Petroleum and Coal

Article Open Access

COMPOSITIONAL SIGNIFICANCE OF PHENANTHRENES FOR GEOCHEMICAL CORRELATION OF TWO COMMINGLED NIGER DELTA CRUDE OILS

Nwannedi C. Okoroh, Mark O. Onyema, and Leo C. Osuji

Petroleum and Environmental Geochemistry Research Group, Department of Pure and Industrial Chemistry, University of Port Harcourt, P.M.B 5323 Choba, Port Harcourt, Rivers State, Nigeria

Received August 21, 2018; Accepted November 19, 2018

Abstract

This research focuses on the geochemical correlation of phenanthrenes peculiar to commingled crude oils for the purpose of deconvolution studies. Two crude oils collected from different parts of Nigeria's Niger Delta were mixed at different proportions of 4:1, 3:2, 2:3 and 1:4 respectively. All the samples were deasphalted, fractionated and the aromatic component analyzed by gas chromatography-mass spectrometry (GC-MS) for C_0-C_4 phenanthrenes. Abundance values of 45 peaks selected for correlation of the samples did not show relationship indicating the abundance of the phenanthrenes did not mix linearly. The correlation coefficient of determination (R^2) for plots of the abundance of some phenanthrenes; Ph, 2Ph, 3Ph, 6Ph2, 8Ph2, 20Ph3, 27Ph3, 31Ph4 and 34Ph4, were low, from 0.022 to 0.285, and for composition were high, from 0.644 to 0.864. The results indicate negligible to weak correlation for the abundance of phenanthrenes and strong to very strong correlation for composition. Ratios of phenanthrene groups (P, P1, P2, P3, and P4) were plotted against all the samples. Plots of P/P_3, P_1/P_3 and P_2/P_3 as well as double ratio plots of P/P_2 vs P_2/P_3 and P/P_2 vs P_1/P_3 had high R^2 values of 0.823 to 0.929 and 0.934 to 0.989 respectively indicating a very strong correlation between the oil samples which could account for 82 to 98% of the mixing pattern of the end member oils in their commingled oils. These results reveal that the composition of these phenanthrenes will better explain the pattern of mixing of the studied Niger Delta crude oils than their abundance.

Keywords: *Phenanthrene; Commingling; Correlation; Crude Oil; Niger Delta; GC-MS.*

1. Introduction

The compounds found in crude oils originate from the chemical and geological transformation of organic matter deposited during sedimentary processes [1]. Petroleum geochemistry utilizes geochemical compounds in crude oils for assessing oil type, depositional environment, maturation level, reservoir compartmentalization and continuity as well as a role in basin development [2-5]. Geochemical compounds typically reviewed in crude oils include polycyclic aromatic hydrocarbons (PAHs), light hydrocarbons (LHs), *n*-alkanes, isoprenoids, terpene, and sterane biomarkers [6-11].

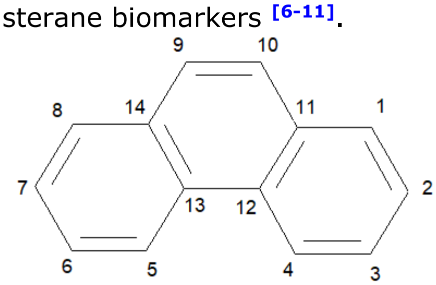

Figure 1. Structure of phenanthrene

Phenanthrene is a PAH composed of 3 benzene (C_6H_6) rings fused together (Fig. 1). Hydrocarbons based on the structure of phenanthrene occur in crude oil, and they include phenanthrene, methyl phenanthrenes, trimethyl phenanthrenes, and tetramethyl phenanthrenes, e.g. 9-methyl phenanthrene, 3-ethyl phenanthrene, and 2,6-dimethyl phenanthrene [12].

The phenanthrenes are relatively stable, highly degradation resistant and source-specific [13]. For light crude oils with similar compositions, characterization of phenanthrenes are essential for source identification, correlation and or differentiation [14].

