



# Aromatic Hydrocarbons as Indicators of Maturation and Source: Correlative Geochemical Evaluation of Commingled Niger Delta Crude Oils

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## Abstract

Two Niger Delta crude oils from Rivers and Delta States (samples A and F) and their compositional mixtures (samples B, C, D and E) were evaluated using a range of geochemical parameters derived from aromatic hydrocarbons and aromatic sulphur compounds to determine their source and maturity. The relative distribution of various plant markers in crude oil samples A and F which were retained in their compositional mixes suggests the contribution of angiosperm higher plants and coniferous higher plants to the source rocks that generated the crude oils. The various maturity parameters computed for the oil samples revealed that both the Rivers and Delta crude oils lie in the high maturity state with sample F significantly more matured than sample A. All alkynaphthalene maturity parameters suggested a peak to late oil generation window for the crude oil samples except the methyl naphthalene ratio (MNR) whose maturity sequence lacks sufficient variation to distinguish maturity differences in the crude oil samples. The maturity characters of TNR-1 and TNR-2 (trimethylnaphthalene ratio) showed a strong correlation between the individual crude oil samples and their mixtures. However, all the other maturity parameters showed moderate or weak correlation between the individual crude oil samples and their mixtures.

**Keywords:** Aromatic hydrocarbons; Maturity; Source; Commingling; Niger Delta

## Introduction

Crude oil consists of a wide range of hydrocarbons that range from saturates, aromatics and nitrogen, sulfur or oxygen (N, S, O) compounds. Embedded within these hydrocarbon compounds are information on the maturity and organic matter source which formed the crude oil [1-3]. Aromatic hydrocarbons found in crude oils are useful as maturity and source indicators in basin analysis and have been found, in some cases, to be more reliable than the aliphatic biomarkers [4,5]. They are more sensitive to maturity differences in the mid to late parts of the oil generation window [6]. Aromatic sulphur compounds have also demonstrated to be very important in evaluating the maturity of crude oils and source rocks [7-9]. Many of the aliphatic biomarker maturity parameters are reported to reach equilibrium before the main stage of oil window and in

some cases show inversion at high maturity levels. As such, they are not effective maturity indicators [4].

Aromatic hydrocarbons are resistant to biodegradation and can span a wide range of thermal maturities under elevated temperatures. These indicators respond to an increase in thermal stress with a predictable alkylation progression of a given parent compound or a shift in the isomer distribution of the alkyl-aromatic homologues towards thermally more stable isomers. The concentrations of the thermodynamically least stable isomers ( $\alpha$ ) are compared with the thermodynamically more stable isomers ( $\beta$ ). The principle behind this is that the methyl group shifts from  $\alpha$ - to  $\beta$ - position with increase in thermal maturity [10]. A number of maturity parameters have been developed based on the distributions of the polycyclic aromatic compounds. In this study therefore, the distributions of alkyl naphthalenes,

biphenyls, phenanthrenes and aromatic sulphur compounds (thiophenes) were applied to determine the maturity and source of two Niger Delta crude oils as well as the trends exhibited by these aromatic geochemical compounds in their compositional mixes.

## Materials and Method

### Study Area

The Niger Delta region is one of Nigeria's five sedimentary basins where oil is produced. It is an extremely prolific hydrocarbon province situated in Southern Nigeria between longitude 5° - 9° E and latitude 4° - 6° N on the West African continental margin, at the apex of the Gulf of Guinea [11,12]. Nine (9) states namely: Ondo, Edo, Delta, Imo, Abia, Bayelsa, Rivers, Akwa-Ibom and Cross-River constitute the oil producing Niger Delta region of Southern Nigeria.

### Samples

Crude oil samples used for the study were obtained from two states in the Niger Delta region namely: Rivers and Delta states. The crude oil samples were collected from two producing oil wells in the states by field technicians with the permission of the Department of Petroleum Resources (DPR) and labelled samples A and F respectively. Mixtures of samples A and F were made at different composition to obtain samples B (4:1), C (3:2), D (2:3) and E (1:4).

