Geochemical Characterization of Some Biodegraded Oils from the Niger Delta Basin, Nigeria

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ABSTRACT

This study aimed to examine the compositional changes resulting from biodegradation, fathom the extent of degradation, and provide clues for interpreting the evolution and the overall effects on the quality of the oils. Ten oil samples from onshore-offshore fields were analyzed using gas chromatography (GC) and GC-mass spectrometry (GC-MS) methods. GC results indicate variable loss of low molecular weight (LMW) alkanes, besides the presence of unresolved complex mixture (UCM). Saturated, aromatic, resins, and asphaltenes (SARA) compositions and low saturate/aromatic ratio confirmed evidence of biodegradation. Biodegradation levels of the considered oils range from light to moderate, based on Peters and Moldowan scale. This influenced shifts in the 'primary compositions' of oils probably from paraffinic or paraffinic-naphthenic oils to aromatic-naphthenic oils. Total ion chromatograms of well 1 and 2 from Northern depobelt, show presence of LMW alkanes, co-existing side by side with UCM, suggesting multiple charges. However, biomarker fingerprints of the oils lack evidence of in-reservoir mixing of biodegraded and non-biodegraded oils. Nevertheless, the possibility of oil mixing cannot be excluded, because biodegradation is progressive and is ongoing. This study, shows the process has dramatically impacted the fluid properties, commercial worth, and economic producibility of the investigated oil accumulations in the basin.

1. INTRODUCTION

The properties and composition of petroleum are principally controlled by complex geological, physiochemical, and biological processes, like source rock organofacies changes, thermal evolution, migration fractionation, in-reservoir alterations, and mixing of fluids from various sources [1-3].

Biodegradation typically changes molecular composition and bulk properties (e.g., API gravity) of crude-oils in the reservoirs. This process poses critical challenges to considerable economic production and commercial value of petroleum in the Niger Delta Basin.

Moreover, Connan [4] and Wenger et al. [5] reported that biodegradation is frequently observed in shallow reservoirs at a critical temperature of about 80°C. Although, 'it depends on certain key factors such as reservoir temperature and nutrients availability to microbes at oil-water contact' [4]. Nevertheless, Larter et al. [6] revealed from field study, a temperature limit of 80°C for biodegradation, thus concluded this temperature as the maximum limit for petroleum degraders in sedimentary basins. Similarly, 'some workers previously reported that, for subsurface biodegradation to occur, reservoir temperature should typically stand less than 80°C, nutrients, and a suitable microbial population must be present' [4, 7, 8].

Meanwhile, Huang et al. [1] suggests that biodegradation is entirely uncontrolled by present-day reservoir temperature, because not all low-temperature reservoirs contain degraded oil [2, 9], and not all deep-seated reservoired petroleum are free of petroleum degraders. Consequently, residency time, together with temperature records, play significant role [1].

Therefore, the complex processes of oil degradation in the reservoirs, and the role of microbes are scarcely understood [1, 10-13].

Biodegradation, water-washing, and fractionation are thought to be the most common petroleum alteration processes in the Niger Delta Basin [9, 14, 15]. These processes are considered to be widespread in the Niger Delta, a deltaic basin with complex structural/tectonic setting, amidst reports of secondary and tertiary migrations, meteoritic water incursions in shallow reservoirs [9, 14, 15]. Mode et al. [9] and Abrakasa and Nwankwo [15] observed variable degrees of biodegradation among some crude oils sampled from different locations in the Niger Delta. It was further stated that 'Niger Delta oils are predisposed to biodegradation because of the potential influx of water into their reservoirs, which provides nutrients to the microbes' [14], and that most reservoirs in the Niger Delta basin had been 'invaded by marine and meteoric waters, through faults, and extensive sand stringers' [15], creating favorable channel for in-reservoir biodegradation to take place. This process overtime impacts the quality of oil via progressive loss of low molecular weight (LMW) hydrocarbons (i.e., saturated), consequently leading to a drop in API value [3, 16].

