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

Mark Obinna Onyema[*], Michael Junior Ajie

Petroleum and Environmental Geochemistry Research Group, Department of Pure and Industrial Chemistry, University of Port Harcourt, Port Harcourt, Nigeria

Email address:

onyemark@yahoo.com (Mark Obinna Onyema)

[*]Corresponding author

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 indicated relatively low abundances of C_{23}, C_{28} and C_{29} tricyclic terpanes, low abundances of homohopanes, a significantly high abundance of oleanane and 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 and 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 the Niger Delta crude oils were generated at high maturity, at top of the oil generation window.

Keywords: Geochemistry, Terpane, Correlation, Niger Delta, Gammacerane, Abundance, Crude Oil

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 [1]. Many of the geochemical compounds identified contain vital information about the fate of the crude oil in which they are found [2, 3]. 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 [4]. 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 [5-7]. 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 $18\alpha/17\alpha$ trisnorhopanes (Ts/Tm), C_{31} to C_{35} homohopanes, gammercerane and oleanane are used as diagnostic parameters for evaluating crude oils [8].

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 [9]. Niger Delta crude oils have been evaluated with their bulk characteristics, light hydrocarbons, triterpanes, and aromatic hydrocarbons [10-14]. 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. Materials 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 mouth 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 [15].

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 for the Niger Delta (Western or Central) sub-region. With authorization from the department of petroleum resources (DPR) and 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 the crude oil samples were weighed into labelled centrifuge tubes. 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) Analysis

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 both 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 and Discussion

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 [8, 16].

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).
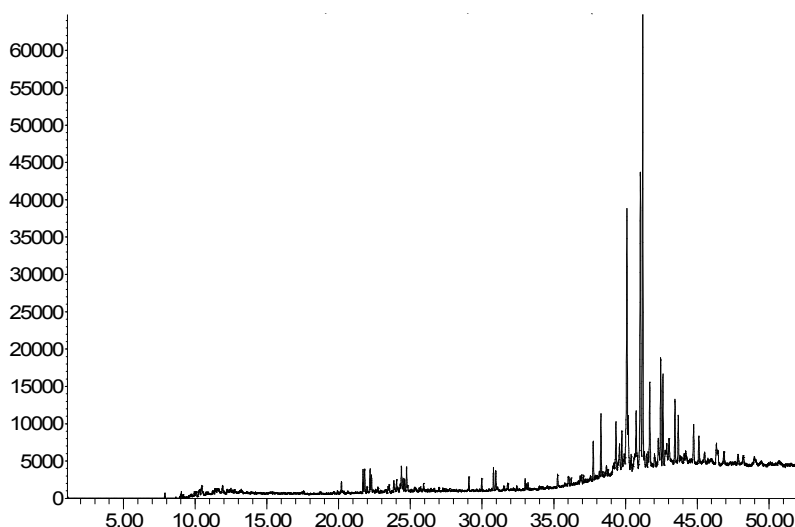

Figure 1. m/z 191 mass chromatogram of crude oil sample-IRD from Western Niger Delta showing the distribution of terpanes.
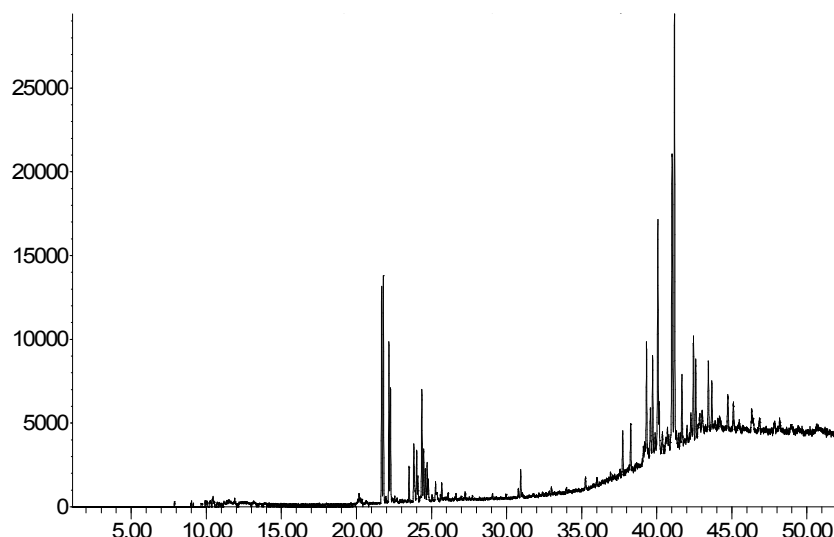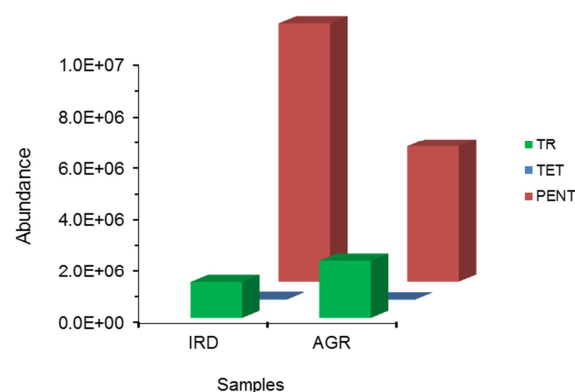
Figure 2. *m/z 191 mass chromatogram of crude oil sample-AGR from Central Niger Delta showing the distribution of terpanes.*

