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The Light Hydrocarbon Components and Oil-Oil Correlation in Niger Delta Crude Oil: Insights into Source, Thermal Maturation, and In-Reservoir Alteration Processes

Omonigho Khalin Egbo[1], Olubunmi Christopher Adeigbe[2], and Onoriode Esegbue[3]

[1]Department of Petroleum Engineering, Global Energy Training Institute, HCCS, Houston, Texas, USA
[2]Department of Geology, University of Ibadan, Nigeria
[3]School of Natural and Environmental Science, Newcastle University, Newcastle, United Kingdom

Corresponding author: omonigho.egbo@gmail.com

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Abstract - Geochemical fingerprints offer useful insight into source inputs, thermal maturity, and alteration processes. Nonetheless, detailed light hydrocarbon (LH) compositional studies across The Niger Delta have not adequately been considered. Thus, twenty-six oil sets from several subbasins (depobelts) were examined, using gas chromatography (GC) approach, aimed at determining the source input and thermal maturity in-reservoir alterations, and then correlating the oils. This provides critical insights for oil characterization in the basin by examining the distribution and abundance of LHs. Mango's invariant K_1 ratio of LHs clearly delineates the oils into two homologous sets, with a narrow range (0.83–0.94 and 0.95–1.13), consistent with the plot of ph/nC_{18} vs. pr/nC_{17} of heavy molecular weight (HMW). The studied oils reflect a modest distribution between Thompson's aliphatic and aromatic curves scheme (Kerogen Type), with heptane ratios varying from 0.64 to 22.04 %, on the average of 16.19 %, indicating contributions from a range of sources typical of type II/III kerogen. The LHs component of the examined oils has an overall six-ring preference, with methylcyclohexane varying from 46.15 to 81.86 %, the average of 56.50 %, dimethyl-cyc %, suggesting a significant input from higher plants. The data suggest expulsions from various source rocks of terrestrial organofacies, with variable contributions from marine sources that were initially laid down in oxic to sub-oxic environments, and range from early to peak oil thermal maturity. Nonetheless, most samples from Greater Ughelli showed varying degrees of evaporative fractionation, suggesting gas washing in the depobelt.

Keywords: light hydrocarbons, gas chromatography, thermal maturity, evaporative fractionation, kerogen type, homologous sets

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INTRODUCTION

The Niger Delta (Figure 1a) is located in a tropical rainforest in southern Nigeria, with dense vegetation and huge biochemical activities. A geologically dynamic region with high sedimentation and subsidence rates, influenced by local and eustatic sea level changes, has complex structural architecture that displays an extensional domain in the northern delta and a compressional thrust zone in the shallow offshore.

Moreover, studies have revealed conflicting origin of oils recovered from the western Niger Delta region (Haack *et al*., 2000; Eneogwe and Ekundayo, 2003), one of Africa's most prolific oil-producing basins. This presents considerable snags for oil-to-oil correlation and characterization due to intricate interactions between various

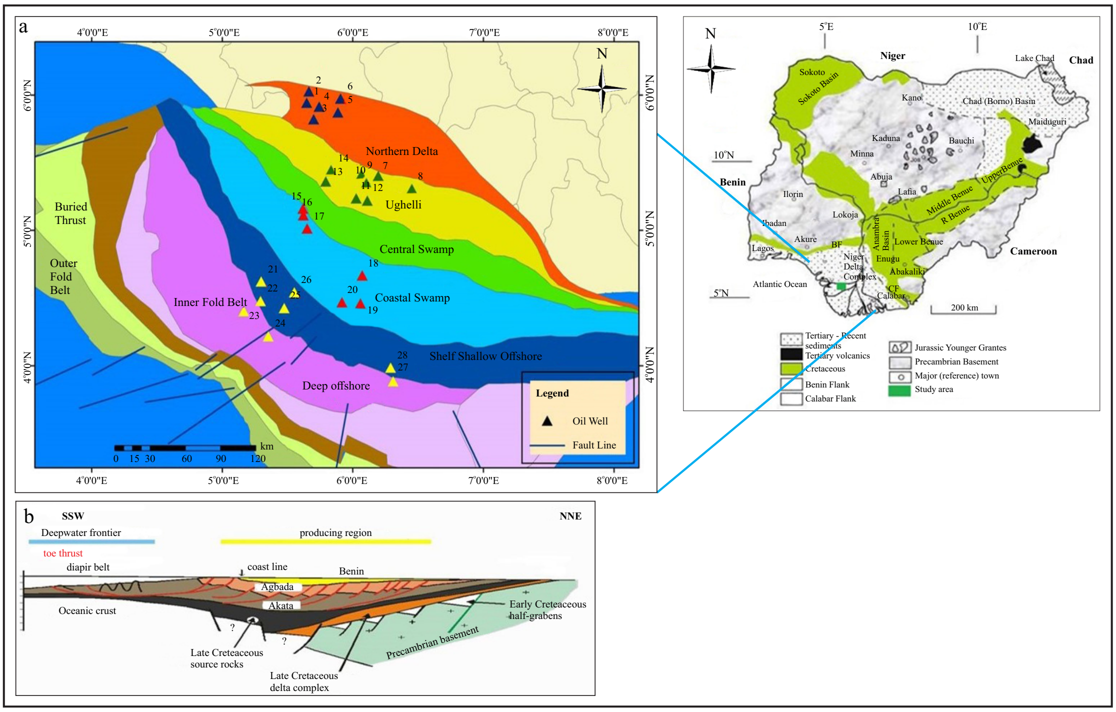

Figure 1. (a) Niger Delta map displaying depobelts and the positions of study oils; (b) The cross-sectional schematic illustration of The Niger Delta, exhibiting stratigraphic units and structural arrangements, after Lehner and De Ruiter (1977).

source rock inputs (Haack *et al*., 2000; Eneogwe and Ekundayo, 2003), oil mixing (Esegbue *et al*., 2020), biodegradation (Egbo *et al*., 2020), and in-reservoir processes.

