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Geochemical Assessment of Naphthalene Homologues (C_0–C_4) in Niger Delta Crude Oils and Their Mixtures

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Abstract **Original Research Article**

This study investigates the distribution patterns and diagnostic utility of C_0–C_4 naphthalene homologues in two Niger Delta crude oils and their binary blends, using Gas Chromatography–Mass Spectrometry (GC-MS). Six samples were analyzed: two unblended oils (Samples A and F) and four volumetric blends (Samples B–E). Results revealed that Sample A exhibited a moderate aromatic profile, dominated by dimethylnaphthalene (33.68%) and trimethylnaphthalene (35.13%), while Sample F showed a more alkylated profile with trimethylnaphthalene (35.70%) and a higher tetramethylnaphthalene content (16.36%), indicative of greater thermal maturity. Blending these oils produced varying aromatic signatures, with Sample C (60:40 blend) displaying an unusual enrichment in tetramethylnaphthalene (30.93%), suggesting non-linear behavior during mixing. Biomarker ratios, including M/P, DM/P, aromaticity index (AI), and C_4/C_0, provided insight into maturity and source input, with Sample F consistently showing the highest AI (14.20) and C_4/C_0 (2.43) values. The findings underscore the diagnostic value of naphthalene homologues in assessing source characteristics, thermal maturity, and compositional alterations in mixed petroleum systems, and support their use in oil correlation, refining strategy, and environmental forensics within the Niger Delta region.

Keywords: Naphthalene Homologues, Crude Oil Blends, Niger Delta, Gas Chromatography–Mass Spectrometry, Thermal Maturity, Oil Correlation, Aromatic Profile.

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1. INTRODUCTION

Crude oil is a natural mixture of compounds that consists predominantly of hydrocarbons like alkanes, cycloalkanes, and aromatics, and traces of sulfur, nitrogen, oxygen, and trace metals. They occur in different concentrations based on the source, thermal maturity, and post-depositional alterations of the oil, which also influence its physicochemical attributes and commercial worth. The geochemical fingerprint of crude oil defined in terms of molecular markers and composition ratios is a valuable source correlation, reservoir description, and environmental forensic technology (Speight, 2020; Hunt, 1996; Tissot & Welte, 2013).

Among the numerous hydrocarbon classes in petroleum crude, polycyclic aromatic hydrocarbons (PAHs) and naphthalene along with its alkylated homologues (C_0–C_4) have gained increasing attention due to their use as geochemical markers for petroleum. They are thermally stable compared to other molecules, highly varied in structure, and sensitive to input from the source and varying thermal maturity. The relative abundance and distribution patterns of naphthalene homologues can therefore be used to monitor oil sources, measure the degree of degradation, and evaluate compositional changes during blending and weathering (Volk et al., 2005; Peters et al., 2005; Osuji & Antia, 2005).

In Africa's most prolific petroleum province, Niger Delta, there is usually more than a single reservoir producing simultaneously and sharing common surface facilities, causing inadvertent or operational mixing of crude oils from geochemically distinct sources (Wang & Stout, 2007; Onyema et al., 2020). This presents difficulties in oil source apportionment, process optimization, and forensic analysis following spill or leaks. Though such mixing processes are important, the behavior of naphthalene alkylates in blended crude oils is yet to be fully explored, especially when viewed in the context of Nigerian petroleum systems.

Previous studies in this area have been predominantly focused on bulk geochemical properties (Okoroh et al., 2018; Onyema et al., 2020), particularly aliphatic hydrocarbon fingerprints and biomarker distributions. However, less is understood about the sensitivity of naphthalene homologues (C_0 to C_4) towards blending and whether their compositional patterns are statistically significant at various mix ratios. These dynamics need to be appreciated in order to build the credibility of molecular markers to play roles in source correlation, spill forensics, and strategy optimization.

This study therefore investigates the distribution and correlation of the C_0 to C_4 naphthalene homologues in two Niger Delta crude oils and their binary mixtures. By the application of Gas Chromatography–Mass Spectrometry (GC-MS) and multivariate statistical analysis, we investigate compositional variations, outlier behavior, and patterns of clustering in the naphthalene fraction. The results open the window of diagnosis stability and variability of these substances in mixed petroleum systems and attest to their utility in geochemical investigation and environmental monitoring.