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	$C_{30}H_{52}$
5	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	$C_{34}H_{60}$

Peak	Terpanes	Code	Empirical formula
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	$C_{35}H_{62}$

The GC-MS analyses of the crude oil samples detected three terpane 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.

	Abundance			
Samples	Tricyclic terpanes (TR)	Tetracyclic terpane (TET)	Pentacyclics 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 (TR), tetracyclic (TET) and pentacyclics (PENT), in the crude oils (samples-IRD and -AGR) from Niger Delta, Nigeria.*

Pentacyclics (PENT) was the most abundant terpane group

in samples -IRD and -AGR with compositions of 87.61% and 70.12%, while tetracyclic (TET) was the least abundant with compositions of 0.31% and 0.15%, respectively. Abundances of tricyclics (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 [17]. This distribution profile of terpane groups indicate that 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 abundance of terpanes to determine the source organic matter type, depositional environment and thermal maturity [18]. 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).

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

Terpanes are used as biological markers (biomarkers) to indicate source organic matter type and depositional environment of crude oils in which they are found. Crude oils from marine sources usually have high C_{23} tricyclic terpane to C_{30} $17\alpha(H)$-hopane ratio with high abundances of C_{28} - C_{30} extended tricyclic terpanes associated with source rocks deposited in an anoxic environment during marine upwelling [17, 19]. Ratios of C_{23} tricyclic terpane (TR23/H30) and extended tricyclic terpanes (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. C_{24} tetracyclic terpane (TET24) is a biomarker that indicates terrestrial higher plant source [20]. 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 [21-24]. Alberdi and Lopez (2000) have used oleanane as a geochemical tool to assess crude oils from two sub-basins of the Venezuelan petroleum system [25]. 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 [26]. 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 [27]. 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 [28, 29]. 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 [30, 31]. 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.*

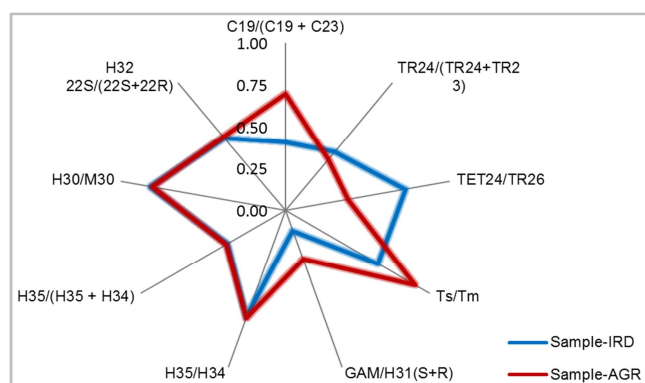| Axis	Terpane ratios	Sample-IRD	Sample-AGR
1.	C19/(C19 + C23)	0.41	0.70
2.	TR24/(TR24+TR23)	0.46	0.40
3.	TET24/TR26	0.73	0.38
4.	Ts/Tm	0.64	0.90
5.	GAM/H31 (S+R)	0.13	0.31
6.	H35/H34	0.68	0.69
7.	H35/(H35 + H34)	0.40	0.41
8.	H30/M30	0.82	0.81
9.	H32 22S/(22S+22R)	0.57	0.58

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 [8, 30]. 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.

Acknowledgements

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