Furthermore, the decline in crude-oil quality associated with biodegradation has taken a critical outlook in recent years. Therefore evaluation of biodegradation status of oil accumulation now become key measure, 'for the oil industries, because of decline in recovery efficiency, drop in oil quality, and increasing challenges associated with economic production and handling' [17]. To such a degree, the relative

biodegradation status of reservoired petroleum is worth profiling. To provide a more authentic picture, about some specific features of reservoirs and its fluid contents, that will assist engineers in designing how best to improve production capacity, and to maximize recovery efficiency of petroleum within a field. This is critical, both for established petroleum accumulations and also for future designs that will enhance the recovery of viscous oil masterminded mediations. This paper aims to establish geochemical evidence, the extent of biodegradation, and to provide clues for interpreting the evolution, and the resultant impacts of biodegradation on the overall quality of the considered oils.
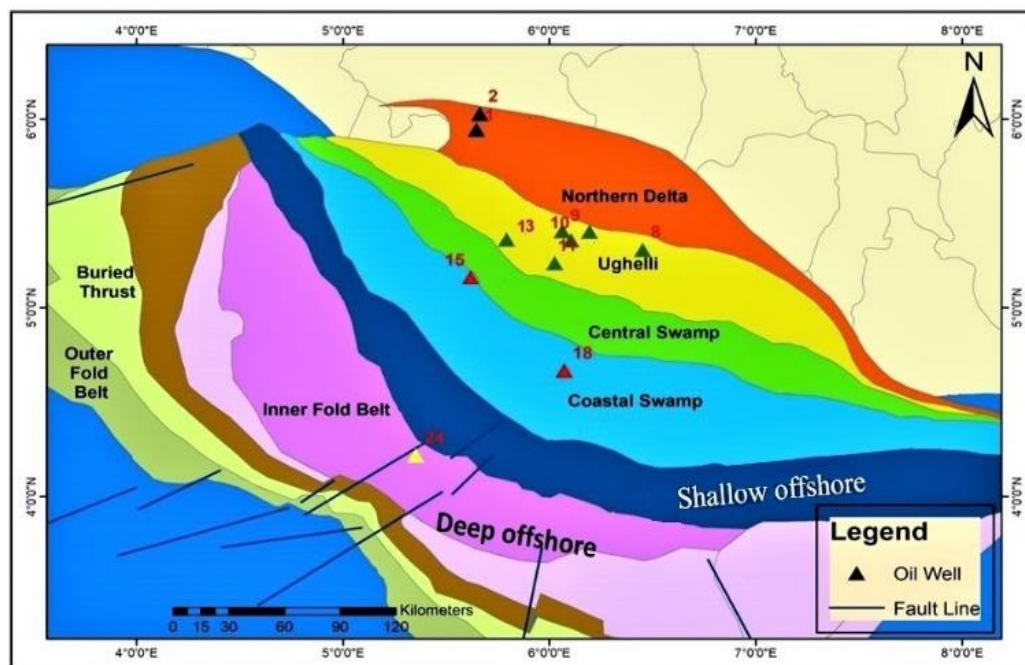

Figure 1. Map of Niger Delta showing depobelts /locations of studied oils

2. GEOLOGICAL SETTING

Niger Delta Basin is strategically located at the complex intersection of the Benue Trough and South Atlantic Ocean, where a triple junction developed during the successful separation of South America and Africa continents. The region has lush vegetation and intense interaction of biological and chemical processes, with siliciclastic sediments that reach a maximum thickness of 9000-12,000m [18, 19].