Samuel *et al*. (2009) postulated that dissimilarities amongst the onshore and offshore oil accumulations, inferred the probability of three source-rock organic matter inputs, with abundant marine organic matters, dominating the deep-water oil pools, abundance of terrestrial intradelta organic matters permeating over the whole delta, and lastly mixed source-rock organic matter predominated the shallow water oil pools. Some other workers (Eneogwe and Ekundayo, 2003; Lehne and Dieckmann, 2010; Esegbue *et al*., 2020) have also investigated and reported that the Niger Delta petroleum accumulations are characterized as having hybrid thermal maturity constituents, which suggest mixtures.

The basin is divided into three key stratigraphic rock units (Figure 1b), and spans a geographical region of around 75,000 km^2, with a siliciclastic sediment infill that may reach the maximum thicknesses of between 9,000 and 12,000 m (Doust and Omatsola, 1990). The latest formation is The Benin Formation (Oligocene-recent), which is made up of sandstone in a river and shoreline setting, and has a thickness that varies around 2,000 m (Doust and Omatsola, 1990). Interbedded sandstones and shales from a transition-marine setting make up The Agbada Formation, which dates back to The Eocene. The real deltaic component of the series is represented by this formation, which is made up of paralic siliciclastics that are almost 3,700 m in the thickness (Doust and Omatsola, 1990).

Underlying The Agbada Formation is The Paleocene-Miocene Akata Formation, made up of massive, overpressure marine shale layers. Doust and Omatsola (1990) estimate the overall formation thickness to be close to 7 km. Nevertheless, in the far offshore portion of the basin, there is compelling evidence of a Cretaceous shale that sits unconformably over the continental-oceanic basement complexes, and has an overall thickness of around 2 km (Eneogwe and Ekundayo, 2003; Bellingham *et al*., 2014). However, the areal extent of this shale is not well defined due to its inaccessible depth by drilling operations (Reijers, 2011). These huge, thick shales of The

Cretaceous sediments, The Akata Formation, and the shale section of the paralic sequence of The Agbada Formation are the probable source rocks of the various crude oils generated within the basin (Eneogwe and Ekundayo, 2003; Samuel *et al*., 2009). The shales are predominantly marine in origin, with significant terrestrial organic material inclusions. Additionally, multiple sources may be anticipated throughout the succession, and it is very likely that there are several tens of meters of alternation between shales and coals (perhydrous and humic) with varying degrees of organic matter preservation and yields. These layer could have generated and contributed to the formation of oil and gas pools.

Undoubtedly, the basin has generated diverse ranges of petroleum types as a result of tectonic activity, sedimentary deposition conditions/ environments, thermal maturation, and post-generation alteration processes in the course of its geologic evolution.

Thus, the geochemical fingerprints of crude oils were critically utilized for predicting oil origin, thermal evolution, and in-reservoir alteration processes based on its LH distribution (Mango, 1997; Eneogwe, 2003, 2006; Peters *et al*., 2005; Akinlua *et al*., 2006).

Characteristically, in resolving, oil-oil as well as oil-source rock tie studies, in the field of petroleum geochemistry during the last forty years, biomarker techniques had played a central role in this development. Application of light hydrocarbon components were barely considered as a routine correlation tools because of their potential origin from thermal-induced cracking of heavier molecules. Hence, studies based on LHs were rarely taken into consideration (Mango, 1997), and were only thought of as useful parameters for describing in-reservoir alteration processes. It was not until Mango (1987) presented a constancy proportionality of the 4-isoheptanes in oil: K_1 = [2-methylhexane (2-MH) + 2,3-dimethylpentane (2,3-DMP)]/[3-methylhexane (3-MH) + 2,4-dimethylpentane (2,4-DMP)]= 1.0, irrespective of their absolute abundances in the oils. In a subsequent work, Mango (1990) suggested the stable-state catalytic reaction model to account for the parent-daughter relationship and the molecular creation of LHs in petroleum.

Similarly, Thompson (1979) introduced two LH metrics, isoheptane, and heptane indices that were extensively used for hydrocarbon thermal maturation and source classification analyses (Wang *et al*., 2010; Yu *et al*., 2014; Han *et al*., 2017; Zhenglu *et al*., 2021; Huang *et al*., 2022). In a subsequent work, Thompson (1988) presented the idea of evaporative fractionation, designating fractionated oils by the toluene/n-heptane ratio. Since then, geochemical correlation studies have often applied Mango's and Thompson's LHs parameters (Thompson, 1988; Chung *et al*., 1998; Obermajer *et al*., 2000; Zhang *et at*., 2005; Wang *et al*., 2010; Yu *et al*., 2014; Han *et al*., 2017; Huang *et al*., 2022). Despite these advancements, there are limited published papers on LH approaches in The Niger Delta; the most prominent ones are those by Eneogwe (2003, 2006), Akinlua *et al*. (2006), and Onyema and Manilla (2010).

Basically, LHs are mostly abundant in mature oil that have not significantly been altered by biodegradation processes. Therefore, the outcome of the current work should be taken as mostly pristine oil that has not been altered by bacterial activities (biodegradation), which is prevalent in the delta (Eneogwe and Ekundayo, 2003; Akinlua *et al*., 2006; Lehne and Dieckmann, 2010; Egbo *et al*., 2020).

Thus, this study aims to use LH characteristics to examine twenty-six oil samples from four depobelts of The Niger Delta. To determine source contributions, thermal maturity, detecting in-reservoir alteration activities, and correlating oils within The Niger Delta petroleum system. This study hopes to shed light on the complexities of oil correlations within The Niger Delta while gaining vital insights for the oil characterization.

MATERIALS AND METHODS

Gas chromatographic analysis was carried out on twenty-six crude oil suites obtained from four major depobelts in The Niger Delta. The LH compound distribution in the studied oils was determined using an Agilent 7890A gas chromatography split/splitless injection technique (280 °C) in conjunction with an Agilent 5975C MSD. All samples were analyzed using the total scan technique (10-235 amu/sec).

The oil samples were fed straight into the GC in a split setting, and the temperature was automated to scale up at the pace of 5 °C per min., starting from 30 °C (which was maintained for five minutes.) to 310 °C (which in turn was held for 15 minutes). At this stage, helium served as the mobile phase, to elute each compound. The Mango and Thompson parameters were then calculated using the standardized peak area computation (see Figure 2).

