# Petroleum Geochemistry of the Central and Eastern Onshore Niger Delta Basin: Oil-oil correlation using Biomarkers and Multi-variate statistic

## ABSTRACT

Petroleum geochemistry of oils in several depobelts of the world has been well documented based on biomarkers. However, there is paucity of data regarding the use of multi-variate statistics in oil-oil correlation study, particularly in the Sub-Saharan African region. The purpose of the study was to gain an insight into the geochemical differences and identify their cause(s) through the application of bulk properties, biomarker indices and multi-variate statistic. Correlation of oils from eight wellheads of three stratigraphic units within the Central and Eastern onshore Niger Delta Basin fields (AG and AS) were undertaken by gas chromatography-flame ionization detector. Utilization of bulk properties, biomarker indices and cross plot parameters somewhat separated the mature AG1-4, AS3 and AS4 oils deposited in oxic/suboxicshaly environment from AS2 oil deposited in anoxic fluvio deltaic environment. In-reservoir alteration and migration differences were the major factors responsible for the observed slight geochemical variability in the studied oils. Nevertheless, multi-variate principal component analysis indicated that the Central and Eastern onshore Niger Delta Basin oils were principally generated from similar organic matter sources. The implication here was that the geochemical variations in the studied oils were not significant, a conclusion corroborated by Pearson correlation model data.

**KEYWORDS**: Depositional environment, lithology, Niger Delta Basin, correlation, Biomarker.

NOMENCLATURE LIST

| **Abbreviation** | **Meaning** |
|---|---|
| API | American Petroleum Institute |
| BL | Biodegradation Level |
| CPI | Carbon Preference Index |
| DBT | Dibenzothiophene |
| DPR | Department of Petroleum Resources |
| DW | Degree of Waxiness |
| GC-FID | Gas Chromatography- Flame Ionization Detection |
| HC | Hydrocarbons |
| OM | Organic Matter |
| PAHs | Polycyclic Aromatic Hydrocarbons |
| PCA | Principal Component Analysis |
| Ph | Phytane |
| Phen | Phenanthrene |
| Pr | Pristane |
| SPDC | Shell Petroleum Development Company |
| TETFUND | Tertiary Education Trust Fund |
| TIC | Total Ion Current |
| UCM | Unresolved Complex Mixture |

## 1. INTRODUCTION

Correlations of oils are on the premise of the capacity to identify unique chemical and physical similarities amongst hydrocarbons in petroleum pool [1]. Biomarkers have been used as instruments to correlate oils based on important aspects of petroleum geochemistry: i. origin of their precursor molecules, ii. Paleo-environmental deposition, iii. Source rocks lithology, iv. Potential source rocks thermal maturity and v. levels of petroleum hydrocarbons (HCs) biodegradation [2; 3; 4; 5; 6].

Multi-variate principal component analysis (PCA) based on co-variability of targeted variables has been applied in source characterization of OM in various components of the environment by many researchers [7; 8], limited number of data are available worldwide that utilize PCA in source correlation of oils (e.g., [3]).

Previous studies revealed that the Niger Delta region oils are of one family of oils which originate from terrestrial and marine organic matter (i.e. mixed Type III/II; 9; 10; 11) with the Central and Western deep offshore Niger Delta oils deposited under an oxic environmental condition [12 and 13], while those for the Coastal and shallow offshore were deposited under oxic/suboxic conditions [4]. Although the oils in this family indicate genetic affinity with source rock, some oil samples show geochemical deviation compared to others. In order to reduce the risks and economic cost associated with exploration, it is important to have an understanding of petroleum systems in the study area. Nevertheless, the necessity to gain an insight into the genetic relationship between the Central and Eastern onshore Niger Delta oils so as to establish any subtle differences or similarities among the studied oils cannot be over emphasized. Thus, to unravel some elements of uncertainty in identification of the petroleum system, a detailed oil-oil correlation of the Central and Eastern onshore Niger Delta basin was for the first time undertaken in the present study. The aim of this work was to gain an insight into the geochemical differences and identify their cause through the application of bulk properties, biomarker indices and multi-variate statistic. The main objectives of the study were to apply biomarker parameters (*n*-alkanes, isoprenoid and aromatic HCs) distributions and multi-variate principal component analysis to correlate and compare the source, thermal maturity, depositional environment, level of biodegradation of HCs and lithology between the Central and Eastern onshore Niger Delta oils.