### Crude Oil Fractionation

50 mg of each crude oil sample was weighed into labelled centrifuge tube and excess pentane added to precipitate the asphaltenes. The samples were allowed to stand for four hours and transferred into a fischer centrifuge set at 1,500 rpm for thirty minutes [13]. The pentane soluble fraction was decanted, concentrated and introduced into a glass chromatographic column (30 cm x 1 cm) stuffed with glass wool at the bottom and packed with activated silica gel. *n*-Hexane was poured into the packed column to elute the

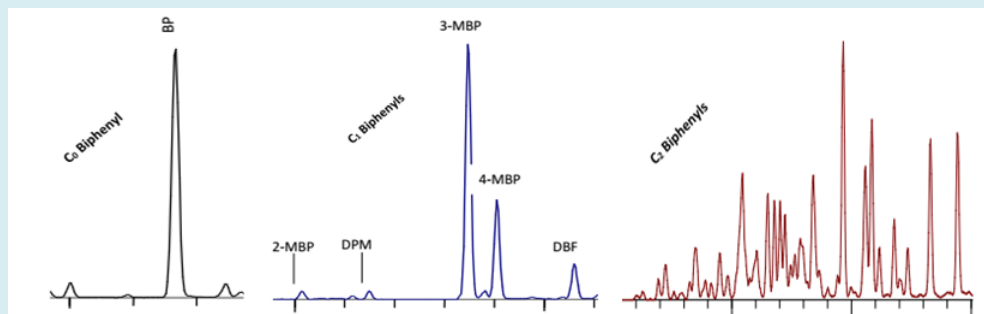
saturates, dichloromethane poured to elute the aromatics and dichloromethane/methanol (1:1) mixture poured to elute the resins. The eluents were collected into pre-weighed vials and the solvents evaporated to dryness under a gentle stream of nitrogen at 40 °C.

### Gas Chromatography-Mass Spectrometry (GC-MS) Analysis

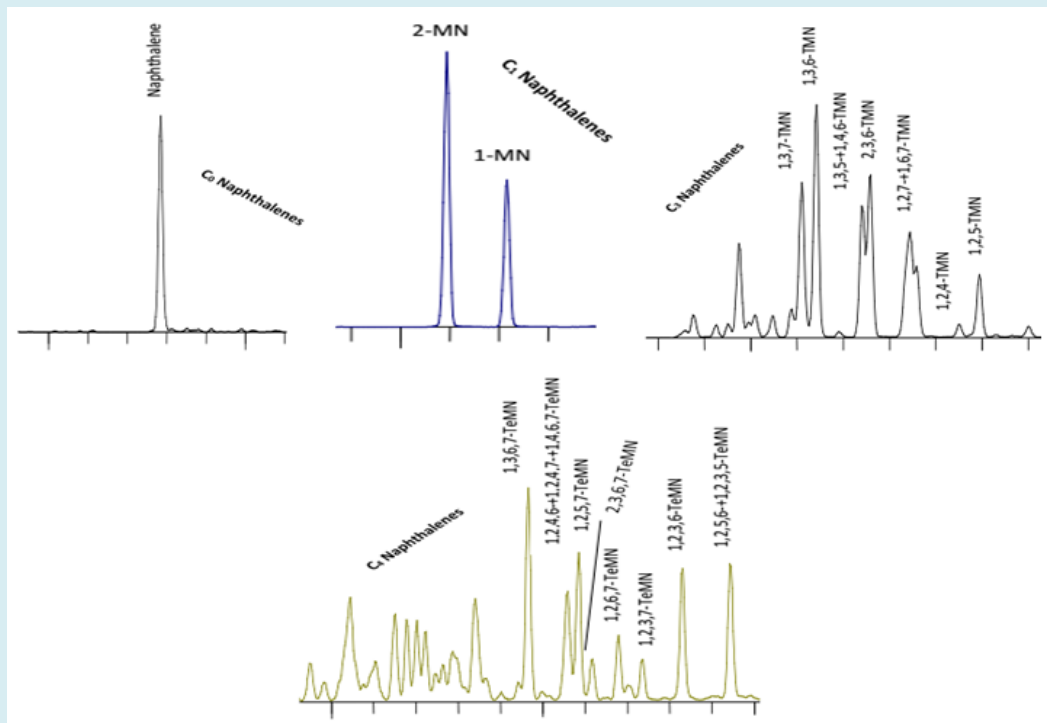
Detailed analysis of the aromatic fractions was facilitated by Agilent 7820A gas chromatography (GC) system fitted to a fused silica capillary column (30m x 0.25µm) and equipped with an Agilent 5975 series mass selective detector (MSD). One microlitre (1µL) of the aromatic component of each fractionated oil sample was injected into the GC capillary column with the aid of a G4513A automatic liquid sampler (ALS) using a split ratio mode of 100:1. The GC oven was initially set at 100°C for 5 min, programmed to 320 °C at 3 °C /min, with a final holding time of 25 min. The temperature of feed ports is fixed at 300 °C. The MS was operated with an ion source temperature of 320 °C, and an ionization energy of 70 eV. Peak identification was by comparison with related literature. Quantification was acquired by area integration of each identified peak which was processed by Chemstation OPEN LAB CDS software.