2. MATERIALS AND METHODS

2.1. Study Area

The Nigerian Niger Delta is an extremely prolific hydrocarbon basin situated between latitudes 4°–6° N and longitudes 5°–9° E, forming part of the West African continental margin. The stratigraphy of the Niger Delta comprises three principal lithostratigraphic units: the basal Akata Formation, which is composed predominantly of marine shales; the Agbada Formation, composed of interbedded sandstones and shales of paralic deposits; and the Benin Formation, an upper unit dominated by continental sands. All these formations together constitute the petroleum system of the region, which has contributed significantly to Nigeria's oil production potential (Tuttle et al., 1999).

2.2. Sampling

Two samples of crude oil, both one litre each, were obtained from Delta State flow stations and Rivers State flow stations in the Niger Delta basin. They were taken with the help of the Department of Petroleum Resources (DPR) and were given the designations Sample A (from Irri Flow Station, Delta State) and Sample F (from Agbada Flow Station, Rivers State). To study the influence of blending on naphthalene distribution, binary blends of these samples were made in 4:1, 3:2, 2:3, and 1:4 volumetric proportions to provide Samples B, C, D, and E, respectively. All blends were thoroughly mixed in clean inert containers and kept at room temperature prior to analysis.

2.3. Crude Oil Characterization

The densities and API gravities of the crude oils were determined using an APAAR DMA 048 density meter. For fractionation, 50 mg of each crude oil sample was weighed into centrifuge tubes, followed by the addition of excess n-pentane. The mixtures were allowed to stand undisturbed for four hours to precipitate the asphaltenes. The supernatant was filtered and concentrated, then introduced into a chromatographic glass column (25 cm × 1 cm) packed with silica gel. Elution was carried out sequentially using n-hexane to obtain the saturates, dichloromethane for the aromatics, and a 1:1 mixture of dichloromethane and methanol for the resins. The respective fractions were collected in pre-weighed vials, and the solvents were evaporated under a gentle stream of nitrogen at 40°C. The resulting weights of the fractions were recorded and normalized to obtain the percentage composition of each sample.

2.4. Gas Chromatography–Mass Spectrometry (GC-MS) Analysis

Aromatic hydrocarbon analysis, specifically for C_0 to C_4 naphthalene homologues, was conducted using an Agilent 7890B gas chromatograph equipped with a mass selective detector (MSD) and an HP-5 silica capillary column (30 m × 320 µm ID × 0.25 µm film thickness). One microlitre (1 µL) of each aromatic fraction was injected using an automatic liquid sampler (model G4513A). The GC oven temperature program began with an initial hold at 40°C for 5 minutes, followed by a temperature ramp to 315°C at 5°C per minute, and a final hold at 315°C for 30 minutes. Helium was used as the carrier gas at a constant flow rate of 1.0 mL/min. Peak identification was performed using the NIST spectral library, and quantification was based on total area normalization using the Chemstation OPEN LAB CDS software.

2.5. Statistical Analysis

Statistical evaluations were performed using Microsoft Excel 2013 and PAST software version 3.22. Pearson correlation coefficients were calculated to assess the degree of similarity between naphthalene homologue distributions across the different samples. Hierarchical cluster analysis (HCA) was conducted to classify samples into compositional groups based on their aromatic profiles (Hammer and Harper 2001).

3. RESULTS AND DISCUSSION

3.1 Quantitative Distribution of Naphthalene Homologues

Gas Chromatography–Mass Spectrometry (GC-MS) analysis was used to determine the distribution of naphthalene homologues (C_0 to C_4) in two crude oil samples from the Niger Delta and their binary mixtures. Samples A and F represent the unblended crudes, while Samples B, C, D, and E are blends prepared in volumetric ratios of 4:1, 3:2, 2:3, and 1:4, respectively. Normalized relative abundances of individual homologues were calculated to evaluate compositional trends across the set.

3.1.1 Naphthalene Homologues in Parent Crude Oils

Sample A (Crude Oil 1) contained a balanced aromatic composition, which was dominated by dimethylnaphthalene (C_2: 33.68%) and trimethylnaphthalene (C_3: 35.13%), with lower percentages of naphthalene (C_0: 9.86%) and methylnaphthalene (C_1: 6.82%). This kind of composition suggests a moderately mature oil with the presence of a mixture of light and mid-range alkylated aromatics. On the other hand, Sample F (Crude Oil 2) had a more alkylation-type nature, with higher concentrations of C_2 (30.41%) and C_3 (35.70%), as well as high tetramethylnaphthalene content (C_4: 16.36%). The lower concentration of C_0 (6.74%) in Sample F also verifies its more thermally mature nature.