The Niger Delta sedimentary succession is stratigraphically divided into three rock units (Figure 1). The Benin Formation (Oligocene-recent), is the youngest rock unit. It composed of sandstone, with about 2000m thickness [18], deposited in a fluvial and coastal environment. The Agbada Formation (Eocene-recent), underlies the Benin Formation. It is made up of interbedded sandstones and shales deposited in a transitional/marine environment. This formation consists of paralic siliciclastic sediments, which are over 3700m thick [18], and represent the actual deltaic portion of the sequence. While the Akata Formation (Paleocene to Miocene), lies underneath the Agbada Formation and is typically composed of thick shale sequences (potential source rocks) and turbidite sand (potential reservoir) with minor amounts of clay and silt of paralic sequence of interbedded sands and massive marine shales generally estimated at 7000m thickness [18].

3. MATERIALS AND METHODS

3.1 Sampling method

Ten crude-oil samples were carefully collected from wellheads from different producing fields, across four depobelts (onshore and offshore), Niger Delta. The sample locations are clearly displayed in Figure 1.

3.2 Analytical methods

The considered oils (approximately 30mg) were carefully separated, into the saturated and aromatic hydrocarbons, and polar compounds, using n-hexane (30 ml), n-hexane/dichloromethane (60:40, vol/vol/ 40 ml) and dichloromethane/methanol (50:50, 30 ml) respectively.

3.3 Gas chromatography (GC) analysis

GC technique was typically used to analyze the saturated fraction, to obtain n-alkanes and acyclic isoprenoid distributions of the investigated crude oils. The GC-Flame ionization detector (FID) analysis of each oil sample was performed on Hewlett-Packard 5890 Series II GC with injector at 280°C and FID at 310°C. 1 µl of the crude-oil samples were injected by an HP6890 auto-sampler in splitless mode. The oven temperature ramp program used was from 50°C (held for 2 minutes) to 300°C at 5°C per min., and held at the absolute temperature of 300°C for 20 minutes. Hydrogen was used as the carrier gas, and separation was accomplished on a fused silica capillary column (30m × 0.25mm i.d), glazed with 0.25µm 5% phenylmethyl polysiloxane (HP-5 phase).

3.4 Gas chromatography-mass spectrometry (GC-MS) analysis

Saturated and aromatic fractions were further analyzed by

GC-MS using single ion monitoring (SIM) mode accompanied by an HP 5890 Series II gas chromatograph, fitted with a 30m x 0.25mm internal dimension fused silica capillary column glazed with DB-5, coupled to an HP5970 Mass Selective Detector (MSD). The oven temperature was carefully held at 40°C for 5 minutes. and programmed, from 40°C to 300°C at 4°C/min. the mass spectrometer was typically operated at an electron energy of 70 eV, an ion source temperature of 250°C, and a separator temperature of 250°C. Terpanes together, with steranes, were mainly identified, employing m/z 191 and 217 fragments, respectively.

4. RESULTS AND DISCUSSION

4.1 Bulk composition of oils

The gross composition of crude oils can be estimated from bulk hydrocarbon fractions, such as the comparable percentage of saturated, aromatic, resins, and asphaltenes (SARA) together with saturate/aromatic ratio. These parameters offer valuable information concerning the general quality of crude oil. The sat/arom ratio is typically constrained by several key factors, such as organic matter facies diversity, thermal maturation, and biodegradation. Thermal maturation provokes cracking of higher molecular weight (HMW), thereby promoting LMW fraction, consequently increasing the ratio. Conversely, biodegradation gradually eliminates the LMW (saturated) fraction, leading to a decline in the ratio, with a corresponding decrease in the API gravity of the oil [16].

The calculated sat/arom ratio and SARA composition of the considered oils are clearly listed in Table 1. The sat/arom ratio ranges from 0.47-2.71. These values, are relatively low indicating that the considered oils have undergone variable levels of biodegradation, with well 15 and 10 representing the least and the most degraded oils, with the limit values of 2.71 and 0.47 respectively.

