

Occurrence and Distributions of Biphenyls and Alkylbiphenyls as Indicators of Maturity in Crude Oils from the Tertiary Niger Delta Basin, Nigeria

Abiodun B. Ogbesejana, Bello Oluwasesan M. and Tijjani Ali

Department of Applied Chemistry, Federal University Dutsin-Ma, P.M.B. 5001, Dutsin-Ma, Katsina State, Nigeria.
E-mail: abiodunogbesejana@gmail.com

Abstract

Crude oils from the Northern and offshore Niger Delta basin, Nigeria have been characterized by gas chromatography-mass spectrometry (GC-MS) in terms of their thermal maturity, based on the distribution of biphenyl and its derivatives. The crude oils were characterized by the dominance of C₂-biphenyl over other alkylated homologues. 3-methylbiphenyl predominated over other methylbiphenyl isomers in the oils samples. 3,3'-dimethylbiphenyl occurred as the most abundant compound among the C₂-biphenyl compounds in the oils samples while 3,5,4-trimethylbiphenyl dominated over other C₃-biphenyl compounds in the oils. The distributions and abundance of the biphenyl and alkylbiphenyls were found not to be influenced by source facies and thermal maturity. The maturity dependent parameter computed from alkylbiphenyl distributions (MBpR, DMBpR-x and DMBpR-y ratios) indicated that the oils have wide variations in maturity status and that the oil samples are within oil window and this is further supported by other maturity parameters computed from the saturate and aromatic biomarkers. This study showed that the abundance and distribution of biphenyl and its derivatives can be used for thermal maturity of crude oil in the Niger Delta Basin.

Keywords: Biphenyl, Alkylbiphenyls, Crude oils, Niger Delta, Maturity.

Introduction

Biphenyl and Alkylbiphenyls are important constituents of petroleum and petroleum source rocks, but have also been found in coal extracts (Alexander et al., 1986a). Their biological origin is uncertain. The compounds are present in organic matter originating from different geological ages and different source types. Their occurrence can

be dated back to the Middle Cambrian, a period that predates the evolution of higher plants (Cumbers et al., 1987). Biphenyl and alkylbiphenyls are combustion products of benzene and alkylbenzenes (Takatsu and Yamamoto, 1993). Kruge et al. (1994) found high proportions of biphenyl in samples that showed high concentrations of semifusinite and pyrofusinite. Semifusinite and pyrofusinite result

from the partial combustion of organic matter. Alexander et al. (1994) showed that the relative abundances of alkylcyclobenzenes and alkylbiphenyls in crude oils are of the same magnitude. The authors therefore suggest, that these compounds are formed via deposition of oxygen-rich source materials in oxic depositional environments. Alkylcyclohexyl-benzenes and alkylbiphenyls may be products of the oxidative coupling of phenols (Alexander et al., 1994). Besides the little knowledge on direct biological precursors of alkylbiphenyls their potential as maturity indicators is also sparse.

It has been reported that many of the aliphatic biomarker maturity parameters do reach equilibrium before the main stage of the oil window and in some cases show inversion at high maturity levels and as such are not effective maturity indicators (Farrimond et al., 1998). Aromatics hydrocarbon maturity parameters have been reported to be more sensitive to maturity differences in the mid to late parts of the oil generation window (Radke, 1988). Biphenyl compounds have also been demonstrated to be very important in evaluating the maturity of crude oil and source rock (Alexander et al., 1986; Cumbers et al., 1987; George and Ahmed, 2002). However, biphenyl and alkylbiphenyls have not been studied or reported in the crude oils from Niger Delta basin. This work is aimed at investigating the occurrence and distributions of biphenyl and alkylbiphenyls in the Niger Delta crude oils in relation to their origin and thermal maturity level.

Materials and Methods

Samples Collection

Forty one crude oil samples were collected in five wells from five fields in the North and offshore of Niger Delta basin. Samples were collected directly from well heads (xmas trees) on the permission of DPR using the oil field operators' staff. Samples collection follow international acceptable standard and procedure. Collected samples were kept in the laboratory before analysis.

Fractionation and Analysis

The oil samples 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 (Li et al., 2012).

