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Terpane Characterization of Crude Oils from Niger Delta, Nigeria: A Geochemical Appraisal

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Abstract: The geochemistry of crude oils from the Niger Delta, Nigeria, were evaluated using the characterization of C_{19} to C_{35} terpanes. Analyses of two representative crude oils from Western and Central Niger Delta showed abundances of C_{19} to C_{29} tricyclic terpanes constituted 12.09% and 29.74%, C_{24} tetracyclic terpane 0.31% and 0.15% and C_{27} to C_{35} pentacyclic terpanes 87.61% and 70.12%, respectively. Diagnostic ratios of terpanes indicate relatively low abundances of C_{23}, C_{28} and C_{29} tricyclic terpanes, low abundances of homohopanes, a significantly high abundance of oleanane and suggested that the Niger Delta crude oils were derived from terrestrial organic matter source rocks deposited in an oxic environment during the Tertiary period. Multivariate oil-oil correlation plot showed the Western and Central Niger Delta crude oils are not distinct, but moderately related (genetically). However, diagnostic ratios of C_{24} tetracyclic terpane, which was high and moderate; gammacerane, which was low and high, revealed crude oils from Western Niger Delta were derived from predominantly terrestrial source and crude oils from Central Niger Delta were derived from terrestrial source with input from marine organic matter, respectively. Tricyclic terpanes/hopanes and isomerization ratios of C_{32} homohopanes indicated that the Niger Delta crude oils were generated at high maturity, at top of the oil generation window.
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1. Introduction

Crude oil originates from the chemical and geological transformation of biomolecules from prehistoric organisms of both marine and terrestrial sources buried deep under the earth's crust during sedimentary processes (Wang et al., 2006). Many of the geochemical compounds identified contain vital information about the fate of the crude oil in which they are found (Osuji et al., 2005; Mobarakabad et al., 2011). One such class of geochemical compounds found in crude oils is terpane, derived from terpenoid found in plants.

Terpanes found in crude oils and source rock extracts range from C_{19} tricyclic terpanes to C_{35} homohopanes and they are detected in a mixture of other types of petroleum hydrocarbons by gas chromatography-mass spectrometry (GC-MS) via monitoring the fragment ion at mass to charge (m/z) 191 (Killops and Killops, 2013). They have been used extensively to indicate organic matter's source, condition of the depositional environment, age of source rock from which the crude oil was derived and maturity at the time of oil generation, as well as correlation and/or differentiation of crude oils and source rocks (El-Gayar et al., 2002; Younes, 2001; Mohialdeen et al., 2013). The relative compositions of terpanes such as C_{19}/C_{23}, C_{23}/C_{24}, and C_{26}/C_{25} tricyclic terpanes, as well as 18α/17α trisnorhopanes (Ts/Tm), C_{31} to C_{35} homohopanes, gammercerane and oleanane, are used as diagnostic parameters for evaluating crude oils (Volk et al., 2005).

The Niger Delta region in southern Nigeria is one of the world's most productive oil regions. As of early 2012, the region possessed an estimated 38 billion barrels of crude oil (Isumonah, 2013). Niger Delta crude oils have been evaluated with their bulk characteristics, light hydrocarbons, triterpanes, and aromatic hydrocarbons (Eneogwe et al., 2003; Onyema and Osuji 2015; Thomas, 1995; Sonibare et al., 2008; Onyema and Ajike 2010). This research utilized the distribution and characterization of C_{19} to C_{35} terpanes for correlation and geochemical appraisal of crude oils from two sub-regions of the Niger Delta, Nigeria.

2. Material and Methods

2.1. Description of Study Area

The Niger Delta region is located in southern Nigeria, between longitudes 5° and 8° E and latitudes 3° and 6° N, at the apex of the Gulf of Guinea. The region formed from the late Cretaceous into the Tertiary period with depositions of sediments south-west ward into the Gulf of Guinea in three sequentially arranged stratigraphic formations: Akata formation, Agbada formation and Benin formation. These formations are distinguished primarily based on the sand-shale ratios. Petroleum system in the region is identified as the Tertiary Niger Delta (Akata-Agbada) Petroleum System (Tuttle et al., 1999).

2.2. Sample Collection

Crude oil samples were obtained from oil flow stations: one each from Delta State (5°28' N, 6°12' E) and Rivers State (4°39' N, 7°16' E) in the Western and Central Niger Delta sub-regions, respectively. Each crude oil obtained, is a mixture of several producing oil wells flowing into the flow station and serve as a representative crude oil sample. With assistance of field technicians, the crude oils were obtained (1 liter each) and labelled sample-IRD and sample-AGR, respectively.