Besides, API gravity is a bulk property that directly relates to the gross composition of crude oils. LMW hydrocarbons (i.e., the gasoline range), usually display high API values. When microorganisms eat up lighter n-alkane components in crude oil, during progressive biodegradation, the residual oil becomes enriched in HMW components (e.g., asphaltenes), which generally correspond to a decrease in API value [16]. To that effect, it can be deduced that the considered oils, undoubtedly have diminished API values as observed from the considerable loss of LMW (paraffin) components, and the corresponding low sat/arom ratio of oils, except well 15 which may have supposedly experienced incipient biodegradation (Figure 2B).

4.2 Normal-alkane and isoprenoid distributions

The results of gas chromatography analysis on the investigated crude-oil samples (Table 1) show varying degrees of oil degradation (Figures 2A, 2B, and 4). Total ion chromatograms (TICs) of the saturated fraction of the investigated oils typically indicate a gradual increase in the levels of biodegradation, corroborating relatively low humps of the unresolved complex mixture (UCM), and significant changes in the n-alkane distributions [16]. The considered Niger Delta oils generally display relatively low UCM humps (whereas biodegraded samples typically have prominent UCM). The n-alkanes are relatively high in abundance, and there is the notable presence of lower molecular weight isoprenoids in addition to alkanes. These key features are consistent with minor to moderate biodegradation [4, 20].

Table 1. Bulk geochemical compositions of studied crude oil samples

Well	Field	Depobelt	Pr/ph	Pr/nC$_{17}$	Ph/nC$_{18}$
1	A	Northern Delta	3.06	1.40	0.47
2	A	Northern Delta	3.32	1.37	0.44
8	D	Greater Ughelli	3.50	1.35	0.83
9	D	Greater Ughelli	3.13	1.03	0.29
10	D	Greater Ughelli	1.88	33.58	2.57
11	D	Greater Ughelli	3.30	6.47	1.17
13	E	Greater Ughelli	4.03	1.48	0.70
15	F	Coaster Swamp	2.49	0.83	0.23
18	G	Coaster Swamp	3.78	1.48	0.70
24	H	Offshore Delta	2.33	1.33	0.41

CPI	Sats.wt%	Arom.wt%	NSOwt%	Sat%Hc	Arom%Hc	Sat/Arom
1.00	52.25	36.40	11.35	58.94	41.06	1.44
1.03	51.05	34.07	14.88	59.97	40.03	1.50
0.97	55.20	31.05	13.75	64.00	36.00	1.78
1.00	36.18	53.92	9.90	40.16	59.84	0.67
1.03	29.32	62.56	8.12	31.91	68.09	0.47
1.05	33.58	55.38	11.04	37.75	62.25	0.61
1.11	41.23	54.81	3.96	42.93	57.07	0.75
1.09	71.82	26.48	1.70	73.06	26.94	2.71
1.16	58.63	39.31	2.06	59.86	40.14	1.49
1.08	63.04	30.33	6.63	67.52	32.48	2.08

