The Presence of 2-Thiaadamantane in Niger Delta Oils may indicate Souring in Niger Delta Reservoirs

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Abstract

Some oil samples from various Nigerian oil fields were examined for the presence of Thermochemical Sulphate Reduction (TSR) derived organo sulphur compounds. Oil samples were diluted with DCM and injected into the GC–MS for full scan analysis. The GC–MS results show the presence 2–thiaadamantane, 1–methyl-2-thiaadamanatane and 5–methyl-2-thiaadamanatane, the compounds were identified by comparison of extracted spectras with literature. The presence of these compounds in oils has been accepted on a wider horizon as indicators of reservoir souring. The plot of 5–Methyl-2-thiaadamantane/Adamantane and Dibenzothiophene/Adamanatane showed a fair correlation, corroborating the presence of 5–Methyl-2-thiaadamantane and fairly high abundance of Dibenzothiophene, the plot of 2-thiaadamantane/Adamantane and 5–Methyl -2-Thiaadamantane/Adamantane corroborating the presence of 2-thiaadamantane and 5–Methyl -2-Thiaadamantane inferring that the presence of 2-thiaadamantane and 5–Methyl -2-Thiaadamantane indicate that reservoir souring is active.

Key words: *2-thiaadamantane, 5–Methyl -2-Thiaadamantane, Thermochemical Sulphate Reduction (TSR), 1–methyl-2-thiaadamanatane, oils, reservoir souring, Niger Delta*

Introduction

Reservoir processes includes biodegradation, water washing, evaporative loss and reservoir souring. Reservoir souring has been of much concern because its potential for wide range damages in the oil field. Reservoir souring is the process of generation of hydrogen sulphide in a petroleum reservoir, souring in petroleum reservoir is associated with Sulphide stress Crossion Cracking (SSCC), Hydrogen Embrittlement, Hydrogen induced Cracking thus H_2S in reservoir not only leads to corrosion but also potential catastrophic failure of equipment used in the oil fields. Reservoir souring can be triggered off by postulated mechanisms which include:

i. Thermochemical sulphate reduction
ii. Bacterial sulphate reduction
iii. Thermal decomposition of organic sulphur compounds
iv. Dissolution of pyritic materials
v. Redox reaction involving bisulphite oxygen scavengers.

The most plausible geochemical mechanism for souring processes in reservoirs is the thermochemical sulphate reduction. This processes have also got literal evidence, the

illustration for possibility of thermochemical sulphate reduction processes is the La Blanc process where Sodium Tetraoxosulphate (VI) [Na2SO4] is reacted with coke [C] at high temperature to give Sodium Sulphide [Na2S] and carbon IV oxide [CO2]. The hydrocarbon could be the source of carbon while sulphate ions are abundant in injected seawater and influxed sea/marine waters. There are substances that are present in crude oil which could serve as reducing agent that can enhance the process at probably a more reduced temperature. However, studies have shown that thermochemical sulphate reduction can occur at temperature between 77ºC–121ºC in the presence of pre–existing hydrogen Sulphide [H2S]. It is also postulated that at temperatures of about 100C, slightly soured reservoirs may become more soured.

The other possible mechanism is the action sulphate reducing bacteria accompanying injection water into the reservoir, the bacteria will source oxygen from the sulphate ions in the injected water to reduce light hydrocarbons to carbon IV oxide [CO2] and H2O and their energy. The temperature of the water will adjust the temperature of the reservoir to much lower temperature hat provides for the bacterial to strife. In the absence of sulphate reducing bacteria [SRB] there will be no biogenic souring in petroleum reservoirs [1]. All green plants fungi and most bacteria can reduce sulphate to Sulphide, most prokaryotes reduce sulphate in an energy yielding processes to obtain energy for growth and maintenance [2]. The North Sea is a resounding example where initial production was characterized with very low H2S, however increase in H2S ensured overtime [1].

In the course of studying Niger delta oils, it was unraveled that the oils contained 2–Thiadiamondoids. Thiadiamondoids are diamond like compounds with a sulfide bond located within the cage structure. The presence of thiadiamondoids in oils have been employed as a molecular proxy/indication for the occurrence and estimation of extent of thermochemical sulphate reduction (TSR) showed that there was increase in thiaadamantane concentration due to reaction of elemental sulphur with adamantane, when subjected to TSR conditions [3-6]. In a study it was observed that the depletion of 34S corresponded with the formation of thaiadamantanes, this observation buttress the fact that the presence of sulphur in oil in the reservoir can trigger the formation of thaiadamantanes [7].

