

Occurrence and Distribution of Chrysene and its Derivatives in Crude Oils and Source Rock Extracts from Niger Delta, Nigeria

Abiodun Busuyi Ogbesejana^{1*}, Oluwadayo Olatunde Sonibare², Zhong Ningning³, and Oluwasesan Michael Bello⁴

¹ Ph.D. Candidate, Department of Applied Chemistry, Faculty of Science, Federal University Dutsin-Ma, Dutsin-Ma, Katsina State, Nigeria

² Professor, Department of Chemistry, University of Ibadan, Ibadan, Oyo State, Nigeria

³ Professor, State Key Laboratory of Petroleum Resources and Prospecting, College of Geosciences, China University of Petroleum, Beijing, China

⁴ Lecturer I, Department of Applied Chemistry, Federal University Dutsin-Ma, Dutsin-Ma, Katsina State, Nigeria

Received: April 25, 2018; revised: May 27, 2018; accepted: June 28, 2018

Abstract

Crude oils and source rocks from the northern and offshore Niger Delta basin, Nigeria, have been characterized by gas chromatography-mass spectrometry in terms of their origin and thermal maturity based on the distribution of chrysene and its derivatives. The crude oils and source rocks were characterized by the dominance of chrysene over benzo[a]anthracene. 3-methylchrysene predominated over other methylchrysene isomers in the oils, while 3-methylchrysenes and 1-methylchrysenes were in higher abundance in the rock samples. The abundance and distribution of chrysene and its derivatives allow source grouping of the oils into three families. However, this grouping disagrees with the results obtained from well-established aromatic source grouping parameters. The maturity-dependent parameters computed from chrysene distributions (MCHR and 2-methylchrysene/1-methylchrysene ratios) indicated that the oils have a similar maturity status, while the rock samples are within an immature to early oil window maturity status, which was further supported by other maturity parameters computed from the saturate and aromatic biomarkers and vitrinite reflectance data. The abundance and distribution of chrysene and its derivatives were found to be effective in determining the thermal maturity of crude oil and source rock extracts in the Niger Delta basin, but they may not be a potential source-dependent biomarker in the crude oils and rock extracts from the basin.

Keywords: Chrysene, Crude Oil, Niger Delta, Maturity, Correlation

1. Introduction

Chrysene (Chy) and its derivatives (see Figure 1) are essential constituents of crude oils and source rock extracts. Chrysene and its derivatives have been identified in both recent and ancient sediments with their occurrence in the recent sediment attributed to the combustion of fossil fuels or plant biomass (Garrigues et al., 1988, 1990; Yunker et al., 2002, 2011, 2014; Li et al., 2012b); however, their presence in ancient sediments are linked with the degradation products of hopanes by the cleavage of ring E and

* Corresponding Author:

Email: abiodunogbesejana@gmail.com

successive aromatization from ring D to ring A (Borrego et al., 1997) or by cleavage from ring A and successive aromatization from ring A to ring D (Laflamme and Hites, 1979). Similarly, Grice et al. (2007) reported that chrysene, benzo[e]pyrene, and benzo[a]pyrene are derived from terrigenous materials (probably the products of combustion) in the Permian sediment from Perth basin, Western Australia, based on the stable carbon isotopic compositions of PAHs in sedimentary organic matter. Chrysene and its derivatives have been detected in crude oils and source rock extracts and applied to thermal maturity studies (Garrigues et al., 1988, 1990; Kruge, 2000; Li et al., 2012b) and petroleum system classification (Li et al., 2012b).

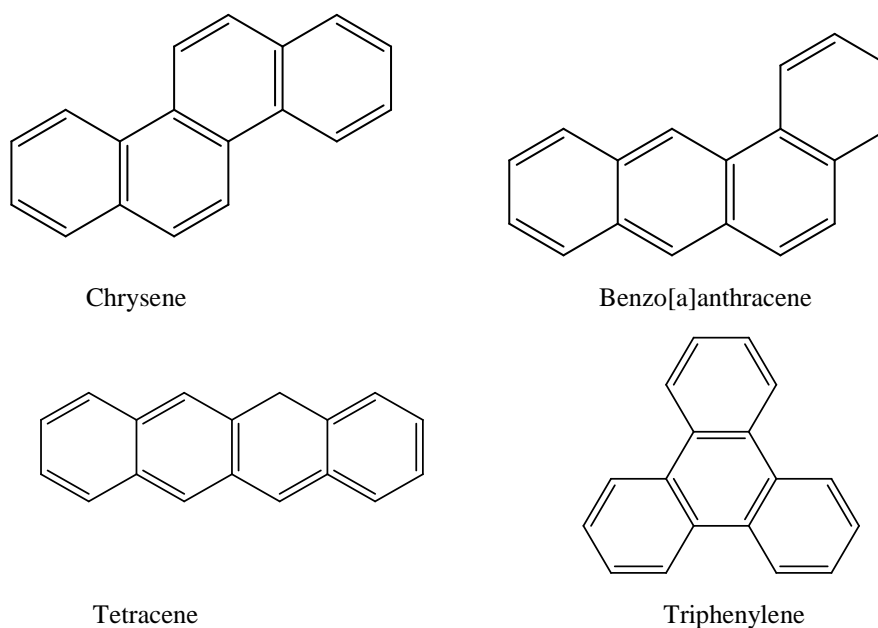


Figure 1

Structures of chrysene and its isomers discussed above.

The Niger Delta is one of the most prolific hydrocarbon provinces of the world with an estimated reserve of about 37 billion barrels of crude oil and 180 trillion cubic feet of natural gas (Tuttle et al., 1999). Petroleum in the Niger Delta is produced from sandstone and unconsolidated sands predominantly in the Agbada formation (Tuttle et al., 1999). However, several directional trends form an “oil-rich belt” having the largest field and the lowest gas to oil ratio (Ejedawe et al., 1984; Evamy et al., 1978; Doust and Omatsola, 1990). The belt extends from the northwest offshore area to the southeast offshore and along a number of north-south trends. It roughly corresponds to the transition between continental and oceanic crust and is within the axis of maximum sedimentary thickness. This hydrocarbon distribution was originally attributed to timing of trap formation relative to petroleum migration. The insight about the source and thermal maturity of crude oils and source rocks can help characterize the hydrocarbons in terms of possible communication between different horizons and describe their migration pattern within the basin.

Chrysene and its derivatives have not been reported before in Niger Delta oils and rock extracts. In the present study, the occurrence and distributions of chrysene, methylchrysenes, benzo[a]anthracene, and methylbenzo[a]anthracenes in the oils and rock extracts were investigated by gas chromatography-mass spectrometry (GC-MS) to understand the source and maturity of the oils and source rocks in the basin.

2. Geological and stratigraphic setting

Niger delta is a sedimentary basin situated in the re-entrant of the Gulf of Guinea, West Africa. The sub-aerial portion of the Niger Delta covers approximately 75,000 km² and stretches about 200 km from the apex to mouth. The total sedimentary prism encompasses 140000 km², with a maximum stratigraphic thickness of about 12 km (Whiteman, 1982). The stratigraphy of the thick sedimentary sequence is divided into three lithostratigraphic units, namely the Akata, Agbada, and Benin formations (Short and Stauble, 1967).

The uppermost unit, the Benin formation, which ranges from Oligocene to recent in age, comprises continental/fluviatile sands, gravels, and backswamp deposits up to a thickness of 2500 m. These are underlain by the Agbada formation of paralic, brackish to marine, coastal, and fluvio-marine deposits. These are mainly interbedded sandstones and shale with minor lignite organized into coarsening upward "offlap" cycles. Underlying this unit is the Akata formation, ranging in age from Paleocene to Miocene, which mainly consists of overpressure shales deposited under fully marine conditions.

The depobelts are partitioned into 6-7 east-west bound blocks corresponding to discrete periods of the deltas evolutionary history starting from the oldest in the north, northern delta, to the youngest offshore, in the south (Doust and Omatsola, 1990). It is believed that each depobelt constitutes a more or less autonomous unit with respect to sedimentation, structural deformation, and hydrocarbon generation and accumulation (Evamy et al., 1978). Available source rocks in the basin exist mainly in the lower parts of the paralic sequence (Agbada formation) and in the uppermost strata of the continuous marine shale (Akata formation; Evamy et al., 1978; Ekweozor and Daukoru, 1994). The hydrocarbon habitat of the Niger Delta is mostly the sandstone reservoir of the Agbada formation, where oil and gas are usually trapped in rollover anticlines associated with growth faults.

3. Experimental

3.1 Samples

41 crude oil samples were collected at different depths in five wells from five fields in the Northern and offshore Niger Delta basin. 21 rock samples from the three wells were also selected and analyzed. Figure 2 shows the Niger Delta stratigraphic depobelts and the sample locations of the studied samples.

