	1,3,6,7-/1,2,5,6-TeMN	1-MP/9-MP	1,7-DMP/X	Re/9-MP
MJI	0.25	0.28	0.55	1.13	0.79	0.87	0.83	0.78	4.27	2.34	0.79	0.88	0.64	0.03
MJI	0.25	0.28	0.55	1.40	0.87	0.92	0.78	1.18	4.70	3.26	0.37	0.90	0.72	0.03
MJI	0.22	0.24	0.53	1.43	0.84	0.90	0.78	1.04	8.55	3.20	0.30	0.93	1.04	0.06
MJI	0.37	0.41	0.62	1.36	0.84	0.90	0.78	1.03	5.39	3.09	0.27	0.87	0.87	0.06
MJI	0.54	0.60	0.72	1.56	0.88	0.93	0.86	0.95	6.19	2.30	0.56	0.81	0.64	0.02
MJI	0.36	0.40	0.62	1.42	0.87	0.92	0.78	1.08	7.20	0.59	1.88	0.92	1.19	0.07
MJI	0.45	0.50	0.67	1.54	0.89	0.94	0.76	1.06	8.86	2.06	0.26	0.99	1.13	0.07
MJI	0.46	0.50	0.68	1.38	0.86	0.92	0.77	0.86	10.63	1.80	0.36	0.94	1.06	0.09
MJI	0.62	0.68	0.77	1.47	0.89	0.93	0.83	0.68	12.69	1.23	0.89	0.88	0.79	0.05
MJO	0.23	0.26	0.54	1.16	0.81	0.88	0.79	0.78	4.19	1.94	0.97	0.78	0.64	0.02
MJO	0.31	0.35	0.59	1.28	0.84	0.91	0.80	0.90	6.65	2.09	0.89	0.77	0.54	0.01
MJO	0.21	0.24	0.53	1.24	0.82	0.91	0.77	0.90	3.93	2.74	0.72	0.73	0.50	0.02
MJO	0.47	0.50	0.68	1.42	0.92	0.95	0.87	0.77	4.87	1.78	0.83	0.83	0.65	0.02
MJO	0.38	0.42	0.63	1.37	0.85	0.91	0.90	0.92	5.50	2.22	0.76	0.80	0.60	0.02
MJO	0.35	0.38	0.61	1.32	0.85	0.91	0.94	0.84	5.15	1.97	0.83	0.84	0.59	0.02
OKN	0.16	0.18	0.50	1.09	0.92	0.95	0.81	0.48	2.98	1.28	1.87	0.87	0.49	0.07
OKN	0.14	0.15	0.48	1.17	0.96	0.97	0.73	0.47	3.18	1.29	1.81	0.82	0.48	0.13
OKN	0.12	0.13	0.47	0.96	0.87	0.92	0.74	0.58	2.90	1.42	1.30	0.76	0.51	0.24
OKN	0.16	0.18	0.50	0.96	0.86	0.91	0.77	0.55	2.97	1.64	1.01	0.84	0.54	0.23
OKN	0.18	0.20	0.51	0.88	0.80	0.88	0.76	0.60	2.94	1.66	0.70	0.78	0.53	0.28
OKN	0.22	0.24	0.53	1.01	0.85	0.91	0.73	0.67	2.78	1.74	0.84	0.87	0.50	0.18

TMN: trimethylnaphthalene; TeMN: tetramethylnaphthalene; 1-MP/9-MP: 1-methyl phenanthrene/9-methyl phenanthrene; 1,7-DMP/X; 1,7-dimethylphenanthrene/(1,3- + 3,9- + 2,10- + 3,10-DMP); MPI-1 = 1.5(2-MP+3-MP)/(P+1-MP+9-MP) [63]; MPI-2 = 3(2-MP)/(P+1-MP+9-MP) [63]; VRc% = 0.55MPI1+0.44 [63]; TMNr-1: trimethylnaphthalene ratio 1 (2,3,6-TMN/1,4,6- + 1,3,5-TMN) [66]; TMNr-2: trimethylnaphthalene ratio 2 (2,3,6- + 1,3,7-TMN)/1,4,6- + 1,3,5- + 1,3,6-TMN). Rcb: 0.40 + 0.6*(TMNr-2) [77]; VRm = 0.073*MDR + 0.51 [62].

(Table 2), showing the C₂₉ predominance, followed by C₂₈. The C₂₈/C₂₉ values below 0.5 were recorded in Ordovician and Lower Paleozoic oils from marine source rocks [48, 50], whereas oils from terrestrial organic matter showed higher ratio values (>0.5) [51]. The distribution and abundance of steranes in the rock samples is thus consistent with source rocks formed from the mixed input of terrestrial and marine organic matter [33, 48, 49]. Also, the cross plots of C₂₇/C₂₈ versus C₂₉/C₂₈ ([48]; Figure 4a), and triplots of the C₂₇, C₂₈ and C₂₉ steranes ([49]; Figure 4b) further support mixed contribution of marine and terrestrial organic matter for the source rocks.

To assess the thermal maturity of source rocks from the Niger Delta basin, a combination of saturated and aromatic hydrocarbon biomarkers have been used. The C₂₇ Ts/(Ts + Tm) ratio for geological samples of similar origin, is a reliable maturity indicator and its values differ from early maturity through the upper main oil-generation stage [52, 53]. The values of C₂₇ Ts/(Ts + Tm) calculated in the rock samples range from 0.18 to 0.59 (Table 3), suggesting immature to early oil window maturity [48, 52, 53]. This interpretation is consistent with the data obtained from the vitrinite reflectance (section 4.1).

The C₃₁ and C₃₂ 22S/(22S + 22R) homohopane values in the rock samples range from 0.24 to 0.59 [16] and 0.23 to 0.58, respectively (Table 3), suggesting immature to early oil window maturity [33]. However, these ratios reach equilibrium in the oil window so have minimal application for studying the relative maturities of crude oils and condensates [33]. The C₂₉ and C₃₀ αβ/(αβ+βα) hopane ratios attain equilibrium values of ~0.9 at considerably higher maturities than homohopane 22S/(22S + 22R) ratios [22, 33, 54]. In this study, the C₂₉ and C₃₀ αβ/(αβ+βα) hopane values calculated for the rock samples range from 0.51 to 0.85 and 0.29 to 0.87, respectively (Table 3), also indicating immature to early oil window maturity [22, 54]. The C₂₉ sterane isomeric distribution has been widely used in petroleum geochemistry to determine the maturity of sedimentary organic matter and crude oils [13, 55]. Factors other than thermal maturity, however, can affect the values of sterane-based maturity ratios such as C₂₉ 20S/(20S + 20R) and

ββ/(ββ+α) [22]. For example, reversal of these ratios could be responsible for the lower values in geological samples at highly mature intervals [22, 56, 57]. In our study, the 20S/(20S + 20R) and ββ/(ββ+α) C₂₉ steranes values are in the range of 0.13–0.52 [16, 17, 41, 45] and 0.25 to 0.55, respectively (Table 3), confirming immature to early window maturity in the rock samples. The plots of hopane and sterane based maturity parameters between C₂₉- and C₃₀ hopanes -αβ/(αβ+βα) [54] (Figure 5a), C₃₁- and C₃₂ homohopanes 22S/(22S + 22R) [35] (Figure 6b), and C₃₂ homohopanes 22S/(22S + 22R) and ββ/(ββ+α) C₂₉ steranes [35] (Figure 5c) support immature to early stage of oil window maturity range for the rock samples.

However, several aliphatic biomarkers maturity parameters reach equilibrium in the early oil window, or are influenced by other factors such as source lithology, depositional environments, and maturity values based solely on aliphatic biomarkers do not reflect the true maturity status of geological materials [22, 33, 53, 58, 59]. Many aromatic biomarkers have been widely documented to be influenced by thermal maturity and are sensitive across the entire oil window, and may be more efficient in evaluating thermal maturity [54, 60, 61, 62]. The methyl phenanthrene index (MPI-1; Radke et al., 1982) appears to be useful to estimate vitrinite reflectance (VRc) [60, 63]. The MPI-1, MPI-2 and calculated vitrinite reflectance (VRc) calculated for the rock samples are in the range of 0.12–0.62 [16, 17, 45, 64] 0.13 to 0.68 [16] and 0.47%–0.77 %, respectively (Table 4), indicating immature to early oil generation window [65]. The trimethylnaphthalene ratio 1 (TMNr-1, Table 4) was compared with the sterane isomerization ratio (20S/20R), showing that the sterane isomerization ratio of the oils reaches equilibrium when the TNR-1 ratio is >1 [66], while the trimethylnaphthalene ratio 2 (TMNr-2) was used to estimate the vitrinite reflectance (Rcb) and shows good agreement with the increase in thermal maturity [67]. In the present analysis, the ranges of TMNr-1, TMNr-2, Rcb and VRm (0.073 x MDR + 0.51) are 0.88–1.56, 0.79 to 0.96, 0.87–0.97 % and 0.73–0.94 % respectively (Table 4). Most rock samples have TMNr-1 values >1, indicating that the source rocks maturity range is beyond the peak of oil

Table 5. Geological information and source facies parameters for crude oils from Niger Delta Basin, Nigeria.

Sample	Depth(m)	Reservoir Formation	Geological Age	Depobelt	Pr/Ph	TPP's/ (TPP's + C ₂₇ Dia)	C ₂₉ H/ (C ₂₉ H + C ₃₀ H)	C ₃₅ H/ (C ₃₅ H + C ₃₄ H)	Oleanane Index	Hopane/ Sterane
ADL1	2602–2607	Agbada	Eocene to Recent	North	3.61	0.72	0.38	0.26	0.23	29.70
ADL2	2602–2607	Agbada	Eocene to Recent	North	3.95	0.73	0.38	0.54	0.24	27.88
ADL3	2759–2763	Agbada	Eocene to Recent	North	4.13	0.75	0.38	0.37	0.23	28.04
ADL4	2766–2770	Agbada	Eocene to Recent	North	4.3	0.74	0.38	0.35	0.23	28.01
ADL5	2905–2908	Agbada	Eocene to Recent	North	4.08	0.70	0.39	0.40	0.24	29.25
ADL6	2964–2967	Agbada	Eocene to Recent	North	3.61	0.71	0.38	0.30	0.24	25.64
ADL7	3064–3052	Agbada	Eocene to Recent	North	3.61	0.83	0.37	0.28	0.24	29.25
OKN-1	1749–1750	Agbada	Eocene to Recent	Offshore	2.39	0.95	0.45	0.33	0.59	8.09
OKN-2	1892–1895	Agbada	Eocene to Recent	Offshore	2.19	0.53	0.46	0.38	0.42	9.60
OKN-3	1905–1907	Agbada	Eocene to Recent	Offshore	2.11	0.55	0.47	0.35	0.42	8.97
OKN-4	1952–1955	Agbada	Eocene to Recent	Offshore	2.39	0.58	0.46	0.39	0.57	8.06
OKN-5	2050–2059	Agbada	Eocene to Recent	Offshore	2.18	0.49	0.46	0.36	0.42	9.22
OKN-6	2369–2555	Agbada	Eocene to Recent	Offshore	2.29	0.66	0.45	0.37	0.42	8.46
OKN-7	2377–2672	Agbada	Eocene to Recent	Offshore	2.1	0.63	0.44	0.37	0.41	8.57
OKN-8	2469–2782	Agbada	Eocene to Recent	Offshore	2.25	0.95	0.35	0.46	0.37	8.73
OKN-9	2485–2793	Agbada	Eocene to Recent	Offshore	2.18	0.62	0.46	0.43	0.41	8.90
OKN-10	2489–2491	Agbada	Eocene to Recent	Offshore	2.72	0.69	0.44	0.32	0.50	10.72
OKN-11	2521–2523	Agbada	Eocene to Recent	Offshore	2.62	0.65	0.47	0.33	0.50	11.95
OKN-12	2530–2537	Agbada	Eocene to Recent	Offshore	2.83	0.63	0.47	0.38	0.55	10.45
OKN-13	2566–2568	Agbada	Eocene to Recent	Offshore	2.49	0.18	0.47	0.33	0.59	8.04
OKN-14	2677–2683	Agbada	Eocene to Recent	Offshore	2.1	0.60	0.46	0.38	0.43	8.55
OKN-15	3148–3154	Agbada	Eocene to Recent	Offshore	2.28	0.64	0.36	0.39	0.35	9.20
OKN16	3593–3605	Agbada	Eocene to Recent	Offshore	2.17	0.95	0.33	0.31	0.36	9.10
MJO-1	2207–2216	Agbada	Eocene to Recent	Offshore	2.93	0.58	0.35	0.35	0.24	7.66
MJO-2	2070–2081	Agbada	Eocene to Recent	Offshore	3.33	0.55	0.09	0.27	0.23	7.22
MJO-3	2091–2104	Agbada	Eocene to Recent	Offshore	3.33	0.50	0.34	0.35	0.23	7.51
MJO-4	2096–2101	Agbada	Eocene to Recent	Offshore	4.37	0.51	0.04	0.32	0.25	9.70
MJI-1	1607–1611	Agbada	Eocene to Recent	Offshore	2.74	0.92	0.55	0.30	0.74	14.16
MJI-2	1777–1779	Agbada	Eocene to Recent	Offshore	3.24	0.93	0.50	0.41	0.73	14.44
MJI-3	1795–1797	Agbada	Eocene to Recent	Offshore	4.71	0.92	0.50	0.31	0.75	11.49
MJI-4	1920–1921	Agbada	Eocene to Recent	Offshore	3.08	0.88	0.47	0.40	0.71	13.64
MJI-5	1936–2342	Agbada	Eocene to Recent	Offshore	3.26	0.92	0.57	0.31	0.74	11.80
MJI-6	1944–1947	Agbada	Eocene to Recent	Offshore	4.43	0.92	0.48	2.74	0.73	13.12
MJI-7	1948–1950	Agbada	Eocene to Recent	Offshore	1.76	0.94	0.51	0.36	0.73	13.68
MJI-8	1979–2398	Agbada	Eocene to Recent	Offshore	1.76	0.90	0.54	0.40	0.74	12.58
MJI-9	2442–2444	Agbada	Eocene to Recent	Offshore	1.68	0.98	0.19	0.45	0.40	17.45
MJI-10	3030–3036	Agbada	Eocene to Recent	Offshore	1.7	0.92	0.45	0.45	0.69	10.12
WZB1	1610–2647	Agbada	Eocene to Recent	Offshore	2.35	0.63	0.45	0.37	0.58	5.23
WZB2	1811–1957	Agbada	Eocene to Recent	Offshore	1.48	0.72	0.37	0.44	0.64	5.68

