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Research Article

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Tricyclics and Tetracyclics in Some Nigerian Oils

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Abstract: Tricyclics and Tetracyclics are intergal part of compounds that constitute crude oils (petroleum) and can be used to characterize crude oils. Oils for this study, were obtained from different fields and treated by diluting to 1mg/1mL using Hexane. The resulting mixture was injected into the column of the GC–MS for whole oil GC–MS analysis. The percent report for EICs (Extractable Ion Chromatograms) for m/z 191 was obtained and the different peak areas for the different peaks that characterizes depositional environment and organic precursors were obtained from the percent report. Linear plots were performed for delineation of depositional environment and organic precursors, the samples were discriminated into various groups such as Lacustrine, Marine and Terrigenous, study also incoperated the depobelt concept and the eustatic sea level at various ages on the geological time frame. MZ 191 EIC peaks such as C_{19}, C_{20} tricyclics and C_{24} tetracyclic defined oils that are predominantly terrigenous, while peaks such as C_{20}, C_{21} C_{25}, (S & R) C_{26} (S & R) tricyclics discriminated Lacustrine oils and marine oils were delineated with combinations of C_{23}, C_{28} (S & R) and C_{29} (S & R) tricyclics peaks.

Keywords: tetracyclics, tricyclics, GC–MS, lacustrine, terrigenous, marine, whole oil analysis,

1. Introduction

Tricyclics and tetracyclics are three and four cyclic compounds respectively and are proposed to have originate or pass through the isoprene unit as a stage in its organic mechanistic pathway. The compounds are easily identified in oils. The tricyclic compounds exist as series from C_{19} to C_{45}. C_{19} to C_{25} tricyclics are most commonly found but C_{25} to C_{31} tricyclics exist as doublets of S and R isomers due to the chiral centre at C_{22}. However, the C_{24} tetracyclics is most commonly detected of the tetracyclics. Most Nigerian oils have C_{19}, C_{20}, C_{21}, C_{23}, C_{24}, C_{25}, C_{26}, with few having C28 and C29.

Studies on some oils from other parts of the world have unraveled the fact that oils from various depositional environments and invariably different organic precursor inputs of organic matter, have different distributions of tricyclics and tetracyclics.

The potential distribution for lacustrine precursors is C_{20}, C_{21} C_{25}, (S & R) C_{26} (S & R) tricyclics, the distribution for marine precursors are C_{23}, C_{28} (S & R) and C_{29} (S & R) tricyclics while the major distribution for terrigenous precursors are C_{19}, C_{20} tricyclics and C_{24} tetracyclic. The peaks that constitute the various depositional environment and organic precursors are peaks that predominantly discriminent the oils (Volk et al., (1996) these are being ensemble for use in this study.

Occurrence of Oil in the Niger Delta.

The occurrence of oil in the Niger Delta follows abit of a complex geology of deposition of the bulk of formations. Formations in the Niger Delta were deposited as mega sequences at intervals of 5 to 10 Ma, which may correspond to different eustatic sea levels, which will be reflected on the mix type of organic matter that consist of the matrix of source rock, that will be deposited and each of the megasequences corresponding to a depobelt. The organic matter is mainly of terrigenous type and corresponds to the Cretaceous and Tertiary Eras.

The occurrence is attributed to successful timing and emplacement of oil into the traps, in the Niger Delta most of the trap were in place before the commence of migration of oil. Oils are mostly generated by the Lower Agbada Formations and Upper Akata Formations, while the reservoirs are mostly found in the Agbada and few in the Akata Formations.