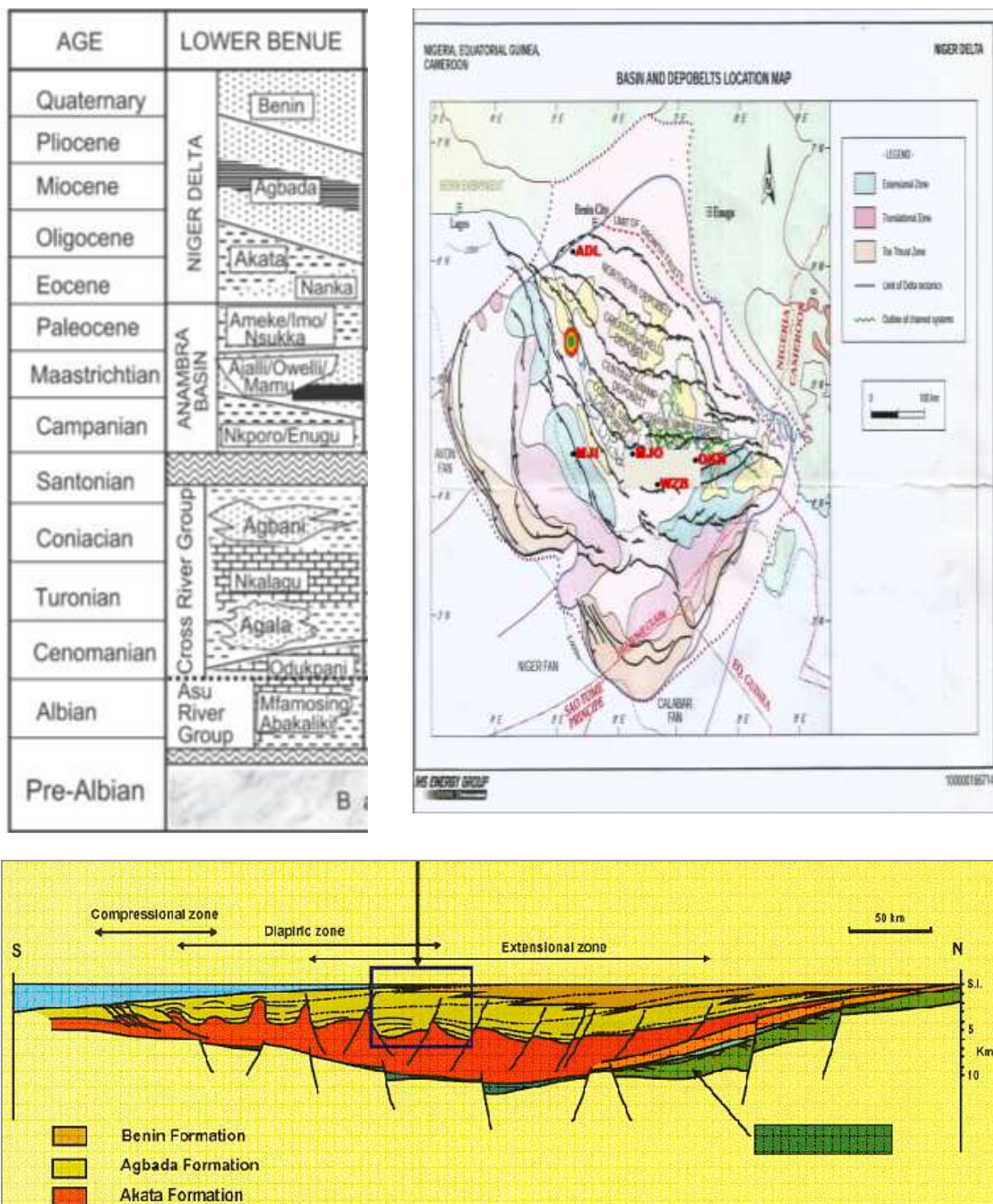


Figure 2
Niger Delta stratigraphy, depobelts and sample locations (after Ekweozor and Daukoru, 1994).

3.2 Sample preparation

The rock samples were crushed with agate mortar and powdered to less than a 100-mesh size prior to extraction.

3.3 Extraction and analysis

About 50 gr. powdered rock samples were extracted in batches in a Soxhlet apparatus with 400 ml dichloromethane and methanol (93:7, vol.:vol.) for 72 hrs. The oil samples and rock extracts were separated into saturated and aromatic hydrocarbon fractions using silica gel/alumina chromatography columns eluted with n-hexane and dichloromethane:n-hexane (2:1, vol.:vol.) respectively (Li et al., 2012b).

The GC-MS analyses of the saturate and aromatic fractions were performed on an Agilent 5975i gas chromatography (GC) equipped with an HP-5MS (5% phenylmethylpolysiloxane) fused silica capillary column (60 m x 0.25 mm i.d., x 0.25 μ m film thickness) coupled to an Agilent 5975i mass spectrometry (MS) (State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, Beijing, China). The GC operating conditions are as follows: the oven temperature was held isothermally at 80 °C for 1 min, ramped to 310 °C at a rate of 3 °C/min, and held isothermal for 16 min (Li et al., 2012a, 2012b, 2012c). Helium was used as the carrier gas at a constant flow rate of 1.2 mL/min. The MS was operated in the electron impact (EI) mode at 70 eV, an ion source temperature of 250 °C and an injector temperature of 285 °C. The identification and elution order of chrysene and its derivatives were determined by comparing their mass spectra and relative retention times in the corresponding mass chromatograms with those reported in literature (Lee et al., 1979; Vassilaros et al., 1982; Kruge, 2000; Li et al., 2012b). The quantification of chrysene and its derivatives were performed using pyrene-d10 (molecular formula: C₁₆D₁₀; molecular weight: 212.31; purity: 98%; State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, Beijing, China) in the rock extracts.

Table 1
Peak identification of the compounds discussed in the text.

Peak	Compound
BaA	Benzo[a]anthracene
Chy	Chrysene
2-MBaA	2-methylbenzo[a]anthracene
9-MBaA	9-methylbenzo[a]anthracene
3-MChy	3-methylchrysene
2-MChy	2-methylchrysene
6-MChy	6-methylchrysene
1-MChy	1-methylchrysene

4. Results and discussion

4.1. Occurrence and distributions of chrysene and its derivatives

The m/z 228 and 242 mass chromatograms showing the distributions of chrysene and its derivatives in the crude oils and rock samples are depicted in Figure 3, and the corresponding peak identities are listed in Table 1. The crude oils and the rock samples are characterized by the predominance of chrysene over benzo[a]anthracene (Figures 3 and 4). The dominance of chrysene over benzo[a]anthracene has been reported in crude oils and rock from the cratonic region of the Tarim basin NW China (Li et al., 2012b). Among the methylchrysene and methylbenzo[a]anthracene isomers in the crude oils, 3-methylchrysene is the dominant compound, while 2-methylbenzo[a]anthracene (2-MBaA) is available in the least quantities (Figure 4). The predominance of 3-methylchrysene over the other isomers of methylchrysene has been reported in Ordovician crude oils from cratonic region of the Tarim basin NW China (Li et al.,

2012b) and sediment extracts (Garrigues et al., 1988; Kruge, 2000). In the rock samples, 3-methylchrysene and 1-methylchrysene are detected in higher amounts compared to the other compounds present in the m/z 242 mass chromatogram (Figure 3, Table 2). This observation is consistent with the result reported in marine shale by Li et al. (2012b).