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 (60m x 0.25mm i.d., x 0.25 μ m film thickness) coupled to an agilent 5975i mass spectrometry (MS). 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 (Li et al., 2012a). 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 70eV, an ion source temperature of 250 °C and injector temperature of 285°C. The identification and elution order of biphenyl 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 (Alexander et al., 1986; Cumbers et al., 1987; George and Ahmed, 2002; Li et al., 2013a, 2013b; Li and Ellis, 2015; Luo et al., 2016). The relative abundance was calculated

from integrated peak areas in the relevant ion chromatograms

Results and Discussion

Occurrence and Distributions of Diphenyl and Its Derivatives in Source Rock Extracts from Niger Delta Basin

The m/z 154+168+182+196 mass chromatograms showing the distributions of biphenyl and its derivatives in the rock samples are shown in Figures 1. The rock samples are characterized by the predominance of C₂- biphenyl over other alkylated homologues as shown in Figure 1 and Tables 1. The dominance of C₂-biphenyl over other alkylated homologues of biphenyl have been reported in rock samples from the cratonic region of the Tarim Basin NW China (Li et al., 2013b), Proterozoic source rocks from middle Velkerri Formation, McArthur Basin, Australia (George and Ahmed, 2002), petroleum and ancient sediments from Australia (Alexander et al., 1986; Cumbers et al., 1987) and crude oils and sediments from Potwar basin, Pakistan (Asif et al., 2010). Among the methylbiphenyl isomers in the source rocks, 3-methylbiphenyl is the dominant compound while 2-methylbiphenyl occur as the least or below detection limit in some source rocks (see Figure 2). The predominance of 3-methylbiphenyl over other isomers of methylbiphenyl have been previously reported in sediments from Tarim Basin NW China (Li et al., 2013b; Li and Ellis, 2015), crude oils and sediment extracts from Potwar basin Pakistan (Asif, 2010). The 3,3'-dimethylbiphenyl (3,3'-DMBP) is the most abundant compound among the C₂-biphenyl isomers while 2,3'-dimethylbiphenyl (2,3'-DMBP) occur as least in the source rocks as presented in Figure. 1. This

pattern of distributions whereby 3,3'-DMBP is the most abundant among the C₂-biphenyl isomers have been previously reported in petroleum and source rocks (Alexander et al., 1986; Cumbers et al., 1987; George and Ahmed, 2002; Asif, 2010). Also, there is predominance of 3,5,4-trimethylbiphenyl (3,5,4-TMBP) over other C₃-biphenyl isomers in the rock samples as shown in Figure. 1. This observation is consistent with the results that have been previously published in the literature (Li et al., 2013b; Luo et al., 2016).

Source facies, depositional environment and thermal maturity of organic matter are important factors controlling the distributions and concentrations of most molecular markers in source rocks and crude oils. In this study, the effect of source, depositional environment and maturity on the distributions of biphenyls in the source rocks were investigated by plotting the abundance of C₀-C₃ biphenyl against well-established source and maturity parameters obtained from the saturate and aromatic distributions in the oils (Figure. 2). Figure 2a shows the cross plots of the abundance of biphenyl (C₀-C₃) against pristane/phytane (Pr/Ph) values in the source rocks. The plots clearly showed no correlation with the source and depositional parameters (Pr/Ph), indicating that source facies has no influence on the distributions and abundance of the biphenyl compounds in the rock samples. Similarly, the abundance of C₀-C₃ biphenyl in the source rocks are plotted against saturate (20S/(20S + 20R) C₂₉ steranes) and aromatic (MPI-1) maturity parameters in Figures 2b, and 2c respectively. The plots also lack any correlation with the maturity parameters showing that thermal maturity has no effect on the

distributions and abundance of the biphenyl and alkylbiphenyls in the source rocks.

Thermal Maturity Status of Niger Delta Crude Oils based on the Distributions of Biphenyl and Alkylbiphenyls

Alexander et al., (1986) proposed MBpR (3-/2-methylbiphenyl ratio) as a thermal maturity parameter while Cumbers et al., (1987) proposed DMBpR-x (3,5-/2,5-dimethylbiphenyl ratio-x) and DMBpR-y (3,3'-/2,3'-dimethylbiphenyl ratio-y) maturity indicators in crude oils and ancient sediments from Australia. George and Ahmed (2002) applied these parameters to maturity study in Mesoproterozoic sediments of the McArthur Basin, Australia and observed that the alkylbiphenyl ratios were sensitive to maturity variations in the peak to late part of the oil window but show little change at lower maturities. Alkylbiphenyl ratios (MBpR, DMBpR-x and DMBpR-y) have also been successfully applied to assess the thermal maturity level of the sediments from Mesoproterozoic Hongshuizhuang Formation, Northern China (Luo et al., 2016).