Note: Pr/ph= pristane/phytane ratio; pr/nC$_{17}$= pristane/nC$_{17}$; ph/C$_{18}$= phytane/nC$_{18}$; CPI= carbon preference index; Sats.wt%= saturated wt%; arom.wt%= aromatic wt%; NSOwt%= polar (resins+asphaltenes)wt%; sat%Hc= saturated %hydrocarbons; arom%Hc= aromatic %hydrocarbons; sat/arom= saturates/aromatic ratio.
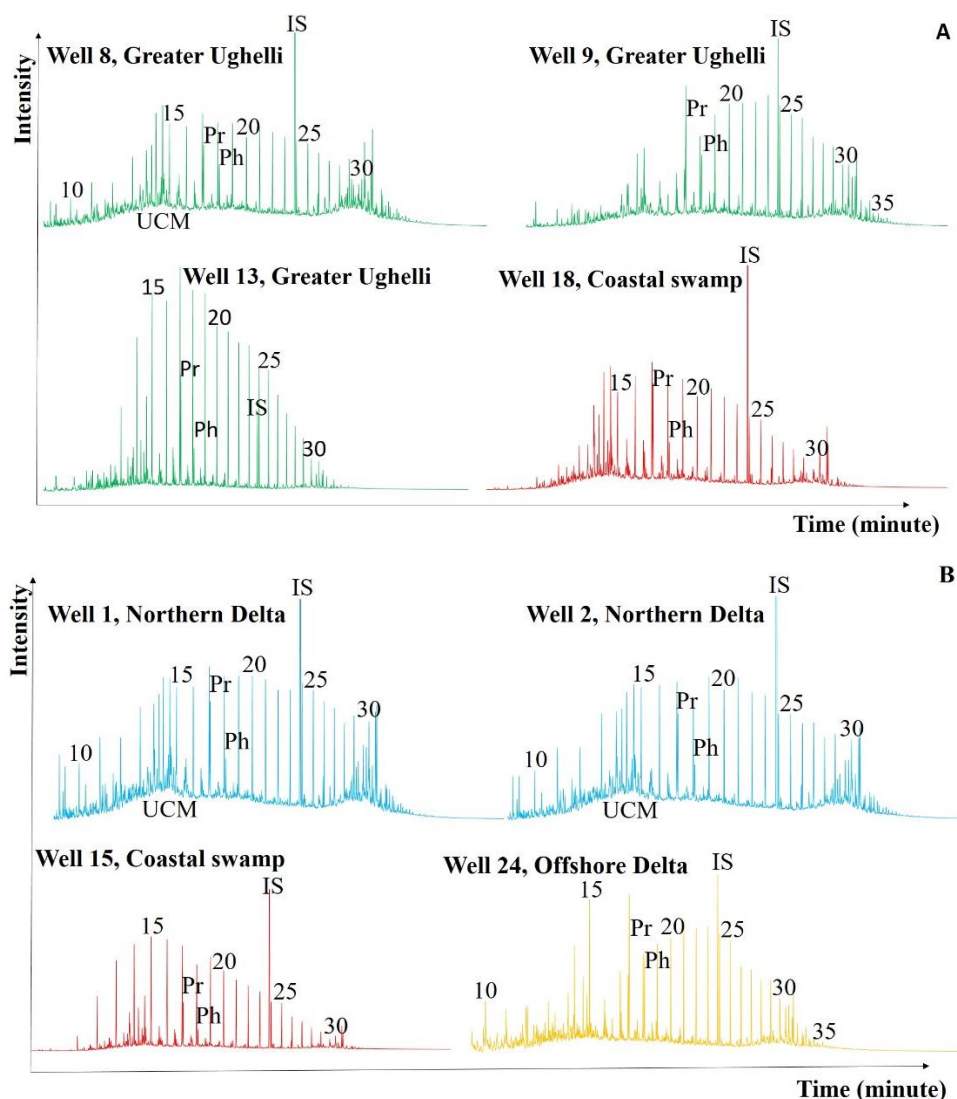
Figure 2. GC of n-alkane profiles of biodegraded oils

(A) Greater Ughelli and Coastal swamp depobelts, (B) Northern, Coastal swamp and Offshore depobelts, of the Niger Delta. Note the different LMW profiles; 20= nC_{20}, Pr =Pristane, Ph=Phytane, UCM= unresolved complex mixture and IS=internal standard (n-heptadecylcyclohexane)

Meanwhile, well 15 from Coastal swamp, displays saturated hydrocarbon distribution that indicates precisely a typical partial biodegradation profile, containing a suite of n-alkanes above C_9. In other words, fractions less than C_9 have been stripped completely. This sample appears to be the least degraded oil, while the rest are degraded up to the fractions in the range (nC_{10}-nC_{19}). Conversely, well 10 from Greater Ughelli depobelt, typically depicts the most degraded oil currently under study. Its chromatogram confirms invariably, the total removal of n-alkanes and extreme reduction in isoprenoids (i.e., pristanes and phytanes) components (Figure 4), typically corresponding to moderate degradation [20].