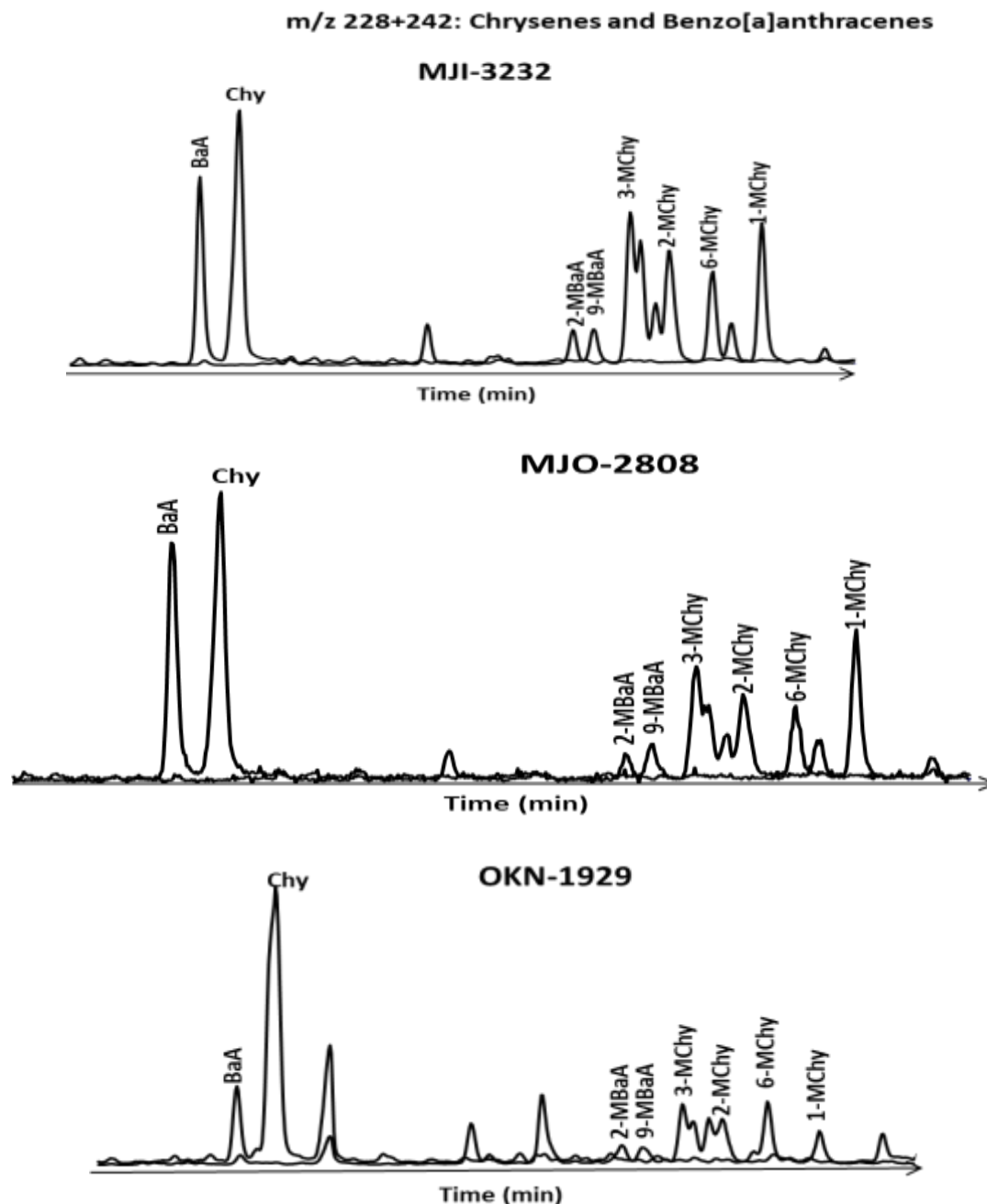


Figure 3

m/z 228+242 mass chromatograms showing the distributions of chrysene, methylchrysenes, and their isomers in source rock extracts from Niger Delta.

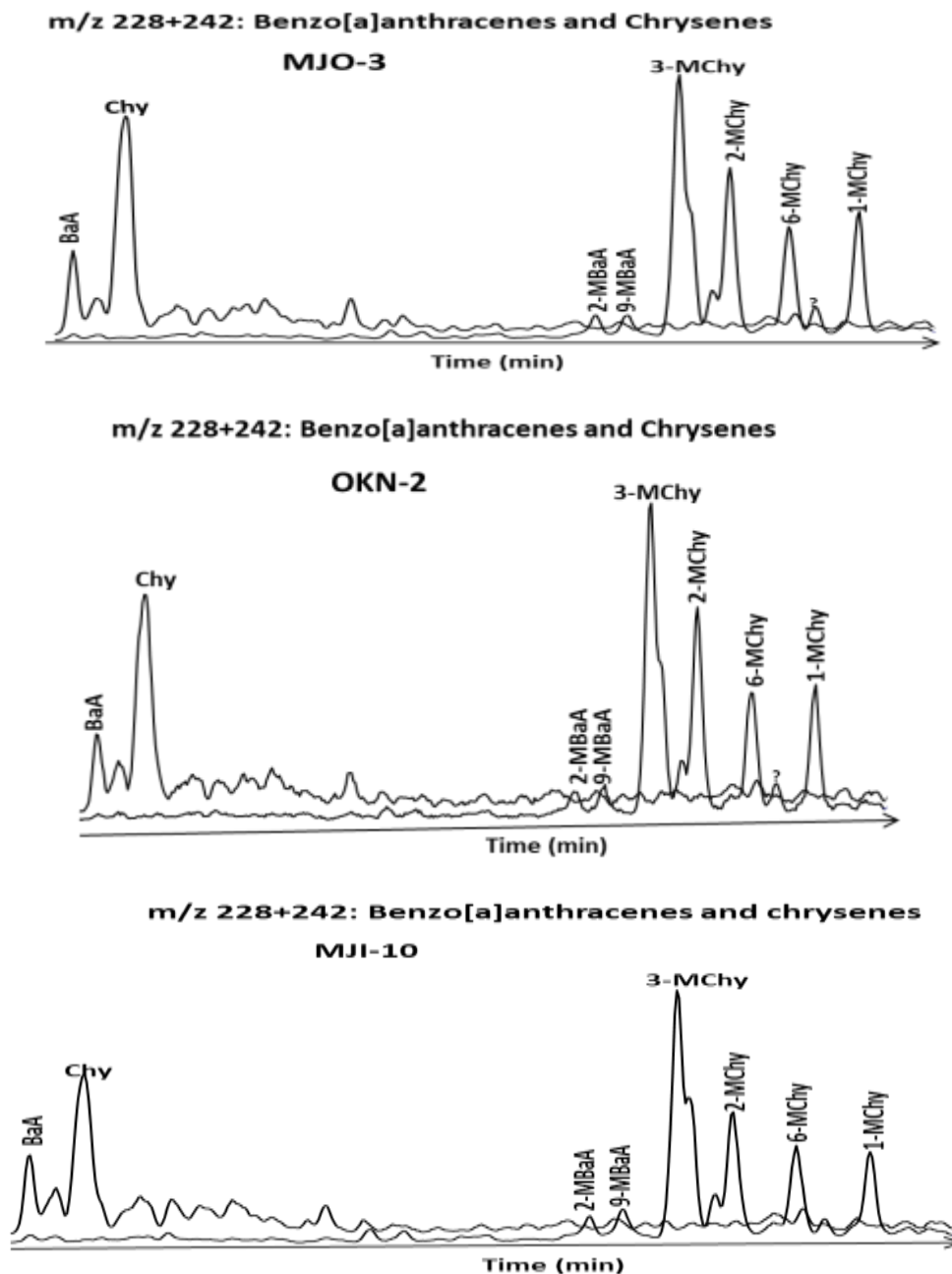


Figure 4

m/z 228+242 mass chromatograms showing the distributions of chrysene, methylchrysenes, and their isomers in crude oil samples from Niger Delta.

4.2. Source and thermal maturity status of Niger Delta source rocks based on the distributions of chrysene and its derivatives

The occurrence of chrysene and its isomers in the rock samples may be due to the degradation products of hopanes by the cleavage of ring E and successive aromatization from ring D to ring A (Borrego et al., 1997) or terrestrial contribution to the source rock organic matter (Jingui et al., 2005). Therefore, the BaA/(BaA+Chy) and MBaA/2-MChy values of the rock samples range from 0.13 to 0.42 and from 0.18 to 0.79 respectively (Table 2), indicating mixed organic sources.