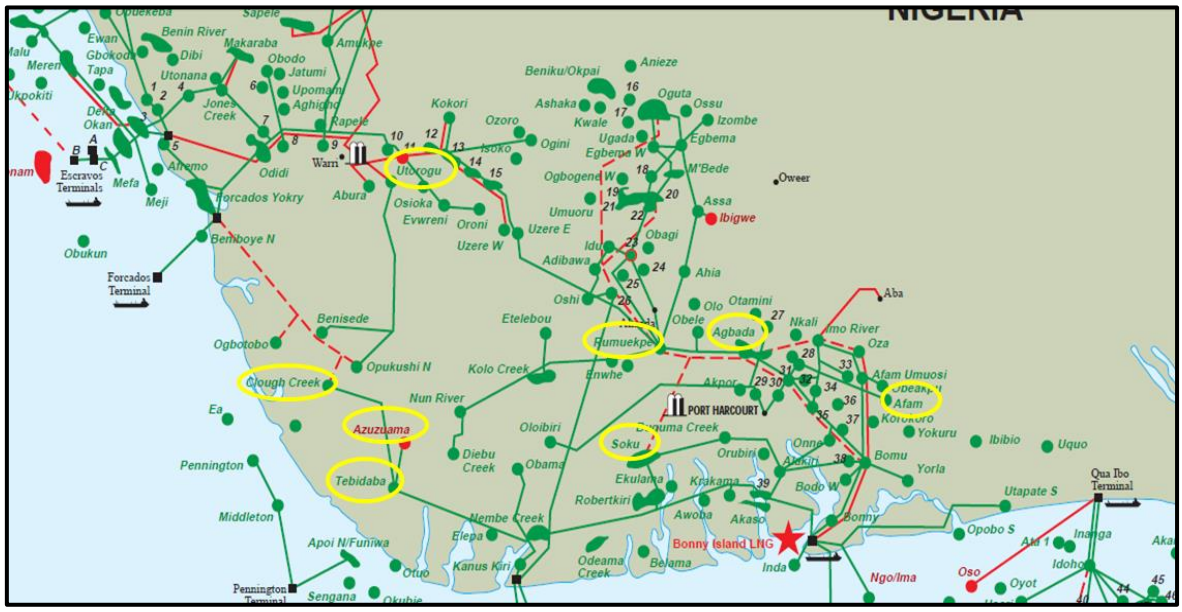

Figure1. *The location of some fields from which oils were obtained for this study*

General Characteristics of Niger Delta Oils.

The Niger Delta oils generally can be classified into two groups, of non-degraded and biodegraded oils. The non-degraded group are light oils with paraffin and wax contents, which mostly occurs in deep reservoirs. The wax content could be about 5%, while the API gravity could be about 30º–40º. The biodegraded oils which constitute the second group are mostly in shallower reservoirs, but non–waxy oils and low API gravity of generally lower than 26ºAPI. Biodegradation and water washing occurs significantly in most of the shallow reservoirs. Biodegraded oils have sulphur content as high as 6%. The characteristics of most oils corresponds to those that are generated from vascular plant materials deposited in suboxic – anoxic bottom waters which is ideal for preservation of organic matter. In this study, the tricyclics and the tetracyclics will be employed in an attempt to classify the oils according to their organic precursors.

2. Samples and Sampling

Samples for this study are crude oils obtained from different oil fields in different depobelts, according to the depobelt concept, the various depobelts are mega sequences that were deposited at various geological time frames, which also account for possible differences in the organic precursor materials. The oil samples were obtained from well heads and stored in sample vials with teflon caps, while in a chest of ice to preserve sample compositional integrity. Sample chain of custody was not broken till analysis.

3. Sample Preparation and Analysis

The samples were treated by dilution using n–hexane to achieve 1ug/uL (Abrakasa & Nwankwo, 2019) for whole oil GC–MS full scan analysis. The GC–MS analysis was performed using a HP5890 II GC which was link to HP 5972 MSD (mass selective detector). The equipment was programmed to ramp from 40ºC–300ºC at 4ºC per minute and held at the final temperature for 20minutes. The MSD was equipped with electron voltage of 70eV.

The acquisition was by a PC chemstation. Peak integration was performed using RTE integrator. Data was obtained from the EICs (Extracted Ion Chromatograms) as percent report from which the peak areas were derived for various parametric ratios.

4. Results and Discussion

Table 1, above consist the sum of the peak area as indicated above on the title panel as data for the discriminatory plots, these data were derived from the percent report, from which the peak areas were obtained for the parametric ratios. The oil fields for which some data are not indicated are those for which the m/z 191 chromatographic peaks do not contain the various peaks. Hence some of the fields may not appear in some plots. This is on the premise that the depositional style has been described with the concept of depobelts, and that each depobelt is a mega sequence which was deposited at different geological time frame, providing for significant or slight differences in environment of deposition and correspondingly the precursor organic matter, which would reflect as variations on the compositional distribution of the tricyclics and tetracyclics of the oils. This study is peformed to explore combination of parameters for discriminating Lacustrine oils from Marine and Terrigenous oils.