The ratios of pr/n-C_{17} and ph/n-C_{18} have proven to be effective indicators of biodegradation [21]. In most cases, these ratios which express n-alkane distributions, in relations to isoprenoids, exhibit diverse range concerning organic matter origins, thermal evolution and biodegradation [3, 22, 23]. Normal alkanes are always present in relatively higher proportion compare to isoprenoids, in matured non-biodegraded oils. The calculated pr/n-C_{17} and ph/n-C_{18} ratio values, for the considered oils, are listed in Table 1, which ranges from 0.83-33.58 and 0.23-2.57, respectively. The value of these ratios increase with rising biodegradation (Table 1 & Figure 3). These values are high, particularly for oil samples

from well (10 and 11), which suggest the light-end hydrocarbons have been significantly depleted. Interestingly, the ratios of pr/n-C_{17}, ph/n-C_{18} of oil samples from well 10 and 15, having the values 33.58, 2.57 and 0.83, 0.23 respectively, affirmed the least and most biodegraded oils earlier interpreted.

4.3 Biomarker fingerprints related to biodegradation

The likely effects of biodegradation on the GC profiles of saturated hydrocarbons of the considered oils are well recognized, particularly where n-alkanes and isoprenoids have been significantly attacked (see well-sample 10 & 11). But this effect cannot be detected directly in GC profiles beyond n-alkane and acyclic isoprenoid distributions. Therefore a more sophisticated GC-MS technique was applied to detect more recalcitrant geochemical molecules (biomarkers) indicator of biodegradation. Meanwhile, considerable resistance of petroleum to biodegradation generally increases in the following order: n-alkanes; alkylcyclohexanes; alkylbenzenes; iso- and anteisi-alkanes; acyclic isoprenoids; alkylnaphthalenes; bicyclic alkanes; (C_{27}-C_{29}) regular steranes; (C_{30}-C_{35}) hopanes; diasteranes; (C_{27}-C_{29}) hopanes; (C_{21}-C_{22}) regular steranes; tricyclic terpanes [4, 20, 24, 25].

Moreover, well-studied demethyled hopane compounds

suggest they might be a useful indicator of severe stage biodegradation of petroleum [20, 26]. Besides, microbially influenced conversion of extended hopanes to 25-norhopanes characteristically begins during petroleum degradation in reservoirs [20, 27-29].

Simultaneously, Moldowan and McCaffrey [30], typically recognized two major biodegradation pathways, viz: the hopane demethylation pathway, where 25-norhopanes traditionally begin to occur before the attack on steranes; and the unique pathway, where hopanes are typically attacked without the possible formation of 25-norhopanes, in other words, steranes are attacked first.