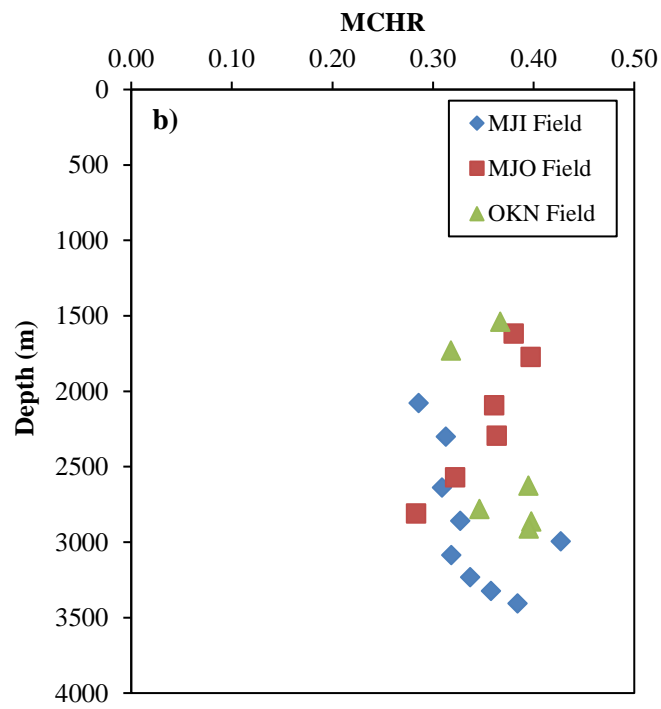
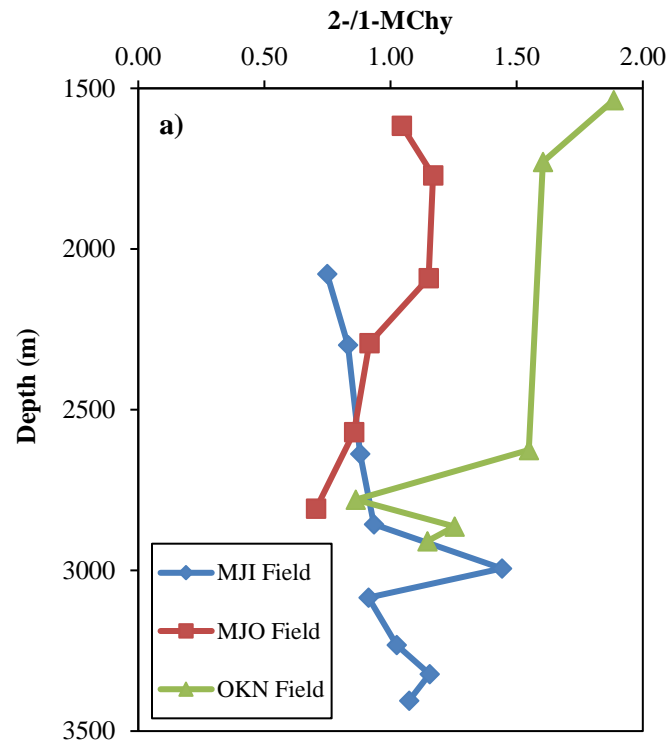
Kruger (2000) and Li et al. (2012b) proposed MCHR ($2\text{-MC}/(\text{MBaA}+6\text{-MC}+2\text{-MC}+1\text{-MC})$) and $2\text{-MChy}/1\text{-MChy}$ as potential thermal maturity indicators. Li et al. (2012b) observed that the 2-methylchrysene to 1-methylchrysene ratio keeps a nearly constant value by increasing maturity at the low maturity stages, and it abruptly increases at the onset of intense C_{15+} hydrocarbon generation. The MCHR and $2\text{-MChy}/1\text{-MChy}$ values of the source rocks range from 0.29 to 0.40 and from 0.75 to 1.88 respectively (Table 2). These values show that the source rocks are within immature to early mature maturity status. The MCHR and $2\text{-MChy}/1\text{-MChy}$ values show no regular increase by raising the burial depth (Figures 5a and b). However, the MPI-1 and $20\text{S}/(20\text{S} + 20\text{R})$ C_{29} steranes values of the MJI and MJO rock samples show an increase by raising the burial depth (Figures 5c and d). The vitrinite reflectance values of the rock extracts range from 0.29 to 0.58% (Table 2), confirming an immature to early mature status already inferred from the chrysene maturity-based parameters in the rock extracts.

Table 2

The absolute concentrations of chrysene and methylchrysene isomers and the related parameters of the source rock extracts from Niger Delta basin, Nigeria.

Field	Depth (m)	Chrysene						$20\text{S}/(20\text{S}+20\text{R})$ C_{29}	MPI-1	MCHR	$2\text{-}/1\text{-Mch}$	BaA/ (BaA+Chy)	MBaA/ 2-Mch	Ro (%)
		$\mu\text{g/g C}_{\text{org}}$	$\mu\text{g/g C}_{\text{org}}$	$\mu\text{g/g C}_{\text{org}}$	$\mu\text{g/g C}_{\text{org}}$	$\mu\text{g/g C}_{\text{org}}$	$\mu\text{g/g C}_{\text{org}}$							
MJI	2079-2098	0.04	0.04	0.02	0.01	0.08	0.15	0.25	0.29	0.75	0.31	0.79	0.29	
MJI	2299-2308	0.10	0.13	0.04	0.03	0.20	0.15	0.25	0.31	0.83	0.33	0.62	0.33	
MJI	2637-2655	0.06	0.11	0.04	0.03	0.14	0.21	0.22	0.31	0.88	0.42	0.74	0.4	
MJI	2857-2875	0.06	0.16	0.03	0.03	0.12	0.29	0.37	0.33	0.93	0.38	0.57	0.41	
MJI	2994-3012	0.17	0.47	0.03	0.02	0.23	0.30	0.54	0.43	1.44	0.20	0.23	0.43	
MJI	3085-3104	0.06	0.10	0.04	0.03	0.12	0.40	0.36	0.32	0.91	0.40	0.60	0.44	
MJI	3232-3250	0.10	0.24	0.05	0.04	0.20	0.46	0.45	0.34	1.02	0.37	0.55	0.37	
MJI	3323-3332	0.23	0.49	0.08	0.07	0.42	0.52	0.46	0.36	1.15	0.31	0.51	0.46	
MJI	3405-3424	0.29	0.43	0.06	0.03	0.50	0.48	0.62	0.38	1.07	0.15	0.24	0.58	
MJO	1616-1707	0.13	0.31	0.02	0.02	0.22	0.16	0.23	0.38	1.04	0.19	0.27	0.3	
MJO	1771-1872	0.86	2.63	0.08	0.08	0.98	0.41	0.31	0.40	1.17	0.13	0.18	0.35	
MJO	2091-2101	0.37	0.86	0.10	0.09	0.57	0.21	0.21	0.36	1.15	0.28	0.43	0.38	
MJO	2293-2366	0.20	0.35	0.08	0.03	0.36	0.13	0.47	0.36	0.92	0.26	0.33	0.35	
MJO	2570-2588	0.14	0.30	0.04	0.04	0.27	0.19	0.38	0.32	0.85	0.31	0.51	0.4	
MJO	2808-2817	0.11	0.22	0.06	0.05	3.00	0.38	0.35	0.28	0.70	0.41	0.72	0.43	
OKN	1537-1555	0.26	0.11	0.09	0.05	0.49	0.18	0.16	0.37	1.88	0.20	0.69	0.23	
OKN	1729-1747	0.38	0.17	0.07	0.08	0.49	0.14	0.14	0.32	1.60	0.15	0.77	0.23	
OKN	2625-2643	0.30	0.35	0.09	0.06	0.34	0.30	0.12	0.39	1.55	0.24	0.50	0.25	
OKN	2780-2799	0.18	0.33	0.07	0.04	0.44	0.24	0.16	0.35	0.86	0.29	0.41	0.29	
OKN	2863-2881	0.12	0.51	0.03	0.03	0.29	0.34	0.18	0.40	1.25	0.27	0.22	0.31	
OKN	2909-2927	0.33	0.87	0.12	0.07	0.67	0.28	0.22	0.40	1.15	0.30	0.28	0.27	

* Mch: methylchrysene; C_{29} : C_{29} steranes; C_{org} : organic carbon; MPI-1: methylphenanthrene index-1; MCHR: methylchrysene ratio; Ro: Vitrinite reflectance.



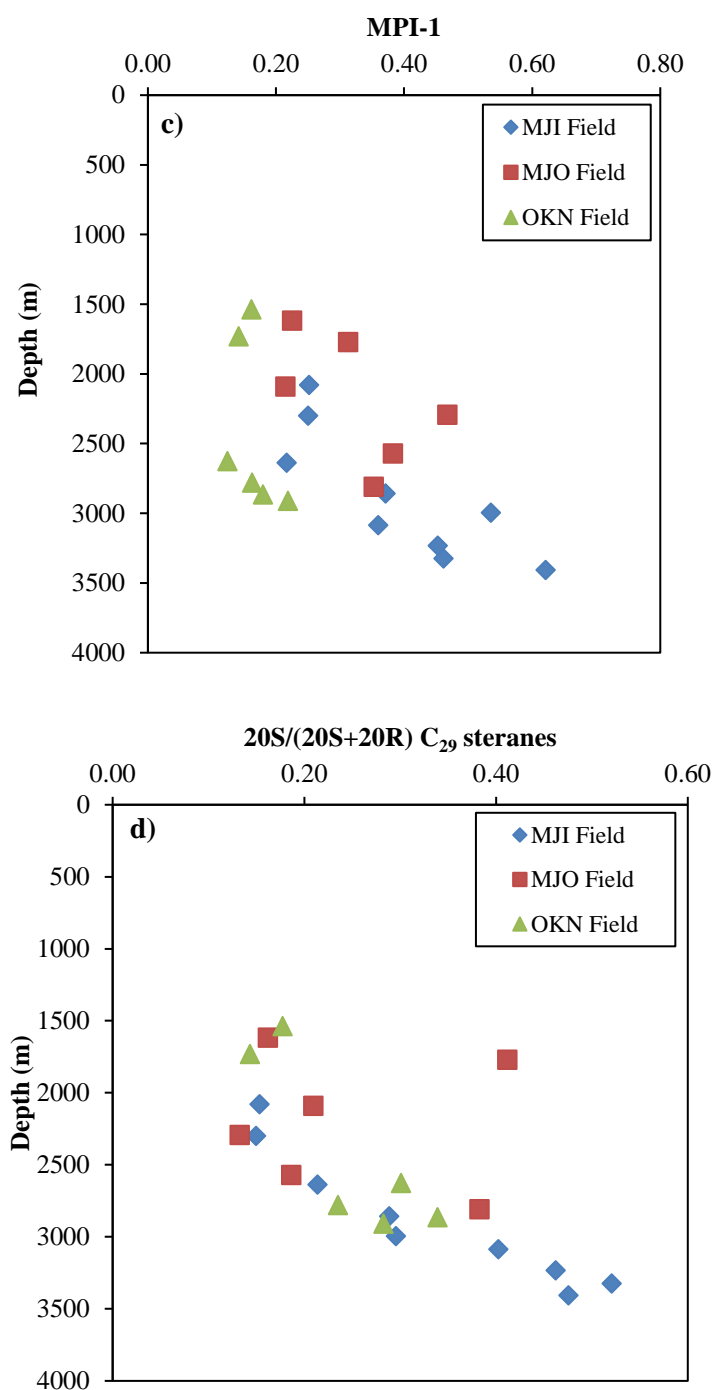


Figure 5

Plots of source rock maturity parameters versus increasing burial depth.