2.3. Crude oil fractionation

50 mg of each crude oil sample was weighed into labelled centrifuge tube. Excess pentane were added to the crude oil samples in the centrifuge tubes, allowed to stand for 3 hours and centrifuged to coalesce the precipitated asphaltenes. The pentane soluble fractions were decanted, concentrated with nitrogen gas at 40°C and each deasphalted crude oil sample transferred onto the top a glass column (30 cm x 1 cm) stuffed with glass wool at the bottom and packed with silica. *n*-hexane, dichloromethane and dichloromethane/methanol (1:1) mixture were poured into the packed columns to elute the saturates, aromatics, and resins, respectively. The eluents were concentrated using nitrogen gas at 40°C.

2.4. Gas chromatography-mass spectrometry (GC-MS) analyses

Agilent 7890A gas chromatograph (GC) system with a HP-5 silica capillary column (50 m x 320 m i.d. and 0.25 m film thickness) and an Agilent 5975 mass selective detector (MSD) was used to analyze the saturate hydrocarbon fractions of the crude oil samples. With the aid of G4513A automatic liquid sampler (ALS), 1 microliter of the saturate fraction of each sample was injected into the GC capillary column in splitless mode. The GC oven was set to an initial temperature of 80°C for 5 minutes (mins.), then ramped to 300°C at a rate of 4°C/min. and held at this temperature for 30 min. Terpanes were monitored using their characteristic fragment ion at mass to charge (m/z) 191. Peaks were identified by comparing their mass spectra to related literature. Quantification of the abundance of each peak was obtained by area integration, which was processed by Chemstation OPEN LAB CDS software.

3. Results

GC-MS analyses of the crude oil samples (-IRD and -AGR) monitored using the m/z 191 fragment ion showed well-resolved peaks (Figures 1 and 2). This fragment ion (m/z 191) is characteristic and indicate the occurrence of terpanes in Niger Delta crude oils (Volk et al., 2005; Eneogwe et al., 2002).

3.1. Distribution of Terpanes

Terpanes in samples -IRD and -AGR elute between 20 and 50 minutes on the m/z 191 mass chromatograms and ranged from C_{19} tricyclic terpane to C_{35} homohopanes (Figures 1 and 2; see Table 1 for peaks identifications). The most abundant terpanes in the Niger Delta crude oil samples were hopane (H30), oleanane (OL), and 30-norhopane (NH30), respectively. It was also observed that tricyclic terpanes, TR20a-d and TR21a-f (see Table 1 for peaks id.), were reduced in sample-IRD and prominent in sample-AGR (Figures 1 and 2).

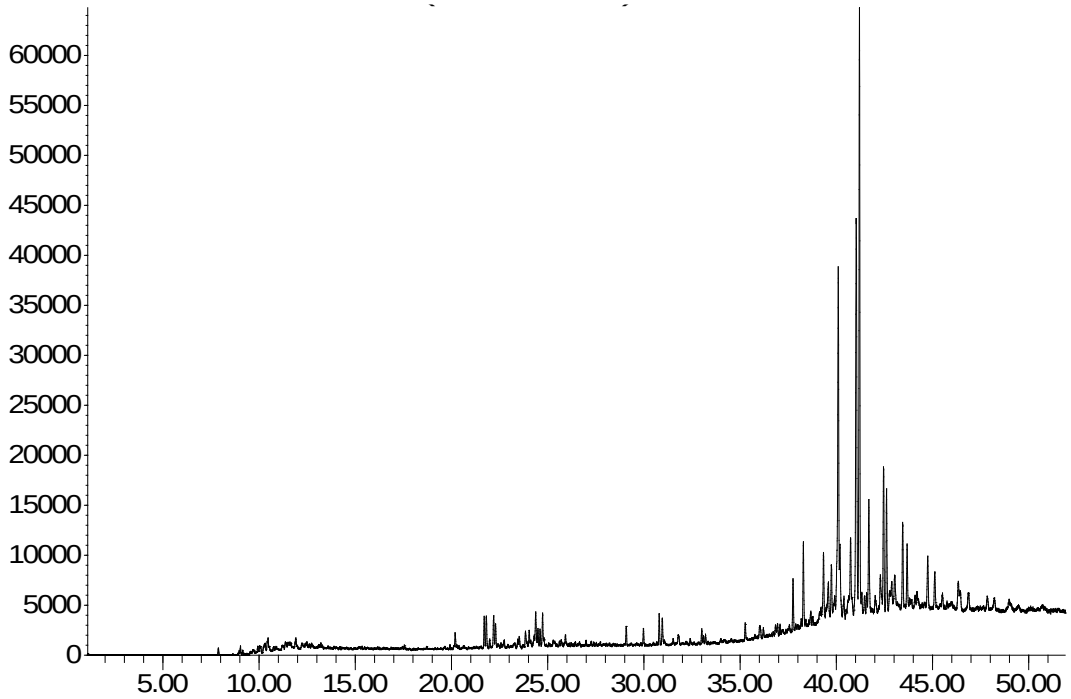


Figure 1. m/z 191 mass chromatogram of crude oil sample-IRD from Western Niger Delta showing the distribution of terpanes