Crude oil is the mainstay of the Nigerian economy. The operations of the oil industry in Nigeria are not isolated from global industrial practices, which include commingling of crude oils. Commingling is a terminology used in the oil and gas sector to refer to the mixing of two or more crude oils from different producing zones, wells or fields [15-16]. The commingling of crude oils is a common practice for sharing facilities and equipment to reduce cost. Adequate assessment of individual field contribution is essential for establishing sales value or tax liability and in effectively managing reservoirs and production operations [17]. According to the 2014 audit report of the Nigerian Extractive Industry Transparency Initiative (NEITI), $4.1bn was lost because of non-existent and inadequate metering systems in the crude oil-producing Niger Delta region [18].

In a bid to restore accuracy, equity, fairness and conformity with international best practices, this research focuses on the development of a flexible, tiered geochemical analytical approach to facilitate the detailed compositional analysis of the phenanthrenes by gas chromatography-mass spectrometry (GC-MS). The distribution of the phenanthrenes would be correlated to identify those peculiar to the mixing of crude oils from the Niger Delta region for the purpose of deconvolution.

2. Materials and method

2.1. Samples

Crude oil samples used for this study were collected from Rivers State (Sample A) and Delta State (Sample F) both in the Niger Delta region of southern Nigeria. The samples were collected from producing oil wells by field technicians with the permission of the department of petroleum resources (DPR). The two crude oil samples (A and F) were mixed at different proportions of 4:1, 3:2, 2:3 and 1:4 to give samples B, C, D, and E respectively.

2.2. Crude oil fractionation

50 mg of each crude oil sample was weighed into labeled centrifuge tubes and excess pentane added to precipitate the asphaltenes. The samples were allowed to stand for four hours and transferred into a fisher centrifuge set at 1,500 rpm for thirty minutes. 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. Different compound classes were eluted with different solvents. Saturates were eluted with *n*-hexane, aromatics eluted with dichloromethane and resins eluted with dichloromethane/methanol (1:1) mixture. All solvents were evaporated in a water bath and then to dryness with nitrogen.

2.3. Gas chromatography-mass spectrometry (GC-MS) analysis

Detailed analysis of the phenanthrenes 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 capillary column of the GC-MS system with the aid of automatic liquid sampler (ALS) using a split ratio mode of 100:1. The GC-MS fragmentation ion was set for phenanthrene (C_0) at m/z 178, methyl phenanthrenes (C_1) at m/z 192, ethyl-/dimethylphenanthrenes (C_2) at m/z 206, trimethyl phenanthrenes (C_3) at m/z 220 and tetramethyl phenanthrenes (C_4) at m/z 234. Peak identification was by comparison with related literature. Quantification was acquired by area integration of each peak which was processed by Chemstation OPEN LAB CDS software.

3. Results and discussions

3.1. Distribution of phenanthrenes

GC-MS analysis of the aromatic component of the studied oil samples identified phenanthrenes at ions (m/z) 178, 192, 206, 220 and 234, which were well resolved (Fig. 2). A total of 45 phenanthrene peaks were selected for geochemical correlation of the two end-member crude oils, from Niger Delta (samples A and F) and their commingled oils (samples B, C, D, and E). One peak was selected for parent phenanthrene (C_0) at m/z 178, 4 peaks for methyl phenanthrenes (C_1) at m/z 192, 11 peaks for ethyl- and dimethyl phenanthrenes (C_2) at m/z 206, 12 peaks for trimethyl phenanthrenes (C_3) at m/z 220 and 17 peaks for tetramethyl phenanthrenes (C_4) at m/z 234.