These findings are consistent with earlier studies by Onyema and Osuji (2015), whose observations were that naphthalene alkylation distributions in Niger Delta oils reflect thermal maturation since an abundance of C_1–C_4 is taken to signify greater maturity and possible terrestrial organic matter input. Mass spectrometry has also proved that such distributions can be related to specific depositional conditions and refining properties (Schaefer & Höltkemeier, 1988).

3.1.2 Effects of Blending on Naphthalene Composition

Blending Crude Oils 1 and 2 resulted in significant impacts on aromatic profiles. Sample B (80:20 blend) already showed early signs of heavier crude influence, with C_1 (22.33%) and C_2 (32.43%) concentration increments. This finding supports the dilution theory, where heavier oils enhance the presence of mono- and di-alkylated compounds (Onyema et al., 2020). Sample C (60:40 mix), however, disrupted this linear pattern. It contained an anomalously high tetramethylnaphthalene (C_4) content (30.93%), despite having an intermediate mixing ratio. The anomaly suggests the presence of non-linear compositional behavior or matrix-induced enrichment during mixing. Akinlua et al. (2007) likewise reported these kinds of irregularities in hydrocarbon mixing, where they observed synergistic effects and co-elution anomalies in mixed Nigerian oils.

Sample D (40:60 mix) was a more normally distributed pattern, with C_2 (33.77%) and C_3 (26.35%) predominating and C_4 dropping off sharply to 1.60%. Sample E (20:80 mix) was very close to Sample F in profile with C_2 and C_3 accounting for over 52% of the total naphthalene profile and a moderate C_4 abundance (17.54%).

These results reflect a compositional shift driven by increased proportions of Crude Oil 2. As blending progresses, the profiles tend to converge with the dominant parent oil's characteristics, particularly for C_2 and C_3 homologues. However, outliers like Sample C demonstrate that aromatic distribution in blends may not always follow additive rules, which complicates interpretation during source correlation studies (Esegbue et al., 2020).

A summary of the normalized abundance data is presented in Table 1. The trends are further visualized in Figure 1, showing the proportional changes in naphthalene homologues across Samples A to F.

Table 1: Percentage Abundance of Naphthalene Homologues (C_0–C_4) in Crude Oil Samples

Sample	**C_0 (%)**	**C_1 (%)**	**C_2 (%)**	**C_3 (%)**	**C_4 (%)**
A	9.86	6.82	33.68	35.13	14.51
B	14.30	22.33	32.43	21.96	8.78
C	14.62	7.52	13.50	33.44	30.93
D	17.44	20.72	33.77	26.35	1.60
E	16.43	13.88	24.27	27.89	17.54
F	6.74	13.14	30.41	35.70	16.36