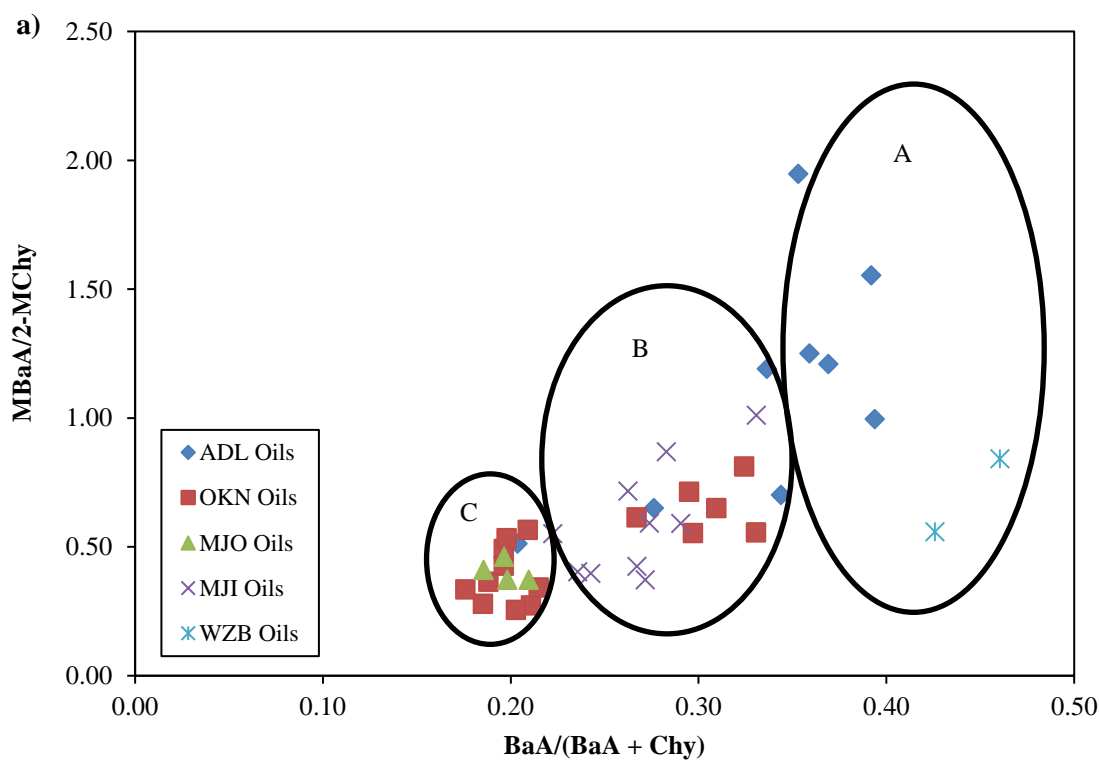
4.3. The absolute concentrations of chrysene and methylchrysenes in Niger Delta source rock extracts

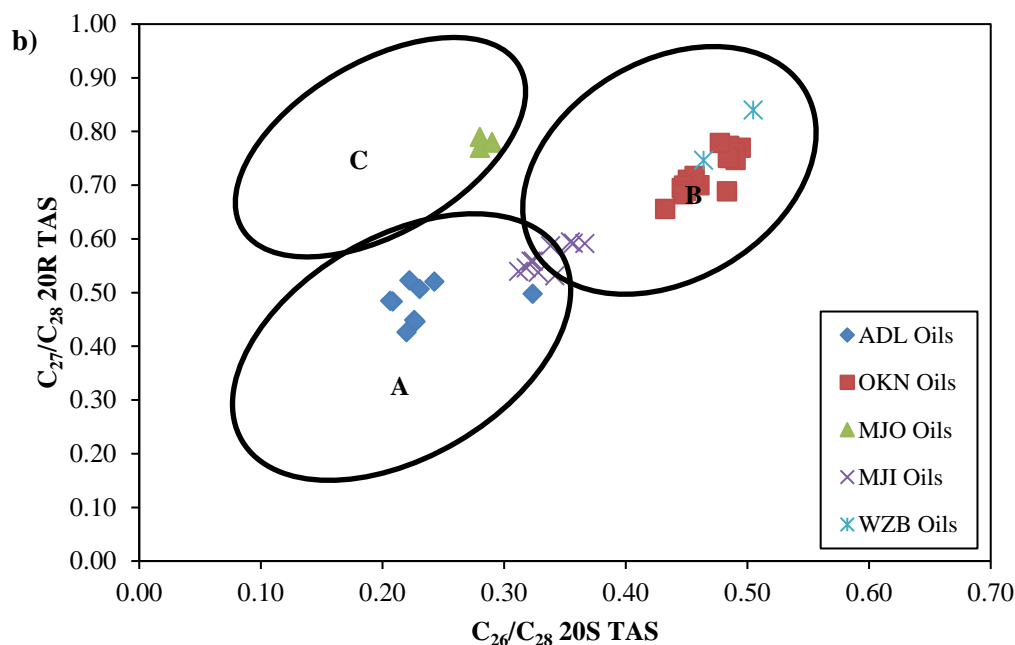
Table 3 shows the absolute concentrations of chrysene and methylchrysenes in Niger Delta source rock extracts. The absolute concentrations of chrysene and methylchrysenes computed for the rock samples are generally low (Table 2), and the low absolute concentration values may be associated with the low maturity status of the rock samples. The absolute concentrations of chrysene and methylchrysenes have

been reported to be low at the immature to low maturity stages of sedimentary rock extracts (Garrigues et al., 1988; Kruge, 2000; Li et al., 2012b).

4.4. The origin and thermal maturity status of Niger Delta crude oils based on the distributions of chrysene and its derivatives

The BaA/(BaA+Chy) and MBaA/2-MChy values of the oil samples range from 0.19 to 0.46 and from 0.27 to 1.55 respectively (Table 3), indicating that the oil is derived from a mixed organic origin (terrestrial and marine) (Borrego et al., 1997; Jingui et al., 2005; Li et al., 2012b). The plot of BaA/(BaA + Chy) versus MBaA/MChy ratios is shown in Figure 6a. This plot has been used to distinguish two petroleum systems in oils from the cratonic region of Tarim basin, China (Li et al., 2012b). The plots were grouped the Niger Delta crude oils into three classes (Figure 6a). However, the plots of C₂₆/C₂₈ 20S triaromatic steroids (TAS) versus C₂₇/C₂₈ 20R triaromatic steroids (TAS) gave an answer different from those of BaA/(BaA + Chy) versus MBaA/MChy ratios (Figure 6b).



**Figure 6**

Cross plots of a) MBaA/2-MChy versus BaA/(BaA + Chy) and b) C₂₆/C₂₈ 20S TAS versus C₂₇/C₂₈ 20R TAS for Niger Delta crude oils.

The MCHR and 2-MChy/1-MChy values computed for the crude oils range from 0.20 to 0.43 and from 0.70 to 1.84 respectively (Table 3). These values show that the crude oils are within an oil generative window (Garrigues et al., 1988; Krugé, 2000; Li et al., 2012b). The plots of the MCHR and 2-MChy/1-MChy ratio values against the reservoir depth lack any significant trend, indicating that these parameters increase irregularly versus reservoir depths (Figure 7). This observation is further confirmed by the plots of well-established saturate (20S/(20S + 20R) C₂₉ steranes) and aromatic (MPI-1) maturity parameters (Figure 7).