In either case, this study explored all necessary channels to ascertain the extent of biodegradation on all affected components. In that respect, the GC-MS mass chromatogram fingerprints (Figure 4), of the two most degraded oil samples (10 and 11) under consideration were specifically examined, for the notable presence of demethylhopanes, and the expressive effect on other hydrocarbons, like steranes, to discretely assess and accurately estimate the ultimate levels of biodegradation on the considered oils. It is well understood that compounds such as 25-norhopanes are associated with crude oil that has undergone significant biodegradation [20, 31]. However, these specific compounds are undetected in the considered oil samples, more also, critical examination on the mass chromatograms (m/z 217), established that sterane components of the investigated oils are intact. Therefore, the biodegradation levels of the considered crude oil can be reliably estimated to a considerable range from light to moderate scale [20].
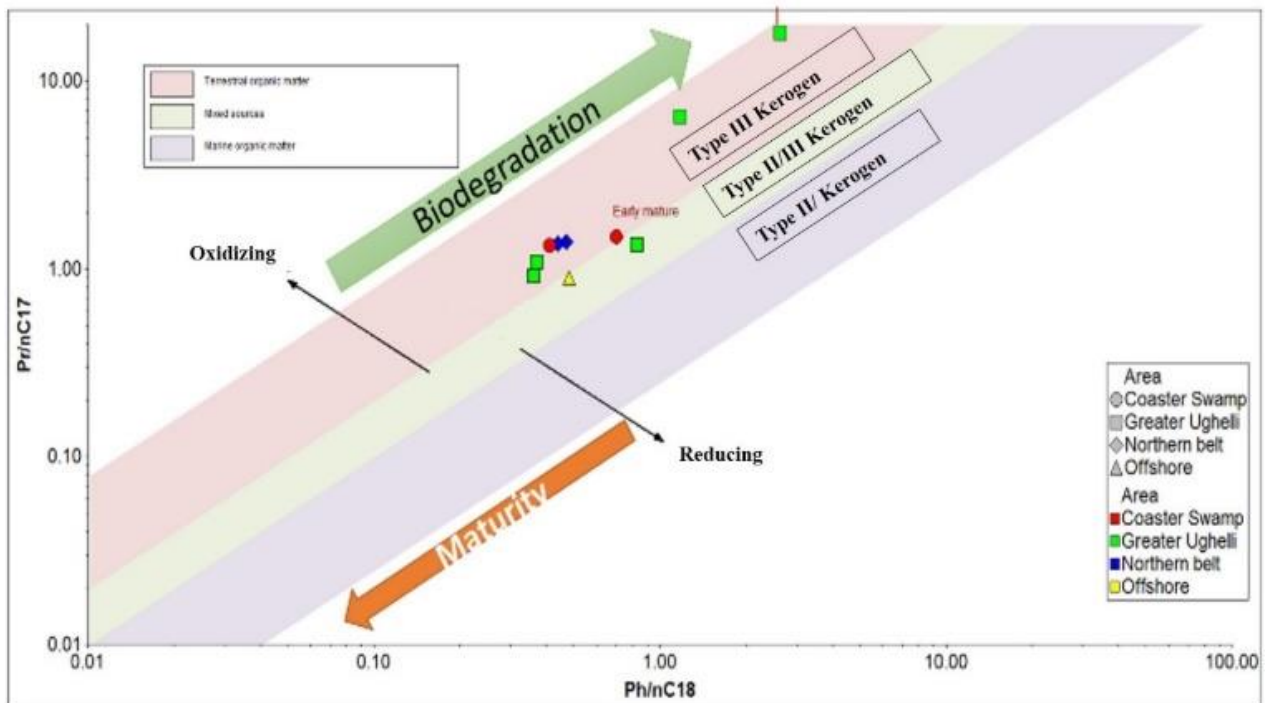

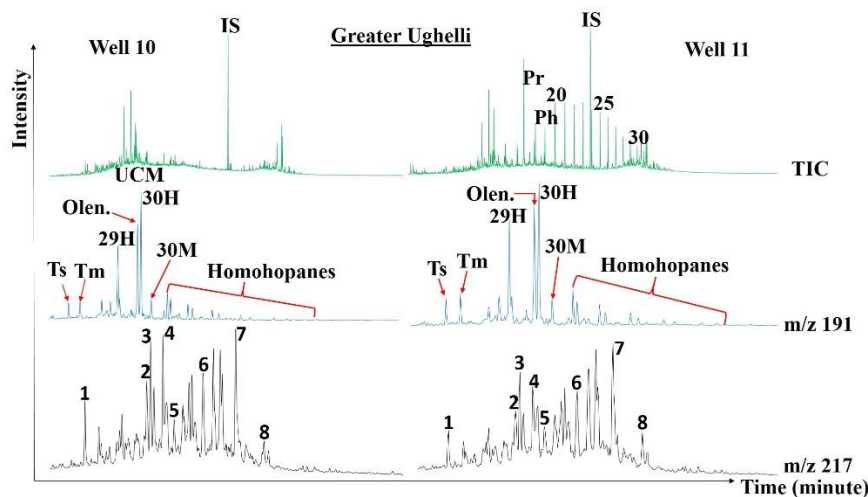**Figure 3.** Plot of pr/n-C_{17} vs ph/n-C_{18} ratios for the studied oils [21]