Table 1. The data for discriminatory plots.

OILS	C19+C20 (tricyclics)+C24 (tetracyclic)	C23+C28+C29 (tricyclics)	C20+C21+C25+C26 (tricyclics)
North Bank	50140	102328	
Afam	41827	65628	99469
Azuzuama	51829	102008	160385
Clough Creek	28758	104437	137130
Rumuekpe	35161	65595	45473
Tebedaba 1	58977	130919	107827
Utorugu	65451	108116	115470
Agbada	65000	141217	
Soku	85974	186540	
Tebedaba 2	92625	232769	
Boscan	83195		165151
Abo	53436		84842
Ahia	49451		44306

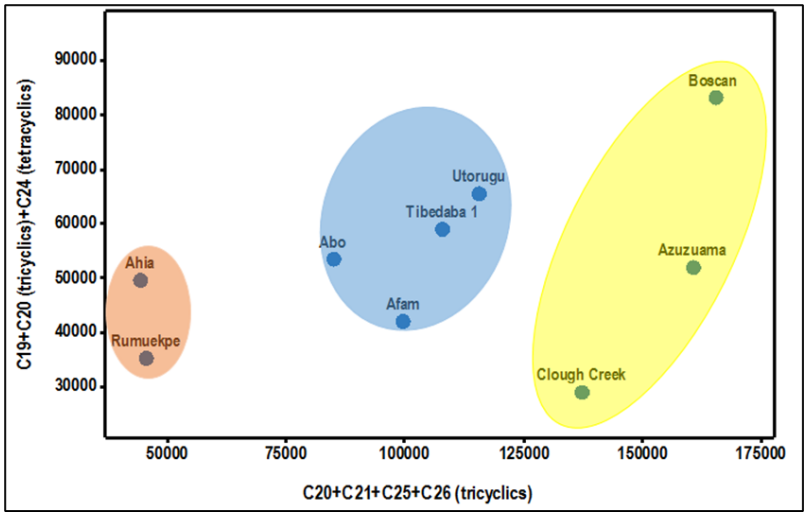

Figure 2. *Plot of C19+C20 (tricyclics)+C24 (tetracyclic) and C20+C21+C25+C26 (tricyclics)*

Inbid to discriminate lacustrine from terrigenous precursors using tricyclics and tetracyclics, the plot on figure 2 was adopted. The plot discriminates the oils with high lacustrine inputs (Boscan, Clough Creek and Azuzuama) from the oil with high terrigenous inputs (Ahia and Rumuekpe). The Boscan oil had already been identified as a lacustrine oil (Onojake & Abrakasa, 2019). In another study, the Afam and Ahia oils has been identified as Central Swamp oils while the Azuzuama and Clough Creek were identified as Offshore/Coastal Swamp oils (Abrakasa & Nwankwo, 2019). These studies validates, that the discrimination in figure 2 is accurate. (Abrakasa

& Nwankwo, 2019). Clough Creek, Azuzuama and Boscan oils show high Lacustrine inputs but increasing terrigenous inputs fom clough Creek to Boscan. By virture of the complex Niger Delta Geology, Clough Creek and Azuzuama are of the Lower Coastal Swamp depobelt, which was deposited during rising sea level and could have foster a lake environment due to a long term inflection point for a revise from the low stand to a rising sea level in the eustatic sea level changes.