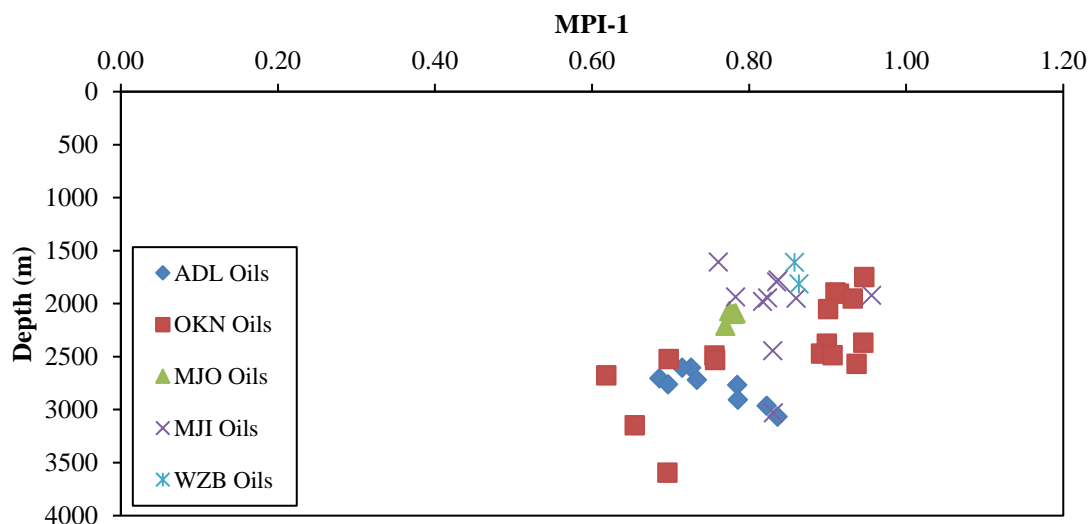
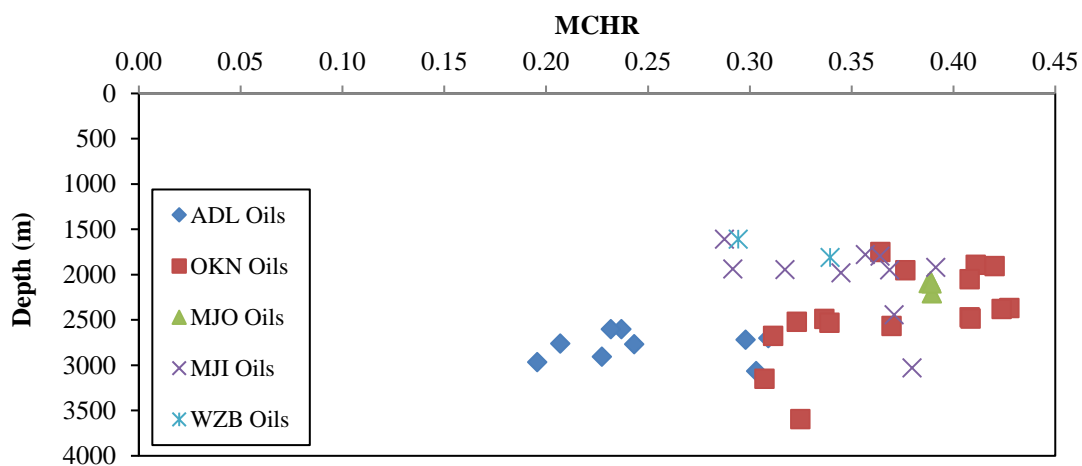
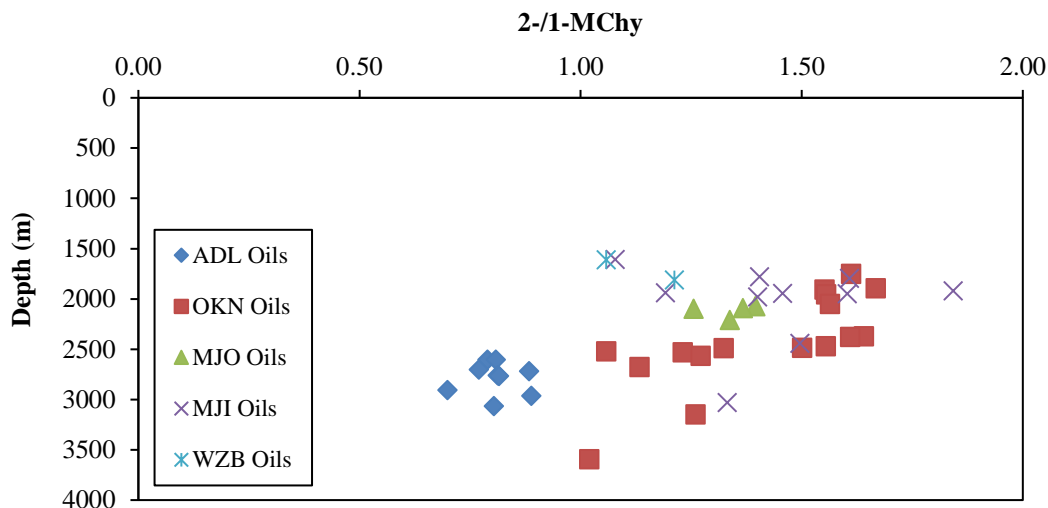
Table 3

Selected geochemical parameters based on the relative concentrations of chrysene, benzo[a]anthracene, and their methylated homologues for the crude oils from Niger Delta basin.

Sample	Depth (m)	BaA/ (BaA+Chy)	MBaA/ 2-Mchy	C ₂₇ /C ₂₈ 20R TAS	C ₂₆ /C ₂₈ 20S TAS	20S/20S+20R C ₂₉	MPI-1	MCHR	2-/1-Mchy
ADL1	2602-2607	0.39	1.00	0.48	0.21	0.41	0.73	0.24	0.79
ADL2	2602-2607	0.39	1.55	0.48	0.21	0.40	0.71	0.23	0.81
ADL3	2702-2704	0.20	0.51	0.50	0.32	0.40	0.69	0.31	0.77
ADL4	2718-2720	0.28	0.65	0.51	0.23	0.44	0.73	0.30	0.88
ADL5	2759-2763	0.35	1.95	0.52	0.24	0.43	0.70	0.21	0.81
ADL6	2766-2770	0.37	1.21	0.45	0.23	0.45	0.78	0.24	0.82
ADL7	2905-2908	0.34	1.19	0.52	0.22	0.45	0.79	0.23	0.70
ADL8	2964-2967	0.36	1.25	0.45	0.23	0.44	0.82	0.20	0.89
ADL9	3064-3052	0.34	0.70	0.43	0.22	0.47	0.84	0.30	0.80
OKN1	1749-1750	0.20	0.49	0.71	0.45	0.36	0.95	0.36	1.61

Sample	Depth (m)	BaA/ (BaA+Chy)	MBaA/ 2-Mchy	C ₂₇ /C ₂₈ 20R TAS	C ₂₆ /C ₂₈ 20S TAS	20S/20S+20R C ₂₉	MPI-1	MCHR	2-/1-Mchy
OKN2	1892-1895	0.21	0.27	0.77	0.49	0.40	0.91	0.41	1.67
OKN3	1905-1907	0.19	0.37	0.77	0.48	0.40	0.91	0.42	1.55
OKN4	1952-1955	0.20	0.53	0.69	0.45	0.33	0.93	0.38	1.56
OKN5	2050-2059	0.20	0.25	0.76	0.49	0.41	0.90	0.41	1.56
OKN6	2369-2555	0.19	0.28	0.75	0.49	0.39	0.95	0.43	1.64
OKN7	2377-2672	0.21	0.34	0.75	0.49	0.43	0.90	0.42	1.61
OKN8	2469-2782	0.18	0.34	0.75	0.48	0.39	0.89	0.41	1.55
OKN9	2485-2793	0.20	0.43	0.78	0.48	0.41	0.91	0.41	1.50
OKN10	2489-2491	0.33	0.56	0.70	0.46	0.36	0.76	0.34	1.32
OKN11	2521-2523	0.32	0.81	0.72	0.46	0.33	0.70	0.32	1.06
OKN12	2530-2537	0.31	0.65	0.70	0.45	0.37	0.76	0.34	1.23
OKN13	2566-2568	0.21	0.57	0.69	0.45	0.35	0.94	0.37	1.27
OKN14	2677-2683	0.30	0.55	0.68	0.45	0.41	0.62	0.31	1.13
OKN15	3148-3154	0.29	0.71	0.69	0.48	0.38	0.65	0.31	1.26
OKN16	3593-3605	0.27	0.61	0.66	0.43	0.41	0.70	0.32	1.02
MJO1	2207-2216	0.20	0.37	0.70	0.44	0.45	0.77	0.39	1.34
MJO2	2070-2081	0.19	0.41	0.70	0.44	0.46	0.77	0.39	1.40
MJO3	2091-2104	0.21	0.37	0.70	0.45	0.45	0.78	0.39	1.37
MJO4	2096-2101	0.20	0.46	0.71	0.44	0.45	0.78	0.39	1.26
MJI1	1607-1611	0.33	1.01	0.59	0.35	0.28	0.76	0.29	1.08
MJI2	1777-1779	0.27	0.59	0.56	0.32	0.40	0.84	0.36	1.40
MJI3	1795-1797	0.27	0.42	0.56	0.32	0.36	0.83	0.36	1.61
MJI4	1920-1921	0.27	0.37	0.55	0.32	0.37	0.96	0.39	1.84
MJI5	1936-2342	0.28	0.87	0.59	0.36	0.35	0.78	0.29	1.19
MJI6	1944-1947	0.29	0.59	0.54	0.33	0.34	0.82	0.32	1.46
MJI7	1948-1950	0.24	0.40	0.54	0.31	0.39	0.86	0.37	1.60
MJI8	1979-2398	0.26	0.72	0.59	0.34	0.36	0.82	0.34	1.40
MJI9	2442-2444	0.24	0.40	0.53	0.34	0.38	0.83	0.37	1.50
MJI10	3030-3036	0.22	0.55	0.59	0.37	0.38	0.83	0.38	1.33
WZB1	1610-2647	0.46	0.84	0.84	0.50	0.42	0.86	0.29	1.06
WZB2	1811-1957	0.43	0.56	0.75	0.46	0.37	0.86	0.34	1.21