## 2. METHODOLOGY

### 2.1 Study area, geological setting and sample

The Niger Delta is considered as one of the copious regions in the globe with high hydrocarbon production, having an approximate reserve of forty billion barrels of crude oil with greater than forty trillion cubic feet of natural gas. The Niger Delta is confined in the Gulf of Guinea and encompasses an approximate area of 75,000 km$^2$ with siliciclastic deposits of about 9000 – 12,000 m wideness [4]. Its stratigraphic units are made up of an upper delta top lithofacies of continental sands and gravels, delta front paralicfacies of mostly sands and pro-delta marine shales. The region is subdivided into a series of independent depobelts representing successive stages of the delta development [13; 14].The occurrence of oleanane in Nigerian oils points to Late cretaceous or younger source rocks [9]. Detailed description of geological settings of the Niger Delta Basin is provided in [3].

The study sites consisted of the AG (about 15 km south-east of Sapele, Delta state) and AS (about 11 km south-west of Port Harcourt city, Rivers State) fields (Fig. 1). AG is located Central onshore Niger Delta at longitude 5.3881$^o$E and latitude 5.8732$^o$N, while AS is located Eastern onshore Niger Delta at longitude 7.0602$^o$E and latitude 4.9693$^o$N and are about 178 km apart.

With the consent of Shell Petroleum Development Company (SPDC) and Department of Petroleum Resources (DPR), eight (8) selected crude oils were obtained at atmospheric conditions from 4 wellheads in field AG and from another 4 wellheads in field AS. These oil samples were selected among others as representative of the oil fields based on the spacing between wells about 200-300 m apart.

### 2.2 Materials

Dichloromethane and petroleum ether (Boiling point: 40-60 $^0$C) were obtained from ShaghaiRuizheng Chemical Technology Ltd, China. Other chemicals used were Chromatographic grade *n*-hexane and methanol purchased from Sigma Aldrich (St Louis, MO, USA). Silica gel 40 (0.063-0.200 mm), anhydrous aluminium oxide 90 active neutral (0.063-0.200 mm) used for column chromatography were also obtained from Merck.

### 2.3. Crude oil analysis and instrumentation

Deasphaltation of the oils was carried out following procedures described in [4] involving precipitation in a petroleum ether (boiling point: 40–60 $^0$C)-dichloromethane (30:1 v/v) in a centrifuge at 2500 rpm for about 20 min. The separation of the deasphalted fractions into saturate, aromatic and heterocompounds (resins or NSO) was made possible by open glass chromatography using alumina (neutral, activated 2 h at 700 $^0$C) promoted with silica gel (70/230 mesh, activated 6 h at 400 $^0$C). About 40 mL *n*-hexane was used to elute the saturate fraction, while dichloromethane (40 mL) was used to elute the aromatic fraction. Finally, a mixture of methanol-dichloromethane (40 mL; 1:2 v/v) was used to remove the resin fraction. The eluents were reduced to near dryness using rotary evaporator [4].

The gas chromatography-flame ionization (GC-FID) analysis was carried out on an HP 5890 GC serial II. The separation was on a 30m long HP5 column with inner diameter of 0.25mm and film thickness of 0.25μm. Hydrogen gas at flow rate of 2 mL/minute was "used as carrier gas. The GC oven was" initially held at 50 $^{0}$C for 2minutes and then ramped at 4 $^{o}$C / minute to 300 $^{o}$C where it was held for 20minutes. Identification of peaks on GC-FID was done using relative retention time in comparison to standards, while peak quantification was done by relating the peak and concentration of each compound to standard. The mean and standard deviation values were calculated for the generated data set. The data sets were also analyzed by Pearson correlation model to understand the relationship between paired variables and principal component analysis (PCA), frequently employ to obtain components required to describe variance of detected data in a geochemical environment. The multi-variate technique handles large variables concurrently, and has been employ by geochemists in the determination of the sources of organic matter as well as their degradation in aquatic systems [7; 8] etc.

