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

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ABSTRACT

Crude oils and source rocks from the Northern and offshore depobelts of the Niger Delta basin, Nigeria have been characterized based on the distribution of pyrene and its derivatives by gas chromatography-mass spectrometry. Moreover, the crude oils have been characterized by the dominance of pyrene over fluoranthene while fluoranthene generally predominated over pyrene in the rock samples. Also, 4-methylpyrene has been the dominant compound among the methylpyrene isomers in the crude oils and source rocks while benzo[a]fluorene (BaF) predominated over benzo[b]fluorene (BbF). The pyrene distribution shows that the crude oils and source rocks have been formed from mixed sources (terrestrial and marine) but with higher inputs from terrestrial organic matter. The maturity dependent parameters which have been computed from pyrene distributions indicate that the oils have been thermally matured while the rock samples have been within immature to early oil window maturity status. Finally, the crude oils and the sources of source rocks, and thermal maturities have been further confirmed by other well-established parameters computed from saturate and aromatic parameters and vitrinite reflectance.

At the end, it has been found out that the abundance and distribution of pyrene, and its derivatives have been found to be effective in determining the origin and thermal maturity of crude oils and source rocks in the Niger Delta Basin.

Keywords: Pyrene, Crude Oil, Source Rocks, Niger Delta, Origin, Maturity.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) such as pyrene and its derivatives are important constituents of crude oils and source rock extracts. In addition, pyrene and methylpyrenes have been studied dated back more than half a century. The occurrence of pyrene and its derivatives in recent sediments has been linked with the combustion of fossil fuel or higher plant materials [1,2,3,4] while their appearance in ancient sediments suggests microbial metabolism of fungi, higher plants, or insects [5]. Moreover, they have been unequivocally identified in crude oils and sediment extracts and applied to thermal maturity [4,6,7] and oil-oil correlation studies [4]. Moreover, it has been

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reported by many authors such as Jacob et al in 1986, Mortelmans et al in 1986, and Pahlman and Pelkonen in 1987 that pyrene (Py), methylpyrene (MPy), and fluoranthene (Fla) have potential toxicity, carcinogenicity, and mutagenicity. PAHs including pyrene have also been synthesized from benzene by impact shock waves in the laboratory experiments [8] which suggests that PAHs may be present in the interstellar medium, in atmospheres of Jovian planets, and in carbonaceous chondrites.

The Niger Delta is one of the major 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 [9]. Previous studies have shown that the Niger Delta oils were formed from the source rocks of mixed origin (terrestrial and marine) at the early stage of oil generation within the catagenesis zone [10,11]. In addition, petroleum in the Niger Delta is produced from sandstone and unconsolidated sands predominantly in the Agbada Formation [9]. However, several directional trends form an "oil-rich belt" have the largest field and lowest gas: oil ratio [12,13,14]. The belt extends from the northwest offshore area to the southeast offshore and along a number of north-south trends. In addition, it roughly corresponds to the transition between continental and oceanic crust, and it is within the axis of maximum sedimentary thickness. Also, this hydrocarbon distribution was originally attributed to the time 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 term of possible communication between different horizons; moreover, this insight can describe their migration pattern within the basin.

Pyrene and its derivatives have not been reported before in Niger Delta oils and rock extracts. In the present study, the occurrence and distribution of pyrene and its derivatives in the Niger Delta oils and rock extracts were investigated by gas chromatography-mass spectrometry (GC-MS) and applied in the source and thermal characterization of the oils and source rocks.

Geological and Stratigraphic Setting

Niger delta basin is located at the entrance of the Gulf of Guinea, West Africa. The sub-aerial portion of the Niger Delta covers approximately 75,000 km^2 and stretches about 200 km from apex to mouth. The total sedimentary prism surrounds 140000 km^2, with a highest stratigraphic thickness of about 12 km [15]. In addition, the stratigraphy of the Niger Delta sedimentary basin is partitioned into three lithostratigraphic parts: the Akata, Agbada, and Benin Formations [16].

The topmost part, the Benin Formation (Oligocene to recent in age) which is made up of continental/ fluviatile sands, gravels, and backswamp deposits up to 2500 m thick. The Agbada Formation comprises of paralic, brackish to marine, coastal, and fluvio-marine deposits. These are predominantly interstratified sandstones and shale with minor lignite organized into coarsening upward ‹offlap› cycles. Underlying this unit is the Akata Formation (Paleocene to Miocene) which consists of mainly of overpressure shales deposited under fully marine conditions.

According to [14], the Niger Delta depobelts are partitioned into 6 to 7 east-west bound blocks in consistence with the separate times of the deltas developmental background beginning from the oldest in the north, northern delta to the youngest, offshore in the south. It is assumed by Evamy in 1978 that individual depobelt comprises of more or

less independent section relative to sedimentation, structural deformation, hydrocarbon generation, and accumulation [13]. Available source rocks in the basin occur majorly in Agbada and Akata Formations [13,17]. Moreover, the hydrocarbon habitat of the Niger Delta basin is mainly in the Agbada Formation where oil and gas are usually trapped in rollover anticlines associated with growth faults.

EXPERIMENTAL PROCEDURES

Samples

Forty one crude oil samples were collected at different depth in five wells from five fields in the Northern and offshore Niger Delta basin. Twenty one rock samples from the three wells were selected and analyzed. Also, the samples locations are shown in Figure 1.