Ts/(Ts + Tm), 18a(H)-22,29,30-trisnorneohopane/(18a(H)-22,29,30-trisnorneohopane + 17a(H)-22,29,30-trisnorhopane). $\alpha\beta/(\alpha\beta+\beta\alpha)$ C₂₉Hop: 17a(H),21b(H)-30-norhopane/(17a(H),21b(H)-30-norhopane + 17b(H),21a(H)-30-norhopane); $\alpha\beta/(\alpha\beta+\beta\alpha)$ C₃₀Hop: 17a(H),21b(H)-hopane/(17a(H),21b(H)-hopane + 17b(H),21a(H)-hopane); 22S/(22S + 22R), C₃₁ Hop:17a(H)-homohopane; 22S/(22S+22R) C₃₂ Hop: 17a(H)-bishomohopane; $\beta\beta/(\beta\beta+\alpha\alpha)$ C₂₉-Steranes: 14b(H),21b(H)/[14b(H),21b(H) + 14a(H),21a(H)] 20R ethylcholestane; 20S/(20S + 20R) C₂₉sterane: 14a(H),21a(H)-ethylcholestane.

generation window [22, 66]. Similarly, the reported values of TMNr-2, Rcb and VRm for the rock samples suggest that they have reached the peak of oil generation to late oil window. A cross plot (Figure 6a) of calculated vitrinite reflectance values i.e. Rcb (TMNr-2) versus VRC (MPI-1) clearly indicates that the thermal maturity of the source rocks from the Niger Delta Basin have reached the peak of oil generation window and beyond. The VRC vs. VRm cross plot (Figure 6b) also shows that the maturity parameters vary over a small range, suggesting similar maturity rank [62]. This study showed that the saturated biomarker maturity parameters for Niger Delta source rocks indicated immature to early oil generation window. Such parameters, however, often reach equilibrium values, thus showing minimal use for maturity evaluation. Thus, it is concluded that the equivalent vitrinite reflectances (VRC and Rcb) determined from MPI-1 and TMNr-2 support that the Niger Delta Basin source rocks are within immature to early oil window while the

VRm and other aromatic maturity parameters showed that the rock samples have reached the peak of oil generation and beyond. These results show that the estimated maturity of the samples, based on the aromatic maturity ratios, can differ significantly depending on the ratios employed.

Source precursors for 1,2,5-TMN and 1,2,5,6-TeMN isomers were identified as β -amyryn and aromatic seco-hopanes [68]. Non-angiosperm biological precursors, by comparison, are also related to the source of 1,2,5-TMN and 1,2,5,6-TeMN [69]. Abundance of the 1,2,5-TMN and 1,2,7-TMN isomers were associated with higher plant angiosperm markers and were derived from biological precursors of the oleanane type [70]. The 1,2,5-TMN isomer is also supposed to be formed from the dehydrogenation of a different biological component present in gymnosperms [71, 72]. Similarly, significant abundance of both 1,2,5-TMN and 1,2,5,6-TeMN has been recorded in aromatic fractions of the Abietites linkii, a

Table 6. Source facies and thermal maturity parameters calculated from the saturated biomarkers in the Niger Delta crude oils.

Sample	Ts/ (Tm + Ts)	$\alpha\beta/\alpha\beta + \beta\alpha$ C ₂₉ Hop	$\alpha\beta/\alpha\beta + \beta\alpha$ C ₃₀ Hop	22S/22S + 22R C ₃₁ Homo.	22S/22S + 22R C ₃₂ Homo.	20S/20S + 20R C ₂₉ sterane	$\beta\beta/\beta\beta + \alpha\alpha$ C ₂₉ sterane	Sterane, %			$\alpha\alpha$ 20R steranes		
								C ₂₇	C ₂₈	C ₂₉	C ₂₇ /C ₂₈	C ₂₉ /C ₂₈	C ₂₈ /C ₂₉
ADL1	0.48	0.87	0.85	0.56	0.53	0.41	0.37	20.8	27.8	51.5	0.75	1.85	0.54
ADL2	0.52	0.86	0.85	0.56	0.56	0.40	0.37	19.7	26.6	53.7	0.74	2.02	0.49
ADL3	0.5	0.87	0.86	0.56	0.55	0.43	0.38	20.2	28	51.8	0.72	1.85	0.54
ADL4	0.51	0.87	0.86	0.56	0.56	0.45	0.38	21.9	27.2	50.9	0.80	1.87	0.54
ADL5	0.49	0.88	0.86	0.56	0.55	0.45	0.39	20.1	30.4	49.5	0.66	1.63	0.61
ADL6	0.51	0.87	0.86	0.56	0.53	0.44	0.39	21.1	28.1	50.8	0.75	1.81	0.55
ADL7	0.61	0.89	0.87	0.57	0.57	0.47	0.38	24.9	25.5	49.5	0.98	1.94	0.52
OKN-1	0.4	0.83	0.81	0.52	0.53	0.36	0.36	31.3	30.3	38.4	1.03	1.26	0.79
OKN-2	0.43	0.83	0.82	0.53	0.53	0.40	0.39	31.1	31.9	37.1	0.98	1.16	0.86
OKN-3	0.43	0.83	0.83	0.53	0.54	0.40	0.40	32.8	31.3	35.9	1.05	1.15	0.87
OKN-4	0.41	0.84	0.82	0.53	0.53	0.33	0.41	30	32.3	37.7	0.93	1.17	0.86
OKN-5	0.46	0.83	0.83	0.53	0.54	0.41	0.39	33.6	31.8	34.6	1.05	1.09	0.92
OKN-6	0.43	0.86	0.84	0.53	0.53	0.39	0.38	31.7	30.3	38	1.05	1.26	0.80
OKN-7	0.43	0.85	0.84	0.53	0.57	0.43	0.39	32.5	32.6	34.9	1.00	1.07	0.93
OKN-8	0.61	0.89	0.87	0.53	0.57	0.39	0.42	31.7	29.3	39	1.08	1.33	0.75
OKN-9	0.43	0.86	0.84	0.53	0.54	0.41	0.37	32.6	32.1	35.3	1.01	1.10	0.91
OKN-10	0.47	0.83	0.84	0.54	0.55	0.36	0.39	31	31.8	37.2	0.97	1.17	0.85
OKN-11	0.46	0.83	0.83	0.54	0.55	0.33	0.38	30.8	32	37.2	0.96	1.16	0.86
OKN-12	0.48	0.86	0.84	0.53	0.56	0.37	0.37	31.2	30.3	38.5	1.03	1.27	0.79
OKN-13	0.39	0.83	0.81	0.53	0.53	0.35	0.36	30.4	31	38.6	0.98	1.25	0.80
OKN-14	0.43	0.86	0.84	0.53	0.55	0.41	0.37	31	32	37	0.97	1.16	0.86
OKN-15	0.51	0.85	0.86	0.54	0.55	0.38	0.39	33.1	31.1	35.8	1.07	1.15	0.87
OKN-16	0.62	0.89	0.88	0.53	0.56	0.41	0.42	33.3	30.5	36.2	1.09	1.19	0.84
MJO-1	0.47	0.88	0.87	0.55	0.57	0.45	0.43	26	27.9	46.1	1.17	1.23	0.82
MJO-2	0.78	0.09	0.83	0.61	0.59	0.46	0.42	26.7	27.9	45.4	1.34	1.29	0.78
MJO-3	0.46	0.89	0.88	0.56	0.56	0.45	0.41	26.5	26.2	47.4	1.13	1.16	0.86
MJO-4	0.47	0.21	0.78	0.85	0.60	0.45	0.42	26	26.5	47.5	1.12	1.17	0.86
MJI-1	0.45	0.82	0.81	0.54	0.53	0.28	0.33	25.2	31	43.9	0.93	1.65	0.61
MJI-2	0.45	0.87	0.83	0.54	0.53	0.40	0.40	25.9	29.7	44.4	0.96	1.63	0.61
MJI-3	0.47	0.90	0.84	0.54	0.52	0.36	0.43	23.7	27.8	48.5	1.01	1.81	0.55
MJI-4	0.55	0.90	0.85	0.54	0.54	0.37	0.39	25.2	28.2	46.5	0.98	1.79	0.56
MJI-5	0.43	0.84	0.82	0.55	0.53	0.35	0.36	24.6	32.5	42.9	0.81	1.42	0.71
MJI-6	0.58	0.88	0.82	0.54	0.54	0.34	0.36	24.6	32.5	42.9	0.87	1.50	0.67
MJI-7	0.45	0.88	0.83	0.54	0.52	0.39	0.40	34.6	30.4	36	0.85	1.74	0.57
MJI-8	0.42	0.87	0.82	0.54	0.53	0.36	0.37	36.9	27.6	35.5	0.89	1.65	0.61
MJI-9	0.48	0.87	0.83	0.54	0.54	0.38	0.39	34.4	30.4	35.2	0.76	1.32	0.76
MJI-10	0.48	0.87	0.83	0.54	0.54	0.38	0.39	34.1	30.4	35.5	0.76	1.32	0.76
WZB1	0.39	0.84	0.80	0.55	0.58	0.42	0.44	43.3	26.6	30.1	1.63	1.13	0.88
WZB2	0.4	0.81	0.81	0.55	0.56	0.37	0.43	37.7	26.4	35.9	1.43	1.36	0.74

Note: See definitions of terms in Table 3.