The MBpR, DMBpR-x and DMBpR-y values in the oil samples range from 3.59 to 120.79, 7.84 to 54.31 and 3.49 to 71.09, respectively (Table 1). These values showed that oils have a wide range maturity variations and also suggest that the oils are within immature to peak of oil generation stage (George and Ahmed, 2002; Luo et al., 2016). The 20S/(20S + 20R) C₂₉ sterane and MPI-1 values range from 0.28 to 0.47 and 0.61 to 0.96, respectively (Table 2), indicating that the oils are within oil generation window (Peters et al., 2005). The cross plots of MBpR, DMBpR-x and DMBpR-y values against reservoir depths are shown in Figures 3a, 3b and 3c respectively. The

plots lack any correlation with increasing burial depths (Fig. 3). Also, for the purpose of comparison, MBpR, DMBpR-x and DMBpR-y values are plotted against other maturity parameters such as 20S/(20S + 20R) C₂₉ steranes and MPI-1 in Figures 4a, 4b and 4c, respectively. The plots of MBpR, DMBpR-x and DMBpR-y clearly show a disagreement between 20S/(20S + 20R) C₂₉ steranes and MPI-1, indicating lack of relationship among the maturity parameters.

Conclusion

The occurrence and distributions of biphenyl and its derivatives in the Niger Delta crude oils have been investigated by gas chromatography-mass spectrometry (GC-MS). Geochemical characterization of the oils based on the distributions of biphenyl and its derivatives show that the oils have been sourced from source rocks within oil window. The crude oils were characterized by the dominance of C₂-biphenyl over other alkylated homologues. The 3-methylbiphenyl predominated over other methylbiphenyl isomers in the oils samples. The 3,3'-dimethylbiphenyl occurred as the most abundant compound among the C₂-biphenyl compounds in the oils samples while 3,5,4-trimethylbiphenyl dominated over other C₃-biphenyl compounds in the oils. The distributions and abundance of the biphenyl and alkylbiphenyls in the oils were found not to be influenced by source facies and thermal maturity. The maturity dependent parameter computed from alkylbiphenyl distributions (MBpR, DMBpR-x and DMBpR-y ratios) indicated that the oils have wide variations in maturity status and that the oil samples are within oil window and this is further supported by other maturity parameters computed

from the saturate and aromatic biomarkers. This study showed that the abundance and distribution of biphenyl and its derivatives can be used for

thermal maturity of crude oil in the Niger Delta Basin.

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Table 1a: Geochemical Parameters Computed from Biphenyl Compounds and related Parameters in Niger Delta Crude Oil

Sample	Depth (m)	Biphenyl (%)				MBp R	DMBpR -x	DMBpR -y	Pr/P h	20S/20S+20 R	MPI-1
		C ₀	C ₁	C ₂	C ₃					C ₂₉	
ADL-1	2602-	3.4	21.8	42.7	31.9						
	2607	0	4	7	9	15.81	9.26	19.98	3.61	0.41	0.73
ADL-2	2602-	3.1	21.6	42.6	32.6						
	2607	1	6	3	1	17.29	15.90	30.48	3.95	0.4	0.71
ADL-3	2702-	1.1	15.0	47.1	36.6						
	2704	7	5	3	5	23.16	11.59	24.97	5.48	0.4	0.61
ADL-4	2718-	3.6	21.8	44.9	29.5						
	2720	5	5	9	1	32.79	9.69	20.78	5.4	0.44	0.73
ADL-5	2759-	2.6	20.9	43.5	32.8						
	2763	8	0	6	7	19.74	10.14	24.97	4.13	0.43	0.7
ADL-6	2766-	4.2	24.8	42.4	28.4						
	2770	5	3	8	4	17.83	9.49	20.78	4.3	0.45	0.78
ADL-7	2905-	3.5	23.6	43.2	29.4						
	2908	5	8	7	9	19.66	10.38	21.92	4.08	0.45	0.79
ADL-8	2964-	4.5	24.8	42.3	28.1						
	2967	9	5	7	9	18.28	10.22	23.70	3.61	0.44	0.82
ADL-9	3064-	5.8	26.5	40.9	26.6						
	3052	0	8	5	7	18.58	9.88	21.51	3.61	0.47	0.91
OKN-1	1749-	3.8	20.9	38.5	36.6						
	1750	5	9	1	5	40.73	13.94	25.79	2.39	0.36	0.95
OKN-2	1892-	0.9	16.1	49.2	33.6						
	1895	9	3	5	3	72.61	20.05	34.73	2.19	0.4	0.91
OKN-3	1905-	2.3	18.0	49.2	30.4						
	1907	0	5	5	0	26.52	14.18	24.43	2.11	0.4	0.91
OKN-4	1952-	3.6	20.8	39.6	35.9						
	1955	4	4	1	2	35.67	11.67	25.67	2.39	0.33	0.93
OKN-5	2050-	2.6	19.2	48.3	29.7	32.98	18.44	26.58	2.18	0.41	0.9