### Results and Discussion

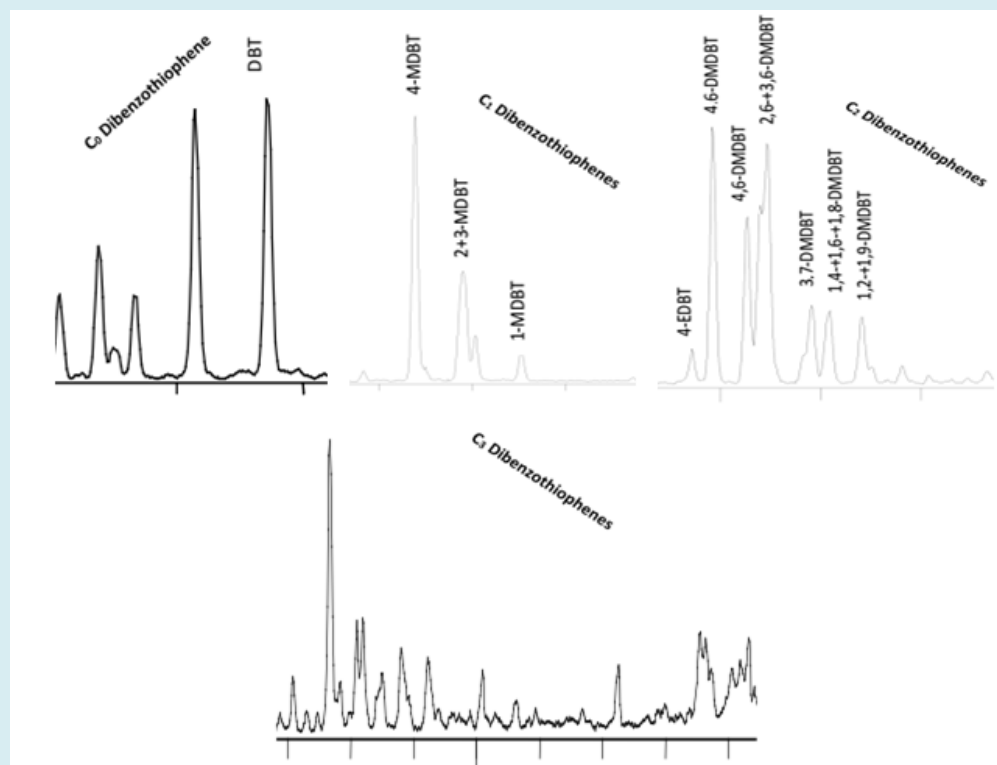
GC-MS analysis identified aromatic hydrocarbons in all the crude oil samples. The identified aromatic hydrocarbons include C<sub>0</sub> - C<sub>2</sub> biphenyls (m/z 154, 168 and 182), C<sub>0</sub> - C<sub>4</sub> naphthalenes (m/z 128, 142, 156, 170 and 184), C<sub>0</sub> - C<sub>3</sub> dibenzothiophenes (m/z 184, 198, 212 and 226) and C<sub>0</sub> - C<sub>4</sub> phenanthrenes (m/z 178, 192, 206, 220 and 234). Representative mass fragmentograms of the identified aromatic hydrocarbons are presented in Figures 1-4 and their names listed in Table 1. From these a total of 98 aromatic hydrocarbon compounds were selected and used for analysis of the source origin and maturity of the two Niger Delta crude oil samples as well as the trend they exhibit in their compositional mixes.