gymnosperm source, fluorinite filling of needles [73]. Previous study reported the values of 1,2,5-/1,2,7-TMN, 1,2,6-/1,2,4-TMN, 1,2,5,6-/1,2,5,7-TeMN and 1,3,6,7-/1,2,5,6-TeMN in the ranges 1.03 to 2.44, 1.36 to 1.64, 0.76 to 1.17 and 2.60 to 8.30, respectively, for oils from marine organic matter [74], whereas values ranged from 1.15 to 1.140, 1.77 to 2.20, 0.53 to 0.60 and 9.0 to 11.40, respectively, for oils from terrestrial-marine organic matter [74], while values of 3.46, 2.49, 1.73 and 1.40, respectively were also reported for predominant terrestrial oils [74]. In our study, the 1,2,5-/1,2,7-TMN, 1,2,6-/1,2,4-TMN, 1,2,5,6-/1,2,5,7-TeMN and 1,3,6,7-/1,2,5,6-TeMN are in the ranges of 0.47–1.18, 2.78 to 12.69, 0.59 to 3.26 and 0.26 to 1.88, respectively (Table 4), indicating source rocks formed from the mixed input of terrestrial and marine organic matter [74]. This finding is consistent with the recent reports on Niger Delta source rocks [16, 17, 41, 42, 46] and crude oils from Potwar Basin, Pakistan [74]. Different relative abundances of specific alkylphenanthrenes were related to both, source and maturity. For example, a higher abundance of 9-MP was attributed to marine organic

matter whereas the predominance of 1-MP was attributed to terrestrial organic matter [75]. The ratios between these various origin isomers may be used to determine the contribution of the organic source material in sediments. 1,7-DMP was suggested as an abundant biomarker of pimarane-type diterpenoids in ambers and resins [71, 76]. The 1,7-DMP/X and 1-MP/9-MP ratios (See Table 4) [74, 77] has been successfully used in oil correlation studies to determine different sources and ages of the organic matter [74, 78]. The 1,7-DMP/X and 1-MP/9-MP values in the ranges of 0.69–0.85 and 0.24 to 0.28, and 0.72 to 0.79 and 0.32 to 0.34, respectively have been previously reported in marine and terrigenous-marine oils from Potwar Basin, Pakistan by Asif and Fazeelat [74], whereas values of 0.84 and 0.53 were also reported for the two ratios in terrestrials oils from the same basin [74]. In the present study, the 1-MP/9-MP, 1,7-DMP/X and retene/9-MP (Re/9-MP) values are in the ranges of 0.73–0.99, 0.48 to 1.19 and 0.01 to 0.28, respectively (Table 4), further indicating mixed input of marine and terrigenous organic matter for the rock samples [74, 77, 78].

Table 7. Source facies and thermal maturity parameters calculated from the aromatic biomarkers in Niger Delta crude oils.

Sample	MPI-1	MPI-2	VRc (%)	TMNR-1	TMNR-2	Rcb (%)	VRm (%)	1,2,5-/1,2,7-TMN	1,2,6-/1,2,4-TMN	1,2,5,6-/1,2,5,7-TeMN	1,3,6,7-/1,2,5,6-TeMN	1-MP/9-MP	1,7-DMP/X	Re/9-MP
ADL1	0.73	0.73	0.84	0.66	0.66	0.80	0.75	2.36	4.35	1.73	0.69	0.59	0.49	0.12
ADL2	0.71	0.71	0.83	0.66	0.67	0.80	0.74	0.99	4.37	1.75	0.68	0.59	0.50	0.12
ADL3	0.70	0.70	0.82	0.66	0.66	0.80	0.69	2.48	4.33	1.77	0.68	0.58	0.48	0.13
ADL4	0.78	0.77	0.87	0.68	0.68	0.81	0.74	2.67	4.09	1.77	0.64	0.63	0.53	0.10
ADL5	0.79	0.77	0.87	0.69	0.69	0.81	0.62	2.36	4.89	1.78	0.64	0.71	0.54	0.08
ADL6	0.82	0.81	0.89	0.69	0.69	0.81	0.70	2.51	4.39	1.80	0.67	0.71	0.53	0.06
ADL7	0.84	0.82	0.90	0.70	0.69	0.81	0.73	2.75	4.52	1.87	0.58	0.80	0.58	0.08
OKN-1	0.95	0.98	0.97	1.55	1.05	1.03	0.77	0.64	5.02	2.17	0.82	0.64	0.34	0.04
OKN-2	0.91	0.95	0.95	0.92	0.78	0.87	0.79	0.57	4.20	1.65	1.17	0.64	0.43	0.03
OKN-3	0.91	0.95	0.95	0.87	0.77	0.86	0.78	0.53	4.11	1.59	1.24	0.63	0.42	0.03
OKN-4	0.93	0.97	0.96	1.03	0.84	0.91	0.77	0.62	3.98	2.13	0.86	0.64	0.35	0.05
OKN-5	0.90	0.93	0.94	0.92	0.79	0.87	0.80	0.54	4.62	1.62	1.20	0.64	0.43	0.04
OKN-6	0.95	0.99	0.97	1.00	0.79	0.87	0.78	0.64	4.01	1.79	1.03	0.63	0.43	0.03
OKN-7	0.90	0.93	0.94	0.84	0.77	0.86	0.80	0.51	4.20	1.60	1.24	0.64	0.42	0.02
OKN-8	0.89	0.92	0.93	1.15	0.91	0.94	0.82	0.50	5.48	1.60	1.18	0.65	0.43	0.02
OKN-9	0.91	0.94	0.94	0.92	0.77	0.86	0.79	0.57	4.35	1.65	1.16	0.65	0.43	0.03
OKN-10	0.76	0.77	0.85	0.91	0.77	0.86	0.81	0.64	3.98	1.60	1.07	0.62	0.47	0.05
OKN-11	0.70	0.70	0.82	0.82	0.74	0.85	0.75	0.65	3.69	1.61	1.02	0.62	0.52	0.07
OKN-12	0.76	0.76	0.85	0.87	0.76	0.86	0.79	0.61	4.21	1.61	0.99	0.63	0.51	0.05
OKN-13	0.94	0.96	0.96	1.07	0.86	0.92	0.79	0.68	4.24	2.18	0.83	0.64	0.34	0.03
OKN-14	0.62	0.63	0.77	0.73	0.72	0.83	0.78	0.50	3.16	1.38	1.43	0.62	0.42	0.02
OKN-15	0.65	0.66	0.79	0.81	0.73	0.84	0.79	0.55	3.13	1.42	1.35	0.62	0.41	0.03
OKN16	0.70	0.72	0.82	0.83	0.75	0.85	0.84	0.51	3.62	1.34	1.45	0.64	0.43	0.03
MJO-1	0.77	0.80	0.86	3.29	1.83	1.50	0.81	0.31	8.34	1.78	1.28	0.67	0.43	0.03
MJO-2	0.77	0.81	0.86	2.09	1.32	1.19	0.80	0.39	6.78	1.63	1.32	0.67	0.43	0.04
MJO-3	0.78	0.81	0.87	2.46	1.49	1.29	0.81	0.36	7.51	1.68	1.30	0.67	0.43	0.03
MJO-4	0.78	0.81	0.87	1.38	1.00	1.00	0.82	0.47	5.89	1.56	1.35	0.67	0.43	0.01
MJI-1	0.76	0.78	0.86	0.43	0.59	0.75	0.81	2.47	3.28	1.56	0.19	0.66	0.53	0.05
MJI-2	0.84	0.86	0.90	1.80	1.14	1.08	0.90	0.42	8.01	1.57	0.84	0.71	0.49	0.06
MJI-3	0.83	0.86	0.90	1.13	0.85	0.91	0.90	0.52	6.96	1.53	0.86	0.70	0.49	0.06
MJI-4	0.96	0.99	0.97	1.09	0.83	0.90	0.93	0.45	6.00	1.53	0.94	0.69	0.45	0.03
MJI-5	0.78	0.80	0.87	0.47	0.60	0.76	0.78	2.09	3.53	1.54	0.21	0.63	0.53	0.08
MJI-6	0.82	0.85	0.89	0.89	0.78	0.87	0.84	0.55	4.87	1.53	0.71	0.70	0.49	0.04
MJI-7	0.86	0.89	0.92	1.47	0.99	0.99	0.89	0.46	7.84	1.56	0.86	0.71	0.49	0.08
MJI-8	0.82	0.85	0.89	0.87	0.76	0.86	0.82	0.78	4.19	1.56	0.53	0.69	0.52	0.07
MJI-9	0.83	0.86	0.90	1.34	0.96	0.97	0.86	0.46	6.69	1.54	0.85	0.71	0.49	0.06
MJI-10	0.83	0.86	0.90	1.05	0.82	0.89	0.85	0.53	5.95	1.50	0.98	0.71	0.49	0.05
WZB1	0.86	0.89	0.91	3.99	2.18	1.71	0.68	0.20	7.04	1.20	1.67	0.71	0.44	0.04
WZB2	0.86	0.88	0.92	4.17	2.26	1.76	0.71	0.24	7.91	1.39	1.03	0.76	0.46	0.05

Note: see definitions of terms in Table 4.

4.3. Geochemical characteristics of Niger delta crude oils based on biomarker distribution

The source facies, depositional environments and thermal maturity parameters based on saturated and aromatic biomarkers are used to assess the origin, environments of deposition and thermal maturity of the crude oils (Tables 5, 6, and 7). The Pr/Ph ratio shows a range of values from 1.48 to 4.71 [41,64] (Table 5), suggesting crude oils derived from terrestrial-marine organic matter and deposited in a lacustrine-fluvial/deltaic environment under oxic to suboxic conditions [42, 43, 44]. For some of the samples, the Pr/Ph values >3 indicate crude oils derived from predominant terrestrial organic matter [33, 42, 43, 44]. The ratios TPP's/(TPP's + C₂₇ Dia), C₂₉H/(C₂₉H + C₃₀H), C₃₅H/(C₃₅H + C₃₄H), Hopane/sterane and oleanane index were successfully applied to differentiate crude oils from different basins of the world into different origins and depositional environments with high, moderately high and low values of these ratios indicating oils from terrigenous, terrestrial-marine and marine organic matter respectively [13]. In the

present study, the values of TPP's/(TPP's + C₂₇ Dia), C₂₉H/(C₂₉H + C₃₀H), C₃₅H/(C₃₅H + C₃₄H), Hopane/sterane and oleanane index in the crude oils are the ranges of 0.18–0.98, 0.04 to 0.57, 0.26 to 0.54, 5.23 to 29.70 and 0.23 to 0.75, respectively (Table 5), indicating crude oils derived from source rocks of mixed origin of terrestrial and marine organic matter [13, 33]. This interpretation is consistent with the recent studies on Niger Delta crude oils [16, 17, 64, 79]. The cross plots of hopane/sterane versus Pr/Ph (Figure 7a), TPP's/(TPP's + C₂₇ Dia) versus hopane/sterane (Figure 7b) and C₂₉H/(C₂₉H + C₃₀H) versus C₃₅H/(C₃₅H + C₃₄H) (Figure 8c) further support terrestrial-marine organic matter for the oil samples.