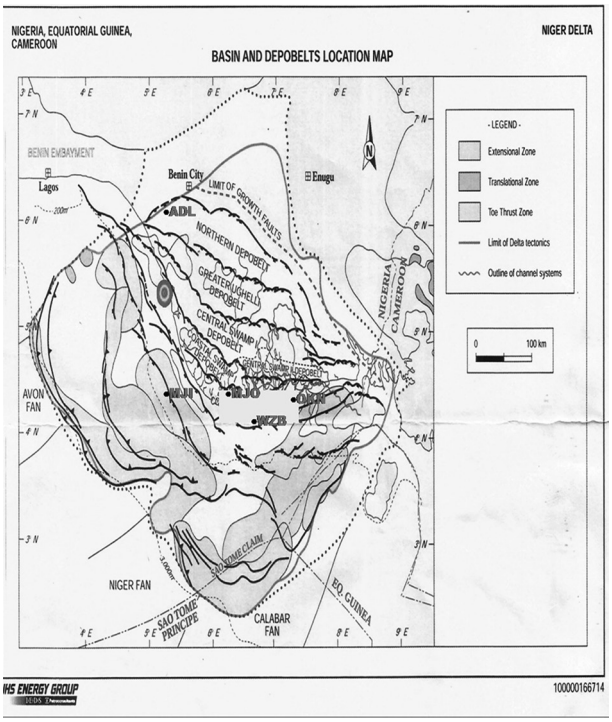

Figure 1: Niger Delta depobelts and sample locations [9].

Vitrinite Reflectance Measurement

The samples were crushed and milled after which they were placed in 50-mL polycarbonate test tubes for kerogen concentration. Also, $ZnBr_2$ was added to each tube to wet the samples and stirred with a stirring motor and paddle. Thin slurries were centrifuged to separate organic from inorganic material. In addition, the kerogen concentrate was then cast in epoxy on standard petrographic slides. Qualitative microscopic analysis of the organic materials was carried out using reflected light microscope equipped with white incident light and blue light irradiation. The reflectance was measured on polished sections by means of a photometer mounted on a microscope. The VR measurements were carried out with oil objectives 320 λ and 40/0.85 interference filter (54 nm).

Extraction and Analysis

The 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 hours. 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, v:v) respectively [18]

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. (internal diameter), x 0.25µm film thickness) coupled to an agilent 5975i mass spectrometry (MS). In addition, the GC operating conditions are as follows: the oven temperature was held isothermally at 80 °C

for 1 min, ramped to 310 °C at 3 °C/min and held isothermal for 16 min [19]. Helium was used as the carrier gas with 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 injector temperature of 285 °C. The identification and elution order of pyrene and its derivatives were determined by comparison of their mass spectra and relative retention times in the corresponding mass chromatograms with those reported in literature [20,21,7,4]. In addition, the quantification of pyrene and its derivatives were done using pyrene-d10 in the rock extracts.

RESULTS AND DISCUSSION

The Occurrence and Distributions of Pyrene and its Derivatives in Crude Oils and Rock Extract from Niger Delta

Figures 2 and 3 show the distributions of pyrene, fluoranthene, and their isomers in the crude oils and rock extracts from Niger Delta. Also, the peak identities are listed in Table 1.

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

Peak	Compound
Fla	Fluoranthene
APA	Acephenanthrylene
Py	Pyrene
2-MFla	2-methylpyrene
MFla	methylpyrene
MFla	methylpyrene
BaF	Benzo[a]fluorene
BbF	Benzo[b]fluorene
2-MPy	2-methylpyrene
4-MPy	4-methylpyrene
1-MPy	1-methylpyrene

The crude oils are characterized by the predominance of pyrene over fluoranthene (Figure 2).

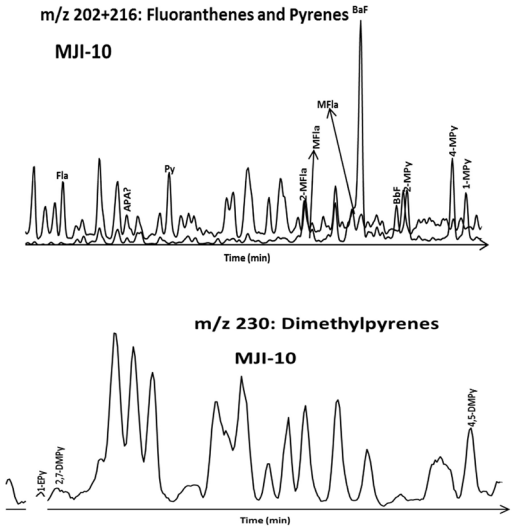

Figure 2: m/z 202 + 216 and 230 mass chromatograms showing the distributions of pyrene, fluoranthene, methylfluoranthenes, methylfluoranthenes and dimethylpyrenes in the Niger Delta crude oils.

The dominance of pyrene over fluoranthene has been reported in crude oils from the cratonic region of Tarim Basin, NW China by Fang et al [4], and coal from Mahakam Delta, Indonesia [6]. However, the rock extracts are characterized by higher abundance of fluoranthene over pyrene (Figure 3).

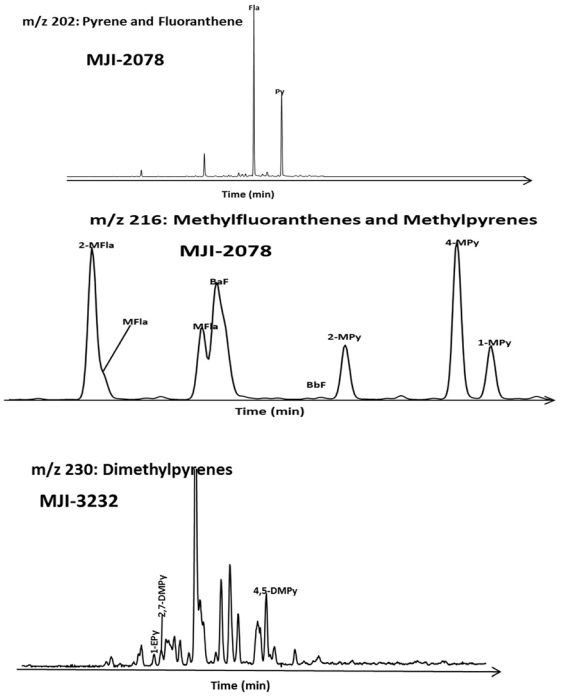

Figure 3: m/z 202 and 216 mass chromatograms showing the distributions of pyrene, Fluoranthene, methylfluoranthenes, and methylpyrenes in source rock extracts from Niger Delta, Nigeria.