## 3. RESULTS AND DISCUSSION

### 3.1 API gravityanddegree of waxiness

The results of American Petroleum institute (API) gravity for the AG oils were in the range 45.4$^{o}$ - 49.9$^{o}$ (mean = 48.2±2.1), while those for the AS oils were in the range 37$^{o}$ - 43.2$^{o}$ (mean = 40.6±3.1) (Table 1). API gravity is used as a crude oil quality indicator. Oil samples having API gravities in the range 20° - 45° are considered as normal crude oils, those < 20° are often times biodegraded, whereas those higher than 50° are ranked as condensate oils [15; 16]. However, API gravities can also be classified in the range of light to heavy oils thus: Extra heavy oils: < 10° API, heavy oils: 10° - 22.3° API, medium oils: 22.3° - 31.1° API, light oil**s**:> 31.1° API. [1]. The results implied that the studied oils fell within the range of normal light crude with the AG crude oils not only showing greater degree of lightness than the AS oils but also suggesting lesser biodegradation of the former, supported by different bulk fraction compositions and n-alkane GC traces for the studied oils (see below). It also revealed that the AG lubricants are sunnier than the AS, and thus will have improved market value than the AS. The higher mean API value found for the AG oils relative to the AS suggested that this difference in API gravity was controlled by in-reservoir alteration rather than by differential entrapment of sediment. This assertion was based on the narrow depth differences between the AG field (Central Basin; 9303 m - 9913 m) and the AS field (Easten Basin; 7408 m – 8670 m) as well as within each field where the studied oils were located (Table 1) [17]. As in the case of the studied oils, light oils are typically generated more from terrestrial than algal OM [1].

Degree of waxiness (DW) for the AG and AS oils ranged from 1.4 – 1.8 (mean = 1.6±0.2) and 0.7-1.4 (mean = 1.1±0.3), respectively (Table 1). Wax precipitation is a serious problem in oil production and transportation facilities. This canister outcome causes numerous harms such as decrease in the rate of production, increased power requirement and failure of facilities [17]. DW, expressed here as DW= $\sum C_{21}$-$C_{31}$/$\sum C_{15}$-$C_{20}$ (where $C_{21}$-$C_{31}$ represent carbon numbered n-alkanes predominance in terrestrial OM and $C_{15}$-$C_{20}$ carbon numbered n-alkanes predominance in algal OM), is used to classify the proportion of terrestrial OM in oils, presumptuous that land-derivedmaterials donate a great molecular mass than usual component of paraffin to oils [19]. Popularly, DW <1 shows nature of low waxy and suggests organic algal marine source, whereas DW > 1 are mostly of higher plant deposited under reducing condition [20]. The results of DW indicated not only the fact that oils from these two fields were moderately waxy and economically valuable but also suggested that the AG and AS oils were predominantly generated from terrestrial OM source except the AS1 oil most likely generated mainly from an algal OM source.

### 3.2 Saturate, aromatic, resin and asphaltene contents

Saturate fractions for AG oils ranged from 54% to 65.3% (mean=58.5±4.8), while those for the AS oils ranged from 48 % to 57.7% (mean=52±4.1). Aromatic fractions for AG oils ranged from 22.7% to 33.2% (mean=27.7±5.1), whereas a range of 22.2% to 38.7% with a mean of 31.8±6.9 was found for AS (Table 1). Resin fractions for the AG oils were in the range 10.4 - 15.1% with a mean of 11.9±2.2, and those for the AS oils were in the range 9.0% - 18.2% with a mean of 13.8±5.1. Asphalthene fractions for AG oils ranged from 0.9% to 3.0% (mean=1.9±0.9), while in the case of AS oils the asphaltene fractions were in the range 1.1 - 5.2% with a mean of 2.41. ±1.9% (Table 1).

The results of percentage aromatic indicated greater tendency of AS oils to adversely impact the environment than the AG oils. Environmental samples contaminated with more sulphur compounds (resin) such as dibenzothiophene were reported to be more resistant to biodegradation than those infested with lesser hetero-compounds due to the fact that sulphur poisons OM degrading microorganisms [21]. The results of percentage resin suggested that the AG oils with lesser mean hetero-compounds were more environmentally friendly and lesser tendency to resist biodegradation than their AS counterpart. Heavy oils are reported to contain 14% and above asphaltene with low API gravity values and are formed when specific species of algae degrades hydrocarbon deposits, leading to the loss of its lighter fractions and leaving behind their heavier counterparts [2]. The relatively low percentage asphaltene in the studied oils supported the light nature of these oils and their economic viability.

Comparing data in the present study with other fields within the Niger Delta Basin, higher mean percentage saturate fraction was recorded for the Eastern coastal and shallow offshore oils [4], whereas similar values were found for the Western offshore oils [3]. The implication here was that the studied oils were of lower fuel value than those of the Eastern coastal and shallow offshore Niger Delta.

Higher mean percentage aromatic fraction was recorded for the studied oils than those for the Western offshore oils [3] and the Eastern coastal/shallow offshore Niger Delta oils [4]. The implication here was that the studied oils were less ecofriendly than oils from the compared fields.