The relative percentages of C₂₇, C₂₈ and C₂₉ steranes in the oil samples range from 19.7 to 43.3 %, 25.5–32.6 % and 30.1 to 53.7 %, respectively (Table 6). The distribution of the steranes in the oil samples occurs in the order C₂₉ > C₂₈ > C₂₇ and C₂₉ > C₂₈ < C₂₇ (Figure 8a), suggesting crude oils derived from source rocks of mixed origin (terrestrial and marine) [33, 48, 49]. The $\alpha\alpha\alpha$ 20R C₂₇/C₂₈, C₂₉/C₂₈ and C₂₈/C₂₉ steranes ratios were used to determine the source organic matter in Crude oils from Potwar Basin, Pakistan [22] and Ordovician oils from the

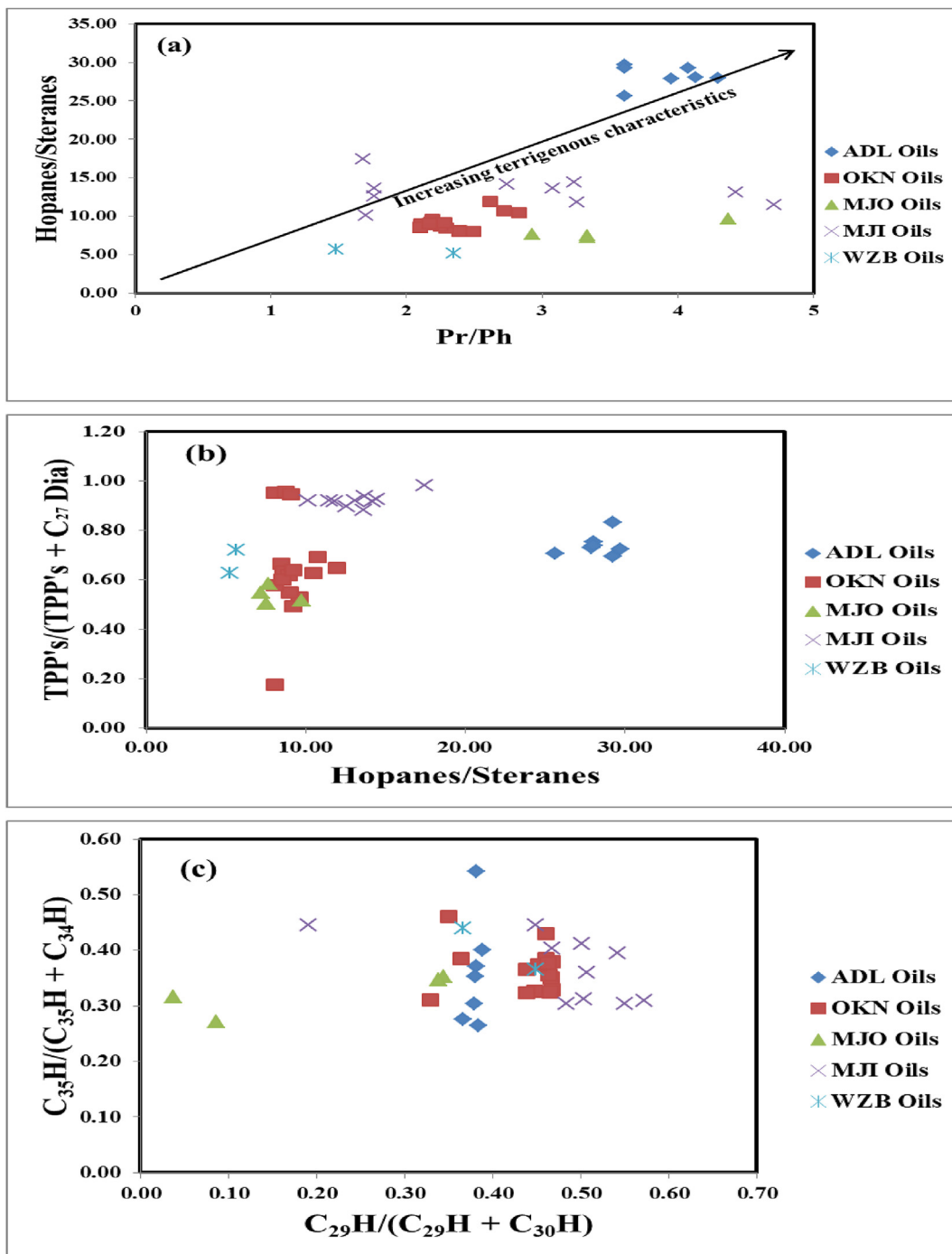


Figure 7. Cross plots of hopane/sterane versus (a) Pr/Ph, (b) TPP's/(TPP's + C₂₇ Dia), and (c) C₃₅H/(C₃₅H + C₃₄H) versus C₂₉H/(C₂₉H + C₃₀H) in Niger Delta crude oils. Note: see Figure 3 for definitions of terms.

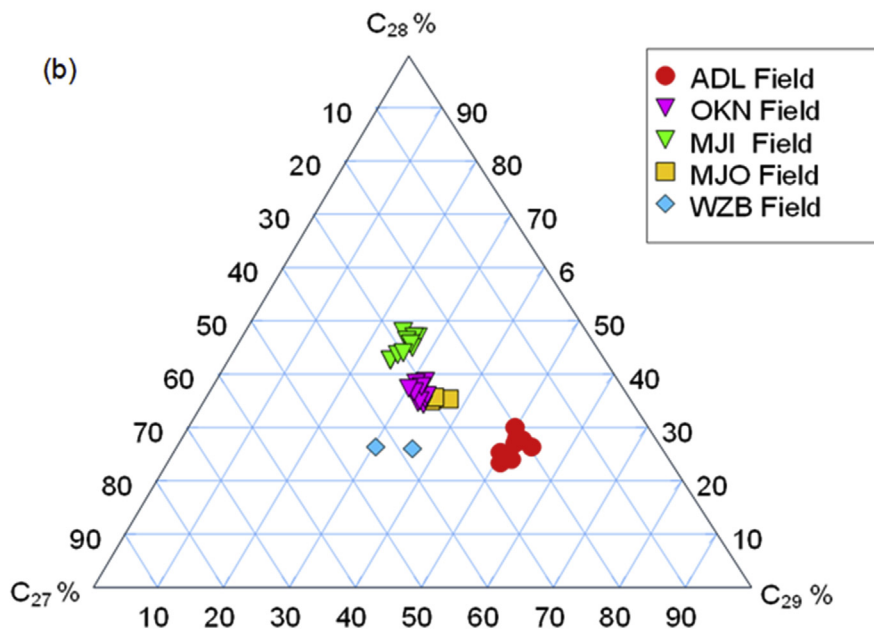
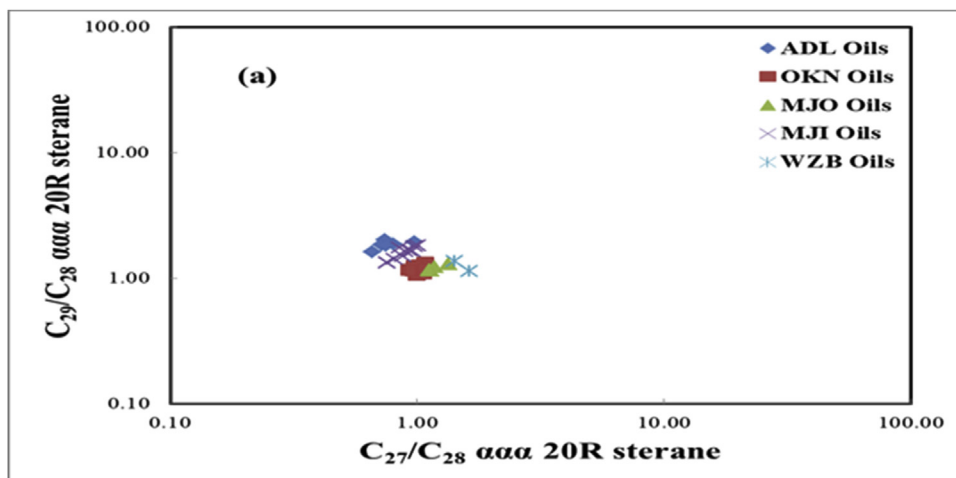


Figure 8. (a) Cross plots of C_{29}/C_{28} $\alpha\alpha$ 20R steranes versus C_{27}/C_{28} $\alpha\alpha$ 20R steranes and (b) Triplots of C_{27} to C_{29} regular steranes in Niger Delta crude oils. Note: see Figure 4 for definitions of terms.

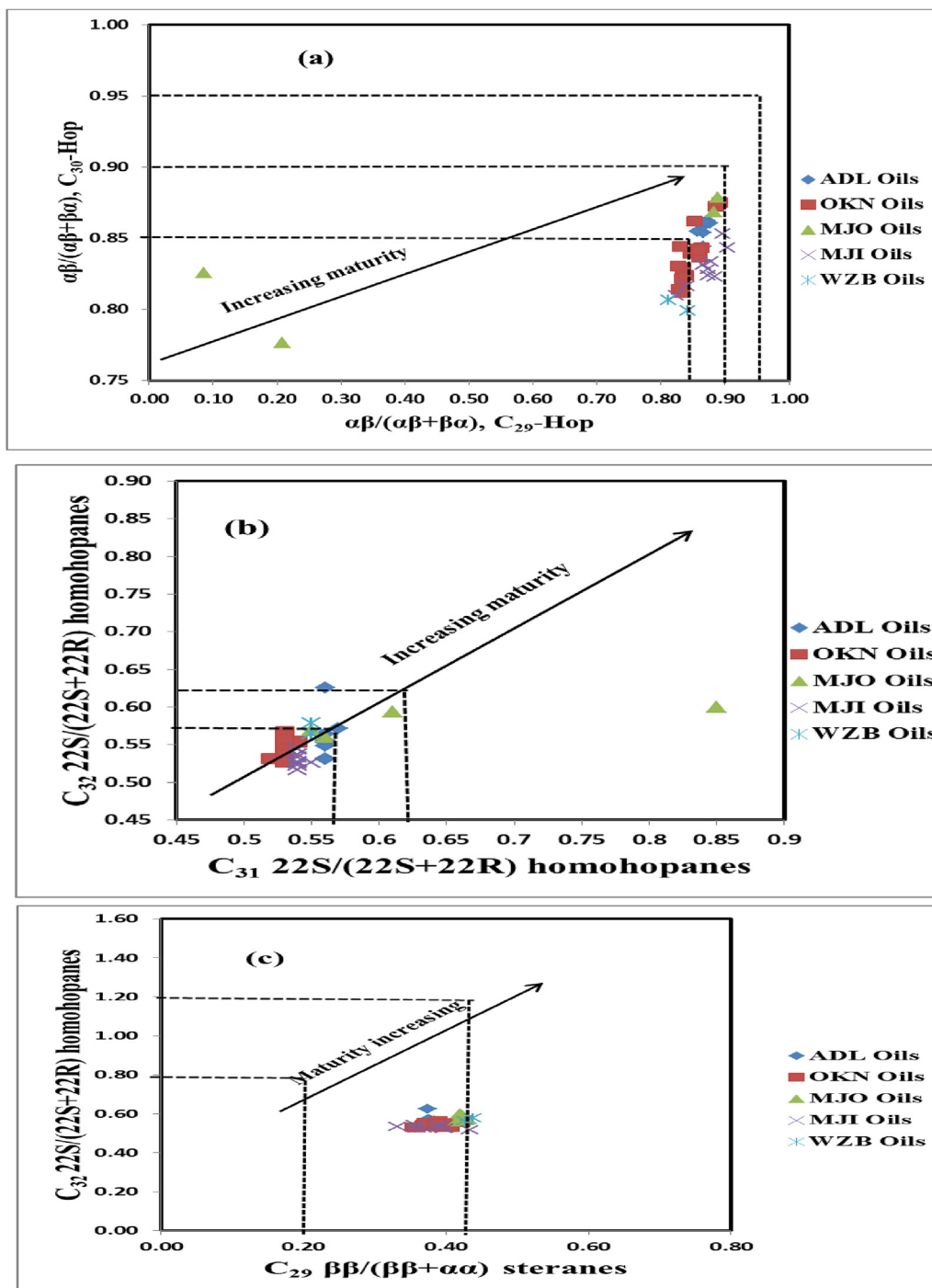


Figure 9. Cross plots of (a) $C_{30} \alpha\beta/(\alpha\beta+\beta\alpha)$ hopanes versus $C_{29} \alpha\beta/(\alpha\beta+\beta\alpha)$ hopanes, (b) $C_{32} 22S/(22S + 22R)$ homohopanes versus $C_{31} 22S/(22S + 22R)$ homohopanes, and (c) $C_{32} 22S/(22S + 22R)$ homohopanes versus $C_{29} \beta\beta/(\beta\beta+\alpha\alpha)$ steranes in Niger Delta crude oils. Note: see [Figure 5](#) for definitions of terms.