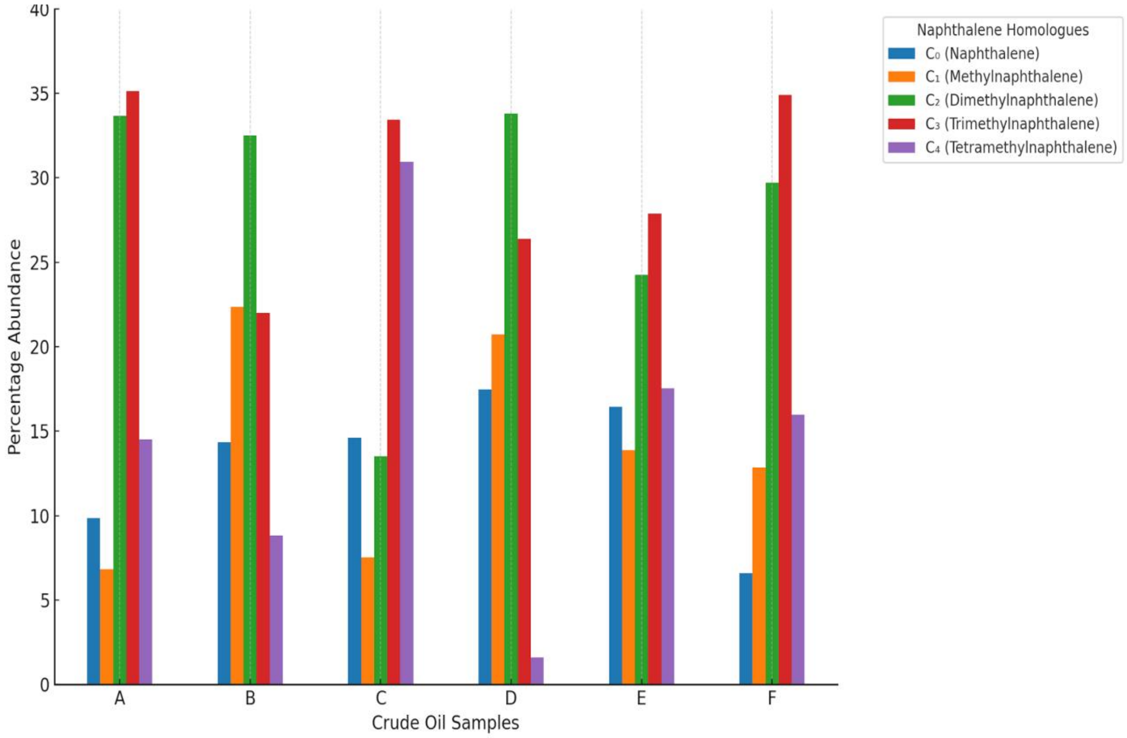

Figure 1. Percentage Abundance of Naphthalene Homologues (C_0–C_4) in Crude Oil Samples A–F Based on GC-MS Analysis

3.2 Correlation and Biomarker Ratios

To evaluate thermal maturity and compositional variation of the crude oil samples, four diagnostic biomarker ratios were determined based on the relative abundances of the naphthalene homologues: mono-/parent ratio ($M/P = C_1/C_0$), dimethyl-/parent ratio ($DM/P = C_2/C_0$), aromaticity index ($AI = (C_1 + C_2 + C_3 + C_4)/C_0$), and tetramethyl-/parent ratio (C_4/C_0). These ratios are established indicators of thermal maturity and aromatic substitution and are increasingly being utilized in oil–oil correlation and maturity analysis (Peters et al., 2005; Zhou, 2008; Onyema et al., 2020).

Sample F recorded the highest values for all the indices ($M/P = 1.95$; $DM/P = 4.52$; $AI = 14.20$; $C_4/C_0 = 2.43$), reconfirming it as the most thermally mature of the six samples. The dominance of more alkylated naphthalenes in the sample supports its classification as a more evolved and deeper-sourced crude (Tissot & Welte, 1984; Oyo-Ita et al., 2023).

Sample C, despite being a 60:40 mix, contained a very high ratio of C_4/C_0 (2.12), which does not agree with linear mixing behavior. The finding may be suggestive of non-proportional compositional effects such as matrix enrichment, co-elution effects, or chemical interaction among components of disparate geochemical origins (Akinlua et al., 2007; Borrett et al., 1991).

Conversely, Sample D had the lowest value of C_4/C_0 (0.09), which could imply dilution of the heavier aromatics or suppression effects upon analysis. This steep decrease in tetramethylated naphthalenes can be indicative of lower maturity or less aromatic input in the mixture, in agreement with findings on immature or biodegraded crudes (Asif & Tahira, 2007).

The ratios of biomarkers computed for all six samples are presented in Table 2.

Table 2.Diagnostic Biomarker Ratios Derived from Naphthalene Homologue Distributions

Sample	**M/P (C_1/C_0)**	**DM/P (C_2/C_0)**	**AI (($C_1+C_2+C_3+C_4)/C_0$)**	**C_4/C_0**
A	0.69	3.42	9.14	1.47
B	1.56	2.27	5.98	0.61
C	0.51	0.92	5.84	2.12
D	1.19	1.94	4.73	0.09
E	0.84	1.48	5.09	1.07
F	1.95	4.52	14.20	2.43