### 3.3 Normal alkanes and isoprenoid hydrocarbons

The *n*-alkanes and isoprenoid HCs concentrations for the studied oils are presented in supplementary information 1 (SI -1). The total ion current (TIC) chromatograms of representative samples of AG and AS oils are shown in Fig. 2 a and b. N-alkanes in the range $C_{8-38}$ with isoprenoid HCs (e.g. pristane and phytane) were observed and *n*-alkanes < $C_8$ were absent, most likely due to evaporate loss during laboratory protocols. The TIC peak areas were employed in the calculation of isoprenoid and *n*-alkane parameters presented in Table 2.

AG and AS oils exhibited Carbon preference index (CPI) values of around 1 (Table 2). CPI is a good indicator of OM type in immature samples in which greater abundance of $C_{16-18}$ *n*-alkanes imply an aquatic source, whereas a $C_{27-33}$ odd abundance of *n*-alkanes are reflective of terrigenous OM [22]. Maturation of OM considerably modifies *n*-alkane abundance. CPI around 1 is observed in typical mature crude oils. Values of CPI recorded for the studied oils indicated mid-oil window thermal maturities at time of expulsion.A more robust thermal maturation aromatic biomarker parameters is needed to delineate the level of thermal maturity of the studied oils and details including terpane biomarkers will be available in our subsequent report.

The pristane/phytane (Pr/Ph) ratios for the AG and AS oils ranged from 1.2 – 1.3 (mean=1.2±0.1) and 0.8-2.7 (mean=1.4±0.9), respectively (Table 2). Pr/Ph is one of those parameters employed as markers of the environment of deposition. Low values of Pr/Ph< 1 indicate highly anoxic/reducing hypersaline conditions, Pr/Ph between 1-2 indicate suboxic sea depositional environment including freshwater, brackish and marine, while Pr/Ph ratios between 2-4 indicate oxicfluvio-deltaic environment [22;2]. Values of Pr/Ph indicated that source rocks of AG oils were deposited in an environment under suboxic condition, while those for the AS oils were mainly deposited under oxic/suboxic conditions except the AS2 which tended toward anoxic depositional condition.

The isoprenoids/*n*-alkanes ratios ($Pr/nC_{17}$ and $Ph/nC_{18}$) for the AG oils were in the range 1.3 -1.5 (mean=1.4±0.1) and 1.7 - 2.3 (mean=2.0±0.3), respectively, while 1.1-1.8(Mean=1.3±0.3) and 0.5-1.7 (mean=1.3±0.5) were the respective $Pr/nC_{17}$ and $Ph/nC_{18}$ values recorded for the AS oils (Table 2). Generally, the $Pr/nC_{17}$ and $Ph/nC_{18}$ values for the AG and AS oils were greater than 1 except for AS1 oil with $Ph/nC_{18}$ value of 0.5. In oil-correlation study, $Pr/nC_{17}$ and $Ph/nC_{18}$ give indication of type of OM but are also influenced by biodegradation and thermal maturity [23]. These authors were of the opinion that *n*-alkanes are generated faster than isoprenoids with increasing maturityin contrast to biodegradation. $Pr/nC_{17}$ and $Ph/nC_{18}$ ratios decrease with thermal maturity of oils [24], and a cross plot of $Pr/nC_{17}$versus$Ph/nC_{18}$ has been applied to classify source rocks and oils [25; 26; 27; 28]. The $Pr/nC_{17}$ and $Ph/nC_{18}$ results implied that the studied oils were generally non-biodegraded and that AS1 oil was not only less thermally mature but also relatively more biodegraded. Biodegradation is the mechanism that influences most of the world's oils and their geochemical properties. Therefore, the exploration of oils is affected by the high costs of refining biodegraded oils.

Also, AyobamiInengite, *et al.,* 2017) [29] has reported high Pr/n-$C_{17}$ and Ph/n-$C_{18}$ and assigned these high values to oxic depositional environment. Mohammed and Ahmed 2016 [30] has also reported that a low Pr/n$C_{17}$ and Ph/n-$C_{18}$ ratios indicates a source rock deposited in an anoxic environment. Therefore the depositional environment of the Eastern and Central Niger Delta basin is mainly dissimilar to those of Eagle Ford shale East Texas as reported by [31] and Biluo Co Oil Shale located in the northern Tibetan Plateau [32] but aligned with that of coastal and offshore Niger Delta oils [4]and Western offshore Niger Delta oils [3] which showed oxic-suboxic environmental conditions of deposition.The Pr/n$C_{17}$ and Ph/n$C_{18}$ results implied that the AS1 oil was from rocks deposited under open water condition, while the rest of the oils were from inland peat swamps [22]. A cross plot of Pr/n$C_{17}$ versus Ph/n$C_{18}$ (Fig. 3) revealed two main groups of oils based on OM type and their thermal maturity status. Although both the AG and AS oils were of similar mixed genetic origins (terrestrial over algal OM-Type III over II kerogen), the AS1 originated more from algal than terrestrial OM -Type II over III kerogen). Most of the AS oils (positioned in the lower portion of the plot) were slightly thermally less mature than the AG oils. In contrast, Abubakar et al., (2022) reported a predominance of marine algae (Type II) over terrestrial (Type III) OM sources in oils from similar Cretaceous Tanos Basin, Ghana as that of the studied Basin.