All isomeric compounds including BaF, BbF, three methylfluoranthene isomers, and 2-MPy, 4-MPy and 1-MPy are present in the oils and rock samples (Figures 2 and 3). Moreover, the abundance of BaF is generally higher than that of BbF in all the oils and rock samples. In addition, 4-methylpyrene is the dominant compound among all the methylpyrene isomers in both the crude oils and rocks (Figures 2 and 3). The dominance of benzo[a] fluorene (BaF) over benzo[b]fluorene (BbF) and the higher abundance of 4-methylpyrene over other methylpyrene isomers have been reported in fluvial/deltaic oils from Beibuwan Basin, South China Sea, and coal extracts from Mahakam Delta Indonesia [4,6,7]. Among the C_2 alkyl pyrenes, 4,5-DMPy is the most prominent isomer in the oils and rock extracts while the 2,7-DMPy isomer and 1-EPy are the least abundant (Figures 2 and 3).

Distributions of Pyrene and its Derivatives in the Niger Delta Source Rocks as Source and Maturity Indicators

Table 2 shows the source and maturity parameters computed from pyrene, methylpyrene, and their isomers in the source rocks from Niger Delta, Nigeria. The Fla/(Fla + Py) and MFla/(MFla + Mpy) ratios have been successfully applied to distinguished two petroleum systems in the oils from the cratonic region of Tarim basin NW China based on the difference in their origin [4]. The Fla/(Fla + Py) and MFla/(MFla + Mpy) values computed for the rock samples range from 0.57 to 0.75 and 0.27 to 0.56 respectively (Table 2).

Table 2: Geochemical parameters computed from pyrene, methylpyrene isomers and Vitrinite Reflectance for Source Rock Extracts from Niger Delta.

		Pyrene	2-Mpy	4-Mpy	1-Mpy	2-/1-Mpy	MPYR	MPyl1	MPyl-2	%Ro
Field	Depth(m)	(µg/g Corg)	(µg/g Corg)	(µg/g Corg)	(µg/g Corg)					
MJI	2079-2098	0.01	0.05	0.91	0.01	1.03	0.51	0.18	0.26	0.29
MJI	2299-2308	0.02	0.08	2.08	0.02	1.44	0.59	0.17	0.43	0.33
MJI	2637-2655	0.03	0.07	1.76	0.02	1.34	0.57	0.33	0.43	0.4
MJI	2857-2875	0.03	0.06	1.55	0.02	1.46	0.59	0.45	0.46	0.41
MJI	2994-3012	0.03	0.07	1.82	0.02	1.64	0.62	0.54	0.43	0.43
MJI	3085-3104	0.02	0.05	2.67	0.02	1.58	0.61	0.51	0.50	0.44
MJI	3232-3250	0.04	0.08	3.80	0.03	1.51	0.60	0.64	0.48	0.37
MJI	3323-3332	0.07	0.16	3.66	0.05	1.30	0.57	0.58	0.43	0.46
MJI	3405-3424	0.04	0.09	3.22	0.02	2.10	0.68	0.57	0.48	0.58
MJO	1616-1707	0.01	0.07	0.84	0.01	1.87	0.65	0.06	0.35	0.3
MJO	1771-1872	0.05	0.35	7.28	0.04	1.17	0.54	0.17	0.29	0.35
MJO	2091-2101	0.06	0.22	3.04	0.06	1.46	0.59	0.05	0.45	0.38
MJO	2293-2366	0.03	0.11	6.52	0.02	2.19	0.69	0.45	0.50	0.35
MJO	2570-2588	0.02	0.09	4.09	0.02	2.11	0.68	0.24	0.51	0.4
MJO	2808-2817	0.03	0.10	4.88	0.03	2.38	0.70	0.28	0.59	0.43
OKN	1537-1555	0.02	0.14	2.18	0.01	1.88	0.65	0.02	0.36	0.23
OKN	1729-1747	0.02	0.25	1.02	0.02	1.10	0.52	0.05	0.22	0.23
OKN	2625-2643	0.04	0.30	1.25	0.03	0.99	0.50	0.10	0.24	0.25
OKN	2780-2799	0.02	0.19	2.05	0.03	1.08	0.52	0.05	0.28	0.29
OKN	2863-2881	0.02	0.08	1.71	0.02	1.28	0.56	0.06	0.39	0.31
OKN	2909-2927	0.05	0.18	5.11	0.06	1.71	0.63	0.03	0.54	0.27

Note: Fla/(Fla + Py): the relative concentration of fluoranthene to pyrene; MFla/(MFla + MPy): the relative concentration of all methylfluoranthene isomers to methylpyrene isomers; %Ro: Vitrinite Reflectance.

These values indicates source rocks formed from mixed organic matter (terrestrial and marine) but with higher contributions from terrigenous organic matter [2,3,4,5,22]. In addition, the values also vary over a small range indicating that the rock samples have received similar organic materials. The pristane/phytane (Pr/Ph) ratios for the samples range from 1.51-4.53 (Table 3).