In their study, it was postulated that the thiaadamantane found in the oils, indicates that the oils have undergone thermochemical sulphate reduction [6]. Some aromatic sulphur compound have been postulated to serve as generic indicator of souring in petroleum reservoirs. In a study, dibenzothiophene (DBT) and related analogues were observed to occur in significant high amounts [8]. The DBT/P (Dibenzothiophene–Phenanthrene ratio were high for oils from reservoir that have undergone souring processes [8]. In another study, it was observed that Methyl dibenzothiophene to methylphenanthrene ratio (MDBT/ MPH) were higher for reservoirs that were suspected to have undergone souring by thermochemical sulphate reduction [9]. MDBT/ MPH range from 0.71–1.38 for TSR suspected reservoir and 0.33–0.65 for non–soured reservoirs. The study also stated that most souring in global scale is a result of TSR.

In the Niger delta, continental runoff that are deposit in proximal and distal environment and are fairly rich in ferrogenious materials which help to scrub off the sulphur in the form of ions from marine incursion and are deposited as pyrite framboids on the reservoir walls, on the infill of petroleum the pyrite could be the source of sulphur and H2S (hydrogen sulphide) during matrix acidization for reservoir stimulation for enhanced fluid flow and petroleum production. The presence of that initial H2S as a pre-existing H2S generated by reservoir stimulation can initiate, foster and enhance souring process [1]. The presence of mercaptans in Nigeria reservoirs may also be an indication of souring processes in Nigeria oil industry. The authors stated that flared gases which are mostly associated gases do contain H2S [10].

The temperature regime of the reservoirs may also be a key factor to the potential for thermochemical sulphate reduction. In the Niger Delta most of the reservoirs are within the Lower Agbada and the Upper Agbada formation. The Niger delta is mostly characterized by intercalated reservoirs within the Agbada Formation [11]. The Akata–Agbada formational boundary is within 3.4km to 4.3km [11]. This invariably infers that most of the Niger Delta reservoirs will be at about 100ºC, this represented high possibility of the occurrence of thermochemical sulphate reduction in Niger Delta reservoir especially with a pre–existing H2S in the reservoir which serve as an initiator and will enhance souring.

Methods and Materials

This entails the samples used, methods of sampling, sample preparation and analysis.

Samples and Sampling

Samples used in the study are crude oil samples obtained from different wells in the corresponding oil fields. Oil fields from which samples were obtained are Ahia, Nembe Creek, Kolo Creek, Obagi, Oluma, Utorugu, Soku, Abo and Escravos (figure 1) Samples were collected in sample vials with Teflon caps. Samples were preserved in refrigerator till analysis was performed. Samples were treated by dilution with hexane for analysis, the concentration injected into the GC–MS is 1mg/ml [12].

GC–MS Analysis

All the oils from different oil fields were subjected to GC–MS analysis using a HP5890 II GC with a split/spiltless injector linked to a HP 5972 MSD (Mass Selective Detector). The GC was temperature programmed for 40ºC–300ºC at 4ºC per minute and held at final temperature for 20 min. The carrier gas was Helium (flow rate 1ml/min., pressure of 50kPa, slit at 30ml/min). The ionization and identification was carried out in the HP 5972 MSD, which was equipped with electron voltage of 70 eV, filament current of 220μA, source temperature of 160ºC, a multiplier voltage of 1600V and interface temperature of 300ºC. The acquisition was monitored by HP Vectra 48 PC chemstation computer in both full scan mode (30ions 0.7 cps 35m dwell). HP is currently known as Agilent, UK. 2-Thiaadamantane and the methyl analogues were detected and identified by extracting m/z=154 and m/z=168 chromatograms respectively, the spectras of the 2-Thiaadamantane and the methyl analogues were extracted and compared with those from literature. Peak integration was done using the RTE integrator [12]. Data was obtained from the percentage report derived from the Enhanced MSD ChemStation 2011 software by Agilent Technologies.