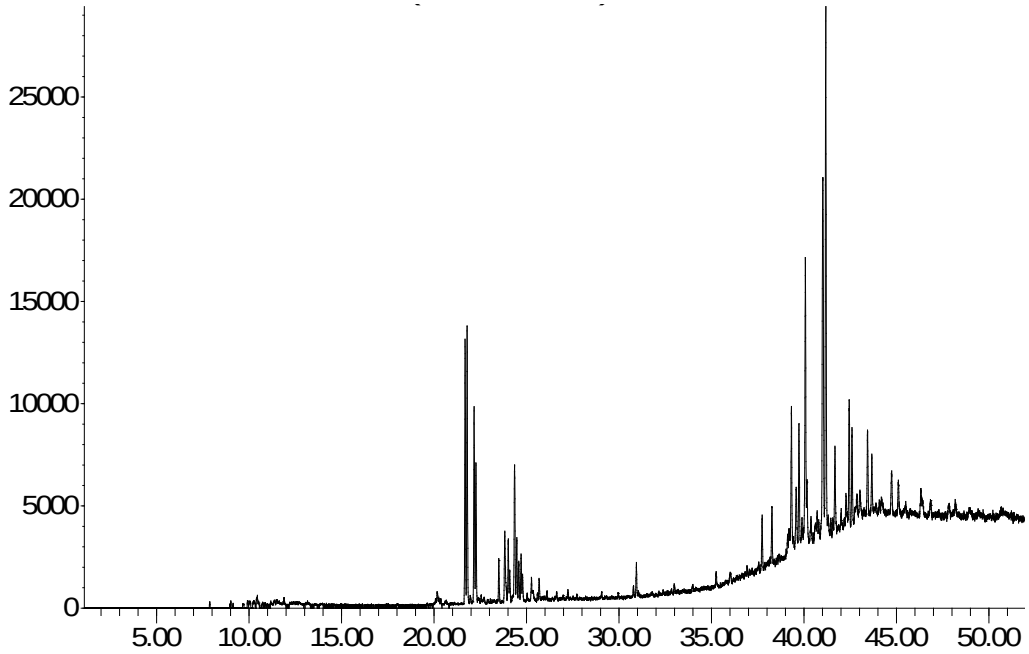


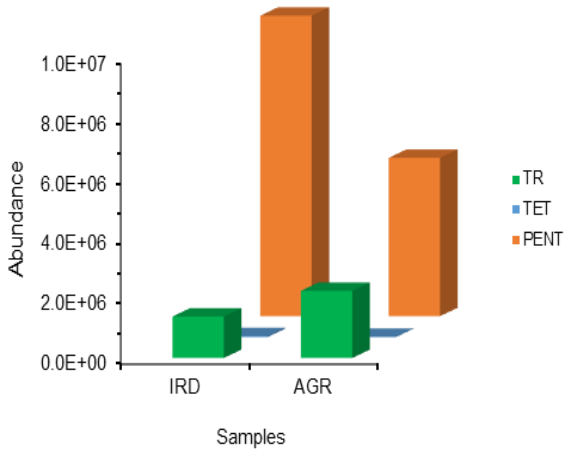
Figure 2. m/z 191 mass chromatogram of crude oil sample-AGR from Central Niger Delta showing the distribution of terpanes

Table 1. Identifications of terpane peaks on the m/z 191 mass chromatograms of the crude oil samples from Niger Delta, Nigeria