Results and Discussion

Source Related Ratios

Typically, the profile of chromatograms often displays the relative composition of oil in terms of its components, which are mainly traceable to the source contributions from the organic matter inputs. Conversely, the effect of maturation transformation often masks the source signatures of pristine oil in most cases. Figure 2 above shows the various chromatograms of representative oils from the four depobelts under investigation, displaying their unique profiles.

The dominant peaks of methylcyclohexane (peak 15) indicate a major contribution from humic sources (Han *et al*., 2017; Huang *et al*., 2022). On the other hand, the dominant peaks of toluene (peak 17) seen in Greater Ughelli and Offshore depobelts from Figure 2 can be attributed to post-generational transformation in the oils (Thompson, 1988; Han *et al*., 2017; Huang *et al*., 2022).

The 2,3-DMP + 2-MH and 2,4-DMP + 3-MH of the studied oils show a positive correlation with coefficient $R^2 = 0.998$ and $K_1 \approx 1.0$ (Figure 3), suggesting that the oils belong to the same homologous set, in keeping with Mango's invariance scheme (Mango, 1987). However, closer examination of these data indicates slight variation in the K_1 values of some oils from the offshore depobelt and a sample from the Greater Ughelli depobelt (Table 1, Figure 3), with K_1 values ranging from 0.83 to 0.94 and the rest of the oils having higher K_1 values (0.95-1.13). This can apparently be distinguished from the rest of the

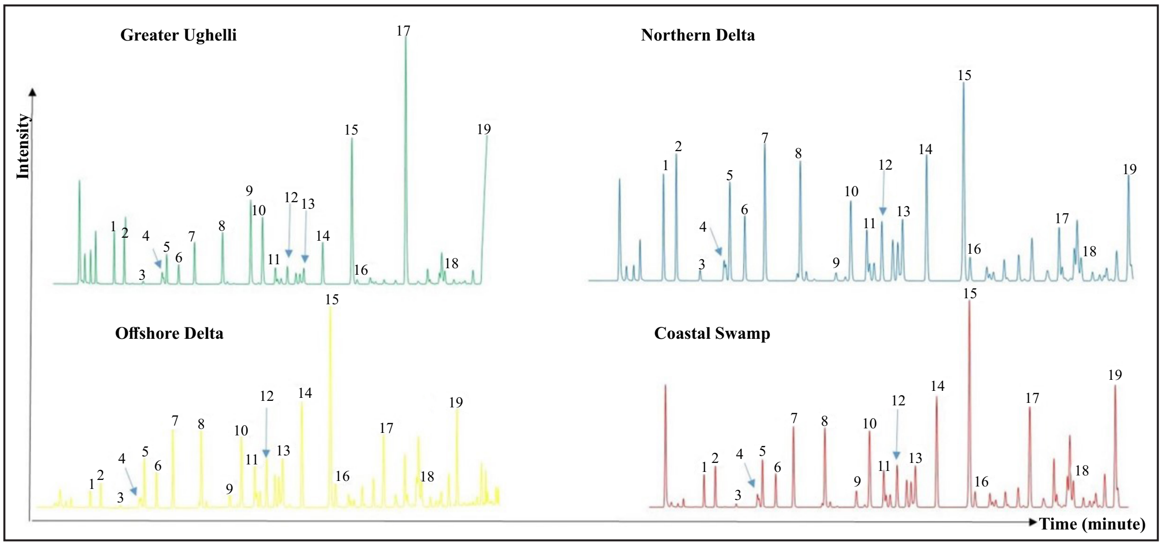

Figure 2. Partial whole oil gas chromatograms, showing relative peak intensities of the light hidrocarbon comonents in crude oils from the respesentative study depobelts, Niger Delta. (1=isoentane; 2= n-pentane; 3=cycloopentane; 4=2,2-dimenthylbutane; 5=2-methylpentane, 6=3-methylpentane; 7=n-hexane; 8=methylcyclopentane; 9=benzane; 10=n-heptane; 11=2-methylhexane; 12=3-methylhexane; 13=1-trans-2dimethycyclopentane; 14=cyclohexane; 15=methylcyclohexane; 16=1-cis-2-dimethylcyclopentane; 17=toluene; 18=3-methyleheptane; 19=n-octane).

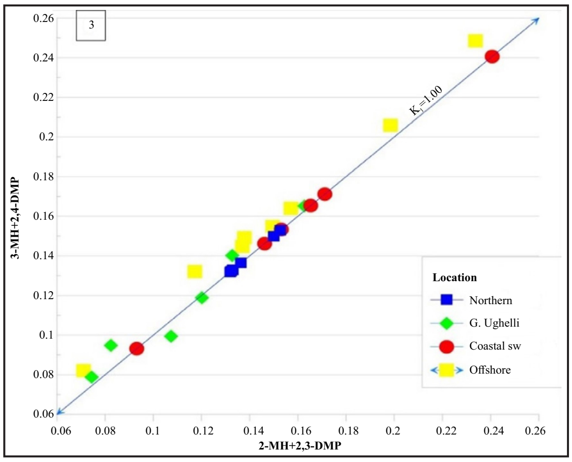

Figure 3. Cross-plot of 2-MH+2,3-DMP versus 3-MH+2.4-DMP, showing Mango's remarkable invariant scheme (K_1) for the studied crude oil samples (Mango, 1990).

oils, as they follow relatively different regression lines plotted above the rest of the oils. Generally, this plot indicates that the studied oils clearly demonstrated compositional linearity.

Additionally, Figure 4 displays the plot of the heptane and isoheptane value dispersions for the examined oils, based on Thompson (1983). The average values for heptane and isoheptane are 16.19 and 0.87, respectively, with values varying from 0.64 to 24.04 and 0.21 to 1.76, respectively. Nevertheless, most of the studied samples plotted between the aliphatic and aromatic curves (Type II/III), while fewer samples plotted slightly above the aliphatic curve (Type II). This suggests generation from mixed terrigenous-marine and marine organic matters. The heptane values of the studied oils slightly distribute over Thompson's aliphatic and aromatic curves (Peters *et al*., 2005), suggesting a higher heptane content for The Niger Delta oils. But these are lesser compared to that of the Tarim Basin, NW China (Song *et al*., 2016).

