GEOCHEMICAL CHARACTERIZATION AND CORRELATION STUDIES OF CRUDE OIL FROM WELLS OF OKPOHO/OKONO, OBEN AND QUA IBOE OIL FIELDS IN NIGER DELTA, NIGERIA

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ABSTRACT

Geochemical Study of oil extracts from Oben (OB), Okpoho (OK) and Qua Iboe (QIT) crudes from Niger Delta was carried out. Elution liquid chromatography, gas chromatography – mass spectrometry, gas chromatography–flame ionization detector, atomic absorption spectroscopy, X-ray florescence spectroscopy,ultraviolet-visible spectroscopy and statistical methods were used to analyse the oils based on some hydrocarbon diagnostic ratios and cross-plots as parameters. Analysis of the oil samples revealed that the concentrations of the saturates, aromatics and biomarkers present varied tremendously from one oil to the other. Some diagnostic ratios and cross-plots used classified the oils produced into oxicand transitional environments of deposition with terrestrial organic input. Pristane to plytane ratio (Pr/Ph) for OB, OK and QIT were 3.74, 2.84 and 1.66 indicating that OB was derived from more oxidizing depositional environment and a typical of oil mainly from coastal swamp, while OK and QIT were deposited in a less oxidizing environment and typical of oils derived from fluviomarine source. Pristine to nC_{17} (pr/nC_{17}) values for OB, OK and QIT were 0.62, 0.83 and 0.95 while phytane to nC_{18} (phy/nC_{18}) values were 0.16, 0.31 and 0.68 respectively, showing that the oil were non-biodegradable. A cross-plot of pr/nC_{17} versus ph/nC_{18} classified the oil into transitional (marine and terrestrial) environment. The monoaromaticsterane and triaromaticsterane values were 0.56, 0.49, 0.55 and 0.53, 0.47, 0.77 for OB, OK and QIT respectively indicating that the oils were resistance to biodegradation. Anthracene to anthracene plus phenanthrene ratio for OB, OK and QIT were 0.47, 0.46 and 0.46 revealing the origin of polycyclic aromatic hydrocarbon as autochthonous sources of hydrocarbons. Statistical analysis of geochemical data and oil locations revealed that they were reliable tools for characterization and correlations of the oils.

Introduction

Niger Delta of Nigeria is important in crude oil correlation studies because it is one of the major hydrocarbon provinces of the world with an estimated reserve of about 23billion barrels of oil and 103 trillion cubic feet of natural gas (Onojake*etal.*, 2013). An appreciable number of studies have been carried out on the Niger Delta crude oil including the works of Odebunmi and Adeniyi (2004),Akinlua*et al*., (2007),Sonibare*et al*., (2008), Onyemaand Ajike(2010) andOnojake*et al*., (2013), in order to ascertain the sources of organic matter, environment of deposition, level of maturity and sources of oil pollution through correlation and characterization. Geochemical parameters used include n-alkanes and isoprenoids, biomarker distribution and their diagnostic ratios and cross-plots, polycyclic aromatic hydrocarbons (PAHS) as well as trace elements geochemistry.

These specific geochemical parameters have been assessed with the aid of elution liquid (column) chromatography, Gas Chromatography-Mass spectrometry/flame ionization detector techniques, Atomic Absorption spectrometry (AAS), ultraviolet-visible spectrophotometry, x-ray fluorescence spectrophotometry following American Standard for Test and Materials (ASTM)Methods.Low molecular weight hydrocarbons might not have been observed probably because of sample processing and preparation, water washing and biodegradation (Onyema and Ajike., 2010). Analysis of the PAHS characteristics show predominance of high molecular weight–PAH with 4-7 rings (HMW-PAH), which is typical of a polycyclic source of hydrocarbon while petrogenic source contain relatively high concentration of individual low molecular weight-PAH (LMW-PAH) with 2-3 rings (Onojake*et al*., 2013).

Biomarker analysis also monitortriterpanes at mass to charge ratio (m/z) 191 and steranes at m/z 253 to ascertain the source of organic matter and environment of deposition (Onojake*et al*., 2013). Transition metals of proven association with organic matter have been used as reliable correlation tools. Nickel and vanadium (referred to as biophile elements) are such examples (Sonibare, 2007,Akinlua*et al*., 2007). It has been proved that high V/Ni ratio is associated with anoxic environment of deposition, indicator of oil maturity as well as differentiating oils from various locations (Onyema, 2010). Moreover, the highest concentrations of metals are found in low maturity crude oils.

Statement of Problem

Owing to the growing concern of the degradation of environment through oil spill especially on land, seas and oceans, and also growing disputes among oil companies regarding whose oil spills and from which wells, there is need for geochemical analysis of hydrocarbons, biomarkers, trace elements as well as sulphur and nitrogen contents that will generate information of great importance to environmental forensic investigators in terms of determining the sources of spills, differentiating and correlating oils and monitoring the degradation process and weathering states of oils under a wide variety of conditions; so that environmental degradation be prevented.

Objectives of Study

The objective of the study was to:

Carry out geochemical characterization and correlation of Crude Oils from different oil wells of Oben, Okpoho/Okon and Qua Iboe oil fields through their extracts, using saturated and polycyclic aromatic hydrocarbon distributions, biomarker and trace elements geochemistry as well as nitrogen and sulphur contents in order to understand the organic matter distribution, source identification, biodegradation, maturity assessment and environment of deposition

Geological setting of Niger Delta

The Niger Delta is one of the world's largest tertiary delta system and an extremely prolific hydrocarbon province. It is situated on the West African continental margin at the apex of the gulf of guinea. It occupies an area of about 75000km^2 with clastic sequence which reaches a maximum thickness of 9000-12000m of sediment and a total sediment volume of 500,000km^3 (Sonibare*et al.*, 2008). Stratigraphically, the thick sedimentary sequence is made up of three principal lithostratigraphic units namely, the Benin, Agbada and Akata formations. The Benin formation is the alluvial or upper coastal plain depositional environment of the Niger Delta complex. It consists of mainly fluvial gravels and sands. It has a thickness in excess of 1820m.