Peak	Terpanes	Code	Empirical formula
1	C_{19} tricyclic terpane	TR19	$C_{19}H_{34}$
2	C_{20} tricyclic terpane (a)	TR20a	$C_{20}H_{36}$
3	C_{20} tricyclic terpane (b)	TR20b	$C_{20}H_{36}$
4	C_{20} tricyclic terpane (c)	TR20c	$C_{20}H_{36}$
5	C_{20} tricyclic terpane (d)	TR20d	$C_{20}H_{36}$
6	C_{21} tricyclic terpane (a)	TR21a	$C_{21}H_{38}$
7	C_{21} tricyclic terpane (b)	TR21b	$C_{21}H_{38}$
8	C_{21} tricyclic terpane (c)	TR21c	$C_{21}H_{38}$
9	C_{21} tricyclic terpane (d)	TR21d	$C_{21}H_{38}$
10	C_{21} tricyclic terpane (e)	TR21e	$C_{21}H_{38}$
11	C_{21} tricyclic terpane (f)	TR21f	$C_{21}H_{38}$
12	C_{22} tricyclic terpane	TR22	$C_{22}H_{40}$
13	C_{23} tricyclic terpane	TR23	$C_{23}H_{42}$
14	C_{24} tricyclic terpane	TR24	$C_{24}H_{44}$
15	C_{25} tricyclic terpane (a)	TR25a	$C_{25}H_{46}$
16	C_{25} tricyclic terpane (b)	TR25b	$C_{25}H_{46}$
17	C_{24} tetracyclic terpane	TET24	$C_{24}H_{42}$
18	C_{26} S tricyclic terpane (S)	TR26S	$C_{26}H_{49}$
19	C_{26} tricyclic terpane (R)	TR26R	$C_{26}H_{50}$
20	C_{28} tricyclic terpane (a)	TR28A	$C_{28}H_{52}$
21	C_{28} tricyclic terpane (b)	TR28B	$C_{28}H_{52}$
22	C_{29} tricyclic terpane (a)	TR29A	$C_{29}H_{54}$
23	C_{29} tricyclic terpane (b)	TR29B	$C_{29}H_{54}$
24	C_{27} 18α trisnorhopane	Ts	$C_{27}H_{46}$
25	C_{27} 17α trisnorhopane	Tm	$C_{27}H_{46}$
26	C_{28} bisnorhopane	H28	$C_{28}H_{48}$
27	C_{29} 17α 25-norhopane	NH25a	$C_{29}H_{50}$
28	C_{29} 17β 25-norhopane	NH25b	$C_{29}H_{50}$
29	C_{29} 17α 30-norhopane	NH30	$C_{29}H_{50}$
30	C_{30} 17α diahopane (Lupane)	LUP	$C_{30}H_{52}$
31	C_{29} normoretane	M29	$C_{29}H_{50}$
32	Oleanane	OL	$C_{30}H_{52}$
33	C_{30} hopane	H30	$C_{30}H_{52}$
34	C_{30} moretane	M30	$C_{30}H_{52}$
35	C_{31} 22S homohopane	H31S	$C_{31}H_{54}$
36	C_{31} 22R homohopane	H31R	$C_{31}H_{54}$
37	Gammacerane	GAM	$C_{30}H_{52}$
38	C_{32} 22S bishomohopane	H32S	$C_{32}H_{56}$
39	C_{32} 22R bishomohopane	H32R	$C_{32}H_{56}$
40	C_{33} 22S trishomohopane	H33S	$C_{33}H_{58}$
41	C_{33} 22R trishomohopane	H33R	$C_{33}H_{58}$
42	C_{34} 22S tetrakishomohopane	H34S	$C_{34}H_{60}$
43	C_{34} 22R tetrakishomohopane	H34R	$C_{34}H_{60}$
44	C_{35} 22S pentakishomohopane	H35S	$C_{35}H_{62}$
45	C_{35} 22R pentakishomohopane	H35R	$C_{35}H_{62}$

Terpanes detected by GC-MS analyses of the crude oil samples were of three groups: C_{19} to C_{29} tricyclic terpanes, C_{24} tetracyclic terpane and C_{27} to C_{35} pentacyclic terpanes. Figure 3 shows the profile of the three terpane groups detected in the crude oil samples. Total abundance of terpanes in the crude oils were high with the abundance in sample-IRD 1.52 times higher than sample-AGR (Figure 3). This indicate terpanes were more abundant in crude oils from Western Niger Delta than Central Niger Delta.

Pentacyclic terpanes (PENT) was the most abundant terpane group in samples -IRD and -AGR with compositions of 87.61% and 70.12%, while tetracyclic terpane (TET) was the least abundant with compositions of 0.31% and 0.15%, respectively. Abundances of tricyclic terpanes (TR) was low with compositions of 12.09% and 29.74%, respectively (Figure 3). According to Huang and Meinschein (1979), tricyclic terpanes are commonly in high abundances in marine-derived oils.



Samples	Abundance Tricyclic terpanes (TR)	Tetracyclic terpane (TET)	Pentacyclic terpanes (PENT)	Total
IRD	1,378,329 (12.09%)	34,811 (0.31%)	9,991,502 (87.61%)	11,404,642
AGR	2,232,170 (29.74%)	11,072 (0.15%)	5,263,550 (70.12%)	7,506,792

Figure 3. Profile of three terpane groups: tricyclic terpanes (TR), tetracyclic terpane (TET) and pentacyclic terpanes (PENT), in the crude oils (samples-IRD and -AGR) from Niger Delta, Nigeria

This distribution profile of terpane groups indicate the Niger Delta crude oils are characterized by high abundance of pentacyclic terpanes and mostly derived from non-marine/terrestrial organic matter sources. The abundance of tricyclic terpanes (TR) was more in sample-AGR (29.74%) than sample-IRD (12.09%) suggesting crude oils from Central Niger Delta received more marine organic matter input than those from Western Niger Delta.