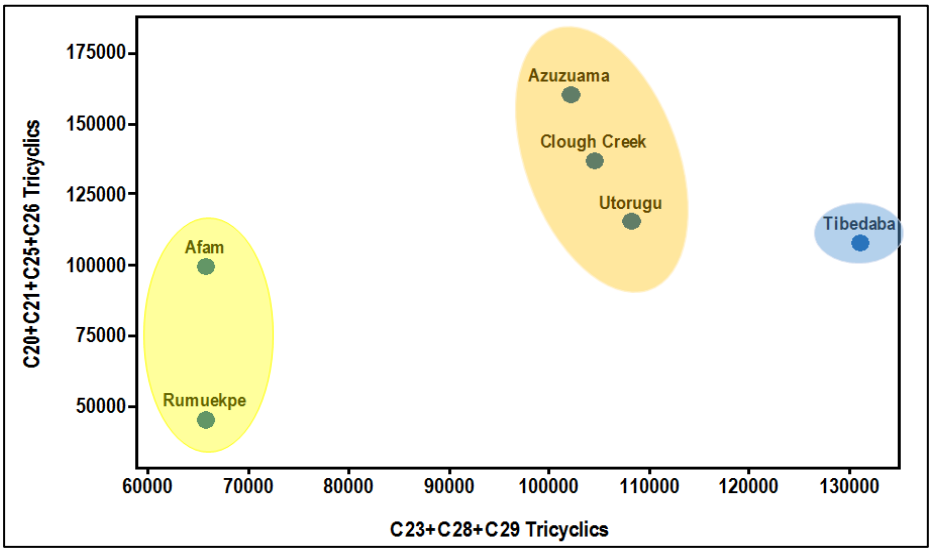

Figure 3. *A plot of C_{20}+C_{21}+C_{25}+C_{26} tricyclics against C_{23}+C_{28}+C_{29} tricyclics.*

Figure 3 is a plot of C_{20}+C_{21}+C_{25}+C_{26} tricyclics against C_{23}+C_{28}+C_{29} tricyclics for discriminating oils derived from Lacustrine precursors and Marine precursors. However, some oils will show a mixed of the parameters but the most prominent/dominant peaks had been identified for each precursor organic matter. The C_{20}+C_{21}+C_{25}+C_{26} tricyclics are synonymous with lacustrine precursor while C_{23}+C_{28}+C_{29} tricyclics are synonymous with marine organic precursors. The plot discriminates the oils, showing Tebedaba to be more marine, while Afam and Rumuekpe are both more less Marine and less lacustrine which may imply terrigenous oils. While the group of Azuzuama, Clough Creek and Utorugu Oils show appreciable Marine features and higher Lacustrine characteristics Azuzuama and Clough Oil are of lower Coastal Swamp depobelt, while Utorugu is of Greater Ughelli Depobelt for which the source rock was deposited during rising sea level which may account for its mix lacustrine and Marine properties.

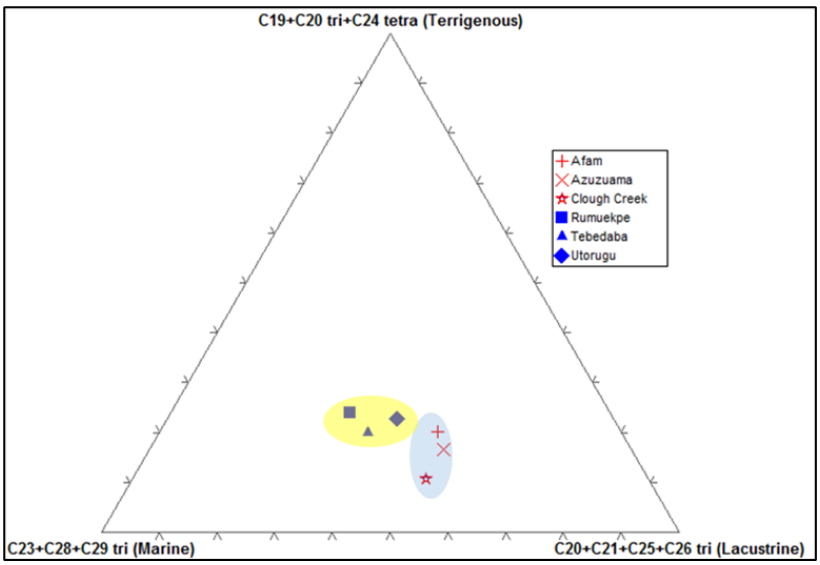

Figure 4. *This is a tenary a plot for Terrigenous, Marine and Lacustrine precursor matter.*

Figure 4, which is a ternary plot can be used to discriminate the samples to their organic precursors origin, it can be observed that the blue and yellow circles are hosting the samples which consists the suite of samples for which complete data are avaliable. Samples in the yellow circle in the ternary plot show Marine samples while those in the blue circle are the Lacustrine Samples. Ternary plots are always used for the delineating depositional environments, however, the depositional environments are always synonymous to the organic precursor materials.