Study/sample locations

Oben oil is produced from an onshore field located in OML4, in Edo State, south-south of Nigeria. It covers an area of 267km^2. The block is located 78m north East of Warri, Delta state. Seplat is the operator of the field. Okpoho/Okono oil is produced from offshore fields located in Block OML119 (formerly Block OPL91), 34 miles (55km) from Nigeria coast of River State.It is in water depth ranging from 210-250ft (65-75m), the produced oil is exported through permanently stationed FPSO mystras with offloading via shuttle Tanker.

Qua Iboe crude oil is produced from numerous offshore fields in the south-south region of Nigeria, East of Oso fields, located in OML13,the crude from fields 20-24 miles offshore are brought to the shore via a sea bed pipeline system to the Qua Iboe terminal (QIT). Qua Iboe terminal is an oil pipeline terminal and is located in EketAkwa Ibom State. The estimated terrain elevation above sea level is 7 meters, latitude 4^{o}22^{1}54.24", longitude 8^{o}0'45.7", Exxon Mobil is field operator. QIT is located on the eastern side of the Qua Iboe River estuary and contains nine oil storage tanks with a total capacity of 4.5million billion barrel of oil.

LITERATURE REVIEW

Chemical composition of crude oil

Crude oils consist of complex mixtures of hydrocarbons and non-hydrocarbons that range from small, volatile compounds to large, non volatile ones. Hundreds of thousands of compounds have been identified in crude oils. Ultrahigh-resolution fourier transform ion cyclotron resonance mass spectrometry has recently revealed that crude oil contains heteroatom organic components having more than 20,000 distinct elemental compositions (Mascareili, 2010). In general, petroleum components are classified in bulk groups of saturates, olefins, aromatics, resin (wide variety of compounds containing sulfur, oxygen and nitrogen), and asphaltenes.

Saturates are a group of hydrocarbons composed of only carbon and hydrogen with no carbon-carbon double bonds. Saturates are the predominant class of hydrocarbons in most crude oil. Saturates include straight chain and branched chain (also called paraffins) and cycloalkane

(naphthenes). Biomarker terpanes and steranes are branched cycloalkanes consisting of multiple condensed five –or six-carbon rings. Sesquiterpanes and diamondoids are smaller cyclic biomarkers, which can be particularly valuable for source identification of lighter petroleum products (Mobarakabad et. al., 2011).

Aromatic hydrocarbons are cyclic, planar compounds that resemble benzene in electronic configuration and chemical behavior. Aromatics in petroleum include the monoaromatic hydrocarbons such as benzene, toluene, ethylbenzene, P-xylene isomers and other alkyl-substituted benzene compounds and polycyclic aromatic hydrocarbons (PAHS), which include oil-characteristic alkylated Co to C_4-naphthalene, phenanthrene, dibenzothiophene, fluorene and crysene homologous series (Farmenand Harman, 2010).

Polar compounds are those with distinct regions of positive and negative charge, as a result of bonding with atoms such as nitrogen, oxygen and sulplur. Heavy oils generally contain greater proportions of high-boiling, more aromatic and heteroatomic and metallic constituents. In the petroleum industry, the smaller polar compounds are called resins. Asphaltenes are a class of very large heteroatom-containing compounds.

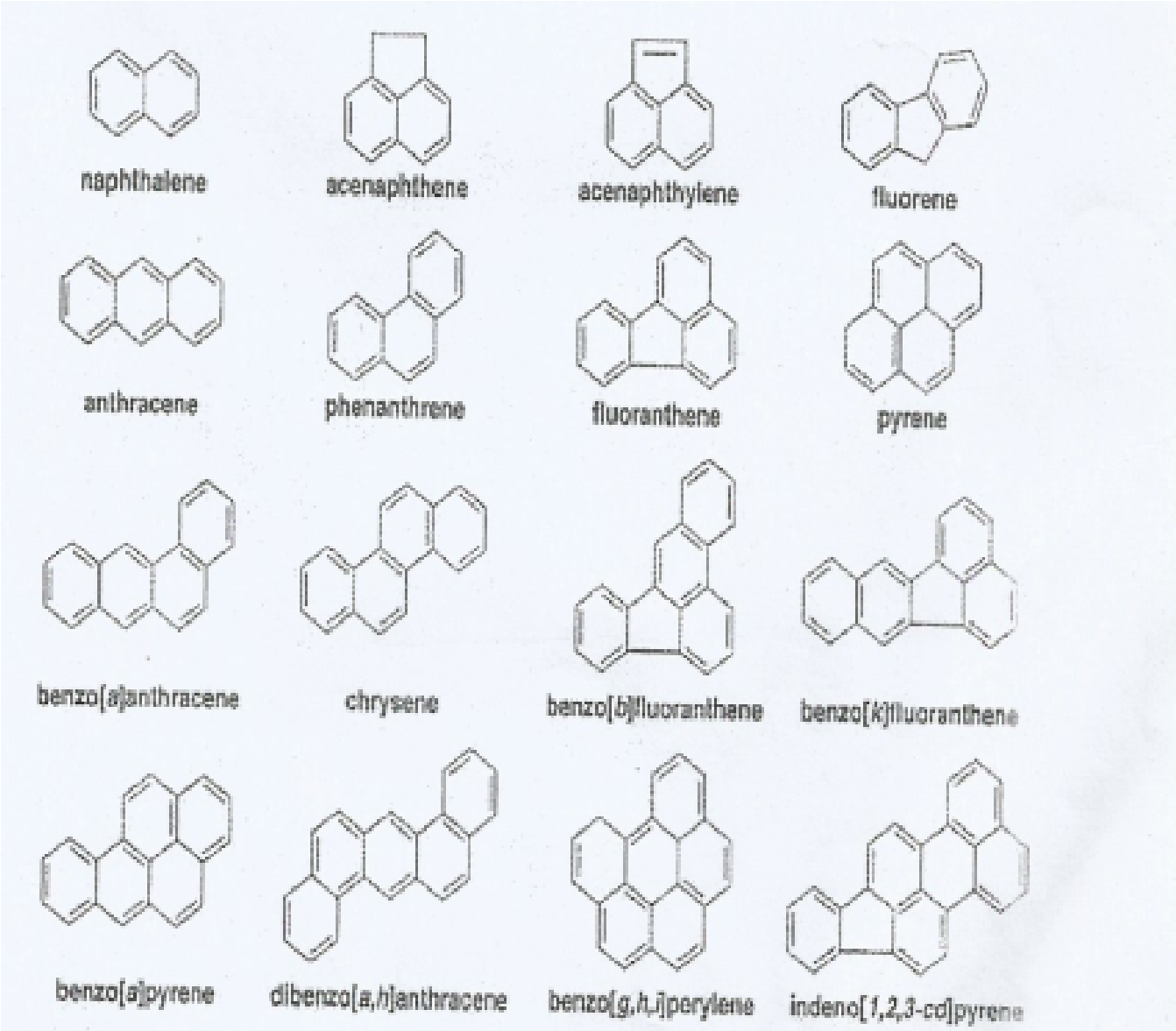
Polycyclic aromatic hydrocarbons in aquatic environments