This finding, however, differs from the chart of the ph/nC_{18} vs. pr/nC_{17} ratios of HMW components of the examined oils, suggesting that the analyzed oils were mostly composed of mixed Type II/III along with some Type III kerogens (Figure 5).

Table 1. Light Hydrocarbon Geochemical Parameters Computed for The Studied Niger Delta Crude Oil Samples

Well	Field	Location	Hept val	Isohep val	Tol/nC_7	nC_7/MCH	nC_7	$DMCC_5$	MCC_6	K_1
			%	a/b	a/b	a/b	%	%	%	a/b
1	A	Northern Delta	12.97	0.81	1.39	0.31	27.03	16.37	56.60	1.12
2	A	Northern Delta	13.04	0.75	1.34	0.31	27.33	15.63	57.04	1.06
3	B	Northern Delta	18.24	0.83	1.05	0.50	31.63	16.57	51.80	1.04
4	B	Northern Delta	16.83	0.97	0.86	0.40	31.83	13.11	55.06	0.98
5	C	Northern Delta	17.79	1.20	1.48	0.47	31.41	21.96	46.63	1.02
6	C	Northern Delta	18.44	1.09	0.77	0.49	34.12	13.52	52.36	1.00
7	D	Greater Ughelli	14.87	0.77	1.27	0.36	27.85	16.44	55.71	0.95
8	D	Greater Ughelli	18.17	0.60	0.33	0.53	34.79	5.44	59.77	0.99
9	D	Greater Ughelli	12.09	0.80	6.83	0.26	37.21	14.16	48.63	0.94
12	D	Greater Ughelli	14.43	0.94	2.75	0.35	23.75	30.10	46.15	1.03
13	E	Greater Ughelli	1.88	0.27	2.80	0.04	17.39	4.87	77.74	1.13
14	E	Greater Ughelli	0.64	0.21	8.59	0.01	12.92	5.22	81.86	0.83
15	F	Coastal Swamp	16.39	0.79	0.76	0.48	32.18	11.28	56.54	0.95
16	F	Coastal Swamp	16.97	0.70	0.65	0.48	32.20	9.82	57.98	0.97
17	F	Coastal Swamp	18.36	1.28	1.10	0.50	33.92	18.53	47.55	1.04
18	G	Coastal Swamp	19.54	1.32	0.87	0.53	36.87	14.97	48.16	1.04
19	G	Coastal Swamp	17.20	1.06	1.61	0.45	31.60	21.19	47.21	0.98
20	G	Coastal Swamp	20.95	1.71	0.55	0.52	39.32	9.74	50.94	1.08
21	H	Offshore Delta	16.17	0.88	1.26	0.40	28.94	17.28	53.78	0.92
22	H	Offshore Delta	15.54	0.64	0.79	0.41	30.09	11.53	58.38	0.89
23	H	Offshore Delta	16.00	0.79	0.89	0.45	31.59	12.49	55.92	0.89
24	H	Offshore Delta	15.42	0.17	20.25	0.01	12.90	7.75	79.35	0.87
25	H	Offshore Delta	16.29	1.00	0.69	0.39	32.21	10.36	57.43	1.00
26	H	Offshore Delta	16.02	0.96	1.56	0.31	24.91	19.06	56.03	0.96
27	I	Offshore Delta	17.79	0.72	0.59	0.52	34.53	9.27	56.20	0.95
28	I	Offshore Delta	22.04	1.28	0.83	0.48	31.88	13.98	54.14	0.93

Note: Hept val =Heptane value; Isohep val =Isoheptane value; Tol/nC_7=Toluene/n-heptane; nC_7/MCH = n-Heptane/methylcyclohexane; nC_7=Heptanes; MCC_6 = Methylcyclohexane+Toluene; $DMCC_5$ = Dimethylcyclopentanes; K_1 = (2,3-dimethylpentane +2-methylhexane)/(2,4-dimethylpentane +3-methylhexane).

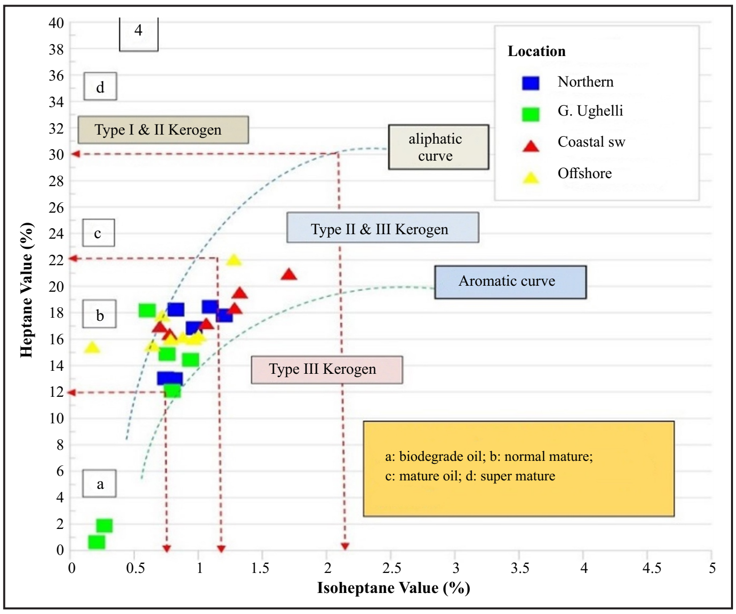

Figure 4. Cossplot of isoheptane value versus heptane value %, showing maturity level of and aliphatic and aromatic kerogen type curves, for the studied crude oils (Thompson, 1983).