	2059	2	6	4	8						
OKN-6	2369-	0.4		46.9	45.6				2.29	0.39	0.95
	2555	1	7.04	0	5	53.54	38.84	65.06			
OKN-7	2377-	6.4	23.3	44.7	25.4				2.1	0.43	0.9
	2672	6	2	6	6	13.98	11.20	18.98			
OKN-8	2469-	6.5	25.6	44.1	23.7				2.25	0.39	0.89
	2782	3	0	5	1	24.33	17.63	24.19			
OKN-9	2485-	1.2	16.4	49.2	33.0				2.18	0.41	0.91
	2793	0	6	9	5	53.68	18.97	31.36			
OKN-10	2489-	1.5	24.1	47.6	26.6	120.7			2.72	0.36	0.76
	2491	7	6	5	3	9	24.35	42.42			
OKN-11	2521-	4.9	29.1	42.4	23.4				2.62	0.33	0.7
	2523	6	0	9	5	46.95	15.72	27.65			
OKN-12	2530-	7.9	32.8	39.6	19.5				2.83	0.37	0.76
	2537	5	5	2	7	44.57	17.33	29.58			

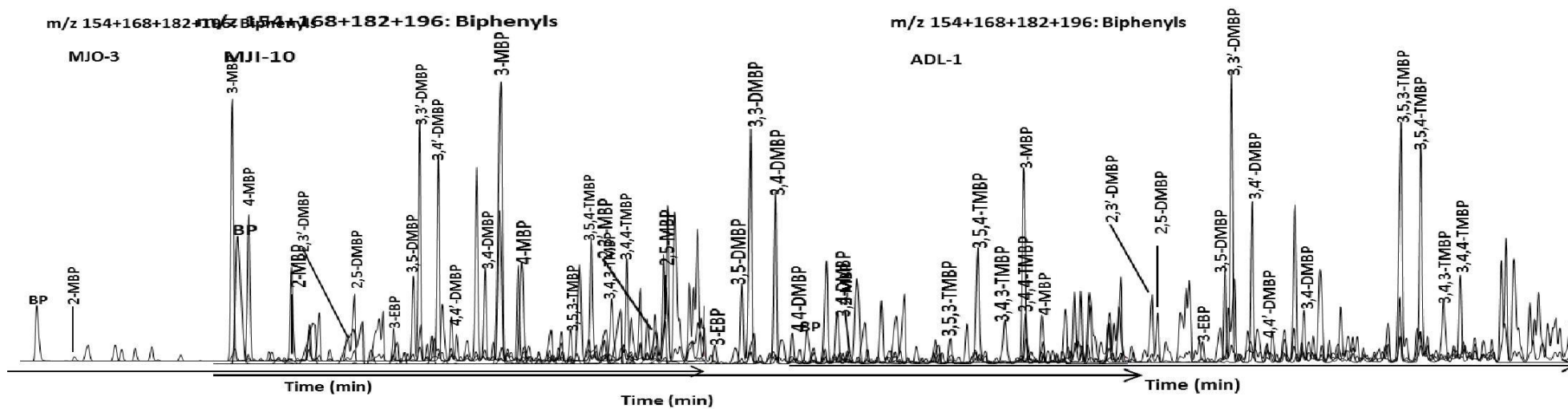
Table 1b: Geochemical Parameters Computed from Biphenyl Compounds and related Parameters in Niger Delta Crude Oil