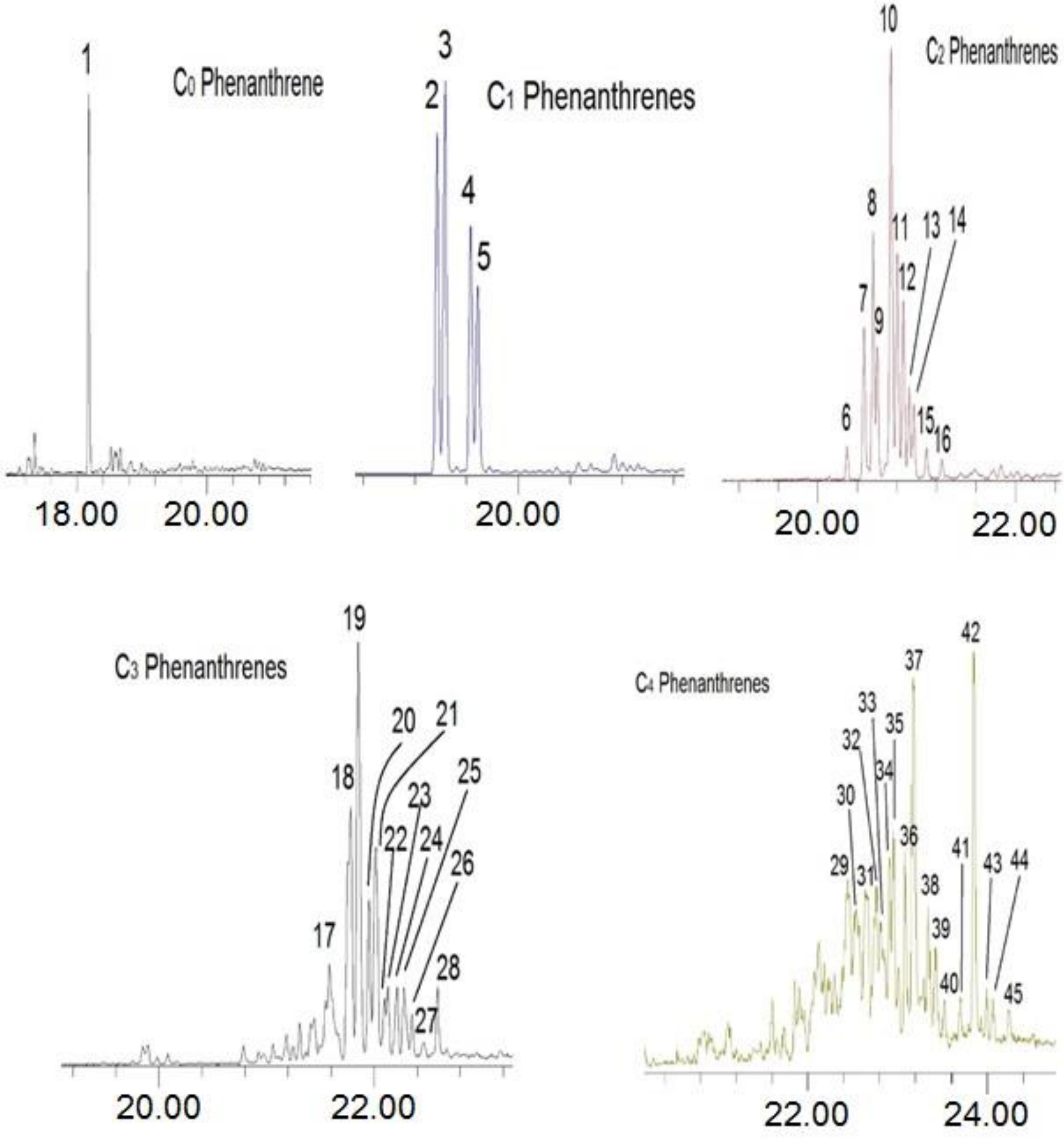

Figure 2. Representative GC-MS fragmentogram of C_0-C_4 phenanthrenes at ions (m/z) 178, 192, 206, 220 and 234 showing the selected peak distributions in crude oil (sample B)

Area integration of each selected peak calculated by the GC-MS system gives the abundance of that peak. The abundances of the 45 selected phenanthrene peaks (C_0-C_4) for the end-member and commingled crude oils used for the study are presented in table 1.