Results and Discussion:

Identification of 2-Thiaadamantane and Methyl Analogues

2–thiaadamanatane, 1-methyl–2–thiaadamanatane and 5–methyl–2–thiaadamanatane were detected in some Niger Delta oils used in this study. 2–thaiadamanatane was detected by extraction of the EIC (extracted ion chromatogram) on m/z 154 (figure 2). The chromatogram was compared with that from literature [5]. Identification of 2–thaiadamanatane was accomplished, by extraction of the mass spectra for 2–thaiadamanatane (figure 3) which was compared to the literature reference, high similitude was observed. This was done with Enhanced MSD ChemStation 2011 software by Agilent Technologies. The detection of 1-methyl–2–thiaadamanatane and 5–methyl–2–thiaadamanatane was accomplished by extraction of EIC (extracted ion chromatogram) on m/z 168 (figure 4) it was also compared to literature (Jiang et al., 2008). Identification of 1-methyl–2–thiaadamanatane and 5–methyl–2–thiaadamanatane was achieved by extraction of the respective mass spectras (figures 5 and 6), the mass spectras were compared to literature [5].

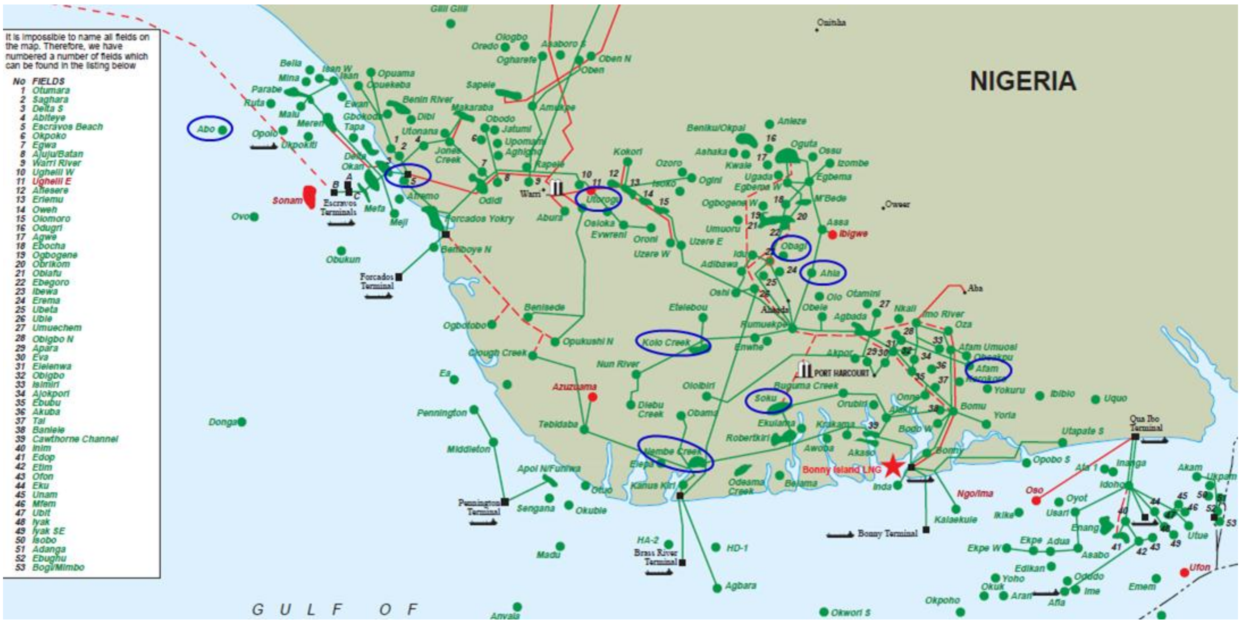
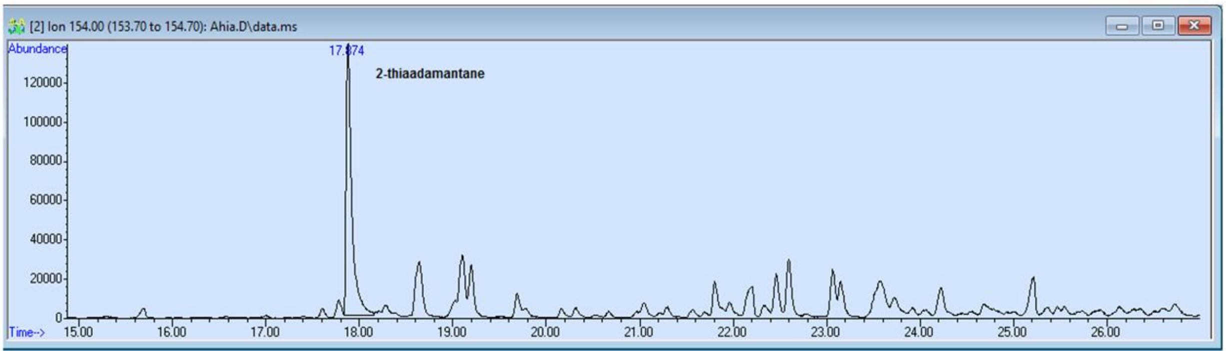