3.2. Characterization of Terpanes

Geochemical characterization of crude oils utilize the abundances of terpanes to determine the source organic matter type, depositional environment and thermal maturity (Peters et al., 2005). From the abundances of terpanes in samples -IRD and -AGR, diagnostic ratios were calculated and used to characterize the Western and Central Niger Delta crude oils (Table 2). Crude oils from marine sources usually have high C_{23} tricyclic terpane to C_{30} 17α(H)-hopane (TR23/H30) ratio with high abundances of C_{28} - C_{30} extended tricyclic terpanes associated with source rocks deposited in an anoxic environment during marine upwelling (Huang and Meinschein, 1979; Holba et al., 2003). Ratios of TR23/H30, TR28/H30 and TR29/H30 in samples -IRD and -AGR, which ranged from 0.02 to 0.05, were relatively low (Table 2). The absence of C_{30} extended tricyclic terpane and the relatively low abundances of C_{23}, C_{28} and C_{29} tricyclic terpanes suggest that Niger Delta crude oils were generated from terrestrial organic matter deposited in an oxic environment.

Table 2. Diagnostic ratios of terpanes utilized for geochemical characterization of crude oil from Niger Delta, Nigeria

Diagnostic ratios	Sample-IRD	Sample -AGR
TR23/H30	0.03	0.02
TET24/TT24+TR26	0.42	0.27
TR28/H30	0.05	0.05
TR29/H30	0.04	0.04
TR/Hop	0.18	0.54
OL/H30	0.90	0.95
GAM/H30	0.06	0.16
GAM/H31	0.13	0.31
HH/Σ (H31-H35)	0.40: 0.25: 0.17: 0.11: 0.07	0.35: 0.33: 0.17: 0.09: 0.06
HHI = H35/Σ (H31-H35)	0.07	0.06
H32S/H32R	1.30	1.38
H32S/(H32S+H32R)	0.57	0.58

C_{24} tetracyclic terpane (TET24) is a biomarker that indicates terrestrial higher plant source (Disnar and Harouna, 1994). It was detected in both crude oil samples with abundances, as determined by TET24/TET24+TR26 ratio (see Table 1 for peak id), high (0.42) in sample-IRD and moderate (0.27) in sample-AGR (table 2). This suggest terrestrial organic matter source for the Niger Delta crude oils with the Western oil receiving a greater input than the Central oil. Oleanane is another biomarker indicating terrestrial higher plant (angiosperm) source, which appeared from the Cretaceous period (<130 million years) with growing abundance in the Tertiary period, but not found in older rocks and oils (Ekweozor and Udo, 1988; Riva et al., 1988; Murray et al., 1997; Hans et al., 2002). Alberdi and Lopez (2000) have used oleanane as a geochemical tool to assess crude oils from two sub-basins of the Venezuelan petroleum system. Oleanane abundances (OL/H30) in the crude oil samples were significantly high (0.90 and 0.95; table 2) and indicate the Niger Delta crude oils were predominantly derived from terrestrial organic matter source rocks deposited during the Tertiary period.

Gammacerane is a terpane biomarker used to determine the degree of salinity in the depositional environment of source rocks. Its abundance rises as the salinity of the depositional environment rises, from lacustrine to marine (Sinninghe Damste et al., 1995). Ratios of GAM/H30 and GAM/H31 (see Table 1 for peaks id), used to determine the abundance of gammacerane in crude oils, were low in sample-IRD (0.06; 0.13) and high in sample-AGR (0.16; 0.31),

respectively (Table 2). This abundance of gammacerane suggest that the crude oils from Western Niger Delta (-IRD) were formed from source rocks deposited in a low salinity environment, whereas those from Central Niger Delta (-AGR) were formed from source rocks deposited in a higher salinity environment, typical of a marine habitat.

The relative abundances of C_{31} to C_{35} homohopanes and homohopane index (HHI), abundance of C_{35} homohopanes relative to total homohopanes, are suitable indicators for determining the reduction/oxidation (redox) condition of the depositional environment. Crude oils derived from source rocks deposited under highly reducing (anoxic) marine conditions, generally show increasing relative abundances of C_{31} to C_{35} homohopanes and high HHI, while those deposited under oxidizing (oxic) conditions show decreasing relative abundances and low HHI [18]. For samples -IRD and -AGR, the calculated relative abundances of homohopanes (HH/Σ H31-H35) progressively decreased from 0.40 to 0.07 and 0.35 to 0.06, while the HHI values were 0.07 and 0.06, respectively. These calculated ratio values suggest that Niger Delta oils were derived from source rocks deposited in an oxic environment.