Geochemical correlation of crude oils is based on similarities and/or dissimilarities of features which are usually established on the relative distribution patterns of certain compounds [16]. From Table 1, the abundance values of the phenanthrenes in the end-member oils (samples A and F) and their commingled oils (samples B, C, D, and E) did not show the relationship. This indicates that the abundance of the phenanthrenes did not mix linearly.

3.2. Correlation of phenanthrenes

In a bid to identify particular phenanthrenes which will attempt to explain the pattern of mixing and give the highest chance of allocation, the abundance, and composition of the forty-five selected peaks were plotted against all the studied oil samples. A relationship was observed between the two end-member and their commingled crude oils for some C_0-C_2 phenanthrenes (Fig. 3) and C_3-C_4 phenanthrenes (Fig. 4).

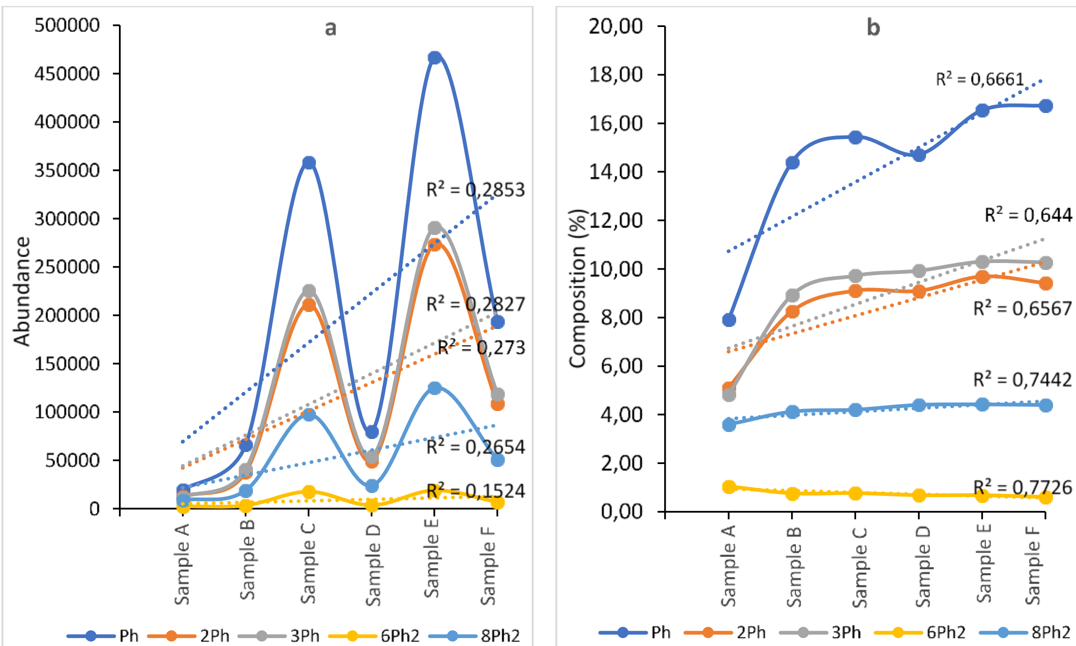

Figure 3. Plot of some C_0-C_2 phenanthrenes (Ph, 2Ph, 3Ph, 6Ph2 and 8Ph2) against all the studied oil samples showing the level of correlation a. abundance b. composition

From Fig 3, the correlation coefficient (R^2) of Ph, 2Ph, 3Ph, 6Ph2 and 8Ph2 (C_0-C_2 phenanthrenes) for abundance range from 0.152 to 0.285 and for composition from 0.644 to 0.773. The R^2 values of 20Ph3, 27Ph3, 31Ph4 and 34Ph4 (C_3-C_4 phenanthrenes) for abundance range from 0.022 to 0.168 and for composition from 0.760 to 0.864. The correlation coefficient (R^2) is a statistical tool used to indicate the strength of a linear relationship between variables. The closer the R^2 value is to one (1) the closer the relationship between the variable and consequently deducing the trend. R^2 values for abundance were low indicating the poor linear relationship of the variable (phenanthrenes) between the end-member and commingled oils (samples A to F). For composition, the R^2 values were higher than that of abundance and indicated considerably linearity of the variable between the end-member oils and commingled oils. The R^2 values from Figs. 3 and 4 reveal that the composition of some phenanthrenes will better explain the pattern of mixing of the studied Niger Delta crude oils than their abundance. Furthermore, from the forty-five phenanthrene peaks selected, peaks Ph, 2Ph, 3Ph, 6Ph2, 8Ph2, 20Ph3, 27Ph3, 31Ph4 and 34Ph4 showed better correlation and a good chance of being used to evaluate contributions from the respective end-member oils to their commingled oil because their R^2 values were high (> 0.6)