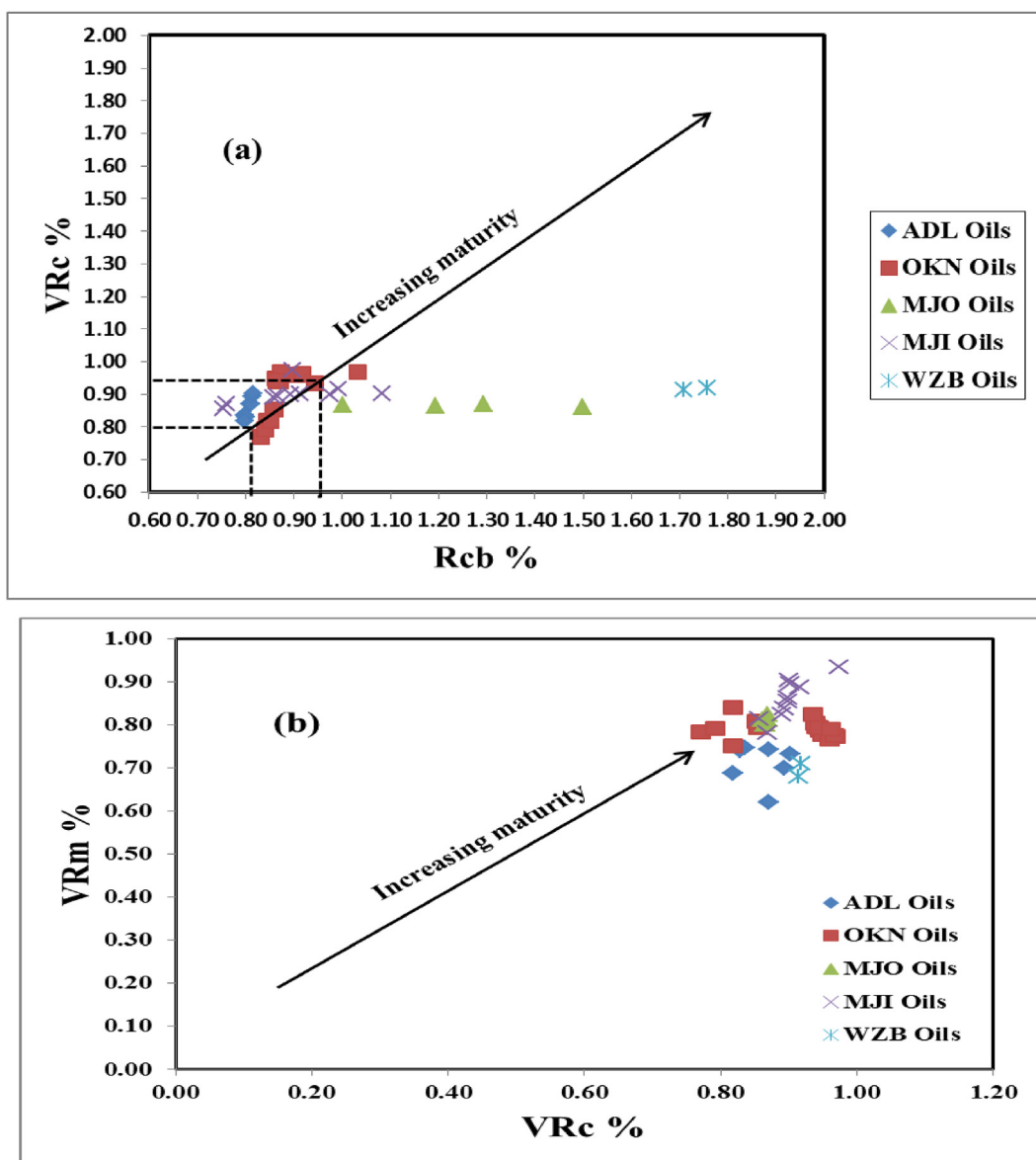


Figure 10. Cross plots of VRc versus (a) Rcb, and (b) VRm in Niger Delta crude oils. Note: see Figure 6 for definitions of terms.

Central Tabei Uplift, Tarim Basin, China [48]. In the present study, the $\alpha\alpha$ 20R C₂₇/C₂₈, C₂₉/C₂₈ and C₂₈/C₂₉ steranes values range from 0.66 to 1.63, 1.07 to 2.02 and 0.49 to 0.93, respectively (Table 6), indicating crude oils of mixed origin. The triplot (Figure 8b) of the C₂₇, C₂₈ and C₂₉ steranes further support mixed origin of terrestrial and marine organic matter for the crude oils. This interpretation is consistent with recent studies on Niger Delta crude oils using aromatic biomarkers [16, 17, 64, 79].

The thermal maturity parameters based on hopane, Ts/(Ts + Tm), 22S/(22S + 22R) C₃₁ homohopanes, 22S/(22S + 22R) C₃₂ homohopanes, $\alpha\beta/(\alpha\beta+\beta\alpha)$ C₂₉ hopanes and $\alpha\beta/(\alpha\beta+\beta\alpha)$ C₃₀ hopanes calculated for the oil samples are in the ranges of 0.40–0.62 [42], 0.52 to 0.85 [9], 0.53 to 0.60, 0.09 to 0.90 and 0.78 to 0.88, respectively (Table 6). These values show that the oil samples are within the oil window [22, 34, 49, 53, 54, 55]. Similarly, the sterane based maturity ratios, 20S/(20S + 20R) and $\beta\beta/(\beta\beta+\alpha\alpha)$ C₂₉ steranes in the oil samples range from 0.28 to 0.47 [16,41,64,79] and 0.33 to 0.44, respectively (Table 6), supporting that the oils have reached oil window [13, 33, 35, 52]. The cross plots of C₂₉- versus C₃₀ hopanes - $\alpha\beta/(\alpha\beta+\beta\alpha)$ [54] (Figure 9a), C₃₁- versus C₃₂ homohopanes 22S/(22S + 22R) [35] (Figure 9b), and C₃₂ homohopanes 22S/(22S + 22R) versus $\beta\beta/(\beta\beta+\alpha\alpha)$ C₂₉ steranes [35] (Figure 9c)

showed that the oils are within the oil window maturity. The distribution of aromatic biomarkers are controlled by the effect of thermal stress [33, 62] with their ratios reported to be more reliable than hopanes and steranes based maturity parameters [22, 33, 35]. The MPI-1, MPI-2, VRc, TMNr-1, TMNr-2, Rcb and VRm calculated for crude oils have the ranges of values from 0.62 to 0.95 [16,17,65,80], 0.63 to 0.99 [16], 0.77–0.97 % [42], 0.43 to 4.17, 0.59 to 2.26, 0.75–1.76 % and 0.62–0.93 %, respectively (Table 7), peak of oil generation to late oil window maturity range [22, 33, 65, 66, 77, 80]. The cross plots of VRc versus Rcb (Figure 10a) [22] further confirmed peak of oil generation to late oil window maturity range for the oil samples. Also, the plots VRc versus VRm (Figure 10b) [62] showed that the oil samples have similar maturity status.

Abundance of polycyclic aromatic hydrocarbons (PAHs) such as alkyl naphthalenes and alkyl phenanthrenes, in crude oils are also influenced by source facies [65, 78]. For example, the relative abundances of phenanthrenes and naphthalenes are lower in marine source rocks and crude oils than those of terrestrial samples and it has been suggested that their biological precursors might derived more from terrestrial organic matter than from a marine one [18, 19, 62]. The values of 1,2,5-/1,2,7-TMN, 1,2,6-/1,2,4-TMN, 1,2,5,6-/1,2,5,7-TeMN, 1,3,6,7-/1,2,5,

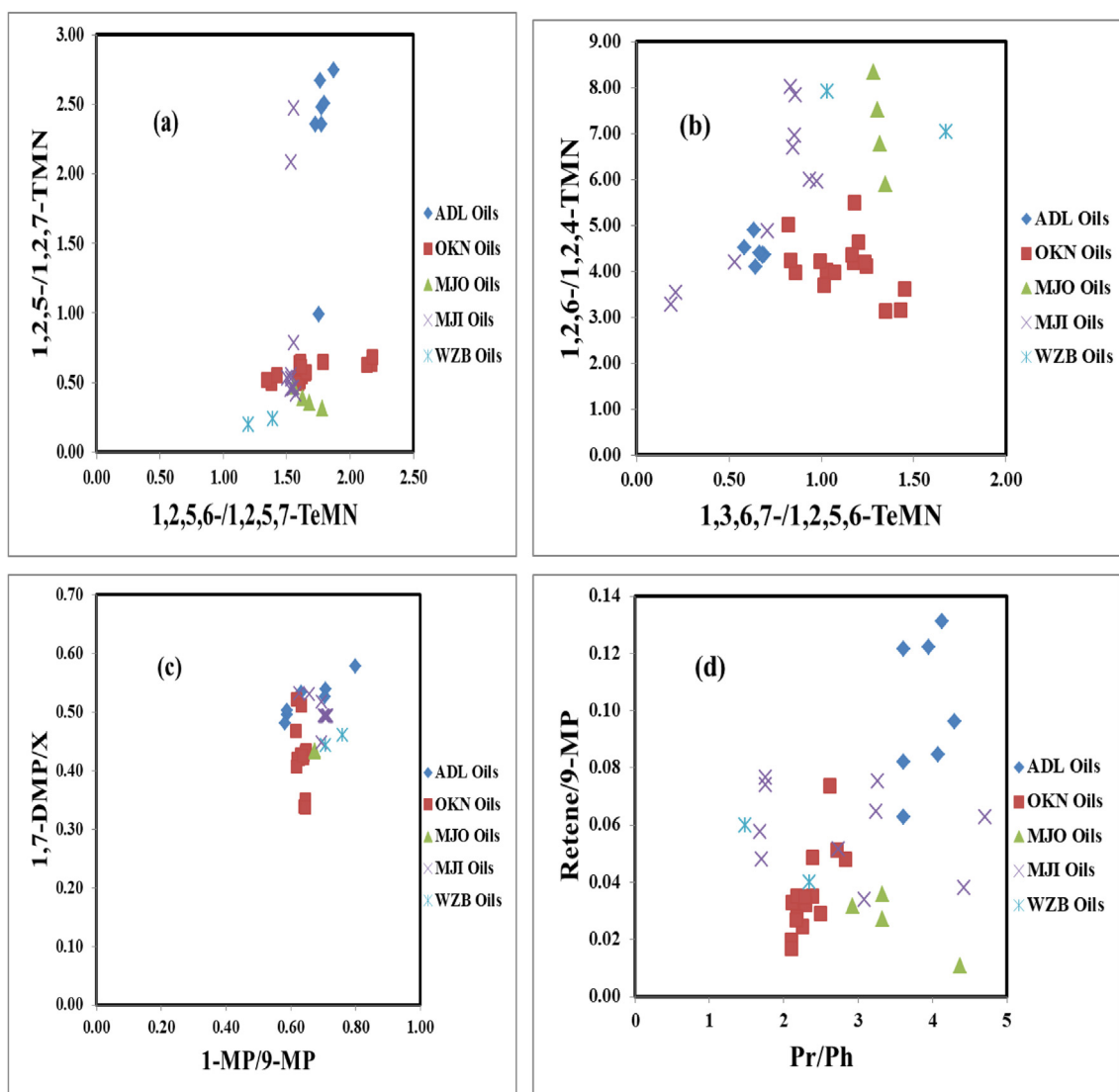


Figure 11. Cross plots of (a) 1,2,5-/1,2,7-TMN versus 1,2,5,6-/1,2,5,7-TeMN, (b) 1,2,6-/1,2,4-TMN versus 1,3,6,7-/1,2,5,6-TeMN, (c) 1,7-DMP/X versus 1-MP/9-MP, and (d) retene/9-MP versus Pr/Ph in Niger Delta crude oils. Note: TMN: Trimethylnaphthalene; TeMN: Tetramethylnaphthalene; DMP: Dimethylphenanthrene; X:/(1,3- + 3,9- + 2,10- + 3,10-DMP); MP: Methylphenanthrene.

6-TeMN, 1-MP/9-MP, 1,7-DMP/X and retene/9-MP (Re/9-MP) range from 0.20 to 2.75, 3.13 to 8.01, 1.20 to 2.18, 0.19 to 1.67, 0.58 to 0.80, 0.34 to 0.58 and 0.01 to 0.13, respectively (Table 7), indicating crude oils formed from source rocks of mixed origin (terrestrial and marine) [22, 66, 74, 78]. Retene has been reported as a biomarker of higher plant in previous study [81]. Thus, its presence in the oils clearly suggest terrestrial organic matter input. The cross plots of 1,2,5-/1,2,7-TMN versus 1,2,5,6-/1,2,5,7-TeMN (Figure 11a) [75], 1,2,6-/1,2,4-TMN versus 1,3,6,7-/1,2,5,6-TeMN (Figure 11b) [74], 1-MP/9-MP versus 1,7-DMP/X (Figure 11c) [78] and Re/9-MP versus Pr/Ph (Figure 11d) [22] showed that the oil samples have received similar inputs of terrestrial and marine organic matter.