Table 3: Geochemical Parameters computed from Saturate and Aromatic Biomarkers in Niger Delta Source Rock Extracts.

					22S/22S+22R	20S/20S+20R		
Field	Depth(m)	Pr/Ph	X/(X + C_{20}T)	Y/(Y + C_{24}T)	C_{31}	C_{29}	MPI-1	MPI-2
MJI	2079-2098	3.2	0.47	0.38	0.24	0.15	0.25	0.28
MJI	2299-2308	2.31	0.47	0.35	0.36	0.15	0.25	0.28
MJI	2637-2655	3.91	0.56	0.54	0.46	0.21	0.22	0.24
MJI	2857-2875	3.98	0.58	0.63	0.52	0.29	0.37	0.41
MJI	2994-3012	4.26	0.69	0.65	0.53	0.30	0.54	0.60
MJI	3085-3104	4.53	0.58	0.61	0.58	0.40	0.36	0.40
MJI	3232-3250	2.87	0.67	0.82	0.59	0.46	0.45	0.50
MJI	3323-3332	4.46	0.77	0.81	0.59	0.52	0.46	0.50
MJI	3405-3424	2.92	0.76	0.78	0.58	0.48	0.62	0.68
MJO	1616-1707	4.31	0.31	0.39	0.25	0.16	0.23	0.26
MJO	1771-1872	2.16	0.38	0.53	0.35	0.41	0.31	0.35
MJO	2091-2101	2.08	0.47	0.45	0.30	0.21	0.21	0.24
MJO	2293-2366	2.96	0.60	0.61	0.42	0.13	0.47	0.50
MJO	2570-2588	3.5	0.59	0.63	0.54	0.19	0.38	0.42
MJO	2808-2817	3.6	0.41	0.66	0.57	0.38	0.35	0.38
OKN	1537-1555	1.85	0.37	0.37	0.29	0.18	0.16	0.18
OKN	1729-1747	2.61	0.43	0.33	0.35	0.14	0.14	0.15
OKN	2625-2643	1.51	0.46	0.39	0.35	0.30	0.12	0.13
OKN	2780-2799	1.73	0.45	0.60	0.35	0.24	0.16	0.18
OKN	2863-2881	2.06	0.56	0.45	0.37	0.34	0.18	0.20
OKN	2909-2927	2.27	0.50	0.43	0.35	0.28	0.22	0.24

***Pr/Ph: Pristane/Phytane; X/X + 20T = unknown tricyclic compound X/X + C_{20} tricyclic terpane, ratio calculated from GC–MS m/z 191 ion chromatogram; Y/Y + 24T = unknown tricyclic compound Y/Y + C_{24} tricyclic terpane, ratio calculated from GC–MS m/z 191 ion chromatogram; C_{31} 22S/22S + 22R = 17a(H),21b(H)-homohopane isomers from GC–MS m/z 191 ion mass chromatogram; C_{29} 20S/20S+20R=5a(H),14a(H),17a(H) sterane from GC–MS m/z 217 ion chromatogram; MPI-1: Methylphenanthrene index; MPI-2: Methylphenanthrene index 2.**

Moreover, the Pr/Ph values are consistent with the source rock formed from mixed (terrestrial and marine) origin and deposited in sub-oxic to oxic paleoenvironment [23,24]. The X/(X + C_{20}T) and Y/(Y + C_{24}T) values computed from tricyclic terpanes, also known as Tricyclic Terpane Terrigenous Index (TTTI), have been successfully applied to distinguished terrigenous crude oils from marine oils in Niger Delta Basin [25,26]. The X/(X + C_{20}T) and Y/(Y + C_{24}T) values in the rock extracts range from 0.31 to 0.77 and 0.33 to 0.82 respectively (Table 3). These values confirm that the rock samples were formed from mixed sources (terrestrial and marine) but with higher inputs from terrestrial materials [25,26].

Pyrene based maturity parameters have been previously proposed by many authors for the maturity assessment of oils and sedimentary organic matter and these include MPyI-1 (3 x 2-Mpy/(1-MPy + 4-MPy + Py)), MPyI-2 (2-MPy/(1-MPy + 4-MPy)) [6,27], MPYR (2-MPy/(2-MPy + 1-MPy)) [7], and 2-/1-Mpy [4]. The MPyI-1, MPyI-2, MPYR, and 2-/1-Mpy values computed for the rock samples range from 0.02 to 0.64, 0.22 to 0.59, 0.51 to 0.70, and 0.99 to 2.38 respectively (Table 2). The vitrinite reflectance (%Ro) values for the rock samples range from 0.23 to 0.58 % (Table 2), confirming the immature to early maturity status inferred from the maturity parameters which have been computed from pyrene distribution. The MPyI-1, MPyI-2, MPYR, and 2-/1-Mpy when plotted against vitrinite reflectance (Ro) values increase with an increase in Ro values suggesting that pyrene based maturity parameters are potential maturity indicators (Figure 4).