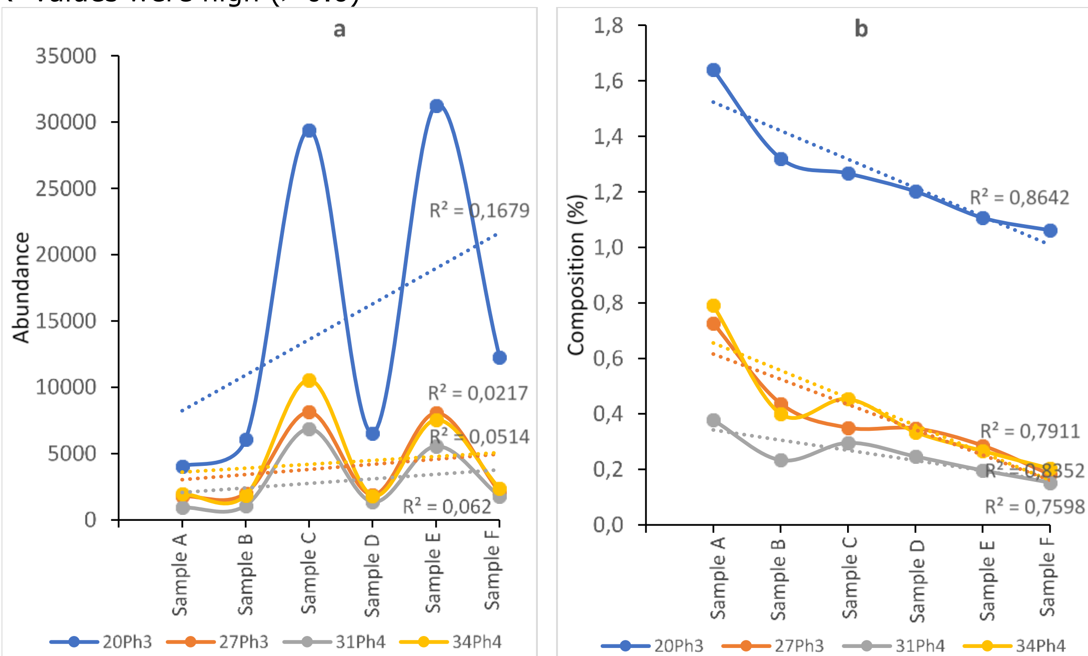

Figure 4. Plot of some C_3-C_4 Phenanthrenes (20Ph3, 27Ph3, 31Ph4, and 34Ph4) against all the studied oil samples showing the level of correlation a. abundance b. composition

3.3. Ratios of the phenanthrenes

The abundance of individual phenanthrenes showed poor correlation and did not mix linearly (Table 1, Figs. 3 and 4). The relative composition of the phenanthrene types in the studied oil samples was used to evaluate the end-member and commingled crude oil samples. The abundance of phenanthrene types (ΣC_0 = P, ΣC_1 = P1, ΣC_2 = P2, ΣC_3 = P3 and ΣC_4 = P4) are shown in table 1 and ratios calculated from it are presented in Table 2.