4.4. Distribution anomalies of fluorene and alkylfluorenes in crude oils and source rock extracts from Niger delta basin

The summed m/z 166 + 180+194 fragmentograms showing the distributions of fluorene and alkylfluorenes in the rock samples and crude oils are shown in supplementary materials 4 and 5, respectively. The relative percentages of fluorene (C_0), methylfluorenes (C_1) and dimethylfluorenes (C_2) in the rock samples are in the ranges of

1.13–30.97 %, 1.02–18.20 % and 51.33–97.85 %, respectively (Table 8) whereas the C_0 , C_1 , and C_2 relative percentage values in the crude oils range from 0.20 to 16.72 %, 29.58–42.12 % and 47.00–64.35 %, respectively (Table 9). The crude oils and the rock samples are characterized by the predominance of C_2 -fluorenes over other alkylated homologues (Figures 12 and 13; Tables 8 and 9). The dominance of C_2 -fluorenes over other alkylated homologues of fluorene have been reported in paleozoic coals from Germany [82] and crude oils and sediment extracts from Potwar basin, Pakistan [11, 83]. The histograms (Figure 14) and triplot (Figure 15) of C_0 , C_1 and C_2 -fluorenes for the source rocks and crude oils further show that the oils and rock samples are characterized by the predominance of C_2 -fluorenes over other alkylated homologues. This pattern of distribution is different from what was observed in the Ordovician and Cambrian source rocks from the Tabei and Tazhong areas, and Triassic and Jurassic terrestrial source rocks from Kuche depression, Tarim Basin, China whereby methylfluorenes dominated other alkylated homologues of fluorenes [21]. [21] also reported the predominance of methylfluorene over all other alkylated homologues of Fluorene in the mudstone and coal extracts from the Kuche depression of Tarim Basin, China. Thus, the distribution patterns of fluorene and alkylfluorenes in the crude oils and rock samples

Table 8. Relative percentages of fluorenes and heterocyclic compounds in Niger Delta source rocks.

Field	Depth(m)	Reservoir Formation	Geological Age	Depobelt	Fluorenes (%)			DBTs %	FLs %	DBFs %
					C ₀	C ₁	C ₂			
MJI	2079–2098	Agbada	Eocene to Recent	Offshore	18.78	15.72	65.5	13.17	17.24	69.59
MJI	2299–2308	Agbada	Eocene to Recent	Offshore	3.04	8.11	88.84	14.77	29.78	55.45
MJI	2637–2655	Agbada	Eocene to Recent	Offshore	15.47	12.02	72.5	16.03	14.86	69.11
MJI	2857–2875	Agbada	Eocene to Recent	Offshore	9.03	9.26	81.71	24.1	16.15	59.75
MJI	2994–3012	Agbada	Eocene to Recent	Offshore	3.36	4.8	91.83	17.21	26.55	56.24
MJI	3085–3104	Agbada	Eocene to Recent	Offshore	7.82	5.15	87.04	13.76	16.1	70.14
MJI	3232–3250	Agbada	Eocene to Recent	Offshore	7.42	5.41	87.16	14.43	13.97	71.6
MJI	3323–3332	Agbada	Eocene to Recent	Offshore	9.91	5.54	84.55	18.81	16.64	64.56
MJI	3405–3424	Agbada	Eocene to Recent	Offshore	3.74	3.06	93.2	10.02	29.65	60.33
MJO	1616–1707	Agbada	Eocene to Recent	Offshore	3.67	7.97	88.37	37.96	26.22	35.82
MJO	1771–1872	Agbada	Eocene to Recent	Offshore	1.24	3.24	95.52	28.01	35.6	36.39
MJO	2091–2101	Agbada	Eocene to Recent	Offshore	2.12	3.22	94.66	32.33	26.14	41.53
MJO	2293–2366	Agbada	Eocene to Recent	Offshore	2.29	1.37	96.33	16.2	27.58	56.22
MJO	2570–2588	Agbada	Eocene to Recent	Offshore	1.13	1.02	97.85	24.02	38.04	37.94
MJO	2808–2817	Agbada	Eocene to Recent	Offshore	3.95	3.17	92.88	22.69	13.71	63.6
OKN	1537–1555	Agbada	Eocene to Recent	Offshore	17.85	12.44	69.71	42.52	9.36	48.12
OKN	1729–1747	Agbada	Eocene to Recent	Offshore	30.97	17.71	51.33	29.75	9.46	60.79
OKN	2625–2643	Agbada	Eocene to Recent	Offshore	22.9	18.2	58.91	28.52	11.1	60.38
OKN	2780–2799	Agbada	Eocene to Recent	Offshore	12.96	9.82	77.22	41.1	12.91	46
OKN	2863–2881	Agbada	Eocene to Recent	Offshore	11.04	7.11	81.85	34.08	16	49.92
OKN	2909–2927	Agbada	Eocene to Recent	Offshore	10.05	11.16	78.78	40.27	17.1	42.63

% DBF, DBT, FL: 100% normalized from peak areas of corresponding ions i.e. dibenzofuran (DBF) (m/z168), dibenzothiophene (DBT) (m/z184) and fluorene (F) (m/z166) [14]. C₀ = fluorene; C₁ = methylfluorenes; C₂ = dimethylfluorenes.

under study might have been influenced by source facies [13, 18, 19, 21]. The predominance of methylfluorenes over other alkylated homologues has been reported in marine rock samples [21]. The rock samples from MJI and OKN fields are characterized by the significant amounts of fluorene while the abundance of fluorene is very low in MJO source rocks (Figure 12). Also, there is high abundance of fluorene in all the crude oils studied in this work (Figure 13). The high abundance of fluorene has been previously reported in crude oils and source rock extracts [12, 13]. Among the methylfluorene isomers in the crude oils and source rocks, 1-methylfluorene is the dominant compound while 4-methylfluorene occur as the least abundant (Figures 12 and 13). The predominance of 1-methylfluorene over other isomers of methylfluorenes have been previously reported in paleozoic coals from Germany [82] and crude oils and sediment extracts from Potwar basin, Pakistan [11, 83]. Also, 1,7-dimethylfluorene (1,7-DMF) is the most abundant compound among the isomers of dimethylfluorene while others occur very low in the source rocks (Figure 12). This pattern of distributions whereby 1,7-DMF is the most abundant among the C₂-fluorene isomers have been previously reported in petroleum and source rocks [11, 12, 83]. The dimethylfluorenes generally occur in significant amounts in all the crude oils (Figure 13). Generally, the fluorene and its alkylated homologues occur in higher abundance in the rock samples compared to the oil samples which have lower abundance (Figures 12 and 13; Tables 8 and 9). The lower abundance of fluorenes in all the oil samples compared to their higher abundance in the rock samples may be related to the effects of migration [21].

4.5. Application of fluorenes, dibenzofurans and dibenzothiophenes as source facies and depositional environment indicators in the source rocks and crude oils from Niger delta basin

Tables 8 and 9 show the geochemical parameters calculated from fluorenes and related compounds in Niger Delta crude oils and source rocks. Variations in the relative abundance of fluorenes (FLs),

dibenzofurans (DBFs) and dibenzothiophenes (DBTs) has been reported as potential indicators of origin and depositional environments of crude oils and source rocks. For instance, the elevated abundance of dibenzothiophenes suggests marine carbonate source rocks while abundance of fluorene and dibenzofurans are high in freshwater source rocks [12, 13, 18, 19, 21]. The FLs %, DBFs % and DBTs % values for the rock samples range from 9.36 to 38.04 %, 35.82–71.60 % and 10.02–42.52 %, respectively (Table 8). The distributions of the FLs, DBFs and DBTs in the rock samples clearly indicate source rocks formed from the mixture of organic matter (terrestrial and marine) [12]. However, the elevated values of DBFs recorded for the rock extracts indicate source rocks with significant inputs from terrigenous organic matter relative to marine and deposited in a marine brackish-saline lacustrine/swampy environments [12, 18, 19, 74]. This finding is consistent with the previous reports on Niger Delta source rocks [16, 17, 41, 45, 84]. The triplot of FLs, DBFs and DBTs is shown in Figure 16a. The plot has been used to delineate the various source rocks and crude oils depositional environments and origins [12, 13, 18, 19]. Source rocks from the same field are grouped together on this plots indicating that they were formed from similar organic materials and depositional conditions (Figure 16a). The triplot indicates the data set is oriented towards higher percent DBF and away from DBT vertex (Figure 16a). This is consistent with the mixed input of terrestrial and marine organic matter but with the dominance of the contribution of terrestrial organic matter to the source rocks and implies that this type of organic matter contains more abundant oxygen species leading to the formation of relatively higher percentage of DBF compared to DBT and FL [13].

The FLs %, DBFs % and DBTs % values for the crude oils range from 18.91 to 56.38 %, 24.90–72.34 % and 5.99–19.02 %, respectively (Table 9). The distributions of the FLs, DBFs and DBTs in the crude oils suggest oil formed the mixture of organic matter (terrestrial and marine) [12]. However, the significant values of FLs and DBFs recorded for the oil samples indicate oil derived from the source rocks with higher contributions from terrigenous organic matter deposited in a marine/swampy

Table 9. Relative percentages of fluorenes and heterocyclic compounds in Niger Delta crude oils.

Sample	Depth(m)	Reservoir Formation	Geological Age	Depobelt	Fluorenes (%)			DBTs %	FLs %	DBFs %
					C ₀	C ₁	C ₂			
ADL1	2602–2607	Agbada	Eocene to Recent	North	16.08	35.65	48.27	7.22	26.74	66.04
ADL2	2602–2607	Agbada	Eocene to Recent	North	16.33	35.79	47.88	7.64	26.15	66.21
ADL3	2759–2763	Agbada	Eocene to Recent	North	16.72	36.45	46.83	7.3	26.74	65.96
ADL4	2766–2770	Agbada	Eocene to Recent	North	13.68	37.48	48.84	5.99	25.23	68.78
ADL5	2905–2908	Agbada	Eocene to Recent	North	16.06	36.2	47.74	6.65	24.66	68.69
ADL6	2964–2967	Agbada	Eocene to Recent	North	0.2	42.12	57.68	7.33	27.56	65.1
ADL7	3064–3052	Agbada	Eocene to Recent	North	14.71	38.28	47	8.75	18.91	72.34
OKN-1	1749–1750	Agbada	Eocene to Recent	Offshore	7.27	29.58	63.16	18.72	56.38	24.9
OKN-2	1892–1895	Agbada	Eocene to Recent	Offshore	8.5	33.97	57.53	17.46	47.84	34.7
OKN-3	1905–1907	Agbada	Eocene to Recent	Offshore	9.32	33.71	56.97	17.18	48.08	34.73
OKN-4	1952–1955	Agbada	Eocene to Recent	Offshore	7.62	30.15	62.23	19.02	54.19	26.79
OKN-5	2050–2059	Agbada	Eocene to Recent	Offshore	9.39	33.57	57.05	16.69	48.57	34.74
OKN-6	2369–2555	Agbada	Eocene to Recent	Offshore	4.87	30.77	64.35	17.37	49.12	33.51
OKN-7	2377–2672	Agbada	Eocene to Recent	Offshore	10.56	34.09	55.35	14.77	48.54	36.69
OKN-8	2469–2782	Agbada	Eocene to Recent	Offshore	10.53	34.33	55.14	14.38	48.86	36.76
OKN-9	2485–2793	Agbada	Eocene to Recent	Offshore	8.16	33.47	58.37	17.1	48.56	34.33
OKN-10	2489–2491	Agbada	Eocene to Recent	Offshore	9.76	35.4	54.84	11.55	40.05	48.4
OKN-11	2521–2523	Agbada	Eocene to Recent	Offshore	11.13	34.86	54	11.03	37.04	51.92
OKN-12	2530–2537	Agbada	Eocene to Recent	Offshore	11.91	35.72	52.37	11.13	38.32	50.55
OKN-13	2566–2568	Agbada	Eocene to Recent	Offshore	7.6	29.78	62.62	17.63	56.04	26.33
OKN-14	2677–2683	Agbada	Eocene to Recent	Offshore	10.97	35.5	53.53	12.42	39.84	47.74
OKN-15	3148–3154	Agbada	Eocene to Recent	Offshore	9.09	35.28	55.63	12.83	40.84	46.33
OKN16	3593–3605	Agbada	Eocene to Recent	Offshore	8.09	34.45	57.46	13.33	42.95	43.72
MJO-1	2207–2216	Agbada	Eocene to Recent	Offshore	6.78	37.46	55.76	17.3	53.56	29.13
MJO-2	2070–2081	Agbada	Eocene to Recent	Offshore	13.71	36.38	49.91	17.2	51.38	31.42
MJO-3	2091–2104	Agbada	Eocene to Recent	Offshore	13.83	35.87	50.3	17.11	51.9	30.99
MJO-4	2096–2101	Agbada	Eocene to Recent	Offshore	11.6	35.87	52.53	16.55	50.82	32.63
MJI-1	1607–1611	Agbada	Eocene to Recent	Offshore	7.27	38.05	54.69	13.05	46.64	40.31
MJI-2	1777–1779	Agbada	Eocene to Recent	Offshore	13.43	36.23	50.34	11.6	44.57	43.83
MJI-3	1795–1797	Agbada	Eocene to Recent	Offshore	13.17	36.61	50.22	10.87	44.46	44.67
MJI-4	1920–1921	Agbada	Eocene to Recent	Offshore	11.21	35.81	52.99	10.98	43.04	45.97
MJI-5	1936–2342	Agbada	Eocene to Recent	Offshore	13.85	36.4	49.74	13.21	45.9	40.89
MJI-6	1944–1947	Agbada	Eocene to Recent	Offshore	15.38	36.82	47.8	12.42	44.31	43.27
MJI-7	1948–1950	Agbada	Eocene to Recent	Offshore	11.95	38.99	49.05	11.33	43.54	45.13
MJI-8	1979–2398	Agbada	Eocene to Recent	Offshore	12.43	38.9	48.67	12.02	44.57	43.41
MJI-9	2442–2444	Agbada	Eocene to Recent	Offshore	12.27	38.85	48.87	11.71	44.17	44.12
MJI-10	3030–3036	Agbada	Eocene to Recent	Offshore	12.75	39.02	48.23	11.11	43.06	45.83
WZB1	1610–2647	Agbada	Eocene to Recent	Offshore	13.28	36.29	50.43	16.95	48.74	34.31
WZB2	1811–1957	Agbada	Eocene to Recent	Offshore	11.3	36.38	52.32	15.91	48.58	35.51