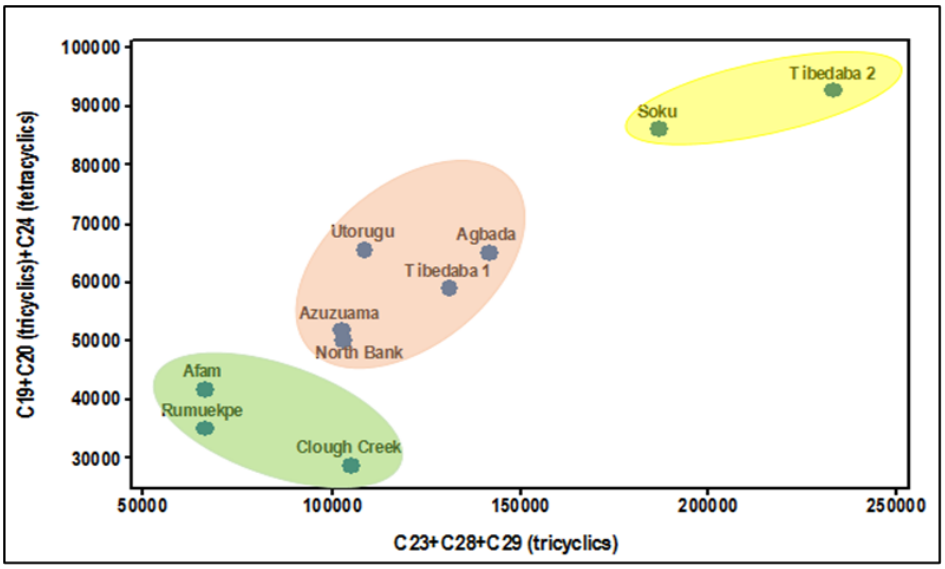

Figure 5. *A plot of C_{19}+C_{20} tricyclics+C_{24} tetracyclics against C_{23}+C_{28}+C_{29} tricyclics*

Figure 5 is a plot of C_{19}+C_{20} tricyclics+C_{24} tetracyclics for terrigenous organic matter against C_{23}+C_{28}+C_{29}Tricyclics for marine organic matter precursors basically to discriminate between terrigenous and marine oils however, in the Niger Delta Basin, all oils are regarded as terrigenous, nonetheless, due to its complex depositional system which takes the form of mega sequences and at intervals of 5 to 10 Ma (million years) which is also a function of eustatic sea level changes. The sea level changes has contributions on the compositional distribution of the types of organic matter that constitute the source rock of various mega sequences and the advent of various forms of organic matter/precursor organism that indicates marine, deltaic and lacustrine environments.

The Afam, Rumuekpe and Clough Creek oils are very low in both marine and terrigenous organic matter for the suite of oils studied on figure 5. The Soku and Tebedaba oils are very high in both marine and terrigenous organic matter, this may be due to the incisions that provided excellent supply of terrigenous organic matter as continental run offs. The Soku and Tebedaba oils are both of the Coastal Swamp depobelt, that was deposited at about the time of incision of the Soku/Buguma Channel that provided for massive deposition of terrigenous materials in near marine environment, this may explain the high terrigenous and Marine features of the Soku and Tebedaba 2 oils. The North bank, Tebedaba 1, Utorogo, Agbada and Azuzuama oils have average contents of both marine and terrigenous features, this could be a contribution of continuous deposition of the Central Swamp When the Coastal Swamp commenced deposition during rising sea level to high sea level.

5. Conclusion:

Tricyclics and tetracyclics are integral part of compounds, that constitute petroleum crude oils, and can classically be used for characterizering oils of Niger Delta origin. Tricyclic and tetracyclic peaks that were characteristics of particular depositional environment and organic precursors were ensembled for delineating depositional environment and organic precursors in this study and the objective was achieved in consideration of the complex geology of the Niger Delta geology. Samples were discriminated into lacustrine, marine and terrigenous oils.

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