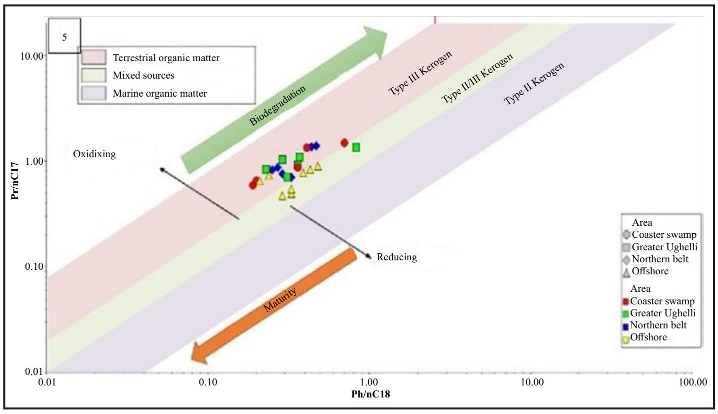

Figure 5. Plot of Pr/n-C17 vs. Ph/n-C18 ratios, showing depositional environmental conditions type of organic matter inputs, post-generational alterations (Peters *et al*., 2005) .

Though, in keeping with Ten Haven (1996) corroboration of Mango's K_1 remarkable invariance, K_1 can vary between homologous series. Moreover, Ten Haven (1996) observed that, where K_1 of homologous sets do not differ significantly, the application of Mango's LH for correlational investigations is constrained, and one has to rely on classical techniques such as biomarker fingerprints. However, it is interesting to note that the chart of ph/nC_{18} vs. pr/nC_{17} of the examined oils (Figure 5) clearly supports this tendency. Nevertheless, the narrow variation (range) in K_1 values can objectively be accepted for terrigenous-derived end-member deltaic oils and the intermediate (mixed terrigenous-marine) derived oils. Ten Haven (1996) noted that tertiary-derived oils typically have narrow heptane and iso-heptane indices and lack distinctive power.

It has been a common practice to employ Thompson’s ternary diagram in Figure 6 to display the relative compositions of heptane, methylcyclohexane, and dimethylcyclopentanes as a source-specific indicator (Thompson, 1988; Peters *et al*., 2005; Han *et al*., 2017; Huang *et al*., 2022). Algae and bacteria constituted organic matter are the main sources of normal heptane,

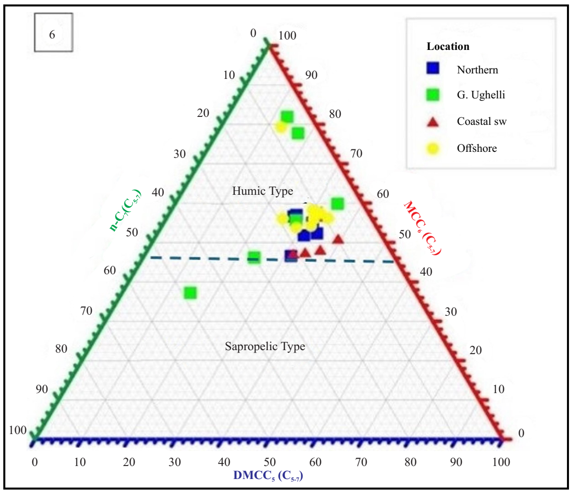

Figure 6. Ternary diagram of nC7, MCC6, and DMCC5 of LHs compositions, showing high preference for 6-ring compounds (6RP in the studied crude oil samples (Peters *et al*., 2005).

suggesting marine sources and also a good indicator of maturity. Methylcyclohexane (MCC_6) has comparatively stable thermal stability, and has the potential to function as a useful clue to original source input from higher plant carbohydrate, lignin, and cellulose. Hence, it is an excellent marker of terrigenous parent materials. On the other hand, dimethyl-cyclopentanes ($DMCC_5$) are primarily synthesized from aquatic plant lipids (Thompson, 1988; Chung *et al*., 1998).

This data suggests that the oils from The Niger Delta contained more terrestrial organic matter supplies. However, the scatter pattern of the samples from Greater Ughelli seen in this plot might possibly be attributed to the onset of secondary alterations (*i.e.* evaporative fractionation and water washing) impacts during migration or phase separation (Dzou and Hughes, 1993), and not totally source controlled. The representative chromatogram of the oils from The Greater Ughelli reinforced this concept with the dominant peak of toluene as seen in Figure 2. Basically, this ternary plot is ineffective in delineating the studied oils into separate groups due to the narrow heptane value range, probably resulting from variable degrees of oil mixing, which cannot be ruled out in The Niger Delta (see Table 1). Nevertheless, the studied oils have a high preference for six-ring compounds (6RP), which plotted close to the field of terrigenous/higher plant predominance, corroborating earlier findings (Eneogwe, 2006; Onyema and Manilla, 2010), suggesting dominant contributions from humic sources, contrary to the finding of Akinlua *et al.* (2006) , that reported the predominance of 3RP in oils from the northwestern Niger Delta, supporting lacustrine source inputs.

Maturity Related Ratio

The maturity of the studied oils was assessed using light hydrocarbon-based parameters like heptane and isoheptane metrics. Thompson (1983) applied heptane *vs*. isoheptane ratio graphs to predict thermal maturity, source, and biodegradation. Table 2 showed the studied oil results, and the heptane versus isoheptane ratio chart revealed that the crude oils ranged from early mature to mature (Figure 4), suggesting that they had attained peak oil window maturity. In general, it should be noted that the concentrations of heptane and isoheptane are considerably impacted by the source material type and thermal maturation (Peters *et al*., 2005).