Note: see definitions of terms in Table 8.

environments [12, 18, 19, 74]. These results further support data obtained from the distributions of C₂₇–C₂₉ steranes (section 4.3) in the oil samples (Table 6). Oils from the same field are grouped together on the ternary plots of FLs, DBFs and DBTs (Figure 16b), indicating similar inputs of organic matter and depositional conditions for oils from the same field [12]. The triplot shows that the data were plotted towards a higher percentage of DBF and away from the DBT vertex (Figure 16), which is consistent with the predominance of terrigenous organic matter contribution to the rocks of source that generate the oils. These findings substantiate the results from the ternary plots of distribution of C₂₇–C₂₉ steranes in the oils (Figure 8b) and agree with the previously reported results on Niger Delta crude oils using aromatic biomarkers [85].

4.6. Oil-source rocks correlation based on fluorene and alkylfluorenes

Fluorene and its alkylated homologues are ubiquitous in the mass chromatograms of the aromatic hydro-carbons in the source rock extracts

and crude oils but C₂-fluorenes (dimethylfluorenes) dominated other alkylated members in both the crude oils and source rocks. The distribution patterns of fluorene and alkylfluorenes in both the rock samples and crude oils are in the order C₂-fluorenes > C₀-fluorene > C₁-fluorenes and C₂-fluorenes > C₁-fluorene > C₀-fluorenes, respectively. Among the isomers of methylfluorenes and dimethylfluorenes in the rock samples and crude oils, 1-methylfluorene and 1,7-dimethylfluorene are the most abundant. The triplot of C₀, C₁ and C₂-fluorenes plotted in Figure 15 also supported that the crude oils and rock samples have similar distribution patterns. The similarity in the distribution between the oils and the source rocks suggest oil-source rock relationships between the oils and rock samples. The differences in the relative abundances of fluorenes, dibenzofurans and dibenzothiophenes is a potential indicator of source facies and depositional environments of source rocks [12, 13, 18, 19, 20, 21]. Previous showed that oils from marine and saline lake environments have high contents of dibenzothiophene while oils from freshwater and brackish lakes are dominated by fluorene, oils of paludal facies and coal

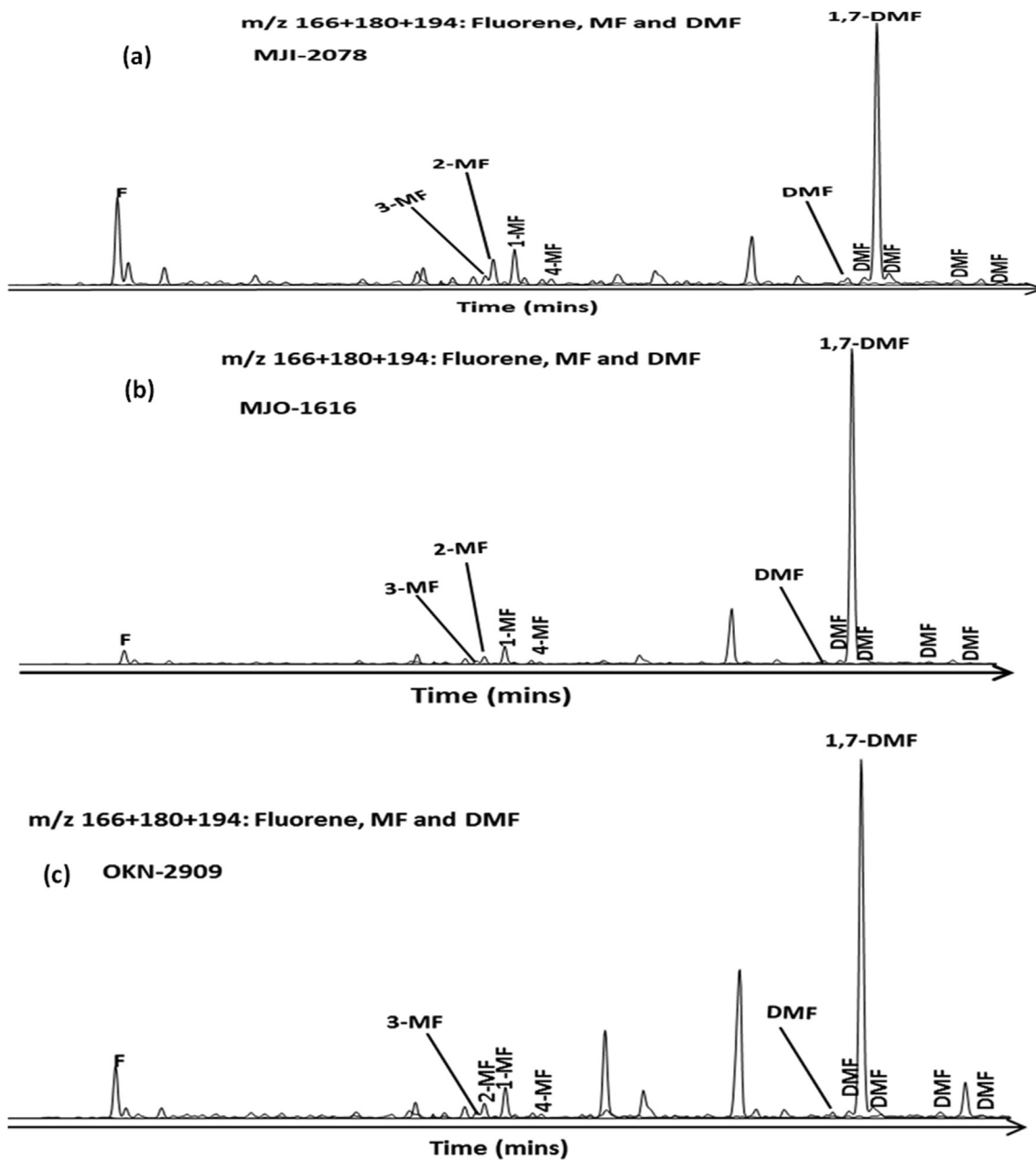


Figure 12. m/z 166 + 180+194 Ion chromatograms showing the distributions of fluorene and alkylfluorenes in the Niger Delta rock samples. Note: F: Fluorene; MF: Methylfluorene; DMF: Dimethylfluorene.

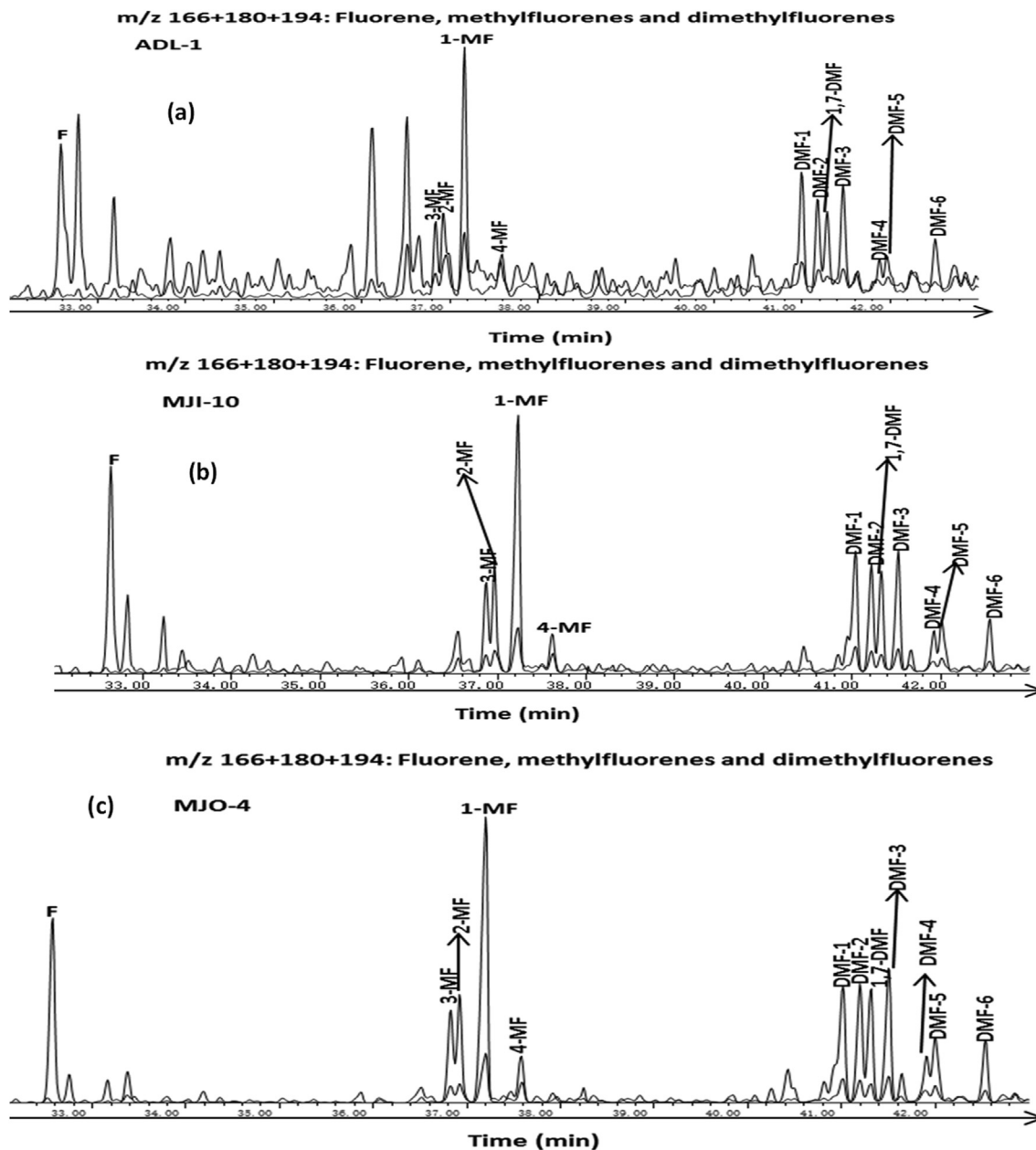


Figure 13. m/z 166 + 180+194 Ion chromatograms showing the distributions of fluorene and alkylfluorenes in the Niger Delta oil samples. Note: see Figure 12 for definitions of terms.