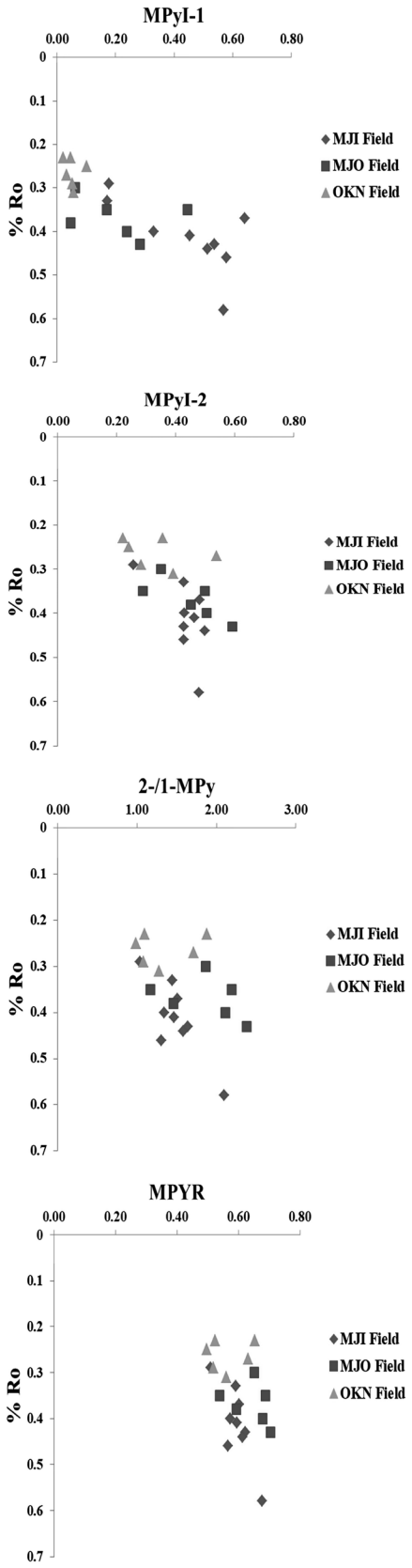

Figure 4: Plots of vitrinite reflectance (%R) versus pyrene based maturity parameters for Niger Delta source rocks.

The 22S/(22S+22R) C_{31} homohopane and 20S/(20S+20R) C_{29} sterane values range from 0.24 to 0.59 and 0.13 to 0.52 respectively (Table 3).Moreover, these values further confirm that the rock samples have immature to early maturity status [24]. The molecular aromatic maturity parameters of the rock samples, MPI-1 and MPI-2 range from 0.12 to 0.62 and 0.13 to 0.68 respectively (Table 3), supporting immature to early mature source rocks already inferred from the pyrene based maturity parameters. The MPyI-1, MPyI-2, MPYR, and 2-/1-Mpy values show the tendency of increase in burial depth (Figure 5).

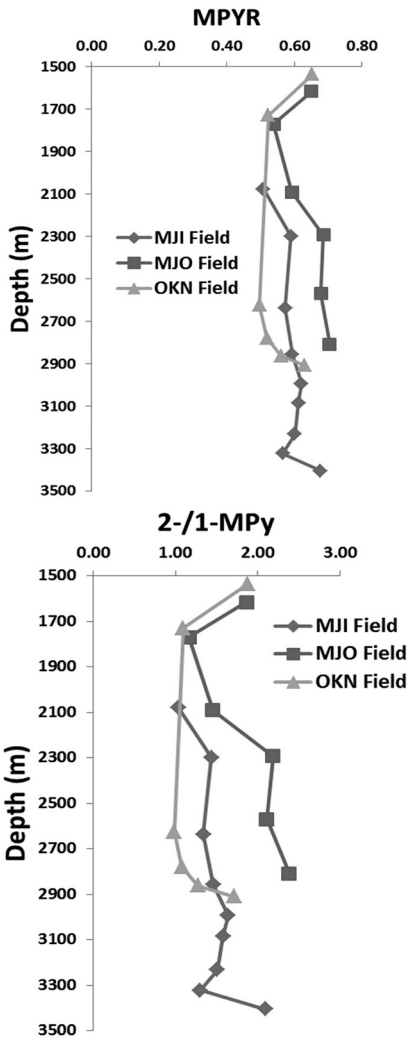

Figure 5: Plots of pyrene based maturity parameters with increasing burial depths in Niger Delta source rocks.

This is further supported by the plots of 20S/(20S + 20R) C_{29} steranes and MPI-1 against burial depths (Figure 6).

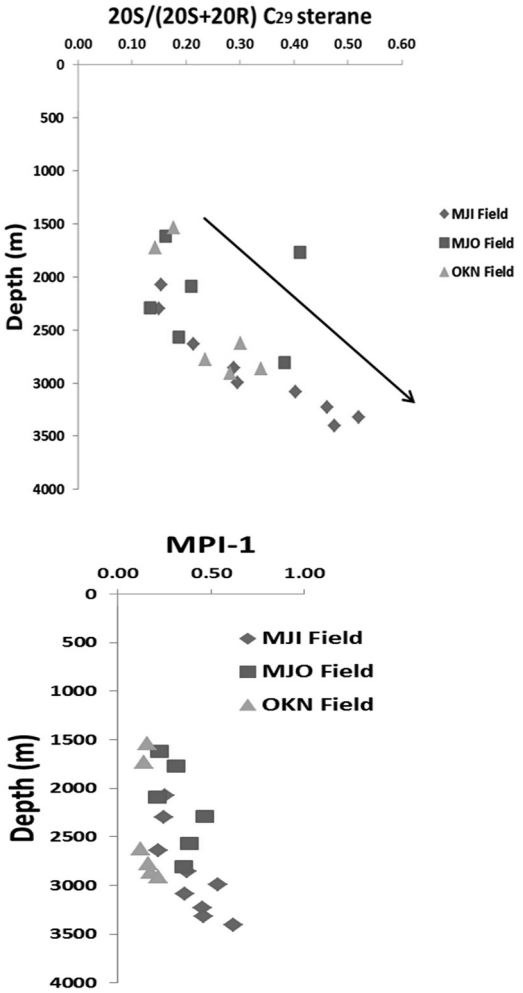

Figure 6: Plots of burial depths versus (a) 20S/(20S + 20R) C_{29} steranes and (b) MPI-1 for Niger Delta source rocks.