Figure 4. GC, GC-MS of the most biodegraded oils from Greater Ughell depobelt, Niger Delta

Note the total and partial removal of n-alkanes profiles, while the steranes and triterpanes profiles are still preserved indicating level 4-5 on the ranking of [20]. [**1**= 13β,17α (20S) Diacholestane; **2**= C_{27} 5α,14α,17α(20S); **3**= C_{27} 5α,14β,17β (20S+20R diasterases); **4** = C_{27} 5α,14α,17α(20R); **5**= C_{29} (20R) diasterane; **6**= C_{28} 5α,14α,17α(20R); **7**= C_{29} 5α,14α,17α(20R); **8**= C_{30} 5α,14α,17α(20R); **Ts**= 18α 22, 29, 30-trisnorneohopane; **Tm** =17α 22, 29, 30-trisnorhopane; **29H**= C_{29} 17αH,21βH 30-nor-Hopane; **Olen**. =18α Oleanane; **30H**= C_{30} 17α 21β Hopane; **30M** = 17β,21α Moretane]

Also, two oil samples from well (1 and 2) from Northern depobelt, show signs of minor (light) degradation with the visible presence of LMW n-alkane distributions within the range≥C_9 and a conspicuous evidence of UCM humps in the TICs (Figure 2B), co-existing simultaneously. This scenario points to likely mixing oils phenomenon, typically resulting from multiple charge episodes. Besides, critically comparing the UCMs of these samples to that of sample 10, (i.e., the most degraded oil Figure 4), indicate an equivalent level of UCM hump. Yet, there exists an abundance of LMW n-alkanes suggesting later charges on the reservoirs. However, critical biomarker distributions lack any firm evidence to support the in-reservoir mixing of biodegraded and non-biodegraded oils. Nevertheless, the possibility of an in-reservoir mixing is not excluded, because petroleum biodegradation is a progressive phenomenon and is ongoing

5. CONCLUSIONS

The study successfully characterizes and estimates the degrees/extent of biodegradation experienced by the studied oils, hence conclude as follows: The results of the analyses show variable loss of LMW alkanes (paraffins) and presence of UCM humps, SARA compositions, and low saturate/aromatic ratios confirmed convincing evidence of biodegradation that infers low API gravity, which negatively impacts the general quality of oils.

Biodegradation effect based on the results of SARA composition and saturate/aromatic ratios influenced shifts in the 'original-oil composition', probably from paraffinic or paraffinic-naphthenic oils to aromatic-naphthenic oils. These biodegradation activities could have been induced by degrading anaerobic bacteria and/or aerobic microbes present in the reservoirs carried in during the influx of meteoric water, especially for the Greater Ughelli crude-oil samples, which are from an onshore fields and are mostly affected.

The levels of biodegradation for the studied oils generally range from light to moderate in the ranking of [20]. These effects have dramatically impacted the fluid properties and hence the commercial worth and economic producibility of the studied oil accumulations in the basin.

Additionally, TICs of well 1 and 2 from the Northern depobelt, show presence of LMW alkanes co-existing side by side with UCM humps, suggesting multiple charge episodes, however, no discrete biomarker fingerprinting evidence for in-reservoir mixing of biodegraded and non-biodegraded oils in the accumulations. However, possibility of in-reservoir mixing cannot be excluded. Therefore, future work shall focus on the used of fliud inclusion to determine the charge history of the oil-reservoirs.

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