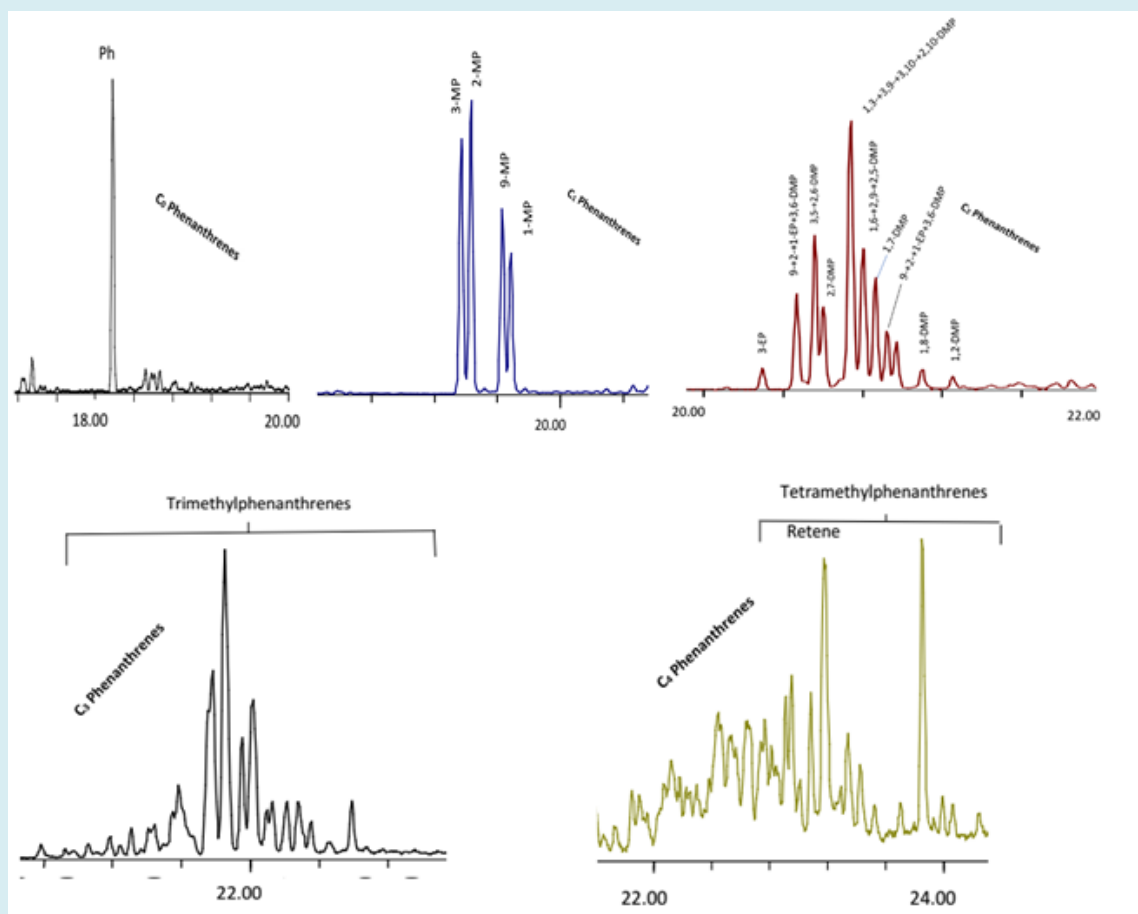
**Figure 1:** Representative mass fragmentograms showing the distribution of C<sub>0</sub> - C<sub>2</sub> biphenyls in the sample crude oil (B) at m/z 154, 168 and 182.



**Figure 2:** Representative mass fragmentograms showing the distribution of  $C_0 - C_4$  Naphthalenes in the crude oil (sample B) at  $m/z$  128, 142, 156, 170 and 184.



**Figure 3:** Representative mass fragmentograms showing the distribution of  $C_0 - C_3$  dibenzothiophenes in the crude oil (sample B) at  $m/z$  184, 198, 212 and 226.



**Figure 4:** Representative mass fragmentograms showing the distribution of  $C_0 - C_4$  Phenanthrenes in the crude oil (sample B) at  $m/z$  178,192,206,220 and 234.

Peaks	Compound
BP	Biphenyl
2-MBP	2-Methylbiphenyl
DPM	Diphenylmethyl
3-MBP	3-Methylbiphenyl
4-MBP	4-Methylbiphenyl
DBF	Dibenzofuran
DBT	Dibenzothiophene
4-MDBT	4-Methyl Dibenzothiophene
2+3-MDBT	2 & 3-Methyl Dibenzothiophene
1-MDBT	1-Methyl Dibenzothiophene
4-EDBT	4-Ethyl Dibenzothiophene
4,6-DMDBT	4,6-Dimethyl Dibenzothiophene
2,4-DMDBT	2,4-Dimethyl Dibenzothiophene
2,6+3,6-DMDBT	2,6 & 3,6-Dimethyl Dibenzothiophene