Sample	Depth (m)	Biphenyl (%)				MBp R	DMBpR -x	DMBpR -y	Pr/P h	20S/20S+2	MPI-1
		C ₀	C ₁	C ₂	C ₃					OR C ₂₉	
OKN-13	2566-		21.9	37.2	36.0				2.49	0.35	0.94
	2568	4.83	1	0	5	29.64	10.28	22.53			
OKN-14	2677-		30.3	41.1	21.9				2.1	0.41	0.62
	2683	6.47	8	7	9	26.81	11.28	18.25			
OKN-15	3148-		24.5	46.4	27.1				2.28	0.38	0.65
	3154	1.89	7	1	4	75.25	18.76	31.27			
OKN-16	3593-		29.5	43.1	23.2				2.17	0.41	0.7
	3605	4.02	6	4	8	47.77	16.64	25.32			
MJI-1	2207-		13.1	36.1	46.0				2.93	0.28	0.76
	2216	4.66	5	2	7	3.59	7.84	3.49			

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MJI-2	2070-2081	8.05	30.8	40.4	20.6	44.92	21.46	36.33	3.33	0.4	0.84	
MJI-3	2091-2104	8.73	30.3	39.8	21.1	35.73	16.93	33.65	3.33	0.36	0.83	
MJI-4	2096-2101	10.1	33.6	38.8	17.4	38.04	17.49	34.42	4.37	0.37	0.96	
MJI-5	1607-1611	5.66	15.2	36.2	42.7	4.23	8.41	4.28	2.74	0.35	0.78	
MJI-6	1777-1779	9.39	29.4	38.9	22.1	23.85	13.06	23.89	3.24	0.34	0.82	
MJI-7	1795-1797	9.63	32.7	39.1	18.5	37.73	17.51	33.06	4.71	0.39	0.86	
MJI-8	1920-1921	9.14	27.3	37.7	25.7	16.80	20.31	26.78	3.08	0.36	0.82	
MJI-9	1936-2342	9.39	31.2	39.0	20.3	36.03	28.59	44.29	3.26	0.38	0.83	
MJI-10	1944-1947	9.39	34.0	35.8	16.3	33.49	15.44	32.20	4.43	0.38	0.83	
MJO-1	1948-1950	4.50	29.6	42.7	23.1	114.0	0	54.31	71.09	1.76	0.45	0.71
MJO-2	1979-2398	4.30	30.7	42.2	22.6	60.24	25.76	35.59	1.76	0.46	0.77	
MJO-3	2442-2444	4.52	29.8	42.7	22.8	55.46	26.10	35.69	1.68	0.45	0.78	
MJO-4	3030-3036	2.65	26.7	44.5	26.0	54.69	19.60	29.79	1.7	0.45	0.89	
WZB-1	1610-2647	6.35	25.7	40.0	27.8	32.83	18.57	22.91	2.35	0.42	0.86	
WZB-2	1811-1957	6.62	16.6	39.9	36.8	11.79	15.37	10.32	1.48	0.37	0.86	

*MPI-1 (methylphenanthrene index-1) = $1.5 \frac{(2- + 3\text{-methylphenanthrene})}{(\text{phenanthrene} + 1- + 9\text{-methylphenanthrene})}$; Pr/Ph = pristane/phytane; MBpR = 3-methylbiphenyl/2-methylbiphenyl; DMBpR-x = 3,5-dimethylbiphenyl/2,5-dimethylbiphenyl; DMBpR-y = 3,3'-dimethylbiphenyl/2,3'-dimethylbiphenyl; $C_{29} 20S/(20S+20R) = 5\acute{a}(H), 14\acute{a}(H), 17\acute{a}(H)-20S/(5\acute{a}(H), 14\acute{a}(H), 17\acute{a}(H)-20S + 5\acute{a}(H), 14\acute{a}(H), 17\acute{a}(H)-20R)$ of C_{29} steranes; C_0 = biphenyl; C_1 = methyl-; C_2 = dimethyl or ethyl-; C_3 = trimethylbiphenyls