Terpanes commonly used for assessment of crude oil thermal maturity are the homohopanes. This is based on the isomerization of the C-22 hydrogen atom of the C_{31} to C_{35} homohopanes from the biologically generated R-isomer to the thermodynamically more stable S-isomer until an equilibrium mixture is reached at maturity. Ratios of C_{32} homohopanes, H32S/H32R and H32S/H32S+H32R (see Table 1 for peaks id), were used to assess the maturity of the samples. For samples -IRD and -AGR, the calculated H32S/H32R ratio were 1.30 and 1.38, while for H32S/H32S+H32R ratio were 0.57 and 0.58, respectively (table 2). At about equilibrium, H32S/H32S+H32R ratio values ranges from 0.57 to 0.62 and indicated the crude oil was formed at top of the oil generation window (Peters and Moldowan, 1993). The isomerization ratio values indicate the thermodynamically stable H32S was more than the biologically generated H32R (i.e. slightly above equilibrium) and that Niger Delta crude oils were generated at peak of the oil generation window at a high maturity, with sample-IRD slightly less mature than sample-AGR. Similarly, tricyclic terpanes to hopanes (TR/Hop) ratio values of 0.18 and 0.54 suggest sample-IRD was less mature than sample-AGR, respectively. This is due to thermal cracking of hydrocarbons from high molecular weight to low molecular weight during crude oil maturation, resulting in the increased abundance of tricyclic terpanes in high-mature oils (Waples, 1985; Farrimond et al., 1999). From the geochemical characterization results of samples-IRD and -AGR, Niger Delta crude oils were generated at peak of the oil generation window at a high maturity, predominantly from terrestrial organic matter with source rocks deposited in an oxic environment during the Tertiary period. However, the abundance of gammacerane suggest that crude oils from Central Niger Delta received a greater marine input and were more mature than those from Western Niger Delta.

3.3. Oil–oil Correlation

Multivariate techniques was used for oil-oil correlation of the Western and Central Niger Delta crude oils. The technique compares hydrocarbon ratios of crude oils and put them in a multivariate plot (Ali et al., 2002; Onyema and Manilla, 2010). Nine (9) selected terpane ratios were determined (table 3) and used for multivariate correlation of oil samples -IRD and -AGR (Figure 4).

Table 3. Selected terpane ratios employed for multivariate correlation of the Niger Delta crude oil samples

Axis	Terpane ratios	Sample -IRD	Sample -AGR
1.	C19/(C19 + C23)	0.41	0.70
2.	TR24/(TR24+TR23)	0.46	0.40
3.	TET24/TR26	0.73	0.38
4.	Ts/Tm	0.64	0.90
5.	GAM/H31(S+R)	0.13	0.31
6.	H35/H34	0.68	0.69
7.	H35/(H35 + H34)	0.40	0.41
8.	H30/M30	0.82	0.81
9.	H32 22S/(22S+22R)	0.57	0.58