Polycyclic aromatic hydrocarbons (PAHs) are aromatic compounds containing from two to eight conjugated ring system. The precursors of PAH found in crude oil are natural products, such as steroids that have been chemically converted to aromatic hydrocarbons overtime (Allan and Smith, 2012).

The PAHs that are present in the marine environments in relevant concentrations are divided into two groups depending on their origin, namely pyrogenic and petrogenic. PAHs are formed by incomplete combustion of organic materials while the petrogenic PAHs are present in oil and some products. In general the pyrogenic PAHs are composed of larger ring systems than the petrogenic PAHs. Sources for pyrogenic PAHs are forest fires, incomplete combustion of fossil fuels and tobacco smoke (Da Silva, 2010). A range of PAHs are naturally present in crude oils and coals and are referred to as petrogenic PAHs. In the coastal zones PAHs enter the water primarily from sewage, runoff from roads, the smeltery industry and oil spills, while offshore PAHs chiefly enter the water through seeps, spills and produced water discharge from offshore oil installations (Farmenand Harman, 2010). Chemical structures of some polycyclic aromatic hydrocarbons are given in Figure 1.

FIG. 1 Chemical structures of Some PAHs

Polycyclic Aromatic hydrocarbons and aromatic sulphur compounds



The abundance and distributions of polycyclic aromatic hydrocarbons (PAHs) and their structural isomers have been useful in maturity assessment of oil, source rock and coal. The presence and abundance of 1,2,5- and 1,2,7-trimethylnaphthalene (TMN) in oils further support higher plants input (Allan and Smith, 2012). The methylphenanthrene index (MPI) is used to estimate the equivalent vitrinite reflectance value (%Rc) for crude oils because of linear relationship with vitrinite reflectance throughout the conventional oil window. Aromatic sulphur compounds are common constituents of sediments and crude oils used in maturity assessment (Antizar, 2009). Dibenzothiophene is an example. A plot of dibenzothiophene/phenanthrene

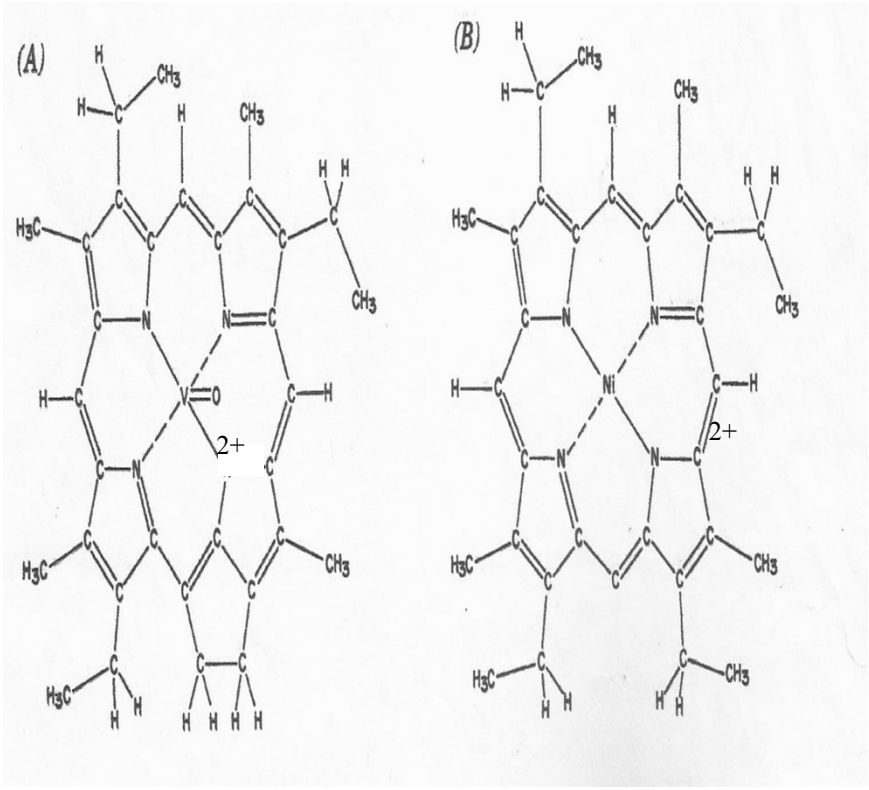
(DBT/PHEN) versus pristane/phytane (Pr/Ph) is used as indicator of source organic matter depositional environment (Wolska, 2008).