Note: BaA/(BaA + Chy), Benzo[a]anthracene/(benzo[a]anthracene + Chrysene); (2+9)-MBaA/(2-MChy), (2+9)-methylbenzo[a]anthracene/2-methylchrysene.



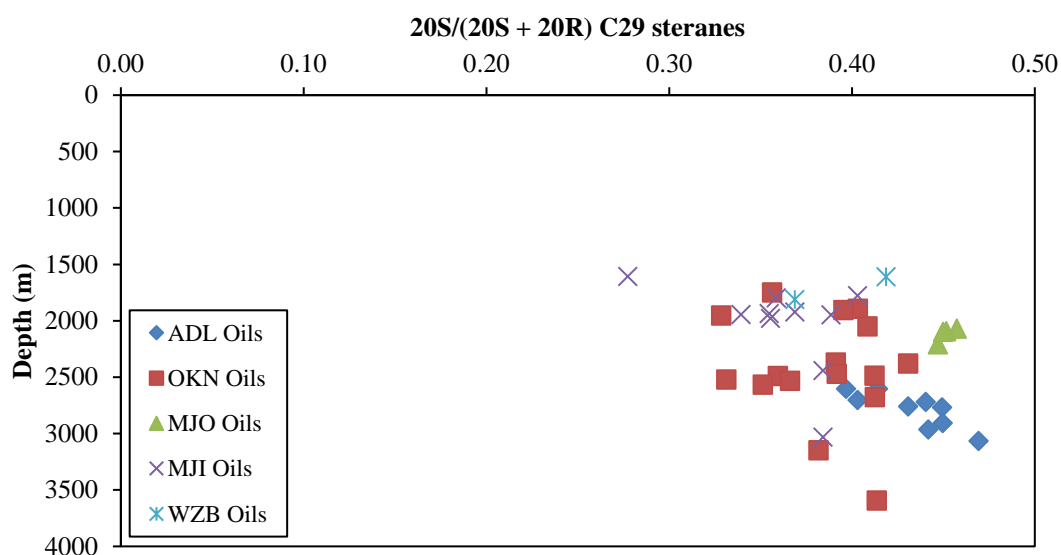


Figure 7

Plots of crude oils maturity parameters versus increasing burial depth.

5. Conclusions

The occurrence and distributions of chrysene and its derivatives in the Niger Delta crude oils and source rocks were investigated by gas chromatography-mass spectrometry (GC-MS). The geochemical characterization of the oils and their presumed source rocks based on chrysene and its derivatives confirmed that the oils have been sourced from source rocks with higher thermal maturity than the analyzed source rocks. The distributions and abundance of the chrysene and its derivatives in the oils permitted the grouping of Niger Delta oils into three families although this grouping disagreed with already established aromatic source parameters. The crude oils and the source rocks were characterized by the predominance of chrysene over benzo[a]anthracene. Among the C₁ chrysenes, 3-methylchrysene occurred in a higher abundance than the other isomers in the crude oils and source rocks. This study indicates that chrysene and its derivatives are useful molecular indicators in petroleum organic geochemistry in Niger Delta basin.

Acknowledgements

The authors thank the Department of Petroleum Resources of Nigeria and Chevron Nigeria Limited for providing the crude oils and rock samples. A.B. Ogbesejana appreciate Cheng Quan and Zhao Jiang for their assistance in the laboratory works.

Funding

The authors gratefully acknowledge the State Key Laboratory of Petroleum Resources and Prospecting, College of Geosciences, China University of Petroleum, Beijing, China for granting A. B. Ogbesejana an international visiting research fellowship towards this research work.

Nomenclature

20S/20S+20R	C ₂₉ Steranes maturity indicator
BaA	Benzo[a]anthracene

Chy	Chrysene
MBaA	Methylbenzo[a]anthracene
MCHR	Methylchrysene ratio
MChy	Methylchrysene
MPI-1	Methylphenanthrene index 1
TAS	triaromatic steroids

Reference

- Borrego, A. G., Blanco, C. G., and Pöttmann, W., Geochemical Significance of the Aromatic Hydrocarbon Distribution in the Bitumens of the Puertollano Oil Shales, Spain, *Organic Geochemistry* Vol. 26, p. 219-228, 1997.
- Budzinski, H., Garrigues, P., Radke, M., Connan, J., and Oudin, J. L., Thermodynamic Calculations on Alkylated Phenanthrenes: Geochemical Applications to Maturity and Origin of Hydrocarbons. *Organic Geochemistry*, Vol. 20, p. 917-926, 1993a.
- Budzinski, H., Garrigues, P., Radke, M., Connan, J., Rayez, J. C., and Rayez, M. T., Use of Molecular Modeling as a Tool to Evaluate Thermodynamic Stability of Alkylated Polycyclic Aromatic Hydrocarbons, *Energy and Fuels*, Vol. 7, p. 505-511, 1993b.
- Doust, H. and Omatsola, E., Niger Delta Divergent/Passive Margin Basins, *AAPG Bull. Mem*, Vol. 45, p. 201-238, 1990.
- Drosos, J. C., Viola-Rhenals, M., and Vivas-Reyes, R., Quantitative Structure-retention Relationships of Polycyclic Aromatic Hydrocarbons Gas Chromatographic Retention Indices, *Journal of Chromatography A*, Vol. 1217, p. 4411-4421, 2010.
- Ejedawe, J. E., Coker, S. J. L., Lambert-Aikhionbare, D. O., Alofe, K. B., and Adoh, F.O., Evolution of Oil-generative Window and Oil and Gas Occurrence in Tertiary Niger Delta Basin, *AAPG* Vol. 68, p. 1744-1751, 1984.
- Evamy, B. D., Haremboure, J., Kamerling, P., Knaap, W. A., Molloy, F. A., and Rowlands, P. H., Hydrocarbon Habitat of Tertiary Niger Delta, *AAPG Bull*, Vol. 62, p. 277-298, 1978.
- Ekweozor, C. M. and Daukoru, C. M., Northern Delta Depobelt Portion of The Akata-Agbada Petroleum System, Niger Delta, Nigeria, in *The Petroleum System from Source to Trap*, AAPG Memoir, Vol. 60, p. 599-613, 1994.
- Fang, R., Li, M., Wang, T. G., Zhang, L., and Shi, S., Identification and Distribution of Pyrene, Methylpyrenes and their Isomers in Rock Extracts and Crude Oils, *Organic Geochemistry*, Vol. 83-84, p. 65-76, 2015.
- Garrigues, P., De Sury, R., Angelin, M. L., Bellocq, J., Oudin, J. L., and Ewald, M., Relation of the Methylated Aromatic Hydrocarbon Distribution Pattern to the Maturity of Organic Matter in Ancient Sediments from Mahakam Delta, *Geochimica Et Cosmochimica Acta*, Vol. 52, p. 375-384, 1988.
- Garrigues, P., Oudin, J. L., Parlanti, E., Monin, J. C., Robcis, S., and Bellocq, J., Alkylated Phenanthrene Distribution in Artificially Matured Kerogens from Kimmeridge Clay and the Brent Formation (North Sea), *Organic Geochemistry*, Vol. 16, No. 1-3, p. 167-173, 1990.