Table 2. Calculated ratios of phenanthrene types all the studied crude oil samples

	P/P1	P/P2	P/P3	P/P4	P1/P2	P1/P3	P1/P4	P2/P3	P2/P4	P3/P4
Sample A	0.42	0.21	0.31	0.84	0.50	0.74	2.03	1.49	4.06	2.73
Sample B	0.50	0.43	0.81	2.52	0.87	1.63	5.07	1.88	5.84	3.10
Sample C	0.50	0.50	0.94	2.59	1.00	1.89	5.20	1.89	5.21	2.75
Sample D	0.47	0.44	0.91	3.15	0.95	1.95	6.73	2.06	7.11	3.45
Sample E	0.51	0.51	1.13	4.30	1.00	2.23	8.43	2.24	8.47	3.79
Sample F	0.52	0.52	1.21	3.18	0.99	2.30	6.07	2.32	6.13	2.64

Ten ratios were calculated and plotted against the end-member and commingled oil samples. The plots of P/P_3, P_1/P_3, and P_2/P_3 ratios had the highest R^2 values of 0.830, 0.823 and 0.929 respectively (figs. V, VI and VII).

R^2 value shows the relationship between variables and explains the percentage variation (y-axis) of the independent variables (x-axis). Values of R^2 range from 0 to 1. A value of 1 indicates a perfect relationship which explains all the variability of the data, while a value of 0 indicates no relationship and explains no variation. The R^2 values from the plots indicate a very strong relationship of P/P_3, P_1/P_3, and P_2/P_3 ratios within the end member and commingled oil samples and that these ratios can account for 83%, 82% and 93% of the mixing pattern of the end member oils in their commingled oils respectively. This reveals a high significance of P/P_3, P_1/P_3, and P_2/P_3 ratios as correlational tools for allocation of commingled crude oils.

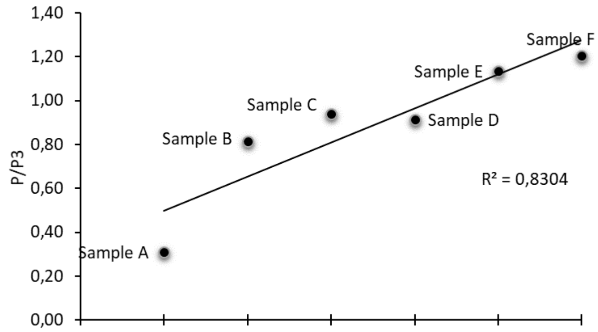

Figure 5. Plot of P/P3 phenanthrenes for the two end-member Niger Delta crude oils (samples A and F) and their commingled oils (B, C, D, and E)

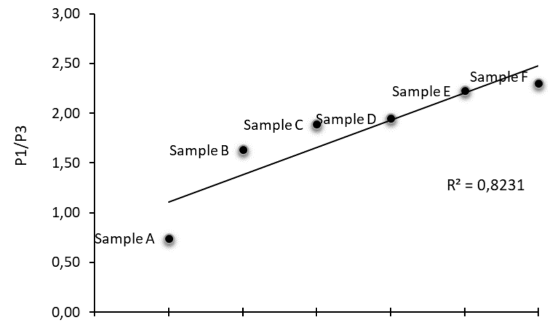

Figure 6. Plot of P1/P3 phenanthrenes for the two end-member Niger Delta crude oils (samples A and F) and their commingled oils (B, C, D, and E)

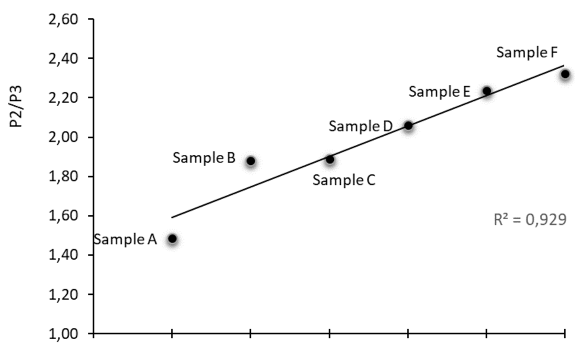

Figure 7. Plot of P2/P3 phenanthrenes for the two end-member Niger Delta crude oils (samples A and F) and their commingled oils (B, C, D and E)