Petroleum biomarkers

Petroleum biomarkers can be defined as complex organic compounds derived from formerly living organisms founds in oil (Mobarakabad*et al* 2011). They show little or no changes in their structure from the parent organic molecules and this distinguishes biomarkers from other compounds (Mailoli*et al.*, 2011). Various biomarkers formed under different geological conditions and ages can occur in different carbon ranges exhibiting different biomarker fingerprints.

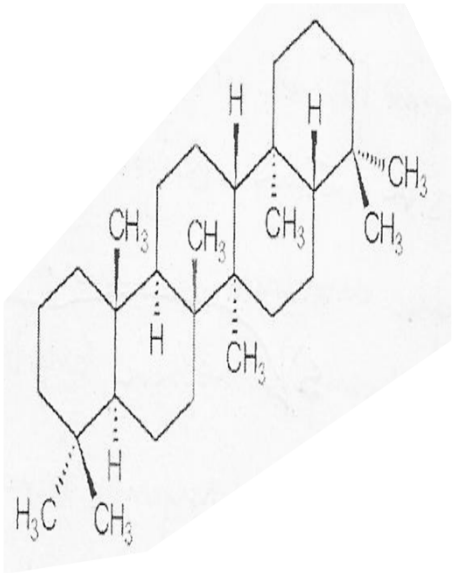
Biomarkers are the most important hydrocarbon groups in petroleum because they can be used for chemical fingerprinting which provide unique clues to the identification of source rocks from which petroleum samples are derived, the biological source organisms which generated the organic matter, the environmental conditions that prevailed in the water column and sediment at the time, the degree of microbial degradation and the thermal maturity of both the source rock and the oil (Roushdy*et al*., 2011).

Biomarkers in petroleum can be identified in form of n-alkanes, iso-alkanes and cyclic alkanes as well as unresolved complex mixture (UCM) profiles, isoprenoid to normal alkanes and alkylated polynuclear aromatic hydrocarbons (PAHs) homologues (Roushdy*et al*., 2010). Relative to other hydrocarbon groups in oil, some of these compoundssuch as pristane, phytane, sterane, triterpanes and porhyrines are more degradable resistant in the environment. Althoughterpanes and steranes are highly resistant to biodegradation but few studies have shown that they can be highly bio-degraded (Silva and Aguiar, 2011).



Vanadylporphyrine Nickelporphyrine

(C)



Gammacerane

FIG.2 Molecular structures of some petroleum biomarkers

Correlation analysis

Correlation analysis include Bulk analysis and Molecular techniques

Bulk analysis: Is the determination of the compositional fraction, elemental composition and isotopic ratios. The bulk properties of the oils include API^{o} gravity, Reid vapour pressure, Kinematic viscosity, moisture, gum contents and cloud point.

Molecular analysis: Molecular analysis is used to determine biomarkers and their thermal fragment. Information from biomarker analysis can be used to determine the migration pathways from a source rock to the reservoir for oil-oil and oil-source rock correlation (Jimenez and Morris, 2012). It can also be used for environmental forensic investigations to determine the sources of spilled oil, differentiating and correlating oils as well as monitoring the degradation process and weathering state of oils under a wide variety of conditions (Maioli*et al*., 2010).

The pressing need for more sensitive and precise analysis, methodologies and combination between those methods to separate, monitor and detect the absolute concentrations and structure of petroleum biomarkers stemmed from the fact that their structures are complex and also present in very low concentrations in petroleum (Onojake*et al*., 2013).

GC-MS can be considered as the most popular method used in characterization of major biomarker groups. GC provides the significant advantages of the separation of different structure of biomarkers while MS can accurately detect and identify the structures (Faramawy and El-Naggar, 2010)

MATERIALS AND METHODS

Materials and Chemical Reagents

All the chemical reagents used in this study were of analar grade and the glassware washed with soap solution, rinsed with distilled water and deionised water and then kept in the oven to dry. Elution liquid (column) chromatography was carried out using standard laboratory columns of about 50cm^3 in volume. They were cleaned with a mixture of chromic acid and tetraoxosulphate (VI) acid. This was followed by rinsing them with distilled water and acetone and allowed to dry in air.

Samples, samples collection and procedure

The crude oil samples were obtained from three producing well heads of the onshore fields of Oben, as well as offshore fields of Okphoho and Qua Iboe of Niger Delta in Nigeria by field technicians. The oils were stored in three plastic containers labeled OB, OK and QIT respectively. They were later taken to the laboratory and cooled in the freezers to prevent evaporation and biodegradation.

Methods

All methods were based on American Society for Testing and Material, ASTM (1993)

Column Chromatography

The oil samples were fractionated using dry packed column with silica gel and alumina (2:1) and mesh sizes of 40-60 ; into saturates, aromatics, nickel porphyrins, Vanadyl porphyrins and heterocompounds (nitrogen, sulphur and oxygen containing compound) using n-hexane, methyl benzene, benzene-ethylacetate (3:1) mixture, dichlormethane-n-heptane (2:3) mixture and methanol-dichlorometane (2:1) mixture respectively. Thirty centimeters cube ($30cm^3$) of each solvent were used for elution after developing the column with $20cm^3$ of n-hexane, hetero-compounds (Nitrogen, sulphur and oxygen) were further separated into nitro-compounds, sulphur and oxo-compounds with nitrobenzene, benzothiol and benzenol respectively. The fractions were eluted based on the solvents polarities. The eluents were collected and stored in sample bottles, labeled and evaporated in fume cupboard and stored in a cool-dry place for further analysis.

Gas chromatography-flame ionization detector (GC-FID)

Gas chromatrographic-Flame ionization detector technique was used for the analysis of aliphatic fractions. Agilent 6890GC equipped with a 30mx0.320mm x0.25um film thickness HP-5 column was used. A flame ionization detector (FID) detected the components. The carrier gas was helium flowing at a rate of 40m/s and the oven was programmed from 45^{o}C to 325^{o}C at 3^{o}C/min. The initial and final temperatures were held for 5min and 20minutes respectively. The peak areas were electronically integrated and identification was based on retention time and comparison with analytical standards. The peak integration was achieved using the Agilent chemstation software (ASTM, 1997).