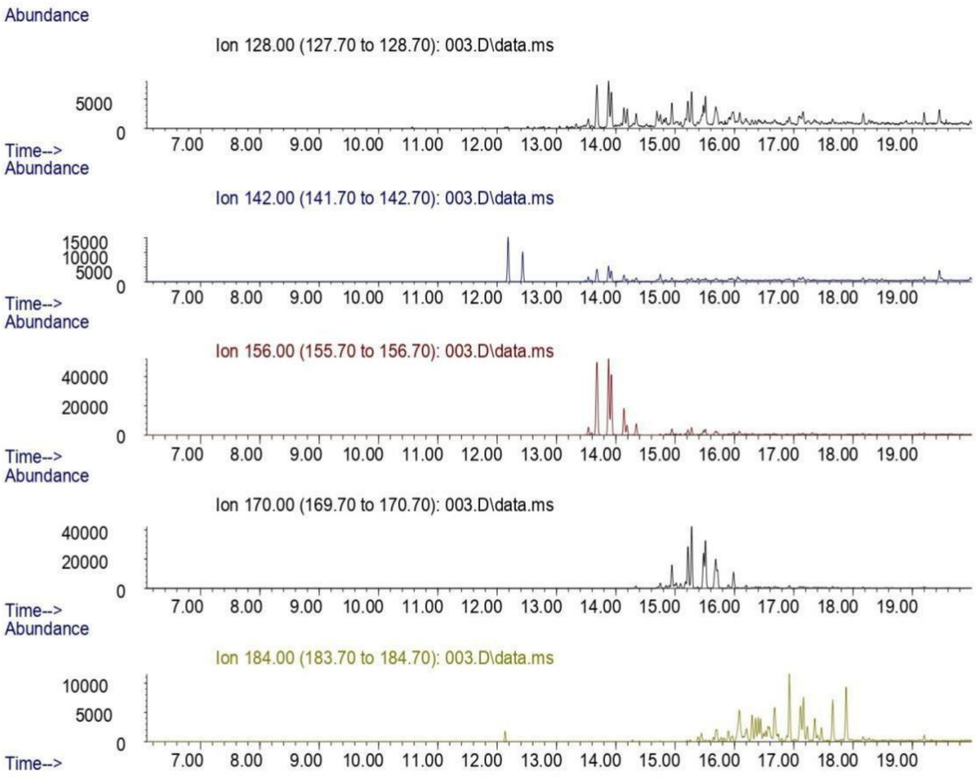

Figure 2. Representative GC-MS Ion Chromatograms

3.2.1 Correlation Analysis

To further elucidate the relationship among the six crude oil samples, Pearson’s correlation analysis was employed to assess the similarity in their naphthalene homologue distributions (C_0–C_4). This statistical method measures the strength and direction of linear association between the relative abundances of individual biomarkers across the samples. A high positive correlation (r close to +1) indicates compositional resemblance, which may point to similar thermal maturity or shared source input. Conversely, lower or negative correlations suggest divergent aromatic patterns, potentially due to varying depositional conditions or blending anomalies.

As shown in **Table 4.3**, most sample pairs exhibited strong positive correlations, particularly between Samples F and E (r = 0.998), and between Samples D and B (r = 0.995), indicating closely aligned aromatic profiles. In contrast, Sample C consistently recorded the lowest correlation values with other samples especially with D (r = 0.801) and B (r = 0.856) reinforcing previous observations of its unusual enrichment in tetramethylnaphthalene. These findings emphasize that crude oil blending does not always result in linear additive patterns, and that outlier behavior such as that seen in Sample C may complicate compositional interpretation in forensic and refining contexts.

Table 3: Pearson Correlation (r) of Naphthalene Homologue Composition (C_0–C_4) in Crude Oil Samples A–F

	A	B	C	D	E	F
A	1.000	0.968	0.916	0.951	0.985	0.994
B	0.968	1.000	0.856	0.995	0.970	0.979
C	0.916	0.856	1.000	0.801	0.954	0.936
D	0.951	0.995	0.801	1.000	0.943	0.957
E	0.985	0.970	0.954	0.943	1.000	0.998
F	0.994	0.979	0.936	0.957	0.998	1.000

4.1.3.3 Multivariate Correlation: Hierarchical Cluster Analysis (HCA)

To investigate the underlying patterns of compositional similarity among the crude oil samples, Hierarchical Cluster Analysis (HCA) was applied to the relative abundances of C_0–C_4 naphthalene homologues. This multivariate technique organizes the samples based on their degree of similarity, generating a dendrogram (Figure 3) that visually depicts the clustering relationships derived from the aromatic profiles.