Correlation and Transformation Related Ratios

Thompson (1988) introduced evaporative fraction parameters; paraffinicity (nC_7/MCH) and toluene (Tol/nC_7) indices, which have been widely used in several basins across the globe (Odden *et al*.,1998; Obermajer *et al*., 2000; Wang *et al*., 2010; Han *et al*., 2017; Huang *et al*., 2022). Nevertheless, the present investigation shows that the paraffinicity index (nC_7/MCH) for the studied oils varied between 0.01 and 0.53, with an average of 0.38. Likewise, the aromaticity ratio (Tol/nC_7) varied between 0.33 and 20.25, with an average of 2.38. Besides, secondary modifications, particularly evaporative fractionation and water washing, both affect the proportion of aromatic to aliphatic hydrocarbons in oils. However, the source facies of the oil play a larger role in this process (Peters *et al*., 2005; Song *et al*., 2016). These elevated values of Tol/nC_7 ratio, seen in some few samples (well 24 for instance), sug-

Table 2. Source-dependent LH And HMW Ratios in The Studied Crude Oil Samples

Well	Location	C1	C2	C3	C4	C5	Pr/n-C_{17}	Ph/n-C_{18}
1	Northern Delta	0.95	0.61	0.73	0.55	0.97	1.40	0.47
2	Northern Delta	0.90	0.68	0.82	0.60	0.76	1.37	0.44
3	Northern Delta	0.88	0.45	0.79	0.50	0.84	0.70	0.33
4	Northern Delta	0.99	0.71	0.62	0.57	0.85	0.87	0.27
5	Northern Delta	0.97	0.56	0.78	0.58	0.96	0.82	0.25
6	Northern Delta	0.89	0.58	0.63	0.53	0.86	0.76	0.29
7	Greater Ughelli	0.92	0.53	0.36	0.51	0.81	1.09	0.37
8	Greater Ughelli	0.78	0.57	0.97	0.66	0.65	1.35	0.83
9	Greater Ughelli	0.96	0.46	0.62	0.57	0.76	1.03	0.29
12	Greater Ughelli	0.94	0.43	0.82	0.56	0.91	0.36	0.36
13	Greater Ughelli	0.73	0.73	0.96	0.58	0.51	0.23	0.23
14	Greater Ughelli	0.93	0.54	0.77	0.52	0.27	0.31	0.31
15	Coastal swamp	0.75	0.33	0.77	0.52	0.87	0.70	0.70
16	Coastal swamp	0.80	0.41	0.54	0.50	0.77	0.41	0.41
17	Coastal swamp	0.83	0.98	0.76	0.76	0.93	0.19	0.19
18	Coastal swamp	0.87	0.84	0.83	0.63	0.95	0.19	0.19
19	Coastal swamp	0.67	0.79	0.91	0.64	0.82	0.36	0.36
20	Coastal swamp	0.87	0.94	0.94	0.61	0.99	0.20	0.20
21	Offshore Delta	0.63	0.55	0.54	0.71	0.90	0.24	0.24
22	Offshore Delta	0.81	0.48	0.69	0.51	0.60	0.43	0.43
23	Offshore Delta	0.66	0.40	0.73	0.58	0.87	0.29	0.29
24	Offshore Delta	0.82	0.48	0.84	0.46	0.33	0.39	0.39
25	Offshore Delta	0.84	0.50	0.38	0.44	0.96	0.48	0.48
26	Offshore Delta	0.93	0.65	0.95	0.68	0.77	0.33	0.33
27	Offshore Delta	0.97	0.49	0.59	0.44	0.74	0.33	0.33
28	Offshore Delta	0.99	0.73	0.94	0.54	0.86	0.21	0.21

Note: C1 =2,2-dimethylpentane/P1; C2 =2,3-dimethylpentane/P1; C3 =2,4-dimethylpentane/P1; C4 =3,3-dimethylpentane/P1; C5 =3-ethylpentane/P1. [P1 = 2,2-dimethylpentane + 2,3-dimethylpentane + 2,4-dimethylpentane + 3,3-dimethylpentane + 3-ethylpentane].

gest a possible alteration often associated with evaporative fractionation. More importantly, regardless of the source type, once gas or light oil migrates up-dip to shallow structures or traps, the accumulated fractionated oil heptane and isoheptane values increase, whereas the Tol/nC_7 value declines (Thompson, 1988; Wang *et al*., 2010). Conversely, the residual oils are invariably enriched with Tol/nC_7 contents, as seen in some samples from Greater Ughelli and one sample from Offshore depobelts (Table 1, Figure 7). Thus, these oils might have experienced variable degrees of fractionation.

To further illustrate the relationship between the oils recovered from The Niger Delta depobelts, two important multivariate chart approaches were used: the inherent C_7 oil correlation star diagram (C_7OCSD) components (Figure 8) and the C_7 oil transformational star diagram (C_7TCSD) (Figure 9), which were modelled after Halpern (1995). These approaches have been widely utilized to correlate oils and to determine the extent of oil transformation in several basins (Halpern, 1995; Can˜ipa-Moralesa *et al*., 2003; Han *et al*., 2017; Huang *et al*., 2022).

The concept behind the used of these charts are to correlate primary oils, based on source-related chemical differences (Table 2), and altered oil via most labile/stable LH components to determine extent of transformation (Table 3).

However, from Figure 8, the correlation parameters of C_7OCSD, graphically shows that most of the studied oils exhibit some degree of homogeneity in terms of source inputs, with the exception of some wells from Greater Ughelli (well 14) and Offshore Delta (well 24), that show significant variance in the recorded LH components, suggesting peculiar source contributions. On the other hand, Figure 9 shows evidence of post-expulsion histories among the oils across The Niger Delta. These characteristics are indicators of migration fractionation (evaporative, water, and gas washings). The application of Halpern's two key multivariate charts (Halpern, 1995), using the parameter of the most stable LH component against the labile component, proved

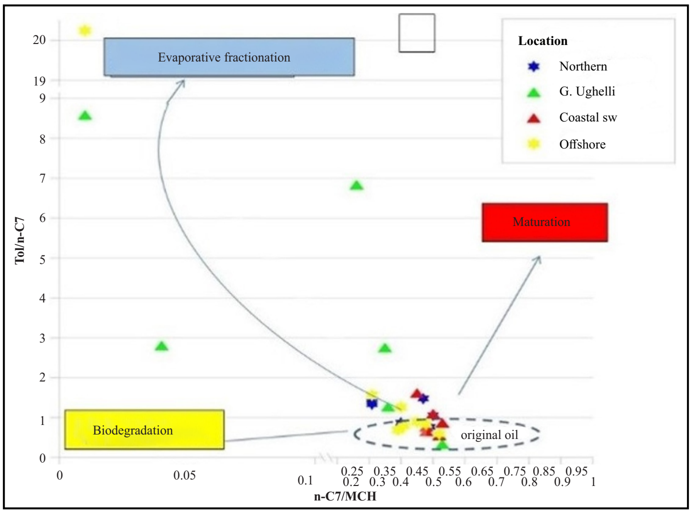

Figure 7. Plot of paraffinicity index versus aromaticity index (BF diagram) showing effects of evaporative fractionation in the studied Niger Delta oils (Thompson, 1988).