Gaschromatography – mass spectometry

Gas chromatographic- mass spectrometric technique was used for the analysis of the aromatics as well as aliphatic and aromatic Biomackers. Aromatics was done using the Agilent 7890GC equipped with a 20m x0.180mm x0.18um film thickness DB-5ms column. The biomarkers were analysed using the Agilent 7890GC equipped with a 30m x0.320mmx0.25um film thickness HP-5 column. An Angilent 5975C mass spectrometer (MS) detected the components.

The carrier gas for aromatics was helium flowing at the rate of 40m/s and the oven was programmed from 55^{o}C. to 200^{o}C at 25^{o}C/min, to 250^{o}C/min at 8^{o}C/min and held for 2 minutes then to 310C at 25^{o}C/min. The carrier gas for Biomarkers was also helium flowing at the rate of $40cm^3$ and the oven was programmed from 45^{o}C to 325oC at 3^{o}C/min. The initial and final temperatures for Aromatics were held for 0.4min and 3 min respectively while the initial and final temperatures for the biomarkers were held for 5 min and 20min respectively.

The peak areas were electronically integrated and identification was based on retention time and comparision with m/z ratio of analytical standards. The selected ions monitoring (SIM) was used to monitor m/z 191 (terpanes) for the saturated biomarkers and m/z 253 (monoaromaticsteranes). The biomarkers and the peak areas were calculated electronically. The peak integration, the ion monitoring and peak area calculations were achieved using the Agilent MSD chemstation software.

Atomic absorption spectroscopy (AAS)

Atomic absorption spectroscopic techniques was used in the analysis of Vanadyl and nicked porphyrins. It was done using AAS Buck scientific accustys 211. The method for the

analysis was based on ASTMD3373 and ASTMD1886 for vanadyl and nickel porphyrins respectively.

Quantitation

Beers Law was applied but deviates at high sample concentrations. This was rectified by diluting standards and samples to fall into the linear range 0.25-0.3AU. Microprocessor and software driven instruments applied linearization algorithms as an auto function mode. A standard curve was applied preceded by a blank to zero the instrument with software designed to calculate direct concentration values.

Beers-Lambert formula is given as $A = \varepsilon lc$ where A is absorbance, ε is molar absorptivity, l is path length of the cuvetand c is molar concentration.

X-ray Fluorescence spectroscopy (XRF)

Weight percent of sulphur (total sulphur) was determined using ASOMA PHOENIX IIXRF analyser with direct excitation optics of 30kV 9W air-cooled x-ray tube. Performance was shown for a measurement time of 200seconds.

Sample preparation

The oil sample was well mixed and stable before it was poured into a commercially available XRF sample cup.

Procedure: This method followed American Standard for Testing and Materials(ASTM) D494. In this analysis x-ray energy disperse mode was used. The voltage used in x-ray tube was 10kv, current 400uAand filter number 5 was used. The instrument was calibrated in the range of 0.001-1.00 wt% by using commercially available Standards Analytical Services Incorporation. The repeatability and reproducibility limit were + 0.0054 to + 0.0309 and ±0.0089 to ±0.1151 respectively for sulphur measurement. The detector for x-rays was capable of measuring in the wave length range of 0.52-0.55nm. ASTM (1997).

UV-VISIBLE SPECTROSCOPY

Weight percent nitrogen contents (total nitrogen) was determined using Uv-visible HACH DR5000 spectrophotometer.

Procedure:

Sample preparation was done according to the Kjeldahlmethod using the digestion apparatus. Five centimeters cube ($5cm^{3)}$ of the digested sample was pipetted into a graduated mixing cylinder followed by the addition of one drop of TKN indicator. Drops of 8.0N KOH were added until a flash of blue appears. 1.0N KOH was then added one drop at a time and stirred after each drop until a permanent blue colour appears. The volume was made up to 200mls using deionized water followed by the addition of 3 drops of mineral stabilizer. Three (3) drops of polyvinyl alcohol dispersing agent was then added and the mixture stirred. The volume was made up of 25mls with deionized water and stirred, 1ml of Nessler's reagent was pipetted into the solution and mixed then allowed to stand for a two minute reaction time. At the end of the reaction time, the prepared sample was transferred into a cell and the total nitrogen concentration was read using the HACH DR5000 at a wavelength of 460nm.

Statistical methods

The null hypothesis stated was that there is no significant relationship between geo-chemical parameters and oil locations in Niger Delta, Nigeria. In order to test the hypothesis, the geochemical parameters were limited to components of saturates, porphyrins and trace elements.

Pearson correlation matrix was obtained from Pearson Product Moment on the geochemical data and tested with critical r-value of 0.996 at 0.05 significant level with one degree of freedom.

RESULTS AND DISCUSSION

RESULTS

The results of the concentrations of saturated hydrocarbons are presented in Tables 1.

TABLE 1
Concentrations of Saturated hydrocarbon of oil samples from OB, OK and QIT in the Niger Delta Nigeria