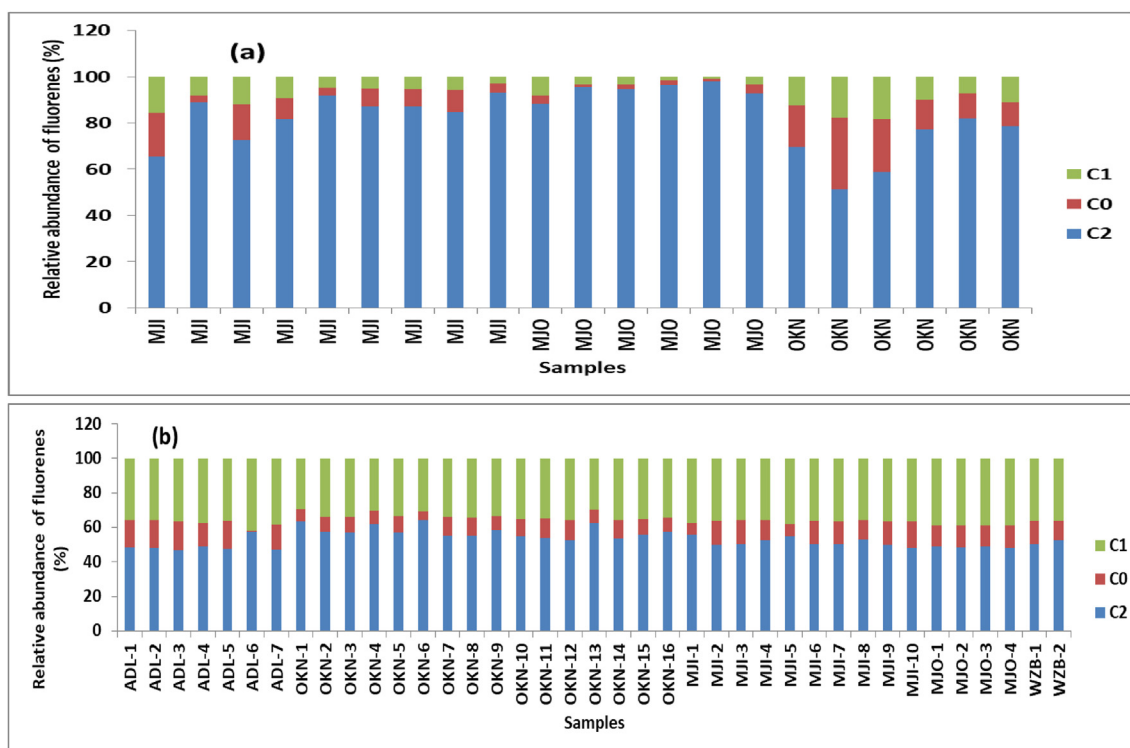


Figure 14. Histograms showing the relative abundance of fluorenes in Niger Delta (a) source rocks and (b) crude oils. Note: C₀, C₁ and C₂ means fluorene, methylfluorenes and dimethylfluorenes, respectively.

measure environment are abundant in dibenzofurans [20]. In order to be firmly sure the possible genetic relationship between the crude oils and source rocks studied, the triplot of fluorenes, dibenzofurans and dibenzothiophenes (Figure 17) is plotted for the source rocks and crude oils. The triplot clearly show that crude oils may likely derived from the studied source rocks.

5. Conclusions

The source rocks and crude oils from Niger Delta Basin, Nigeria, were investigated by optical microscopy and gas chromatography-mass

spectrometry (GC-MS) in terms of their origin and depositional environments based on the distribution of fluorene and alkylfluorenes. The preliminary studies based on maceral compositions, saturated and aromatic biomarkers showed that the rock samples and crude oils were formed from the mixed input of terrigenous and marine organic matter with greater contribution from terrigenous organic matter and deposited under oxic to sub-oxic conditions in a lacustrine-fluvial/deltaic environments. The maturity parameters based on hopanes and steranes showed that the rocks samples and crude oils were within immature to early mature; and early oil generation respectively whereas aromatic maturity ratios indicated that the rock samples and

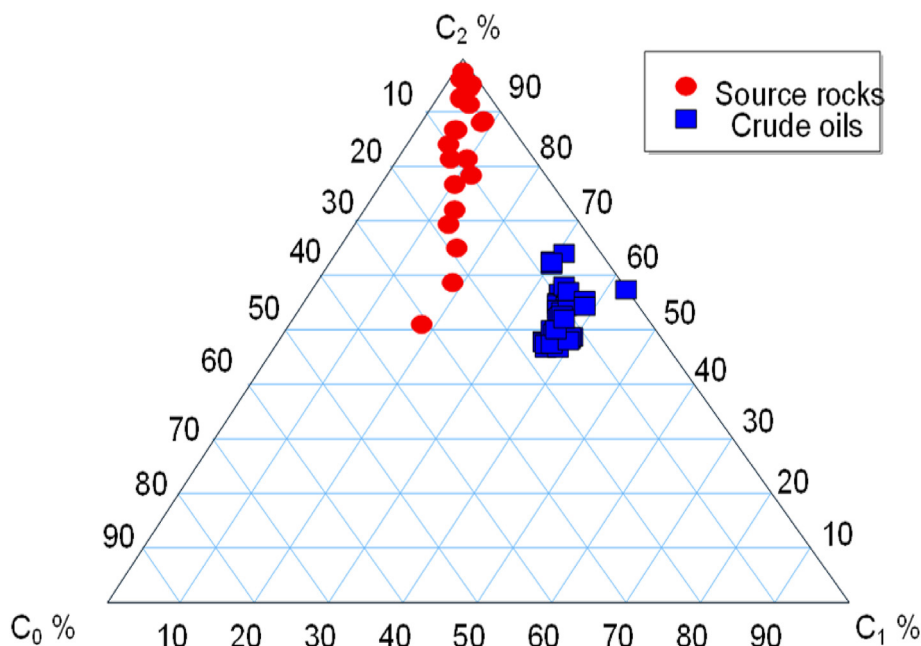


Figure 15. The triplots of C₀, C₁- and C₂-fluorenes in Niger Delta source rocks and crude oils. Note: see Figure 14 for definitions of terms.

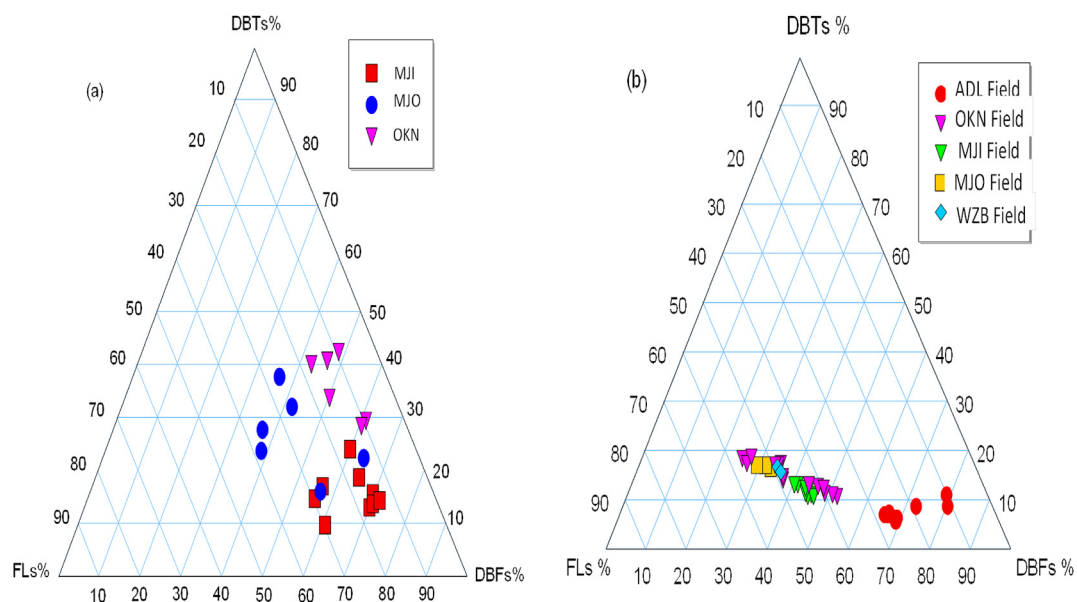


Figure 16. Triplots of fluorenes (FLs), dibenzofurans (DBFs) and dibenzothiophenes (DBTs) in (a) source rocks and (b) crude oils from Niger Delta. Note: DBTs %: DBTs/(DBTs + FLs + DBFs) and same for FLs and DBFs.

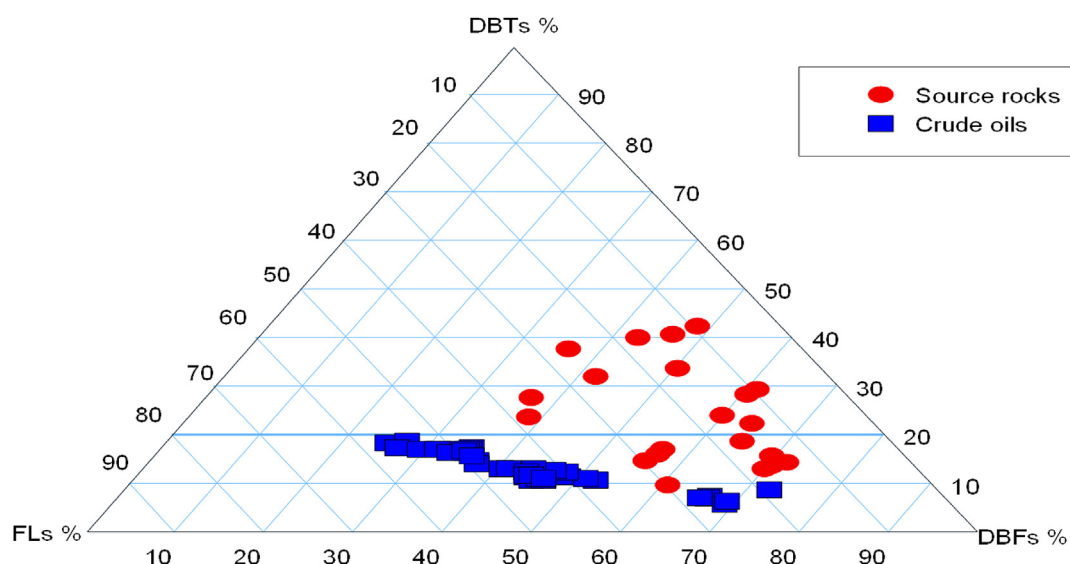


Figure 17. Triplots of fluorenes (FLs), dibenzofurans (DBFs) and dibenzothiophenes (DBTs) in source rocks and crude oils from Niger Delta. Note: see Figure 16 for definitions of terms.

crude oils were within immature to peak of oil generation and beyond; and peak to late oil generative window, respectively. 1-methylfluorene predominated over other methylfluorene isomers in the oils and rock samples. The crude oils and source rocks were characterized by the dominance of C₂-fluorenes over other alkylated homologues. These patterns of distribution might be due to the influence of source facies. The crude oils and source rocks were found to originate from the mixture of organic matter (terrestrial and marine) with significant contribution from terrestrial organic matter and deposited in a marine brackish-saline lacustrine/swampy environments based on the abundance of fluorenes, dibenzofurans and dibenzothiophenes in the oils and source rocks. The abundance and distribution of fluorenes and alkylfluorenes were found to be effective in determining the origin and depositional environments of crude oils and source rocks in the Niger Delta Basin, Nigeria.

Declarations

Author contribution statement

Abiodun B. Ogbesejana: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Oluwasesan M. Bello: Performed the experiments; Contributed reagents, materials, analysis tools or data.

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The authors declare no conflict of interest.

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