3,7-DMDBT	3,7-Dimethyl Dibenzothiophene
1,4-+1,6-+1,8-DMDBT	(1,4 + 1,6 + 1,8)-Dimethyl Dibenzothiophene
1,2+1,9-DMDBT	1,2 & 1,9-Dimethyl Dibenzothiophene
N	Naphthalene
2-MN	2-Methylnaphthalene
1-MN	1-Methylnaphthalene
2-EN	2-Ethylnaphthalene
1-EN	1-Ethylnaphthalene
2,6-+2,7-DMN	2,6 & 2,7-Dimethylnaphthalene
1,3+1,7-DMN	1,3 & 1,7-Dimethylnaphthalene
1,6-DMN	1,6-Dimethylnaphthalene
1,4-+2,3-DMN	1,4 & 2,3-Dimethylnaphthalene
1,5-DMN	1,5-Dimethylnaphthalene
1,2-DMN	1,2-Dimethylnaphthalene
1,3,7-TMN	1,3,7-Trimethylnaphthalene
1,3,6-TMN	1,3,6-Trimethylnaphthalene
1,3,5+1,4,6-TMN	(1,3,5 & 1,4,6)-Trimethylnaphthalene
2,5,6-TMN	2,5,6-Trimethylnaphthalene
1,2,7-+1,6,7-TMN	(1,2,7 & 1,6,7)-Trimethylnaphthalene
1,2,4-TMN	1,2,4-Trimethylnaphthalene
1,2,5-TMN	1,2,5-Trimethylnaphthalene
1,3,6,7-TeMN	1,3,6,7-Tetramethylnaphthalene
1,2,4,6-+1,2,4,7-+1,4,6,7-TeMN	(1,2,4,5 + 1,2,4,7 + 1,4,6,7)-Tetramethylnaphthalene
1,2,5,7-TeMN	1,2,5,7-Tetramethylnaphthalene
2,3,6,7-TeMN	2,3,6,7-Tetramethylnaphthalene
1,2,6,7-TeMN	1,2,6,7-Tetramethylnaphthalene
1,2,3,7-TeMN	1,2,3,7-Tetramethylnaphthalene
1,2,3,6-TeMN	1,2,3,6-Tetramethylnaphthalene
1,2,5,6+1,2,3,5-TeMN	(1,2,5,6 & 1,2,3,5)-Tetramethylnaphthalene
P	Phenanthrene
3-MP	3-Methylphenanthrene
2-MP	2-Methylphenanthrene
9-MP	9-Methylphenanthrene
1-MP	1-Methylphenanthrene
3-EP	3-Ethylphenanthrene
9+2-+1-EP+3,6-DMP	(9 + 2 + 1-EP + 3,6)-Dimethylphenanthrene
3,5-+2,6-DMP	(3,5 & 2,6)-Dimethylphenanthrene
2,7-DMP	2,7-Dimethylphenanthrene
1,3-+3,9-+3,10-+2,10-DMP	(1,3 + 3,9 + 3,10 + 2,10)-Dimethylphenanthrene

1,6+2,9+2,5-DMP	(1,6 + 2,9 + 2,5)-Dimethylphenanthrene
1,7-DMP	1,7-Dimethylphenanthrene
2,3-+1,9-+4,9-+4,10-DMP	(2,3 + 1,9 + 4,9 + 4,10)-Dimethylphenanthrene
1,8-DMP	1,8-Dimethylphenanthrene
1,2-DMP	1,2-Dimethylphenanthrene

**Table 1:** Peak Identification of Some Polycyclic Aromatic Hydrocarbons and Aromatic Sulfur Compounds (Thiophenes) in the Niger Delta Crude Oils.

Generally, variations in relative distribution of geochemical compounds indicate a difference in source and depositional environment of organic matter [14,15]. Aromatic hydrocarbon plant markers such as 1,2,5-trimethylnaphthalene (1,2,5-TMN), 1-methylphenanthrene, 1,7-dimethylphenanthrene and retene, derived from Araucariaceae [16], are all present in crude oil samples A and F. The relative abundance of 1,2,5-TMN among the naphthalenes in samples A (6.33%) and F (6.16%) support significant angiosperm higher plant input to the source rock that generated the oils, which was more in sample A. This feature was retained in their compositional mixes. These data are consistent with the presence of oleanane and/or lupane in the Niger Delta crude oils. Furthermore, log ratios of (1-MP/9-MP), (1,7-DMP/1,3-+3,9-+2,10-+3,10-DMP) and (retene/9-MP) were proposed as a means of detecting organic matter input from coniferous higher plants [17]. These source specific aromatic ratios

did not exceed the thresholds for samples A, F and their mixtures. Their source organic matter however, is consistent with the aliphatic hydrocarbon data for these sets of crude oils which suggested greater higher plant organic matter input as reported by Onyema et al. [12].