Pr/Ph ratios versus API gravity have been used to differentiate oils from many Basins based on depositional environment and maturation level e.g. [2]. A cross plot of Pr/Ph and API gravity presented in Fig. 4 revealed a single oil (i.e. AS1) situated at the right top corner of the plot with highest Pr/Ph (2.7) and API gravity value of 43.2 which was in agreement with an oxic environment of deposition and mature light oil expelled from a mixed OM source. An important feature of the plot was the slight shift of the AG1-4, AS4, AS3 oils deposited under oxic/suboxic condition from the AS2 oil deposited under anoxic condition. This scenario appeared somewhat similar to the groups B, C and D in the Hughes diagram shown below. The main group where most of the oil samples plotted (i.e. group C in the Hughes diagram) showed higher Pr/Ph (>1) and high API gravity values (38.9 –49.9), while AS2 oil showed low Pr/Ph value (<1) and relatively lower API gravity value of 37. The API gravity and Pr/Ph ratios relationship somewhat largely differentiated Eastern and Central onshore Niger Delta Basin crude oils. This slight geochemical variability could not have been caused by sedimentary rock differential entrapment but rather by minor differences in in-reservoir alteration, depositional environment, migration and OM types.

## 3.4. Aromatic hydrocarbons

The concentrations of parent polycyclic aromatic hydrocarbon (PAHs) in the studied oils are presented in SI 2. The fact that mean levels of PAHs were relatively higher in AS (mean = 263.2±150 mg/l) than in the AG oils (mean = 207.8±65.2 mg/l) supported the earlier assertion that the AG oils were of higher quality and more environmentally friendly than their AS counterpart.

Dibenzothiophene (DBT)/Phenanthrene (Phen) ratio for the AG oils ranged from 0.24 to 0.35 with a mean of 0.29±0.4, while those for the AS oils were in the range 0.17 – 0.74 with a mean of 0.36±0.3 (Table 2). DBT/Phen ratio is a good marker of lithology and the values for the studied oils were <1 reflecting mainly a shale lithology for the Eastern and Central onshore Niger Delta Basin [32]. Incorporation of sulfur into OM produces higher DBT level especially in an anoxic depositional environment. The low DBT content of the studied oils derived from an environment where sulfur reacts with iron species in the clay minerals not only supported the oxic-suboxic depositional environment but also the high premium placed on the Nigerian oil in terms of its exploration, production and ecofriendly value. Following Hughes diagram, a cross plot of DBT/Phen against Pr/Ph ratios (Fig. 5) showed that all AG oils, AS3 and AS4 oils fell in the larger group (within zone 3; group C) which indicated that these oils were derived from shale-marine/lacustrine depositional lithology [32]. AS1 oil tended towards fluvial deltaic environment (zone 4; group D), while AS2 fell within zone 2 (group B) indicating hypersaline lacustrine depositional lithology with poor sulfur content [33; 34].The dominant shale lithology observed for the Eastern and Central Niger Delta onshore areas indicated that the sedimentary rock that produced the oils contained high amount of OM and the rocks are most likely deposited in swampy environment conducive for the preservation of OM with good potential to generate large volume of petroleum.

## 3.5. Biodegradation level of the studied oils

Biodegradation is a process that modifies the molecular signatures and bulk properties like API gravity of crude oils and sedimentary OM. The biodegradation level (BL) expresses the degree of loss of the lighter hydrocarbon fractions (aliphatics), which can be seen in the unresolved complex mixture (UCM) as hump at the baseline of the gas chromatograms. The larger the hump, the higher the degree or level of biodegradation. In the study, AS oils exhibited larger UCMs relative to the AG oils (Fig. 2 a and b), implying that the AS oils were slightly more biodegraded than their AG counterpart, supporting the fact that the AG oils have better fuel value than the AS oils. Fig. 6 confirmed the fact that the AS oils were more biodegraded than the AG oils based on Peters and Moldowan, 1993[23] BL scale.