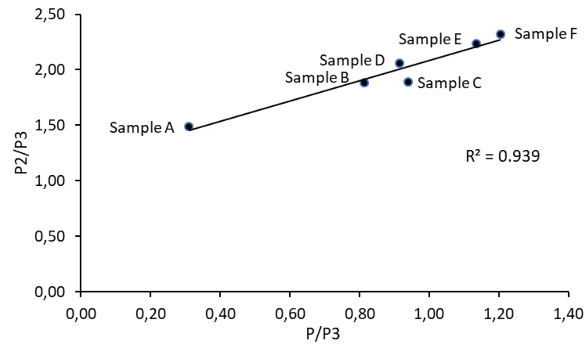

Figure 8. Plot of P/P3 vs. P2/P3 phenanthrenes for the two end-member Niger Delta crude oils (samples A and F) and their commingled oils (B, C, D, and E)

Double ratio plots of P/P_2 vs. P_2/P_3 and P/P_2 vs. P_1/P_3 are shown in Figs. 8 and 9. The R^2 values of these double ratio plots are 0.934 and 0.989 respectively. This R^2 values indicate a very strong relationship of the double ratios with the oil samples and can account for 93% and 98% of the mixing pattern of the end member oils in their commingled oils respectively.

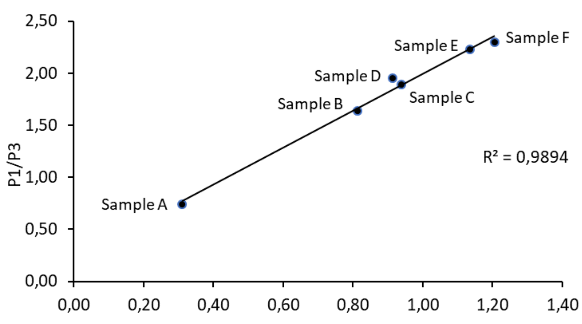

Figure 9. Plot of P/P3 vs. P1/P3 phenanthrenes for the two end-member Niger Delta crude oils (samples A and F) and their commingled oils (B, C, D, and E)

From the R^2 values of Figs. 8 and 9, the double ratio plots of P/P_2 vs. P_2/P_3 and P/P_2 vs. P_1/P_3 exhibited a high significance in the correlation of the phenanthrenes for allocation of the composition of the end member Niger Delta crude oils in their commingled oils. The extrapolation of these ratio values for a hypothetical mixture of two end member Niger Delta crude oils from the y-axis and down to the x-axis can estimate (93 to 98%) the contributions of the different end member oils to their commingled stream.

4. Conclusion

GC-MS was used to analyze for C_0-C_4 phenanthrenes in two Niger Delta crude oils (samples A and F) and their commingled oils (samples B, C, D, and E). Forty-five (45) phenanthrene peaks were selected for geochemical correlation of the oil samples. Abundance plots of some C_0-C_4 phenanthrenes; Ph, 2Ph, 3Ph, 6Ph2, 8Ph2, 20Ph3, 27Ph3, 31Ph4 and 34Ph4, gave low R^2 values which indicate negligible to the weak correlation of these phenanthrenes with the oil samples, while composition plots gave high R^2 values which indicate strong to a very strong correlation. R^2 values from plots of P/P_3, P_1/P_3 and P_2/P_3 ratios, as well as double ratio plots of P/P2 vs P2/P3 and P/P2 vs P1/P3, indicate a very strong correlation between the end member and commingled oils which could account for 82 to 98% of the mixing pattern. The results show the significance of phenanthrenes in Niger Delta crude oils for geochemical correlation and allocation of the composition of end member crude oils in their commingled oils. This method will be of advantage over the metering system as it measures the relative contributions of the end member crude oils production stream (instead of water + oil) and effective reservoir management in the Nigerian oil industry which has suffered from absence/inaccurate metering systems.

References

[1] Tissot BP and Welte DH Petroleum Formation and Occurrence. Springer-Verlag Berlin Heidelberg New York, 1984.