Components	Names	Oil samples (ppm)		
		OBI	OKI	QITI
nC_8	Octane	16.65974	Bdl	bdl
nC_9	Nonane	Bdl	Bdl	bdl
nC_{10}	Decane	Bdl	Bdl	bdl
nC_{11}	Undecane	Bdl	Bdl	bdl
nC_{12}	Dodecane	Bdl	32.5170	bdl
nC_{13}	Tridecane	60.60905	256.596	bdl
nC_{14}	Tetradecane	243.4049	744.6715	bdl
nC_{15}	N-petadecane	577.8615	1257.548	bdl
nC_{16}	N-Hexadecane	893.4846	1397.766	bdl
nC_{17}	N-Heptadecane	1096.3200	1483.696	20.46800
Pristine		682.8918	1228.913	19.42015
nC_{18}	N-Octadecane	1126.318	1400.441	16.94302
Phytane		182.5141	432.5954	11.52125
nC_{19}	N-Nonadecane	1153.498	1425.195	19.12538
nC_{20}	N-Elcosane	1076.738	1311.847	20.78809
nC_{21}	Henicosane	1005.3430	1241.991	21.20086
nC_{22}	Docosane	932.4410	1202.432	21.03289
nC_{23}	Tricosane	893.9592	1231.579	21.61163
nC_{24}	N-tetracosane	809.9799	1172.247	18.87684
nC_{25}	N-pentacosane	737.9325	1129.473	16.03197
nC_{26}	N-Hexacosane	639.5099	1006.973	12.52456
nC_{27}	N-Heptacosane	614.2922	995.0519	bdl
nC_{28}	N-octacosane	493.4991	827.6287	bdl
nC_{29}	N-Nonacosane	413.0655	739.4752	bdl
nC_{30}	Triacontane	282.2485	518.218	bdl
nC_{31}	Hentriacontane	260.5633	537.398	bdl
nC_{32}	N-Dotriacontane	166.8340	345.5519	bdl
nC_{33}	N-tritriacontane	149.4413	325.4539	bdl
nC_{34}	N-tetratriacontane	72.74518	165.8751	bdl

nC_{35}	N-pentatriacontane	48.28431	119.9371	bdl
nC_{36}	N-Hexatriacontane	Bdl	56.48986	bdl
nC_{37}	Heptatriacontane	Bdl	Bdl	bdl
nC_{38}	Octatriacontane	Bdl	Bdl	bdl
nC_{39}	Nonatriacontane	Bdl	Bdl	bdl
nC_{40}	Tetracontane	Bdl	Bdl	bdl
Total conc.		**14613.77884**	**22587.56056**	**219.54464**
Pencentage		**39.1**	**60.4**	**0.6**

TABLE 2
Diagnostic ratios of saturated hydrocarbons for OB, OK and QIT Oil Well

Sample	Pr/Ph	Pr/nC_{17}	Pr/Cn_{18}	CPI	C_{25}/C_{18}	C_{29}/C_{30}	C_{17}/C_{29}	C_{23}/C_{30}	C_{23}/C_{24}	MAS	T
OB	3.74	0.62	0.16	1.46	0.65	1.46	2.65	3.17	1.1	0.56	0
OK	2.84	0.83	0.31	1.48	0.81	1.4	2	2.38	1.05	0.49	0
QIT	1.66	0.95	0.68	1.4	0.95	0	-	-	1.14	0.55	0

MAS = Monoaromaticsterane; TAS =Triaromaticsterane; Pr= pristane
Ph = phytane C_{29}/C_{30} = hopane ratio; CPI = carbon preference index (pr + C_{17}/ph+C_{18})
TAR = Terrigeneous Aquatic Ratio