Low molecular weight PAHs (2-and 3-ring types) are more susceptible to biodegradation than their high molecular weight counterparts (4-, 5-, and 6-ring type) [23; 25]. Naphthalene and acenaphthylene (2- and 3-ring PAHs) in AS oils were lower in their mean percentage (10.7% and 13.2%) than those recorded for the AG oils (11.9% and 14.7%), respectively (SI-2). The implication here is that the AS oils were more degraded than the AG oils, confirming the earlier data obtained from *n*-alkanes on biodegradation status of the studied oils.

### 3.6. Correlation of the studied oils

The study utilized Pearson correlation model to determine the relationship between the AG and AS oils and to estimate the intensity of the links [35]. The results of API gravity for AG and AS oils revealed a very strong correlation ($r^2$ = 0.92), indicating that these oils were generated from the same family and were somewhat of similar quality and economic value. For Pr/Ph ratios, moderate relationship was found ($r^2$ = 0.67). This revealed that some of these oils were not formed under similar redox depositional environment. On the other hand, CPI and BL strongly correlated with $r^2$ values of 0.89 and 0.76 for the studied oils, supporting slight differences in maturity and biodegradation status of the studied oils, respectively (SI-3 a-d).

### 3.7. Principal component analysis (PCA)

To further determine the OM source relationship that existed among the studied oils, comparison of various compositional parameters between the AG and AS oils was achieved using a more robust multi-variate principal component analysis (PCA) method. In other words, all variables were used to examine samples relationship between the two fields based on changes in API gravity, degree of waxiness, saturate, aromatic, resin and asphaltene fractions, *n*-alkanes ($C_8$ – $C_{38}$) and isoprenoid (pristane and phytane) concentrations as well as such ratios as Pr/Ph, Pr/$nC_{17}$, Ph/$nC_{18}$ and DBT/Phen. Fig. 7 shows all samples positioned together in the right top corner of the plot. The implication here was that although bulk and biomarker parameters provided evidence of variations in depositional environment, lithology, biodegradation, OM type and maturity, PCA revealed the Eastern and Central onshore Niger Delta Basin oils were principally generated from similar OM sources.

## 4. CONCLUSIONS

Characterization and correlation of the AG and AS oils based on their depositional environment, OM type, thermal maturity and biodegradation state as well as lithology was undertaken. Bulk and biomarker parameters provided evidence of slight variations in thermal maturity of the studied oils, their environment of deposition, lithology and biodegradation status. These slight geochemical variability in the studied oils could not only be caused by differential entrapment of sedimentary rocks but also by slight differences in in-reservoir alteration, arising from differences in the physical and chemical properties of petroleum, degree of biodegradation it has undergone, depositional environment associated with the degree of oxygenation in the water column , variation in sedimentation rate, migration occasioned by the presence of other geological features, OM types linked to ocean current and circulation as well as the level of primary productivity.The results indicated that majority of the studied oils were generated from a mixed source predominated by terrestrial over algal OM (Type III/II kerogen) deposited in oxic/suboxic shale-marine environment, while others were either deposited in oxichypersaline marine/lacustrine generated from a mixed source predominated by algal over terrestrial OM (Type II/III kerogen) or anoxic fluvio deltaic environment with relatively lower biodegradation level and thermal maturity found for the AG than the AS oils. Nevertheless, multi-variate PCA indicated that the Eastern and Central Niger Delta Basin onshore oils were predominantly generated from similar sources. The implication here was that the geochemical variability in the studied oils were not significant, a conclusion corroborated by Pearson correlation model data.The study can therefore help explorationists locate potential petroleum reservoirs, understand the geological history of Eastern and Central Niger Delta basin, identify potential production zones and design enhanced oil recovery strategies.

To improve our understanding of the subtle geochemical variability in the studied oils, more oil and source rock samples will be needed for analysis of other saturate and aromatic biomarkers including their isotopic compositions.

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## COMPETING INTERESTS

"Authors have declared that no competing interests exist is associated with the manuscript.".

## AUTHORS' CONTRIBUTIONS

Orok Oyo-ita' designed the study, Inyang Oyo-ita performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. 'Ogbonna, Victoria, Akinlua, Akin' managed the analyses of the study. 'Orok Oyo-ita' managed the literature searches…… All authors read and approved the final manuscript."