[2] Hunt JM. Petroleum Geochemistry and Geology, 2nd Ed.; W. H. Freeman and Company, U.S.A, 1996.

[3] Peters KE, Fraser TH, Amris W, Rustanto B, Hermanto E. Geochemistry of Crude Oils from Eastern Indonesia. American Association of Petroleum Geologists Bulletin. 1999; 83: 1927-1942.

[4] Hwang RJ, Baskin DK, Teerman SC. Allocation of Commingled Pipeline Oils to Field Production. Organic Geochemistry, 2000; 31: 1463-1474.

[5] Ekweozor CM. Source Rocks of Giant Hydrocarbon Deposits in Deep Offshore, Niger delta. Abstract of Paper; Nigerian Association of Petroleum Explorationists and American Association of Petroleum Geologists Regional West Africa Deepwater Conference, Abuja, Nigeria; 2004.

[6] Eneogwe CI, Ekundayo O, Patterson BA. Source-Derived Oleanenes Identified in Niger Delta Oils. Journal of Petroleum Geology, 2002; 25: 83-95.

[7] Eneogwe CI. The Distribution of Light Hydrocarbons in Western Niger Delta Oils. Journal of Petroleum Geology, 2003; 26: 479-488.

[8] De Luca G, Furesi A, Leardi R, Micera G, Panzanelli A, Piu PC, Sanna G. Polycyclic Aromatic Hydrocarbons Assessment in the Sediments of the Porto Torres Harbor (Northern Sardinia, Italy). Marine Chemistry, 2004; 86: 15–32.

[9] Osuji LC and Antia BS. Geochemical Implications of Some Chemical Fossils as Indicators of Petroleum Source Rocks. J. Appl. Sci. Environ. Mgt., 2005; 9(1): 45-49.

[10] Onyema MO and Manilla PN Light Hydrocarbon Correlation of Niger Delta Crude Oils. Journal of American Science, 2010; 6(6): 82-88.

[11] Sosrowidjojo IB. Organic Geochemistry: Geographic Location of Crude Oil Based on Biomarker Composition of the Sundr-Asri Basins, Indonesia. Int. J. Phys. Sci., 2011; 6(31): 7291-7301.

[12] Volk H, George SC, Middleton H, Schofield S. Geochemical Comparison of Fluid Inclusion and Present-day Oil Accumulations in the Papuan Forland – Evidence for Previously Unrecognised Petroleum Source Rocks. Organic Geochemistry, 2004; 36: 29-51.

[13] Antle PM, Ziegler CD, Wilton NM, Robbat A. A More Accurate Analysis of Alkylated PAH and PASH and its Implications in Environmental Forensics. Intern. J. Environ. Anal. Chem., 2014; 94(4): 332-347.

[14] Ali FM, Al-Khadrawi RM, Perzanowski H, Halpern HJ. Central Saudi Arabia crude oil: A Geochemical Investigation. J. Petrol. Sci. and Tech., 2002; 20: 633-654.

[15] Hwang RJ, Ahmed AS, and Moldowan JM. Oil Composition Variation and Reservoir Continuity: Unity Field, Sudan. Organic Geochemistry, 1994; 21(2): 171-188.

[16] Kaufman RL, Ahmed AS, and Hempkins WB. A New Technique for the Analysis of Commingled Oils and its Application to Production Allocation Calculations. Presented at IPA 16th Annual Indonesian Petro. Assoc. Indonesia, 1987; 247-268.

[17] Abivin P, Toribio MM, and Indo K. Methods for Allocating Commingled Oil Production. US Patent US2010/0307740 AI, 2010.
[18] Nigeria Extractive Industries Transparency Initiative. Oil and Gas Industry Audit Report. Abuja, Nigeria, 2014.

To whom correspondence should be addressed: Dr. Nwannedi C. Okoroh, Petroleum and Environmental Geochemistry Research Group, Department of Pure and Industrial Chemistry, University of Port Harcourt, P.M.B 5323 Choba, Port Harcourt, Rivers State, Nigeria