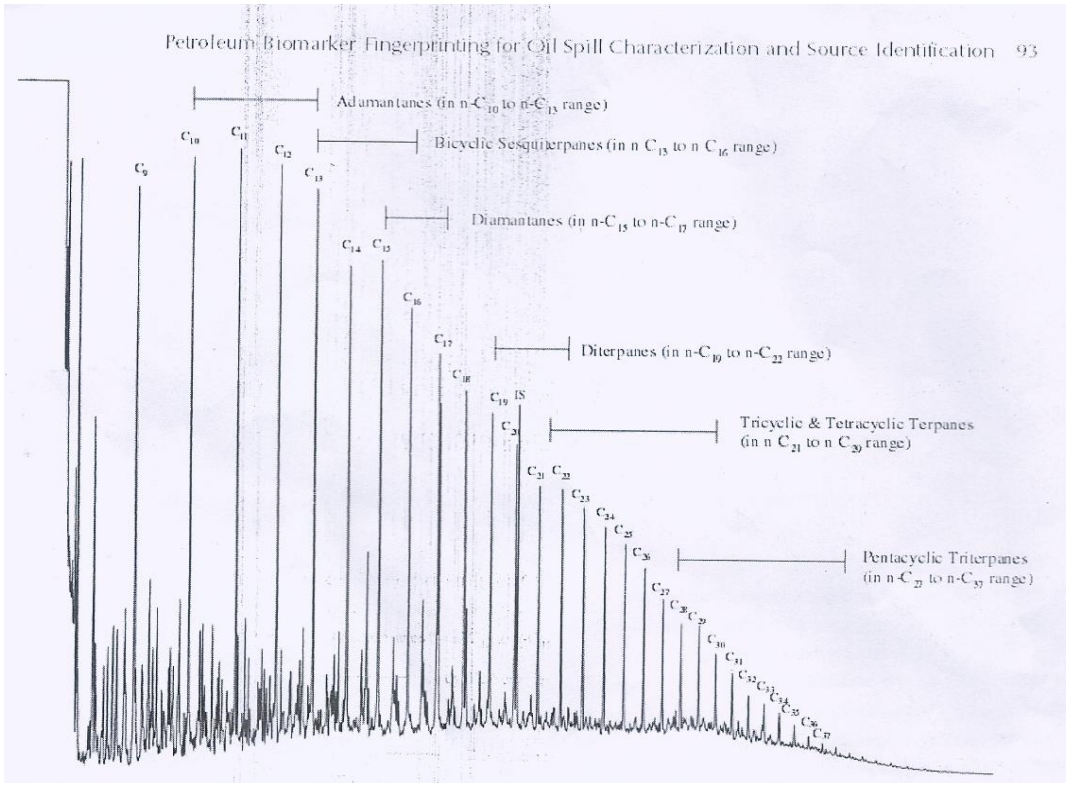
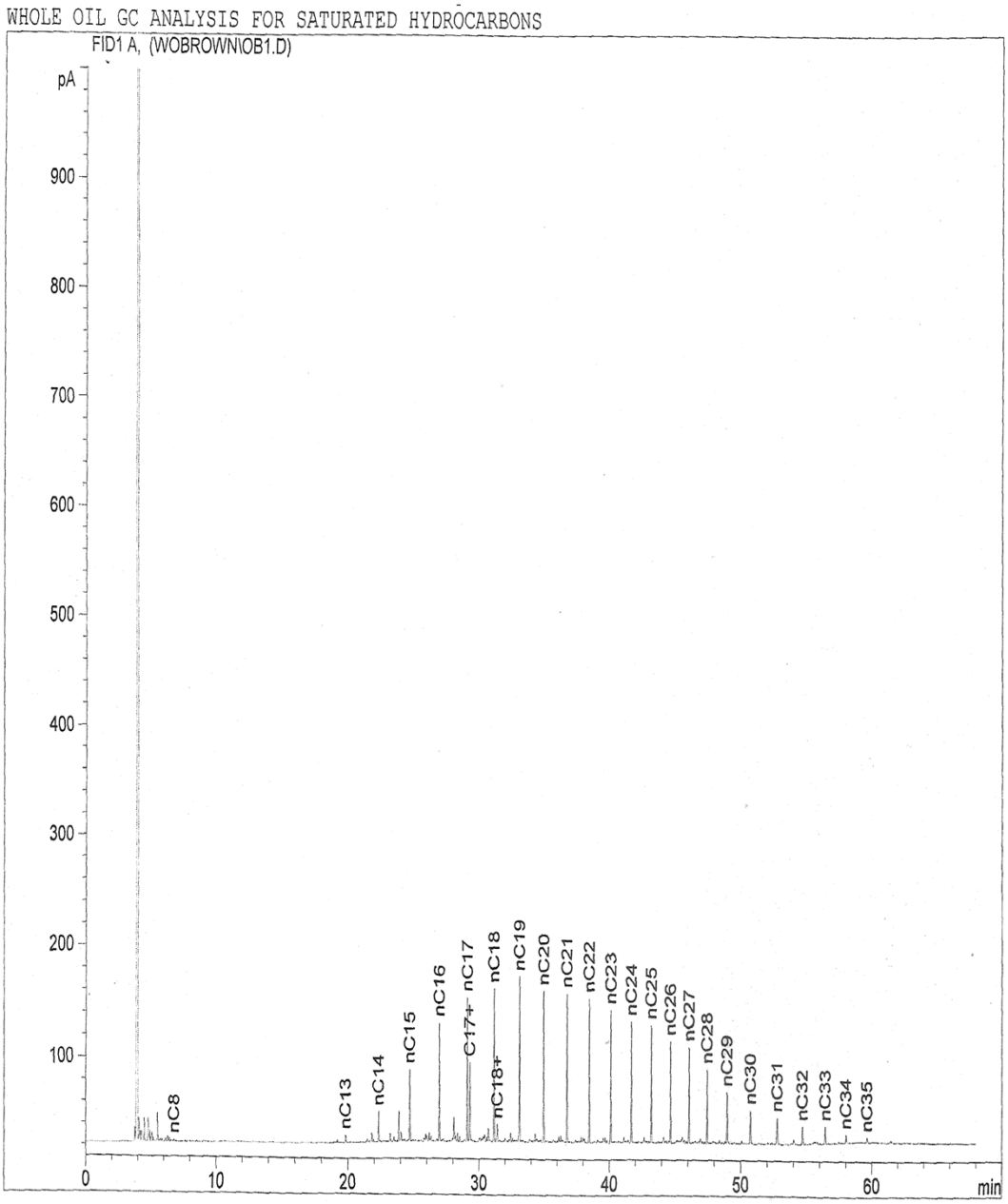


FIG. 3 GC- MS of carbon range of common cyclic biomarkers in petroleum
(Da Silva, 2010)

Fig. 4.0

FIG. 4 Chromatogram of saturated hydrocarbon for Oben Oil Well



DISCUSSION

Normal alkanes and isoprenoid distribution

The saturated hydrocarbon fractions and the chromatograms of oil extracts from OB, OK and QIT are as shown in Table 1 and Figures 3 and 4. The Chromatograms are dominated by n-alkanes in the range of $nC_8 - nC_{36}$, maximizing at nC_{19} for OB, nC_{17} for OK and no distinct peak in QIT. Their diagnostics ratios are also displayed in Table 2.

Pr/Ph ratio

In crude oil correlation, the ratios of isoprenoid to n-alkanes are used to assess the source of organic matter, depositional environment and level of maturity of the oils (DaSilva, 2010). The pristane and phytane ratio (Pr/Ph) for OB, OK and QIT were 3.74, 2.84 and 1.66 respectively (Table 2). The Pr/Ph ratios were used to asses the depositional environment of the oils. Pr/Ph greater than one (> 1) indicates oxidizing depositional environment (Onojake*etal*., 2013). Pr/Ph (> 3) not only indicates oxidizing depositional environment for the source rock but also is typical of oil derived from coal - source (peat swamp) or terrestrial source deposited under oxic environment (Onyemaand Ajike, 2010). However Pr/Ph<3 indicate oil from transitional depositional environment. Therefore Pr/Ph value for OB is above 3.0 indicating oxidizing depositional environment for source rock, while OK and QIT reflects that they were deposited under transitional (reducing–oxidizing) environment. These results show a good correlation between OB, OK and QIT.

Ekwezor and Sonibare (2001); further reported that Pr/Ph ratio is >0.5 in oils derived from source rocks deposited under anoxic conditions. Relatively high Pr/Ph ratios for OB, OK and QIT oils are attributable to their high maturation levels and significant humic organic matter in the source rocks from which these oils were generated, though there were also measurable contributions from marine source. Low Pr/ph values (<2) indicate aquatic depositional environments including marine, fresh and brackish water (reducing conditions). QIT belongs here

Pr/nC_{17} and Ph/nC_{18} ratios

The ratios of Pr/nC_{17} and Ph/nC_{18} have been widely used as indicators of source rock types, depositional environment and organic matter maturation (Akinlua*etal*., 2007). Both Pr/nC_{17} and Ph/nC_{18} decrease with maturation due to increasing prevalence of the n-alkanes. Pr/nC_{17} for OB, OK and QIT were 0.62, 0.83 and 0.95 while values for Ph/nC_{18} were 0.16, 0.31 and 0.68 respectively (table 2). The values for Pr/nC_{17} and Ph/ncC_{18}< 1.0 indicates that the oils are non-biodegradable. Therefore OB, OK and QIT may be termed non–biodegraded. Though the value for QIT is close to unity that reflect much level of biodegradation as evidenced in the absence of HMW hydrocarbons. These values also reflect mostly mature oils and originated mainly from marine organic sources deposited under reducing environment. Therefore one can rightly say that the oils are derived from mixed organic sources.