Also, this shows that pyrene based maturity parameters has exhibited similar characteristics with other well established saturate and aromatic biomarkers.

The absolute concentrations of Pyrene, 2-MPy, 4-MPy, and 1-MPy (ug/g Corg) are shown in Table 2.

Also, this shows that pyrene based maturity parameThe absolute concentrations are generally low in the rock samples. In addition, these low values may be attributed to immature to low maturity status of the rock samples. Also, the absolute concentrations of pyrene and its derivatives have been reported to be generally low within immature to low maturity status [4].

Source and Thermal Maturity Status of the Niger Delta Crude Oils Based on the Distributions of Pyrene and its Derivatives

The source and maturity parameters computed from pyrene, methylpyrene, and their isomers in the crude oils from Niger Delta are shown in Table 4.

Table 4: Geochemical parameters computed from pyrene and methylpyrene isomers for Niger Delta crude oils.

						Fla/	Mfla/
Sample	Depth(m)	2-/1-Mpy	MPYR	Mpyl-1	Mpyl-2	(Fla+Py)	(Mfla+Mpy)
ADL1	2602-2607	0.69	0.41	0.49	0.27	0.43	0.38
ADL2	2602-2607	0.70	0.41	0.47	0.26	0.41	0.35
ADL3	2702-2704	0.71	0.42	0.40	0.27	0.50	0.48
ADL4	2718-2720	0.75	0.43	0.45	0.28	0.48	0.45
ADL5	2759-2763	0.70	0.41	0.48	0.27	0.43	0.40
ADL6	2766-2770	0.73	0.42	0.51	0.28	0.43	0.39
ADL7	2905-2908	0.80	0.44	0.57	0.32	0.39	0.39
ADL8	2964-2967	0.97	0.49	0.67	0.37	0.38	0.38
ADL9	3064-3052	0.98	0.49	0.73	0.41	0.38	0.36
OKN-1	1749-1750	1.33	0.57	1.01	0.49	0.61	0.51
OKN-2	1892-1895	0.94	0.49	0.82	0.38	0.46	0.34
OKN-3	1905-1907	1.04	0.51	0.91	0.43	0.46	0.31
OKN-4	1952-1955	1.39	0.58	0.95	0.46	0.61	0.48
OKN-5	2050-2059	1.10	0.52	0.89	0.43	0.46	0.38
OKN-6	2369-2555	0.88	0.47	0.75	0.36	0.45	0.38
OKN-7	2377-2672	1.05	0.51	0.82	0.40	0.43	0.33
OKN-8	2469-2782	1.15	0.54	0.90	0.45	0.43	0.36
OKN-9	2485-2793	1.04	0.51	0.90	0.42	0.44	0.35
OKN-10	2489-2491	1.39	0.58	1.12	0.56	0.58	0.47
OKN-11	2521-2523	1.10	0.52	0.94	0.47	0.57	0.46

Note: See Table 2 for the definitions of terms.

Table 4: Contd.

Sample	Depth(m)	2-/1-Mpy	MPYR	Mpyl-1	Mpyl-2	Fla/ (Fla+Py)	Mfla/ (Mfla+Mpy)
OKN-12	2530-2537	1.07	0.52	0.91	0.43	0.56	0.45
OKN-13	2566-2568	1.24	0.55	1.00	0.50	0.62	0.51
OKN-14	2677-2683	1.27	0.56	1.00	0.52	0.64	0.53
OKN-15	3148-3154	0.89	0.47	0.78	0.39	0.63	0.52
OKN16	3593-3605	1.22	0.55	1.13	0.53	0.61	0.45
MJO-1	2207-2216	0.91	0.48	0.74	0.37	0.31	0.32
MJO-2	2070-2081	0.86	0.46	0.74	0.36	0.34	0.31
MJO-3	2091-2104	0.92	0.48	0.76	0.37	0.34	0.30
MJO-4	2096-2101	0.95	0.49	0.79	0.38	0.33	0.28
MJI-1	1607-1611	1.29	0.56	1.01	0.51	0.71	0.53
MJI-2	1777-1779	1.15	0.53	0.98	0.48	0.61	0.44
MJI-3	1795-1797	1.06	0.51	0.89	0.42	0.62	0.42
MJI-4	1920-1921	1.08	0.52	0.95	0.45	0.55	0.44
MJI-5	1936-2342	0.90	0.47	0.70	0.35	0.70	0.54
MJI-6	1944-1947	1.18	0.54	0.89	0.45	0.65	0.53
MJI-7	1948-1950	1.38	0.58	1.06	0.52	0.60	0.41
MJI-8	1979-2398	1.11	0.53	0.87	0.44	0.66	0.53
MJI-9	2442-2444	1.16	0.54	0.93	0.46	0.62	0.56
MJI-10	3030-3036	1.06	0.51	0.88	0.43	0.44	0.44
WZB1	1610-2647	0.96	0.49	0.77	0.39	0.43	0.35
WZB2	1811-1957	0.97	0.49	0.70	0.37	0.47	0.40

The Fla/(Fla + Py) and MFla/(MFla + Mpy) ratios for the oils range from 0.31 to 0.70 and 0.28 to 0.56 respectively (Table 4). These values indicate oils formed from source rocks of mixed origin (terrestrial and marine) with significant contributions from terrigenous materials [4,5]. Also, the cross plots of Fla/(Fla + Py) versus MFla/(MFla + Mpy) ratios is shown in Figure 7a.