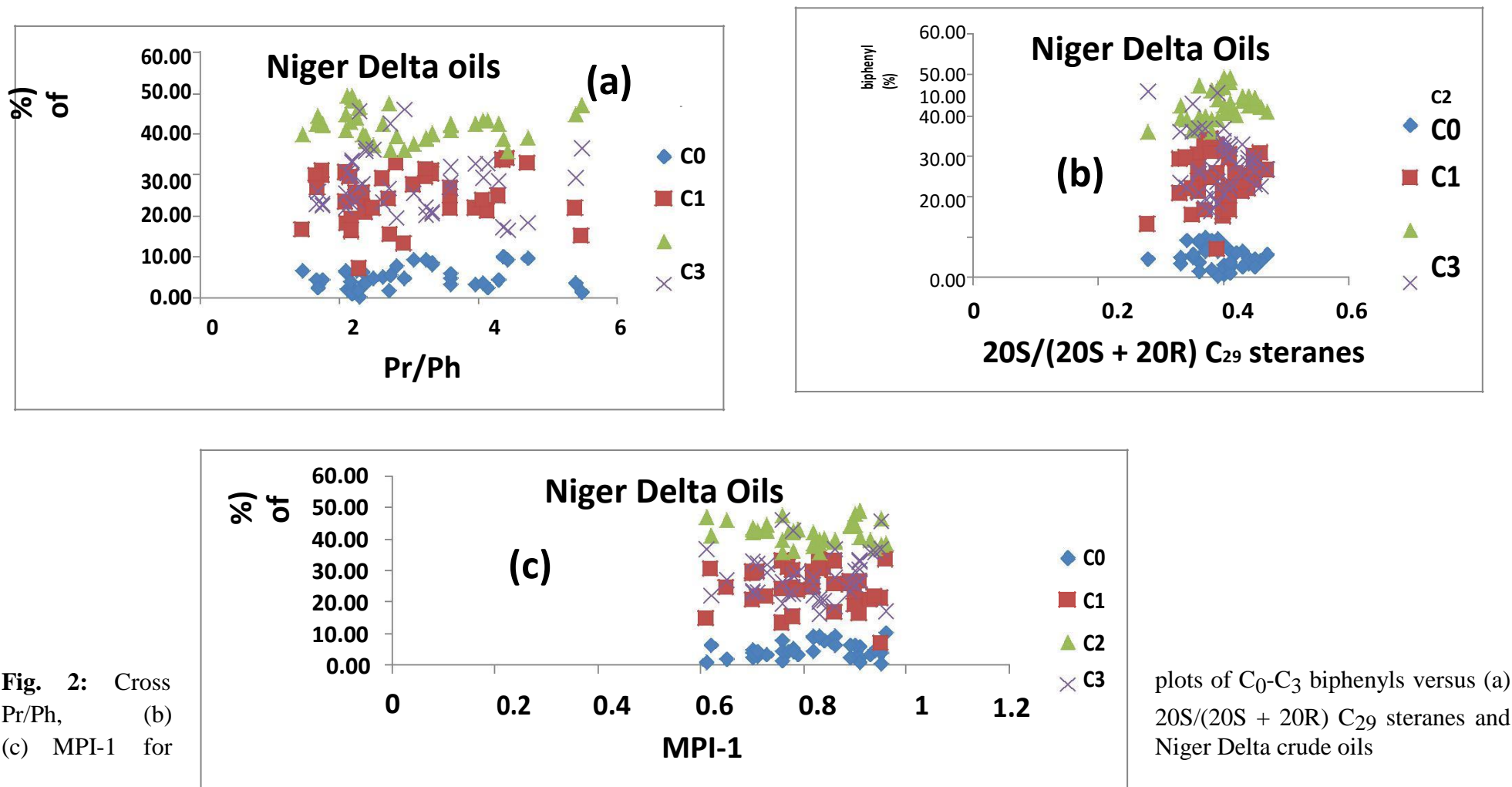


Fig. 2: Cross Pr/Ph, (b) MPI-1 for

plots of C₀-C₃ biphenyls versus (a) 20S/(20S + 20R) C₂₉ steranes and Niger Delta crude oils