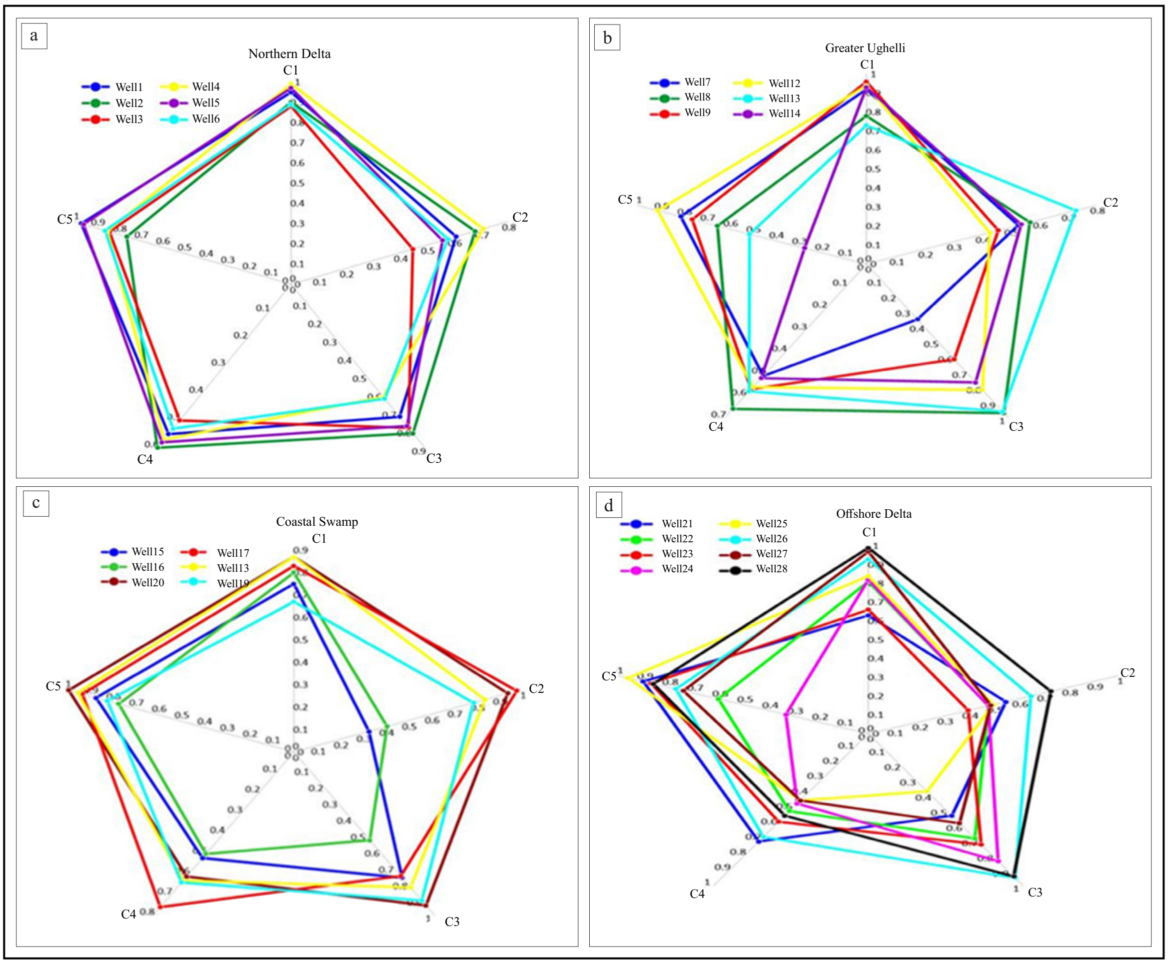

Figure 8. Oil correlation star charts plotted for the studied crude oils from several depobelts in the Niger Delta.

useful in describing links and degrees of variance among the studied oil sets, providing insight into their relationship, original inputs, and of course, their post-expulsion histories.

Table 3. LH Ratios in The Studied Crude Oil Samples Susceptible to Transformation

Well no.	Location	Tr1	Tr2	Tr3	Tr4	Tr5	Tr6	Tr7	Tr8
1	Northern Delta	3.26	0.21	0.43	4.71	1.41	0.31	0.30	0.90
2	Northern Delta	3.24	0.18	0.41	5.35	1.44	0.31	0.24	0.82
3	Northern Delta	2.00	0.24	0.53	5.83	1.12	0.50	0.23	0.97
4	Northern Delta	2.49	0.12	0.35	8.13	0.78	0.40	0.16	0.88
5	Northern Delta	2.11	0.36	0.70	4.68	1.27	0.47	0.04	0.25
6	Northern Delta	2.05	0.09	0.38	8.74	0.79	0.49	0.09	0.94
7	Greater Ughelli	2.81	0.24	0.45	5.49	1.59	0.36	0.31	0.88
8	Greater Ughelli	1.89	0.11	0.18	4.98	0.63	0.53	0.09	0.20
9	Greater Ughelli	3.86	1.35	1.77	3.28	5.89	0.26	2.32	0.43
12	Greater Ughelli	2.82	0.66	0.98	3.64	1.95	0.35	1.00	0.23
13	Greater Ughelli	27.43	0.10	0.10	3.35	2.80	0.04	0.43	0.70
14	Greater Ughelli	81.92	0.01	0.10	37.46	8.59	0.01	0.05	0.86
15	Coastal swamp	2.09	0.23	0.36	4.15	0.76	0.48	0.21	0.79
16	Coastal swamp	2.08	0.24	0.31	3.87	0.65	0.48	0.21	0.46
17	Coastal swamp	2.00	0.21	0.55	4.49	1.10	0.50	0.02	0.63
18	Coastal swamp	1.89	0.28	0.46	4.13	0.87	0.53	0.28	0.62
19	Coastal swamp	2.22	0.47	0.72	4.93	1.92	0.55	0.53	0.93
20	Coastal swamp	1.92	0.17	0.29	7.99	0.66	0.68	0.19	0.33
21	Offshore Delta	2.49	0.30	0.51	4.68	1.35	0.49	0.24	0.77
22	Offshore Delta	2.42	0.22	0.33	3.32	0.79	0.51	0.26	0.50
23	Offshore Delta	2.20	0.34	0.40	3.35	0.91	0.65	0.28	0.49
24	Offshore Delta	114.70	0.02	0.18	29.54	19.75	0.09	0.16	0.58
25	Offshore Delta	2.56	0.16	0.27	5.49	0.67	0.59	0.17	0.54
26	Offshore Delta	3.22	0.14	0.48	23.27	1.09	0.42	0.53	0.78
27	Offshore Delta	1.92	0.22	0.31	4.24	0.57	0.63	0.18	0.45
28	Offshore Delta	2.09	0.19	0.40	16.89	0.84	0.58	0.28	0.43