Most of the maturity parameters computed for the individual crude oils and their compositional mixtures (Table 2) revealed an increase in thermal maturity from sample A to F. Radke [6] established that aromatic hydrocarbons do change in a regular fashion with increasing maturity, thus a number of maturity parameters have been developed based on the distributions of alkyl naphthalene, biphenyl, dibenzothiophene and phenanthrene. Maturity parameters computed from these aromatic hydrocarbon compounds in the oil samples and their mixtures are presented in Table 2.

S.No.	Diagnostic Ratio	Samples					
		A	B	C	D	E	F
1	MNR	1.44	1.45	1.79	1.45	1.84	1.2
2	DNR	6.66	6.86	9.8	3.9	10.99	9.43
3	TNR-1	0.84	1.1	1.15	1.11	1.3	1.47
4	TNR-2	0.74	0.86	0.82	0.83	0.94	0.98
5	TNR-3	0.53	0.58	0.6	0.58	0.72	0.71
6	Log(1,2,7-TMN/1,3,7-TMN	0.15	0.08	0.11	0.09	0.12	0.13
7	TMNr	0.53	0.58	0.6	0.58	0.72	0.71
8	Rcb	0.84	0.91	0.89	0.9	0.96	0.99
9	MPI	0.87	1.25	1.02	1.05	1.04	1.02
10	MPI-2	0.85	1.29	1.05	1.1	1.07	1.06
11	MPI-3:	1.09	0.66	1.54	1.54	1.61	1.61
12	Rc	0.92	1.15	1.01	1.03	1.02	1.01
13	MPDF	0.52	0.59	0.61	0.61	0.62	0.62
14	DPR	0.36	0.45	0.15	0.48	0.48	0.48
15	MBpR	0.3	0.32	0.36	0.33	0.34	0.36
16	P/MP	0.42	0.5	0.5	0.47	0.51	0.52

17	MDR	2.33	5.47	7.42	6.41	9.17	7.45
18	MDR*	0.69	0.85	0.88	0.87	0.9	0.9
19	Rcs	0.68	0.91	1.05	0.98	1.12	1.05
20	DBT/P	0.18	0.09	0.1	0.09	0.1	0.08
21	Log(1-MP/9-MP)	-0.11	-0.13	-0.13	-0.12	-0.12	-0.13
22	Log(Retene/9-MP)	-0.38	-0.76	-0.78	-0.88	-0.96	-1.35
23	Log(1,7-DMP/[1,3 + 3,9 + 2,10 + 3,10-DMP])	-0.26	-0.39	-0.41	-0.42	-0.45	-0.45

**Table 2:** Aromatic hydrocarbon thermal maturity parameters for two Niger Delta crude oils and their compositional mixtures.

MNR: methyl naphthalene ratio (2-MN/1-MN)

DNR-1: dimethylnaphthalene ratio 1 ([2,6- + 2,7-DMN]/1,5-DMN)

TNR-1: trimethylnaphthalene ratio 1 (2,3,6-TMN/[1,4,6- + 1,3,5-TMN])

TNR-2: trimethylnaphthalene ratio 2 (2,3,6- + 1,3,7-TMN/[1,4,6- + 1,3,5- + 1,3,6-TMN])

TMNr: trimethylnaphthalene ratio (1,3,7-TMN/[1,3,7-TMN + 1,2,5-TMN])

TeMNR: tetramethylnaphthalene ratio (1,3,6,7-TeMN/[1,3,6,7- + 1,2,5,6-TeMN])

MPI: methylphenanthrene index 1.5 · [3-MP + 2-MP]/[P + 9-MP + 1-MP]

MPI-2: methylphenanthrene index 2 (3\* 2-MPI (P + I-MP + 9-MP)

MPI-3: Methylphenanthrene Index

Rc: calculated reflectance (0.6 · MPI + 0.4)