- Gilmour, I., Structural and Isotopic Analysis of Organic Matter in Carbonaceous Chondrites, in: *Treatise on Geochemistry*, Oxford, p. 269-290, 2003.
- Grice, K., Nabbefeld, B., and Maslen, E., Source and Significance of Selected Polycyclic Aromatic Hydrocarbons in Sediments (Hovea-3 Well, Perth Basin, Western Australia) Spanning the Permian-Triassic Boundary, *Organic Geochemistry*, Vol. 38, p. 795-1803, 2007.
- Hanson, A. D., Zhang, S., Moldowan, J. M., Liang, D., and Zhang, B., Molecular Geochemistry of the Tarim Basin, Northwest China, *American Association of Petroleum Geologists Bulletin* 84, 1109-1128.
- Hu, L., Fuhrmann, A., Poelchau, H.S., Horsfield, B., Zhang, Z., Wu, T., Chen, Y., and Li, J., Numerical Simulation of Petroleum Generation and Migration in the Qingshui Sag, Western Depression of the Liaohe Basin, Northeast China, *American Association of Petroleum Geologists Bulletin* Vol.89, p. 1629-1649, 2005.
- Huang, H., Pearson, M.J., Source Rock Paleoenvironments and Controls on the Distribution of Dibenzothiophenes in Lacustrine Crude Oil, Bohai Bay Basin, Eastern China, *Organic Geochemistry*, Vol. 30, p.1455-1470, 1999.
- Jiang, C., Alexander, R, Kagi, R. I., and Murray, A. P., Polycyclic Aromatic Hydrocarbons in Ancient Sediments and their Relationships to Paleoclimate, *Organic Geochemistry*, Vol. 29, p. 1721-1735, 1998.
- Killops, S. D. and Massoud, M. S., Polycyclic Aromatic Hydrocarbons of Pyrolytic Origin in Ancient Sediments: Evidence for Jurassic Vegetation Fires, *Organic Geochemistry*, Vol. 18, p. 1-7, 1992
- Koopmans, M. P., De Leeuw, J. W., Lewan, M. D., and Sinninghe Damste, J. S., Impact of Dia- and Catagenesis on Sulphur and Oxygen Sequestration of Biomarkers as Revealed by Artificial Maturation of Immature Sedimentary Rock, *Organic Geochemistry*, Vol. 25, p. 391-426, 1996.
- Kovats, E., Gas Chromatographische Charakterisierung Organischer, Verbindungen Teil 1: Retentionindices Aliphatischer Halogenide, Alkohole, Aldehyde and Ketone, *Helvetica Chimica Acta*, Vol. 41, p. 1915-1932, 1958.
- Kruege, A.M., Determination of Thermal Maturity and Organic Matter Type by Principal Components Analysis of the Distributions of Polycyclic Aromatic Compounds, *International Journal of Coal Geology*, Vol. 43, p. 27-51, 2000.
- Laflamme, R. E. and Hites, R. E., The Global Distribution of Polycyclic Aromatic Hydrocarbons in Recent Sediments, *Geochimica Et Cosmochimica Acta*, Vol. 42, p. 289-303, 1978.
- Laflamme, R. E. and Hites, R. A., Tetra- and Pentacyclic, Naturally-occurring, Aromatic Hydrocarbons in Recent Sediments, *Geochimica Et Cosmochimica Acta*, Vol. 43, p. 1687-1691, 1979.
- Lee, M. L., Vassilaros, D. L., White C. M., and Novotny, M., Retention Indices for Programmed-temperature Capillary-column Gas Chromatography of Polycyclic Aromatic Hydrocarbons, *Journal of Chromatography A*, Vol. 51, p. 768-774, 1979.
- Li, M., Wang, T. G., Simoneit, B. R. T., Shi, S., Zhang, L., and Yang, F., Qualitative and Quantitative Analysis of Dibenzothiophenes, its Methylated Homologues, and Benzonaphthothiophenes in Crude Oils, Coal and Sediment Extracts, *Journal of Chromatography A*, Vol. 1233, p. 126-136. 2012a.

- Li, M., Shi, S., and Wang, T.G., Identification and Distribution of Chrysene, Methylchrysenes and their Isomers in Crude Oils and Rock Extracts, *Organic Geochemistry*, Vol. 52, p. 55-66, 2012b
- Li, M., Zhong, N., Shi, S., Zhu, L., and Tang, Y., The Origin of Trimethyldibenzothiophene and their Application as Maturity Indicators in Sediments from the Liaohe Basin, East China, *Fuel*. [Http://Dx.Doi.Org/10.1016/J.Fuel.2012.09.027](http://dx.doi.org/10.1016/j.fuel.2012.09.027), 2012c.
- Ma, A., Zhang, S., Zhang D., Liang, D., and Wang, F., Organic Geochemistry of TD-2 Well in Tarim Basin, Xinjiang Petroleum Geology, Vol. 26, p. 148-151, (In Chinese with English Abstract), 2005.
- Messenger, S., Amari, S., Gao, X., Walker, R. M., Clement, S. J., Chillier, X. D. F., Zare, R. N., and Lewis, R. S., Indigenous Polycyclic Aromatic Hydrocarbons in Circumstellar Graphite Grains from Primitive Meteorites, *Astrophysical Journal*, Vol. 501, p. 284-295, 1998.
- Mi, J., Zhang, S., Chen, J., Tang, L., and He, Z., The Distribution of the Oil Derived from Cambrian Source Rocks in Lunnan Area, the Tarim Basin, China, *Chinese Science Bulletin*, Vol. 52 (Supp. 1), p. 133-140, 2007.
- Mimura, K., Synthesis of Polycyclic Aromatic Hydrocarbons from Benzene by Impact Shock: its Reaction Mechanism and Cosmochemical Significance, *Geochimica Et Cosmochimica, Acta*, Vol. 59, p. 579-591, 1995.
- Mimura, K. and Toyama, S., Behavior of Polycyclic Aromatic Hydrocarbons at Impact Shock: its Implication for Survival of Organic Materials Delivered to the Early Earth, *Geochimica Et Cosmochimica Acta*, Vol. 69, p. 201-209, 2005.
- Modica, R., Fiume, M., Guaitani, A., and Bartosek, I., Comparative Kinetics of Benzo [A] Anthracene, Chrysene and Triphenylene in Rats after Oral Administration: I. Study with Single Compounds, *Toxicology Letters*, Vol. 18, p. 103-109, 1983.
- Moore, R. J., Thorpe, R. E., and Mohaney, C. L., Isolation of Methylchrysene from Petroleum, *Journal of The American Chemistry Society*, Vol. 75, p. 2259, 1953.
- Myers, S. R. and Flesher, J. W., Metabolism of Chrysene, 5-Methylchrysene, 6-Methylchrysene and 5, 6-Dimethylchrysene in Rat Liver Cytosol, in Vitro, and in Rat Subcutaneous Tissue, in Vivo. *Chemico-biological Interactions*, Vol. 7, p. 203-221, 1991.
- Radke, M., Organic Geochemistry of Aromatic Hydrocarbons, *Advances in Petroleum Geochemistry*, Vol. 2, p. 141-207, 1987.
- Short, K. C. and Stauble, A. J., Outline of Geology of Niger Delta. *AAPG Bull*, Vol. 51, p. 761-779. 1967.
- Tuttle, M. L. W., Charpentier, R. R., and Brownfield, M. E., Tertiary Niger Delta (Akata-Agbada) Petroleum System (No. 719201), Niger Delta Province, Nigeria, Cameroon, and Equatorial Guinea, Africa. A U.S. Geological Survey World Energy Assessment Project. [<http://Greenwood.Cr.Usgs.Gov/Energy/>](http://Greenwood.Cr.Usgs.Gov/Energy/), 1999.
- Vassilaros, D. L., Kong, R. C., Later, D. W., and Lee, M. L., Linear Retention Index System for Polycyclic Aromatic Compounds: Critical Evaluation and Additional Indices, *Journal of Chromatography A*, Vol. 252, p. 1-20, 1982.
- Whiteman, A., 1982, *Nigeria: its Petroleum Geology, Resources and Potential*: London, Graham and Trotman, 394 P.

- Yunker, M. B., Macdonald, R. W., Vingarzan, R., Mitchell, R. H., Goyette, D., and Sylvestre, S., PAHs in the Fraser River Basin: A Critical Appraisal of PAH Ratios as Indicators of PAH Source and Composition, *Organic Geochemistry*, Vol. 33, p. 489-515, 2002.
- Yunker, M. B., Macdonald, R. W., Snowdon, L. R., and Fowler, B. R., Alkane and PAH Biomarkers as Tracers of Terrigenous Organic Carbon in Arctic Ocean Sediments, *Organic Geochemistry*, Vol. 42, p. 1109-1146, 2011.
- Yunker, M. B., Mclaughlin, F. A., Fowler, M. G., and Fowler, B. R., Source Apportionment of the Hydrocarbon Background in Sediment Cores from Hecate Strait, a Pristine Sea on the West Coast of British Columbia, Canada, *Organic Geochemistry*, Vol. 76, p. 235-258, 2014.
- Zhang, S. and Huang, H., Geochemistry of Paleozoic Marine Petroleum from the Tarim Basin, NW China: Part 1, Oil Family Classification, *Organic Geochemistry*, Vol. 36, p. 1204-1214, 2005.