Note: Tr1 =Toluene/D; Tr2 =n-C_7/D; Tr3 =3MH/D; Tr4 =2MH/D; Tr5 =P2/D; Tr6 =1-cis-2-dimethylcyclopentane/D; Tr7 =1-trans-3-dimethylcyclopentane/D; T8 =P2/P1. [P2 = 2-methylhexane + 3-methylhexane; D =1,1-dimethylcyclopentane].

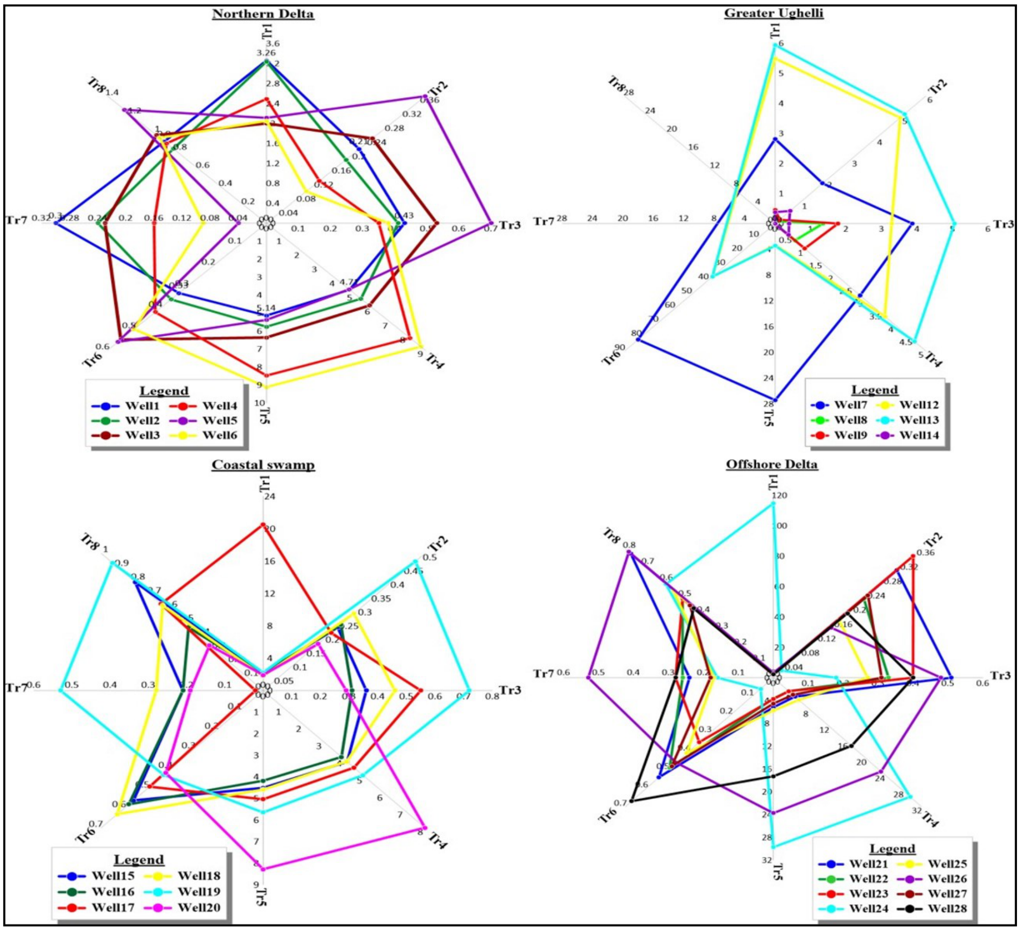

Figure 9. Oil transformation star chart plotted for the studied crude oils from different locations in The Niger Delta.

Nevertheless, these parameters suggest the studied oils had variable post-generation histories varying from evaporative fractionation, water washing to gas washing (Figure 9) (Song *et al.*, 2016; Huang *et al*., 2022). Besides their relative common origins, the oils experienced variable degrees of transformational histories. This is typical of Niger Delta due to the several complex structural plays of the reservoirs vis-a-vis the oils migration pathways.

Conclusion

The investigation into the distribution of LHs in the studied Niger Delta oils, focusing on oil-oil correlations, source contribution, deposition environment, source type, thermal maturation, and in-reservoir alteration, was largely successful. Thus, two homologous oil sets were established. The light hydrocarbon study classified the oils as terrigenous and mixed terrigenous/marine organofacies-derived oils, with a strong predilection for six-ring compounds, implying a dominant higher plant source input with variable contributions from marine/lacustrine sources and thermal maturation in the range of early to peak oil window.

Moreover, the data suggests that the majority of the oils from Greater Ughelli and a few from the offshore have been extensively fractionated, with indications of remobilization.

However, despite the successful outcomes, the present study turn up some key weaknesses which is a focus for future research work, requiring the application of compound specific isotope analysis (CSIA) of LHs of The Niger Delta oils to clearly delineate the impacts of maturation transformation from migration transformation for better understanding of the activities at play within the basin.

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