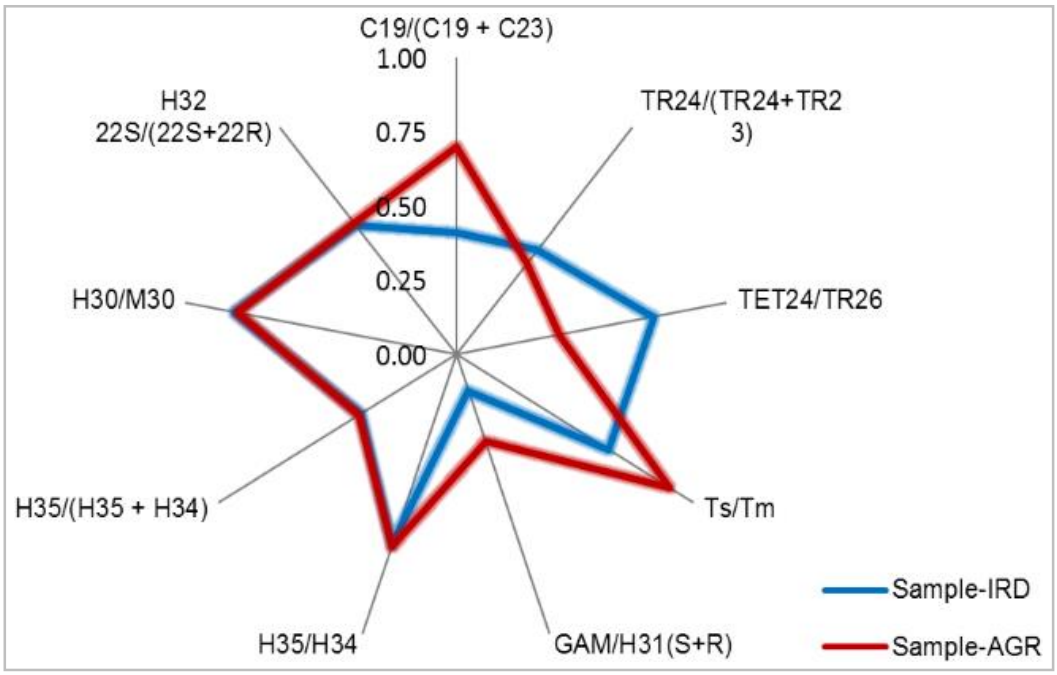


Figure 4. Plot of selected terpane ratios employed for multivariate correlation of oil samples -IRD and -AGR from Niger Delta, Nigeria

From figure 4, the pattern formed on the multivariate plot of selected terpane ratios by sample-IRD was comparable to sample-AGR. The multivariate plot of 9-axis (selected terpane ratios) showed samples-IRD and -AGR followed different paths on axis-1,-2, -3 and -4; similar path with slight deviation on axis-5 and same paths on axis-6, -7, -8 and -9 indicating the crude oil samples are not distinct, but moderately similar. Differences in paths followed by crude oils and source rocks on multivariate plots reflect differences in organic matter source, depositional environment, lithology and/or transformation process (Volk et al., 2005; Ali et al., 2002). This reveal the Western and Central Niger Delta crude oils are genetically related with input from a different organic matter source, depositional environment, lithology and/or transformation process to crude oils from one of the sub-regions.

4. Conclusion

Two representative crude oils from Western and Central Niger Delta were evaluated employing terpane characterization. Diagnostic ratios of C_{23}, C_{28} and C_{29} tricyclic terpanes, C_{24} tetracyclic terpane, oleanane, gammacerane and homohopanes as well as multivariate correlation indicate crude oils from Western Niger Delta were derived from predominantly terrestrial source and Central Niger Delta, derived from mixed marine and terrestrial organic matter source. Source rocks of Niger Delta crude oils were deposited in an oxic environment during the Tertiary period. Ratios of tricyclic terpanes/hopanes and C_{32} homohopane isomerization indicate the Niger Delta crude oils were generated at high maturity, at top of the oil generation window with crude oils from the Central Niger Delta more mature than the Western Niger Delta. These terpanes can furthermore be used to characterize the Niger Delta petroleum system for continuity / compartmentalization and geochemical allocation of commingled crude oils from the region.

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References

[1]. Wang Z, Stout SA, Fingas M. Forensic fingerprinting of biomarkers for oil spill characterization and source identification, *Environmental Forensics*, 7(2) (2006) 105-146.

[2]. Osuji LC, Antia BS, Geochemical implication of some chemical fossils as indicators of petroleum source rocks, *Journal of Applied Science and Environmental Management*, 9 (1) (2005) 45-49.

[3]. Mobarakabad AF, Bechtel A, Gratzer R, Mohsenian E, Sachsenhofer RF. Geochemistry and origin of crude oils and condensates from the Central Persian Gulf, offshore Iran, *Journal of Petroleum Geology*, 34 (3) (2011) 261-275.

[4]. Killops SD, Killops VJ. Introduction to organic geochemistry, John Wiley and Sons, New York. (2013) 138-141.

[5]. El-Gayar MS, Mostafa AR, Abdelfattah AE, Barakat AO. Application of geochemical parameters for classification of crude oils from Egypt into source-related types, *Fuel Processing Technology*, 79 (2002) 13-28.

[6]. Younes MA. Application of biomarkers and stable carbon isotopes to access the depositional environment of source rocks and the maturation of oils, East Zeit Field, Southern Gulf of Suez, Egypt, *Petroleum Science and Technology*, 19 (2001) 1039-1081.

[7]. Mohialdeen IMJ, Hakimi MH, Al-Beyati FM. Biomarker characteristics of certain crude oils and the oil-source rock correlation for the Kurdistan Oilfields, Northern Iraq, *Arabian Journal of Geosciences*, 8 (1) (2013) 507-523.

[8]. Volk H, George SC, Middleton H, Schofield S. Geochemical comparison of fluid inclusion and present-day oil accumulations in the Papuan Foreland - Evidence for previously unrecognized petroleum source rocks. *Organic Geochemistry* 36 (2005) 29-51.

[9]. Isumonah VA. "Armed society in the Niger Delta". Armed forces and Society. 39 (2) (2013) 331-358.

[10]. Eneogwe CI, Ekundayo O. Geochemical correlation of crude oils in the NW Niger Delta, Nigeria, *Journal of Petroleum Geology*, 26 (2003) 95-103.