## REFERENCES

1. Ali A. ElBassoussi, Seham M. El-sabagh, Fatma M. Harb, Mohamed M. El Nady (2018). Characterization and correlation of crude oils from some wells in the North Western Desert, Egypt. Petroleum Science and Technology 36(5), 384-391.
2. Asif, Muhammad, Fazeelat, Tahira, Grice, Kliti (2011). Petroleum geochemistry of the Potwar Basin, Pakistan: 1. Oil–oil correlation using biomarkers, d13C and dD. Organic Geochemistry, 42 1226-1240
3. Ekpo, B.O., Essien, N., Neji, P.A., Etsenake, R.O (2018). Geochemical fingerprinting of western offshore Niger Delta oils, *Journal of Petroleum Science and Engineering* 160: 452–464.
4. Anyanwu, T. C., Ekpo, B. O., Oriji, B. A. (2021).Geochemical characterization of the coastal and offshore Niger Delta crude oils, Nigeria. International Journal of Advanced Academic Research | ISSN: 2488-9849Vol. 7, Issue 12.
5. Abubakar R., Adomako-Ansak K., Marfo S. A., Owosu J. A. &Fenyi C. (2022). Origin and depositional environment of oils and sediments in the cretaceous Deep-Water Tano Basin, Ghana: Constraints from biomarkers. Petroleum Science and Technology, DOI: 10. 1080/10916466.2022.2143804.
6. Husseiny E. (2022). Geochemical variability of oils from Jurassic petroleum system in the east of Persian Gulf. Petroleum Science and Technology, DOI: 10.1080/10916466.2022.2118776.
7. Walker, S. E., Dickhut, R.M., Chisholm-Brause, C., Sylva, S., and Reddy, C. M. (2005). Molecular and Isotopic Identification of PAH sources in a highly industrialized urban estuary, *Organic Geochemistry 36* 619-632.
8. Oyo-Ita, I. O., Patience Y. Nkom, Samuel U. Ugim, Francisca I. Bassey&Orok E. Oyo-Ita (2021) Seasonal Changes of PAHs in Water and Suspended Particulate Matter from Cross River Estuary, SE Nigeria in Response to Human-Induced Activity and Hydrological Cycle. *Polycyclic Aromatic Compounds 42(1)* 1-18.
9. Onyia, V., Adejobi, A., Ibie, E., Nkeme, U. and Haack, R., (2002). Regional chronostratigraphic interpretation in northwestern Niger Delta. *NAPE Buletin,* 16: 81–92.
10. Akinlua, A., Ajayi, T. R. and Adeleke, B. B., (2005). A re-appaisal of the application of Rock- Eval pyrolysis to source rock studies in the Niger Delta. *Journal of Petroleum Geol*ogy 28(1): 39–48.
11. Akinlua, A. and Ajayi, T.R. (2009). Geochemical Characterization of Central Niger Delta Oils. *Journal of Petroleum Geology*, 32(4): 373-382

12. Stacher, P., (1995). Present understanding of the Niger Delta hydrocarbon habitat. In: Oti, M.N., Postma, G., (Eds.), Geology of Deltas. A.A. Balkema Publishers, Rotterdam, 257–267.

13. Reijers, T. J. A., Petters, S. W. and Nwajide, C. S. (1997) The Niger Delta basin, in R. C. Selley, ed., African basins: Amsterdam, Elsevier Science, Sedimentary Basins of the World 3:151–172.

14. Ekweozor, C. M. and Daukoru, E. M. (1994). Northern delta depobelt portion of the Akata – Agbada petroleum system, Niger Delta. In Magoon, L.B. and Dow, W.G. (eds). The petroleum system – from source to trap. *American Association of Petroleum Geologists Memoir*. 460:599 – 613.

15. Makeen, Y. M., W. H. Abdullah, M. H. Hakimi, and K. A. Mustapha. 2015. Source rock characteristics of the Lower Cretaceous Abu Gabra Formation in the Muglad Basin, Sudan, and its relevance to oil generation studies. *Marine and Petroleum Geology* 58:505–16.

16. Collins, E. (2018). Oil Exploration in the Niger Delta : Its ’ Gains and Loss. *International Jouranl of Geopgraphy and Environmental Management*, *4*(3), 24–31

17. Reinhard G., Achim B., Reinhard F., Sachsenhofer, Hans-Gert L., Doris R., Hans-Martin S. (2011). Oileoil and oil-source rock correlations in the Alpine Foreland Basin of Austria: Insights from biomarker and stable carbon isotope studies. MarineandPetroleum Geology28, 1117-1186.