Rcb: 0.40+0.6×(TNR-2)

Rcs: 0.073×MDR + 0.5

MPDF: methylphenanthrene distribution fraction ([3-MP + 2-MP]/RMPs)

DPR: dimethylphenanthrene ratio ([3,5- + 2,6-DMP + 2,7-DMP]/[1,3 + 3,9- + 2,10- + 3,10-DMP + 1,6- + 2,9- + 2,5-DMP])

MBpR: methylbiphenyl ratio (3-MBp/2-MBp)

DBT/P: Dibenzothiophene/Phenanthrene

DMBpR-x: dimethylbiphenyl ratio x (3,5-DMBp/2,5-DMBp)

DMBpR-y: dimethylbiphenyl ratio y (3,30-DMBp/2,30-DMBp)

MDR: methyl dibenzothiophene ratio (4-MDBT/1-MDBT)

MDR\*: Methyl dibenzothiophene ratio (4-MDBT/4-DBT + 1-MDBT)

DMDR: dimethyl dibenzothiophene ratio (4,6-DMDBT/[3,6- + 2,6-DMDBT])

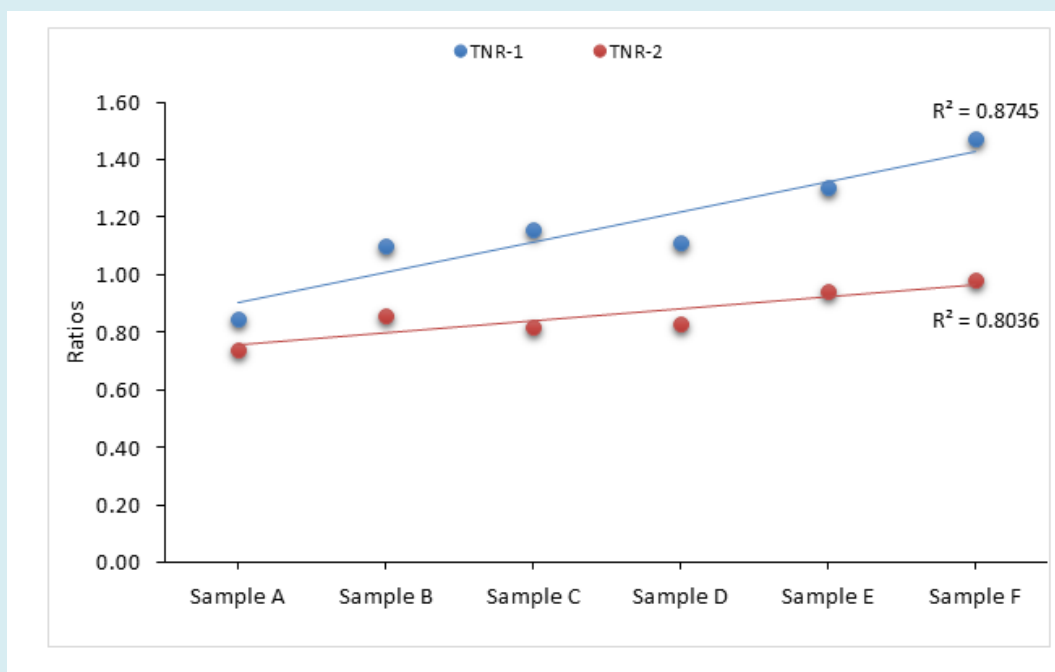
Dimethylnaphthalene ratio (DNR-1) is a useful aromatic hydrocarbon maturity parameter for samples having mean vitrinite reflectance ( $R$ ) equal or higher than 1%. Generally, ratios of DNR-1 > 6.65 (Table 2) suggest that thermal maturity of the two Niger Delta crude oils, samples A and F, reached peak to late oil generation window. The result also reveal that the DNR-1 feature of the two Niger Delta crude oils was expressed in their mixtures, except for sample D with a low ratio of 3.90, but was not relative to the compositional mix. The methyl naphthalene ratio (MNR) as shown on Table 2 does not support the maturity sequence exhibited by other alkynaphthalene thermal maturity parameters. The relative maturities based on MNR appear spurious when compared to other maturity indices as it lacked sufficient variation to distinguish maturity differences in the crude oils. No peculiar trend could be deduced for the MNR ratio which ranges from 1.20 – 1.84 for both the individual and composition mix crude oil samples. It therefore showed a weak to moderate correlation between the individual crude oils and its commingled samples.