[11]. Onyema MO, Osuji LC. Gas Chromatography-Mass Spectrometry (GC-MS) compositional analyses of aromatic hydrocarbons in Niger Delta crude oils. *Petroleum and Coal* 57(5) (2015) 526-531.

[12]. Thomas D. Niger Delta oil production, reserves, field sizes assessed. *Oil and Gas Journal*, 93 (1995) 101-103.

[13]. Sonibare O, Alimi H, Jarvie D, Ehinola OA. Origin and occurrence of crude oil in the Niger Delta, Nigeria, *Journal of Petroleum Science and Engineering*, 61 (2008) 99-107.

[14]. Onyema MO, Ajike KU. Compositional significance of light hydrocarbons in Niger Delta crude oils, Nature and Science 8 (8) (2010) 130-135.

[15]. Tuttle MLW, Charpentier RR, Brownfield ME. Tertiary Niger Delta (Akata Agbada) Petroleum System (No. 719201), Niger Delta province, Nigeria, Cameroon and Equitorial Guniea, Africa. US Geological Survey, Open-File Report 99-50-H.https://pubs.usgs.gov/of/1999/ofr-99-0050/OF99-50H/ChapterA.html. (1999).

[16]. Eneogwe CI, Ekundayo O, Patterson B. Source-derived oleanenes identified in Niger Delta oils. *Journal of Petroleum Geology*, 25 (2002) 83-96.

[17]. Huang WY, Meinschein WG. Sterols as ecological indicators. *Geochimica et Cosmochimica Acta*, 43 (1979) 739-745.

[18]. Peters KE, Walters CC, Moldowan JM. The biomarker guide (2nd Edition): Biomarkers and isotopes in petroleum systems and earth history. Cambridge University Press, Cambridge, (2005) 476-1155.

[19]. Holba AG, Dzou LI, Wood GD, Ellis L, Adam P, Schaeffer P, Albrecht P, Greene T, Hughes WB. Application of tetracyclic polyprenoids as indicators of input from Fresh-Brackish water environments, *Organic Geochemistry*, 34 (2003) 441-469.

[20]. Disnar JR, Harouna M. Biological origin of tetracyclic diterpanes, *n*-alkanes and other biomarkers in Lower Carboniferous Gondwana coals (Niger), *Organic Geochemistry*, 21 (1994) 143-152.

[21]. Ekweozor CM, Udo OT. The oleananes: Origin, maturation and limits of occurrence in Southern Nigeria's sedimentary basins, *Organic Geochemistry*, 13 (1-3) (1988) 131-140.

[22]. Riva A, Caccialanza P, Quagliaroli F. Recognition of 18α(H)-oleanane in several crudes and Tertiary-Upper Cretaceous sediments, *Organic Geochemistry*, 13 (1988) 671-675.

[23]. Murray P, Sosrowidjojo IB, Alexander R, Kagi RI, Norgate CM, Summons RE. Oleananes in oils and sediments: Evidence of marine influence during early diagenesis? *Geochimica et Cosmochimica Acta*, 61 (1997) 1261-1276.

[24]. Hans PN, Jorgen AB, Flemming GC, Fowler MG. Oleanane or lupane? Reappraisal of the presence of oleanane in Cretaceous-Tertiary oils

and sediments, *Organic Geochemistry*, 33 (2002) 1225-1240.

[25]. Alberdi A, Lopez L. Biomarker 18α(H)-oleanane, a geochemical tool to assess Venezuelan Petroleum Systems. *Journal of South American Earth Sciences*, 13 (2000) 751-759.

[26]. Sinninghe Damste JS, Kenig F, Koopmans MP, Koster J, Schouten S, Hayes JM, de Leeuw JW. Evidence for gammacerane as an indicator of water column stratification, *Geochimica et Cosmochimica Acta*, 59 (1995) 1895-1900.

[27]. Peters K.E, Moldowan JW. The biomarker guide: Interpreting molecular fossils in petroleum and ancient sediments, Prentice Hall, New Jersey, (1993).

[28]. Waples D. W., Geochemistry in Petroleum Exploration. International Human Resources Development Corporation, Boston, (1985).

[29]. Farrimond P, Bevan CJ, Bishop AN. Tricyclic terpane maturity parameters: Response to heating by an igneous intrusion, *Organic Geochemistry* 30 (1999) 1011-1019.

[30]. Ali FM, Al-Khadrawi RM, Perzanowski H, Halpern HJ. Central Saudi Arabia crude oil: A geochemical investigation, *Petroleum Science and Technology*, 20 (2002) 633-654.

[31]. Onyema MO, Manilla PN. Light hydrocarbon correlation of Niger Delta crude oils. *Journal of American Science*, 6 (6) (2010) 82-88.

10/22/2023