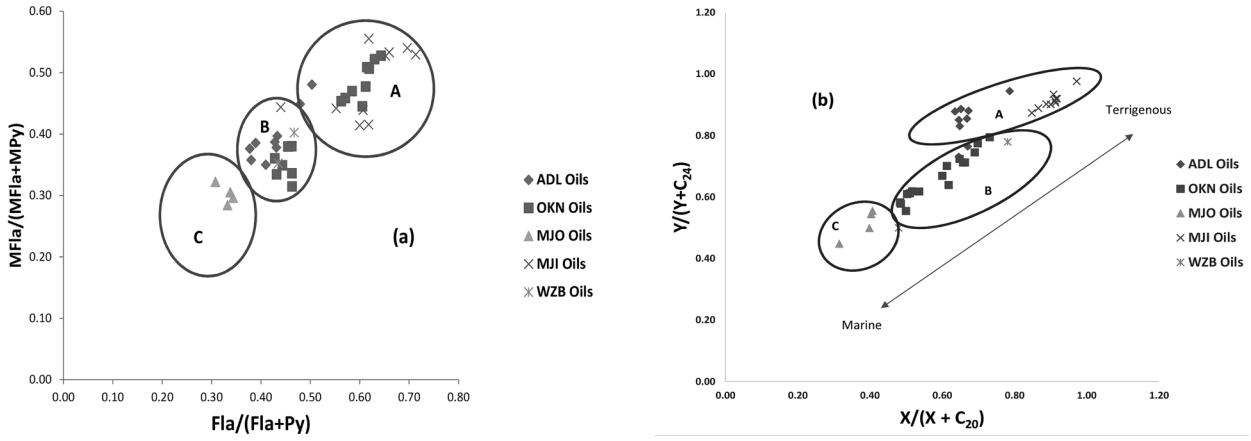

Figure 7: Cross plot of (a) Fla/(Fla + Py) versus MFla/(MFla + Mpy) and (b) X/(X + C_{20}) versus Y/(Y + C_{24}) for Niger Delta crude oils.

The plots have clearly distinguished the Niger Delta oils into three families. Moreover, the Pr/Ph values have been computed for the oils range between 1.48 and 5.48 (Table 5), indicating crude oils formed from the source rocks of mixed origin (terrestrial and marine) with higher inputs from terrestrial organic matter deposited under sub-oxic to oxic paleoenvironment [23]. The $X/(X + C_{20}T)$ and $Y/(Y + C_{24}T)$ values in the crude oils range from 0.31 to 0.92 and 0.45 to 0.95 respectively (Table 5).

Table 5: Geochemical Parameters computed from Saturate and Aromatic Biomarkers in Niger Delta Crude Oils.

Sample	Depth(m)	P_r/P_h	$X/(X + C_{20}T)$	$Y/(Y + C_{24}T)$	$22S/22S+22R\ C_{31}$	$20S/20S+20R\ C_{29}$	MPI-1	MPI-2
ADL1	2602-2607	3.61	0.65	0.83	0.56	0.41	0.73	0.73
ADL2	2602-2607	3.95	0.67	0.77	0.56	0.40	0.71	0.71
ADL3	2702-2704	5.48	0.65	0.73	0.56	0.40	0.69	0.71
ADL4	2718-2720	5.40	0.65	0.85	0.56	0.44	0.73	0.72
ADL5	2759-2763	4.13	0.64	0.88	0.56	0.43	0.70	0.70
ADL6	2766-2770	4.30	0.65	0.89	0.56	0.45	0.78	0.77
ADL7	2905-2908	4.08	0.67	0.88	0.56	0.45	0.79	0.77
ADL8	2964-2967	3.61	0.67	0.86	0.56	0.44	0.82	0.81
ADL9	3064-3052	3.61	0.79	0.95	0.57	0.47	0.84	0.82
OKN-1	1749-1750	2.39	0.70	0.77	0.52	0.36	0.95	0.98
OKN-2	1892-1895	2.19	0.49	0.58	0.53	0.40	0.91	0.95
OKN-3	1905-1907	2.11	0.50	0.61	0.53	0.40	0.91	0.95
OKN-4	1952-1955	2.39	0.69	0.75	0.53	0.33	0.93	0.97
OKN-5	2050-2059	2.18	0.48	0.58	0.53	0.41	0.90	0.93
OKN-6	2369-2555	2.29	0.52	0.62	0.53	0.39	0.95	0.99
OKN-7	2377-2672	2.10	0.50	0.55	0.53	0.43	0.90	0.93
OKN-8	2469-2782	2.25	0.65	0.72	0.53	0.39	0.89	0.92
OKN-9	2485-2793	2.18	0.51	0.61	0.53	0.41	0.91	0.94
OKN-10	2489-2491	2.72	0.66	0.71	0.54	0.36	0.76	0.77
OKN-11	2521-2523	2.62	0.61	0.70	0.54	0.33	0.70	0.70

Note: See Table 3 for the definitions of terms.

Table 5: Contd.