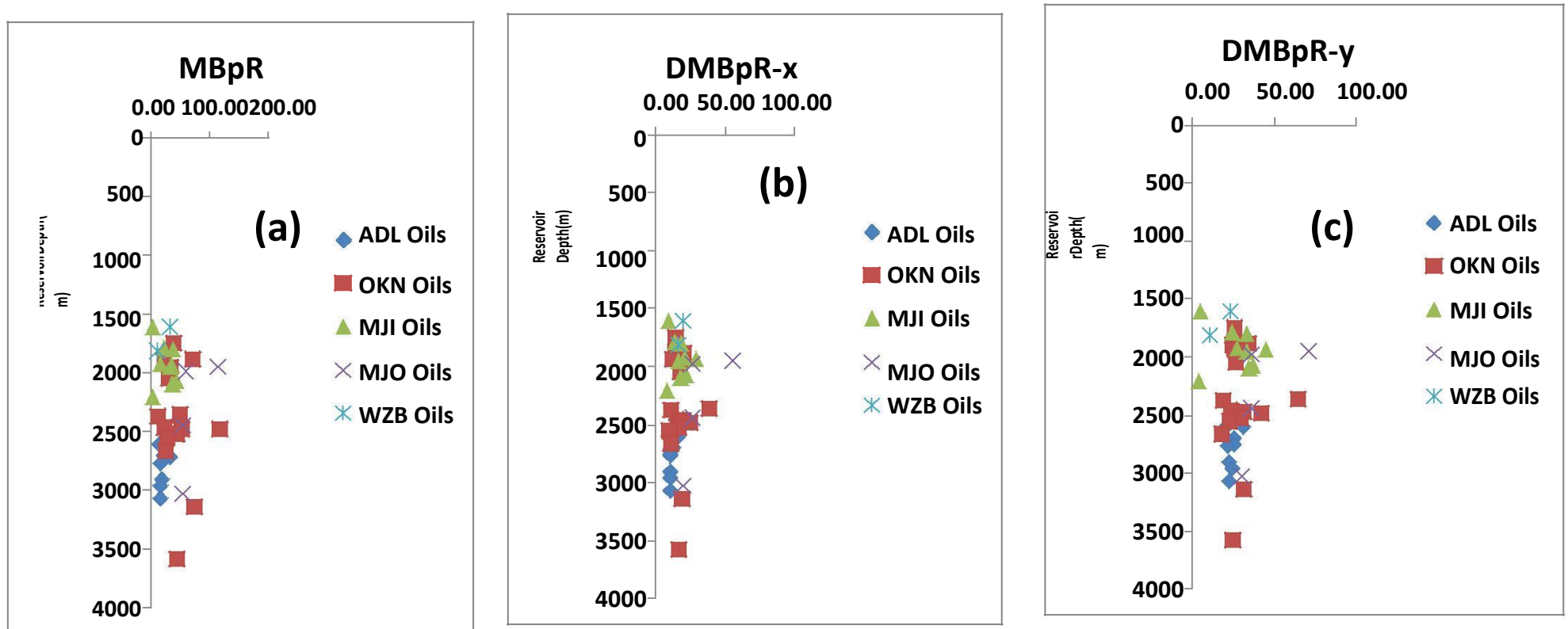


Fig. 3: Cross plots of burial depths versus (a) MBpR, (b) DMBpR-x and (b) DMBpR-y for Niger Delta crude oils.