The methylphenanthrene index (MPI) is a commonly used thermal maturity parameter of aromatic hydrocarbons which is calibrated with mean vitrinite reflectance ( $R_m$ ) for source rocks and crude oils [18]. The calculated vitrinite reflectance ( $R_c$ ) from MPI classifies crude oils thermal maturity into immature (0.70), mature (0.85) and post mature (> 0.95) [19]. The MPI and  $R_c$  for the crude oil samples range from 0.87 to 1.25 and 0.92 to 1.15 respectively. These show high maturity of the source rocks which generated the two Niger Delta crude oils with sample A oil (Rivers state) being slightly less mature than sample F oil (Delta state). The maturity sequence however does not show a linear relationship to the compositional mix of the two Niger Delta crude oils. Methyl dibenzothiophene ratio (MDR; 4-/1-MDBT) is sensitive to maturity changes and shows good correlation with vitrinite reflectance [20]. The commonly used parameter, methyl dibenzothiophene ratio (MDR), is derived based on a methyl shift from thermally less stable isomer (1-MDBT) to thermally more stable isomer (4-MDBT) with increase in thermal maturity. MDR is calibrated with vitrinite reflectance and reported as  $R_{cs}$ . The MDR and  $R_{cs}$  values for

oil samples A and F and their mixtures, samples C – E, ranged from 2.33 to 9.17 and 0.68 to 1.12 respectively. This suggest a peak to late oil generation window thermal maturity of the two Niger Delta crude oils. MDR and  $R_{cs}$  showed a linear relationship between the two Niger Delta crude oils and their compositional mix. Variations in expulsion stages of 1-MDBT and 4-MDBT isomers from kerogen was shown to affect MDR and Chakhmakhev and Suzuki [20] have pointed out its limitations for coal samples where it does not show linear relationship between 0.5 to 1.0%  $R_{cs}$ . However, Radke et al. [7] introduced a revised form of MDR as MDR\* where it was calculated by traditional biomarker maturity parameters i.e.  $4\text{-MDBT}/(4\text{-MDBT} + 1\text{-MDBT})$ . MDR\* values shown in Table 2 range from 0.68 - 1.05 and reveal higher thermal maturity for sample F. The distribution of methylbiphenyl represented

in the methylbiphenyl ratio (MBpR) further validates other maturity parameters which suggest a lower maturity for sample A compared to sample F. The calculated maturity parameter results reveal the two Niger Delta crude oils were of high maturity with the crude oil from Delta State (sample F) being of more matured than Rivers State (sample A).

TNR-1 values  $>1$  for all the samples except sample A indicates that the maturity of source rocks generating these oils reached post mature level. This parameter exhibited a strong correlation between the individual crude oil samples and their composition mixtures. Similarly, TNR-2 a useful aromatic hydrocarbon thermal maturity parameter showed trend with increase in thermal maturity of the crude oil samples and their mixtures (Figure 5).



**Figure 5:** Plot of trimethylnaphthalene ratios (TNR-1 and TNR-2) against the studied crude oils and their compositional mixtures showing the level of correlation.

TNR-2 values (0.74 - 0.98) and the calculated vitrinite reflectance  $R_{cb}$  (0.84 - 0.99) indicate that the thermal maturities of the crude oils reached peak to late oil generation window. The values further showed sample F to be more matured than sample A [21]. In addition, the maturity sequence in the individual samples were expressed in their mixtures and showed a very strong linear relationship (0.8045) with the compositional mix as shown in Figure 5.

## Conclusions

Crude oil samples from Rivers and Delta states of

the Niger Delta exhibited a significant range of thermal maturities reflecting different timing of oil generation and expulsion from their source rocks. Aromatic hydrocarbon maturity results revealed that the two Niger Delta crude oils were of high maturity state as reflected in the maturity parameters. The thermal maturity of the crude oil from Delta State (sample F) was higher than that from Rivers State (sample A) in all the parameters evaluated. All alkyl naphthalene thermal maturity parameters suggest a peak to late oil generation window for the crude oil samples except methyl naphthalene ratio (MNR) whose maturity sequence lacks sufficient variation to distinguish maturity differences

in the crude oils. All the maturity parameters evaluated showed weak to moderate correlation ( $R^2$ ) between the two Niger Delta crude oils and their composition mixtures, except TRI-1 and TRI-2 whose maturity character in the oils and their mixtures showed a strong correlation.

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