Sample	Depth(m)	Pr/Ph	X/ (X + C_{20}T)	Y/ (Y + C_{24}T)	22S/22S+22R C_{31}	20S/20S+20R C_{29}	MPI-1	MPI-2
OKN-12	2530-2537	2.83	0.66	0.71	0.53	0.37	0.76	0.76
OKN-13	2566-2568	2.49	0.73	0.79	0.53	0.35	0.94	0.96
OKN-14	2677-2683	2.10	0.54	0.62	0.53	0.41	0.62	0.63
OKN-15	3148-3154	2.28	0.60	0.67	0.54	0.38	0.65	0.66
OKN16	3593-3605	2.17	0.62	0.64	0.53	0.41	0.70	0.72
MJO-1	2207-2216	1.76	0.40	0.54	0.55	0.45	0.77	0.80
MJO-2	2070-2081	1.76	0.31	0.45	0.61	0.46	0.77	0.81
MJO-3	2091-2104	1.68	0.41	0.56	0.56	0.45	0.78	0.81
MJO-4	2096-2101	1.70	0.40	0.50	0.85	0.45	0.78	0.81
MJI-1	1607-1611	2.93	0.85	0.87	0.54	0.28	0.76	0.78
MJI-2	1777-1779	3.33	0.91	0.93	0.54	0.40	0.84	0.86
MJI-3	1795-1797	3.33	0.91	0.91	0.54	0.36	0.83	0.86
MJI-4	1920-1921	4.37	0.92	0.92	0.54	0.37	0.96	0.99
MJI-5	1936-2342	2.74	0.87	0.89	0.55	0.35	0.78	0.80
MJI-6	1944-1947	3.24	0.90	0.90	0.54	0.34	0.82	0.85
MJI-7	1948-1950	4.71	0.91	0.92	0.54	0.39	0.86	0.89
MJI-8	1979-2398	3.08	0.89	0.90	0.54	0.36	0.82	0.85
MJI-9	2442-2444	3.26	0.97	0.98	0.54	0.38	0.83	0.86
MJI-10	3030-3036	4.43	0.91	0.91	0.54	0.38	0.83	0.86
WZB1	1610-2647	2.35	0.48	0.50	0.55	0.42	0.86	0.89
WZB2	1811-1957	1.48	0.78	0.78	0.55	0.37	0.86	0.88

These values confirm that the oil samples were formed from mixed origin (terrestrial and marine) but with higher inputs from terrestrial materials [25,26]. Moreover, the cross plots of these parameters show that oil samples from the same field have been formed from similar organic matter (Figure 7b).

The $MPyl_1$, $MPyl_2$, MPYR, and 2-/1-MPy ratios have been computed for the oils range from 0.40 to 1.13, 0.26 to 0.56, 0.41 to 0.58, and 0.69 to 1.39 respectively (Table 4).

Moreover, based on these values, it has been shown that the oils are within early stage of oil generation [4,6,7,27]. The 22S/(22S+22R C_{31}) homohopane and 20S/(20S + 20R) C_{29} steranes of the oils range from 0.52 to 0.85 and 0.28 to 0.47 respectively (Table 5). The MPI-1 and MPI-2 values range from 0.62 to 0.95 and 0.63 to 0.99 respectively (Table 5). These values support the fact that the oils were formed within the early stage of oil generation [24]. Finally, this shows that the pyrene based maturity parameters exhibit similar maturity features with already established saturate and aromatic maturity parameters.

CONCLUSIONS

The occurrence and distributions of pyrene and its derivatives in the Niger Delta crude oils and source rocks have been investigated by gas chromatography-mass spectrometry (GC-MS). The crude oils have been characterized by the dominance of pyrene over fluoranthene while fluoranthene shows predominance over pyrene in the rock samples. Moreover, 4-methylpyrene was the dominant compound among the methylpyrene isomers in the crude oils and source rocks while benzo[a]fluorene (BaF) predominated over benzo[b] fluorene (BbF). Geochemical characterization of the oils and their source rocks based on pyrene and its derivatives showed that the oils were generated from source rocks of mixed origin (terrestrial and marine) at the early stage of oil generation while the source rocks were within immature to early maturity stage. The distributions and abundance of the pyrene and its derivatives in the oils have permitted the grouping of Niger Delta oils into three families.

Base on this study, it is shown that the abundance and distribution of pyrene and its derivatives can be used to assess the origin and thermal maturity of crude oil and source rocks in the Niger Delta Basin.

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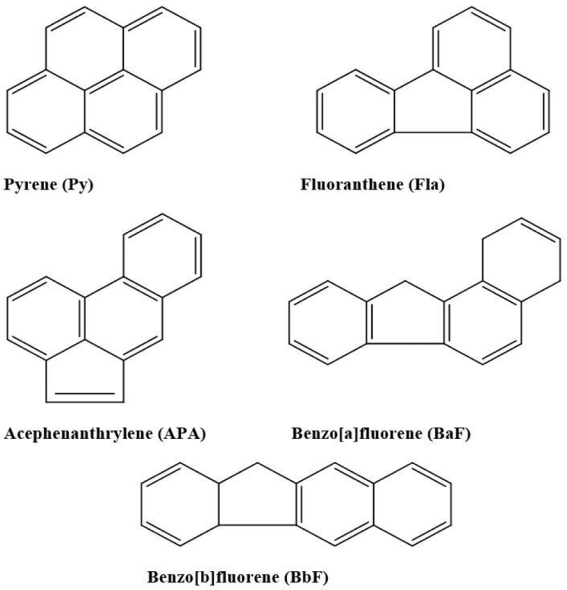
NOMENCLATURES

BaF	: Benzo[a]Fluorene
BbF	: Benzo[b]Fluorene
EI	: Electron Impact
Fla	: Fluoranthene
GC	: Gas Chromatography
GC-MS	: Gas Chromatography-Mass Spectrometry
i.d.	: Internal Diameter
MPy	: Methylpyrene
MS	: Mass Spectrometry
PAHS	: Polycyclic Aromatic Hydrocarbons
Pr/Ph	: Pristane/Phytane
Py	: Pyrene
TTTI	: Tricyclic Terpane Terrigenous Index

APPENDIX



Appendix: The structure of pyrene and benzofluorene isomers discussed in the text.

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