18. Fazeelat, T., Jalees, M.I., Bianchi, T.S., 2010. Source rock potential of Eocene, Paleocene and Jurassic deposits in the subsurface of the Potwar basin, northern Pakistan. Journal of Petroleum Geology 33, 87–96

19. Mohammad, Rehan, Adul-S, Nizami, Osman, T. Basil, O. &Sassi, (2016). Determination of wax contents in crude oil. *Journal of Petroleum Science and Technology* 34(9): 779-804.

20. Lize, M. S. L. Rita, C. P. N., Ygor, L. L. R., Dayane, M. C., Debora, A. A., Julio, C. M. D. & Elizabete, F. L. (2018). Wax behavior in crude oil by pour point analysis: *Journal of the Brazilian Chemical Society*, 29(10): 220-379.

21. Oyo-Ita, O. E., Oyo-Ita, I. O., and Elarbaoui S. (2017).Reassessment of Dibenzothiophene as marker for petroleum and coal contamination in sediments from Imo River, SE Nigeria. *Environmental Forensic,* 18(4)*: 285-295.*

22. Peters, K., Walters, C. &Moldowan, J. (2005). *The Biomaker Guide*: Biomarkers and isotopes in petroleum systems and earth history. 2, 2nd edition, Cambridge University Press, New York.

23. Peters, K. E. &Moldowan, J. M. (1993). The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments. Prentice Hall, Englewood Cliffs, New Jersey, 363

24. Aas, E., Baussant, T., Balk, L., Liewenborg, B. & Andersen, O. K. (2000). PAH metabolites in bile, cytchrome P4501A and DNA adducts as environmental risk parameters for chronic oil exposure: a laboratory experiment with Atlantic cod. *Aquatic. Toxicology*. 51:241-258.

25. Yunker,M. B., S. M. Backus, E. G. Pannatier, D. S. Jeffries, and R.W.Macdonald (2002): Sources and Significance of Alkane and PAHs in Canadian Arctic Rivers. *Estuarine, Coastal & Shelf Science* 55, 1–31.

26. Harb, F. S. D., El Nady, M. M., &Basta, J. S. (2003). Oil: Oil correlation for some oil fields in the North Western part of the Western Desert, Egypt. *Petroleum Science and Technology*, *21*(9–10), 1583–1600.

27. Heinio, P., and Davies, R.J., 2006. Degradation of compressional fold belts: Deep-water Niger Delta: AAPG Bulletin, 90: 753 – 770.

28. Haritash AK, Kaushik CP (2009) Biodegradation aspects of polycyclic aromatic hydrocarbons (PAHs): *A Review of Journal of Hazardous Materials* 169:1-15

29. Ayobami O.A, Allen T. E., Azibaola K. I, Sylvester C.I. (2017). Assessment of some selected heavy metals andtheir pollution indices in an oil spill contaminatedsoil in the Niger Delta: a case of Rumuolukwucommunity. *BiotechnolRes.l 3(1):*11-19.

30. Mohammed H. H. and AhmedAskar, A. N. (2016). Origin of crude oils from oilfields in the Zagros Fold Belt, southern Iraq: Relation to organic matter input and paleoenvironmental conditions. *Marine and Petroleum Geology 78* 547-561

31. Miceli , A. A., Romero, T. N. , and Philp, R.P. (2018). Organic geochemistry of the Eagle Ford Group in Texas. Article in AAPG Bulletin ·1-35.

32. Changiun, J., Guoging, X., Haisheng, Y., Xinhe, W., and Xinhe, W. (2014). Aromatic hydrocarbons in the Biluo Co oil shale of the Shuanghu area, northern Tibetan Plateau, and

33. Najaf, A. A., Al-Dahhan, W. H., & Al Ameri, T. K. (2016). Geochemical correlation of oil and source rocks from selected exploratory wells within Northern Mesopotamian basin, Iraq. *Arabian Journal of Geosciences*, *9*(5) 8-16.

34. Hughes, W.B., Holba, A.G., Dzou, L.I., 1995. The ratio of dibenzothiophene to phenanthrene and pristane to phytane as indicators of depositional environment and lithology of petroleum source rocks. GeochimicaetCosmochimicaActa 59, 3581–359

35. Hughes, W.B., Holba, A.G. &Dzou, L.I.P. (2006). The ratios of Dibenzothiophene tophenanthrene and pristane to phytane as indicators of depositional environment and lithology of petroleum source rocks. In: GeochimicaetCosmochimicaActavol. 59:3581- 3598.