Plot of Pr/nC_{17} Vs Ph/nC_{18}

A cross plot of Pr/nC_{17}vs Ph/nC_{18} is used to classify oil and rock extracts into different groups such as source, maturation, migration, biodegradation and also depositional environment which are the major factors responsible for differences in crude oil composition (Onojake*etal*., 2013). Valuesless than 1.0 are indicative of oils deposited in mixed and transitional environment. Therefore OB, Ok and QIT are deposited in mixed and transitional environment (Akinlua*et al*., 2007). A plot of Pr/nC_{17} versus Ph/nC_{18} of oil from OB, Ok and QIT in Niger Delta is given in Figure 5.

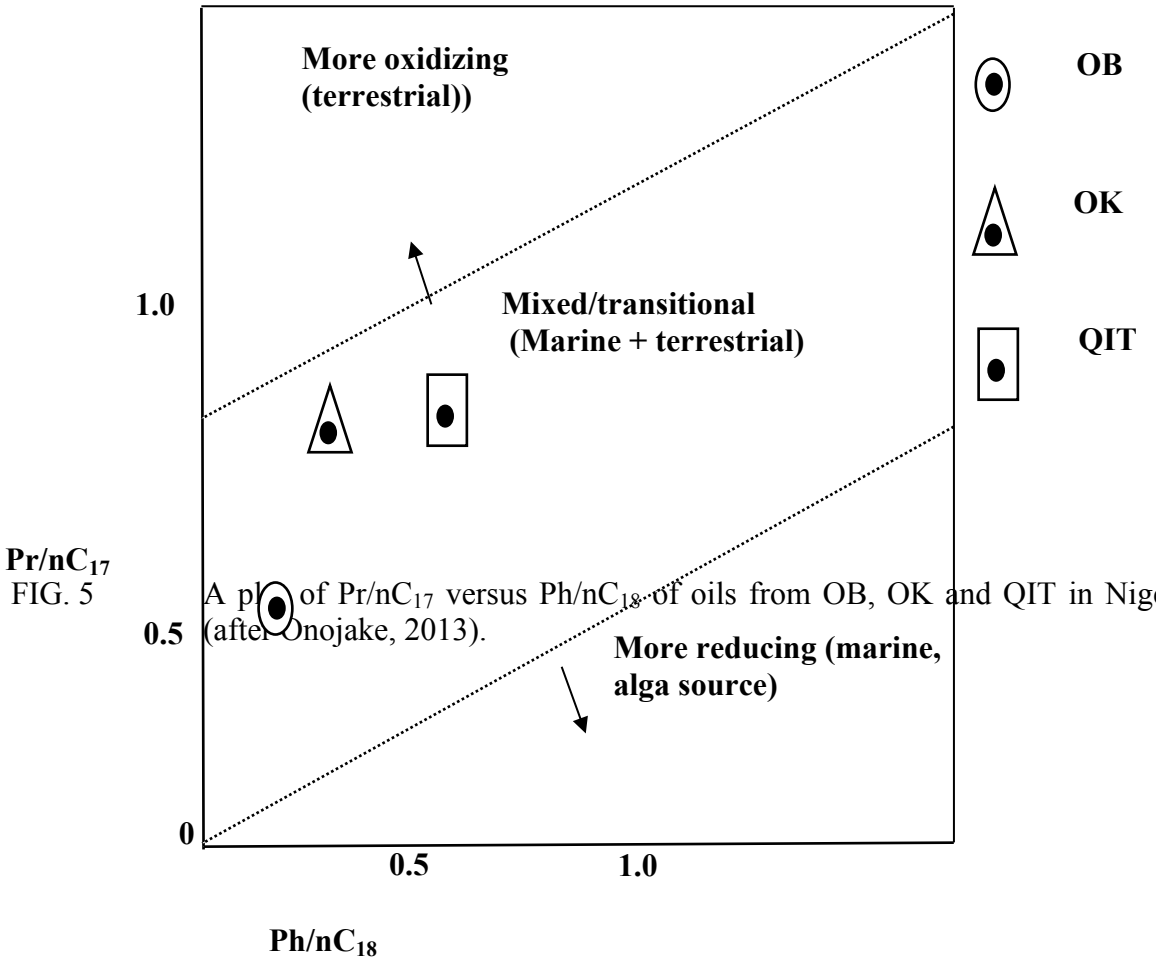


FIG. 5 A plot of Pr/nC_{17} versus Ph/nC_{18} of oils from OB, OK and QIT in Niger Delta (after Onojake, 2013).

Conclusion

In conclusion, oils from Okpoho/Okono, Oben and Qua Iboe wells have been characterized and correlated to show their genetic relationship and differences which may serve as a baseline database for environmental forensic investigation, in the event of oil spillage and environmental pollution occurrence.

Recommendation

It should be noted however that, in any correlation exercise particularly for complex hydrocarbons mixtures and degraded oils residues, a single technique cannotbe used to completely meet the objectives of characterization and correlation of oil to their respective source and depositional environment. Hence, integrated multitools are often necessary under such conditions. Therefore other parameters such as bulk parameters as well as stable carbon isotopic analysis, detailed analyses of organic biomarkers and alkylated PAH and a combined statistical methods are needed to further enhance the utility of OB, OK and QIT characterization and correlation.

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