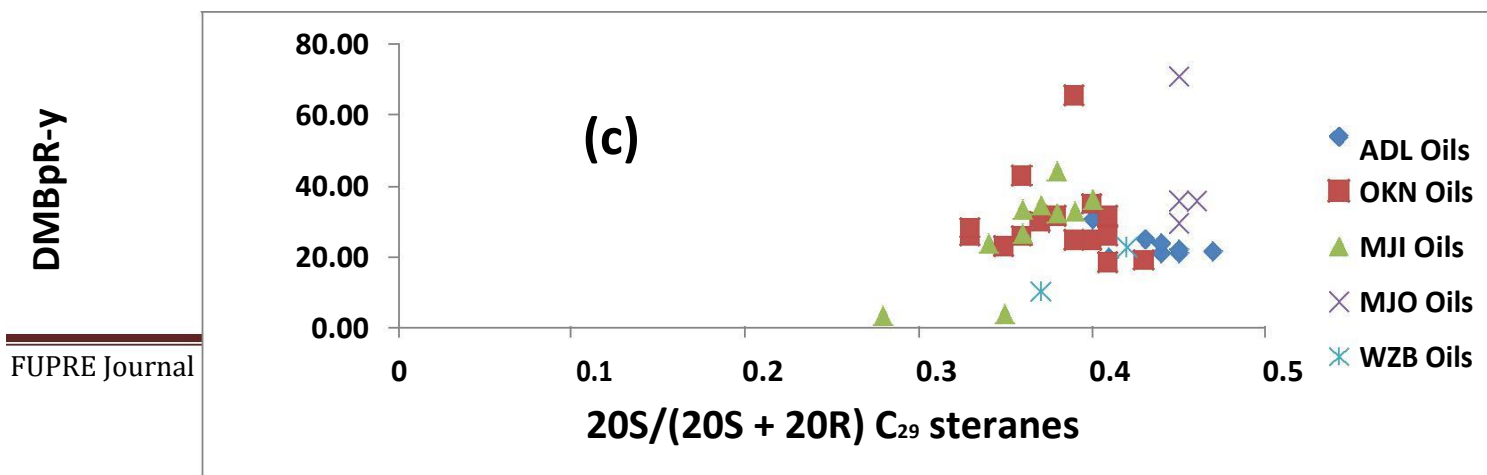
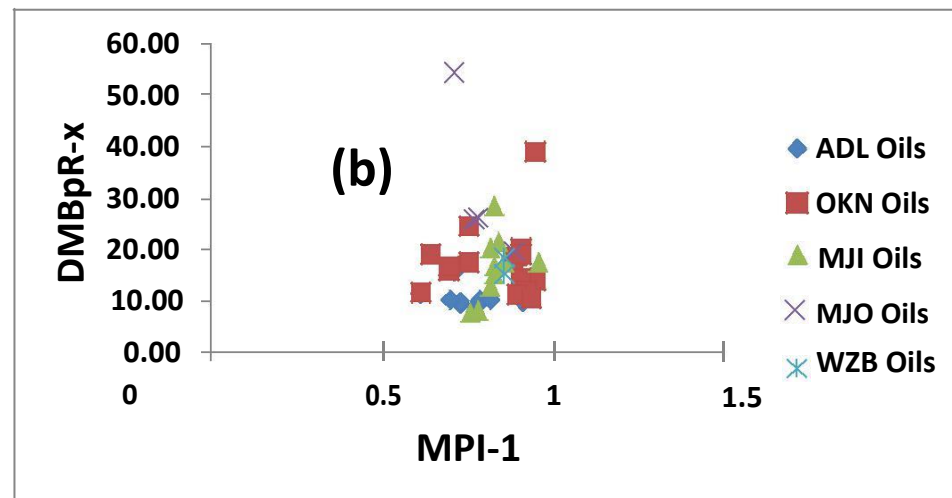
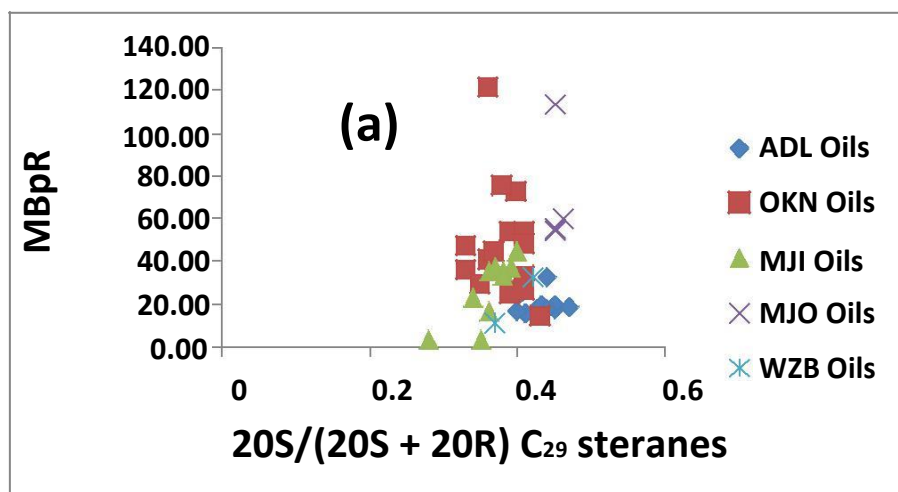


Fig. 4: Cross plots of (a) MBpR versus $20S/(20S + 20R)$ C₂₉ steranes, (b) DMBpR-x versus $20S/(20S + 20R)$ C₂₉ steranes, (c) DMBpR-y versus MPI-1 for Niger Delta crude oils.