The resulting dendrogram reveals two major clusters. Samples A, E, and F form one tightly associated group, indicative of comparable enrichment in higher alkylated naphthalenes such as trimethylnaphthalene (C_3) and tetramethylnaphthalene (C_4), which is consistent with their elevated aromatic maturity indices. A second subgroup consisting of Samples B and D suggests a more moderate degree of similarity, likely attributable to their intermediate blend ratios. Notably, Sample C appears as a distinct outlier, separated at a higher dissimilarity level due to its anomalously high tetramethylnaphthalene content a pattern previously noted in its biomarker ratios.

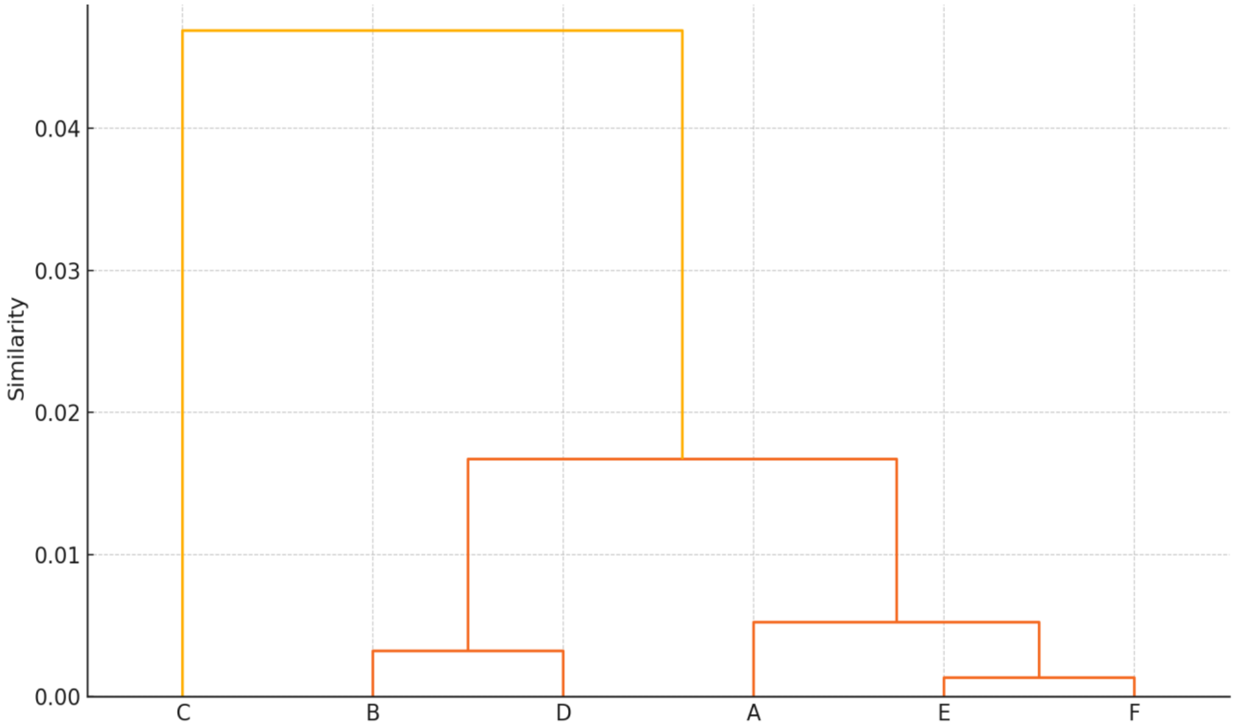

Figure 3: Hierarchical Cluster Analysis (HCA) dendrogram showing the relationship among crude oil samples A–F based on the relative abundance of C_0–C_4 naphthalene compounds.

4. CONCLUSION

This work examined the geochemical distribution and behavior of C_0–C_4 naphthalene homologues in two Niger Delta crude oils and in their binary blends using Gas Chromatography–Mass Spectrometry (GC-MS). Analysis indicated apparent differences in source composition between the two source crude oils, one bearing higher percentages of alkylated naphthalenes, most importantly trimethyl- and tetramethylnaphthalene, which may be described as coming from a more thermally mature source. Combinations of the two oils induced progressive though sometimes non-linear compositional variations in the naphthalene with some blends having unusual enrichment patterns. These disparities were complemented by biomarker ratios calculated quantitatively, which helped distinguish oil types and blending ratios. The result shows that naphthalene homologues can be effective markers of crude oil maturity, source input, and compositional changes induced by blending. These observations have great importance to petroleum geochemistry, refining strategies, and environmental monitoring in regions like the Niger Delta where many oil sources have a tendency to become commingled.

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