Figure 1: Map of oil sample locations used for the study.



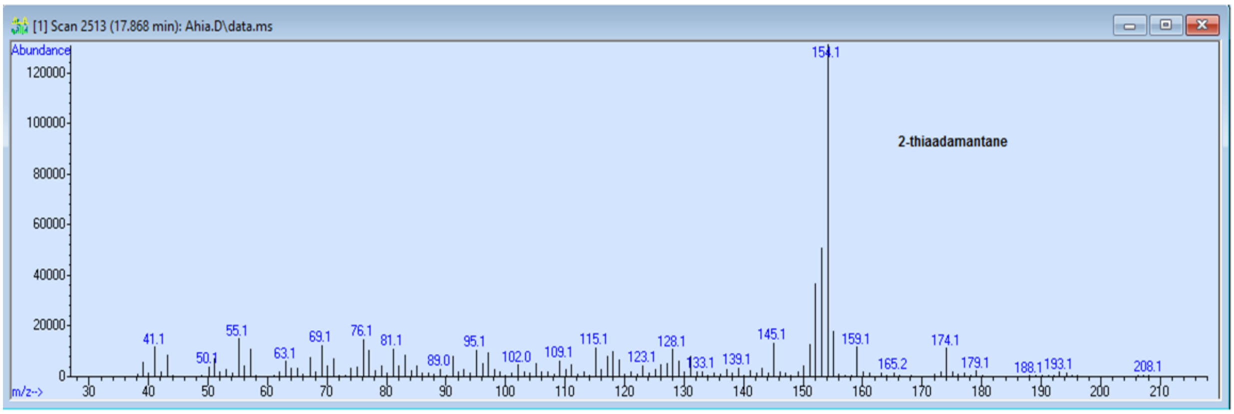


Figure 3: Mass spectra for 2–thiaadamanatane for Ahia oil

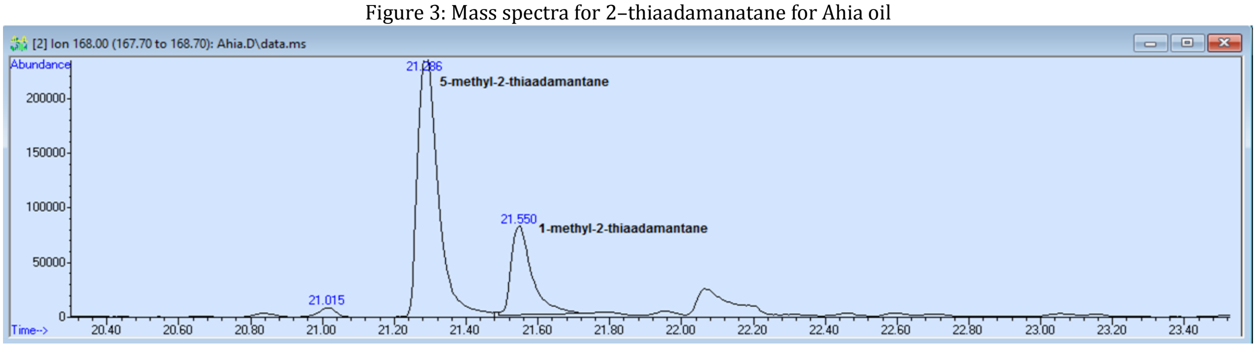


Figure 4: Mass chromatogram for m/z =168, showing 1-methyl–2–thiaadamanatane and 5–methyl–2–thiaadamanatane for Ahia oil

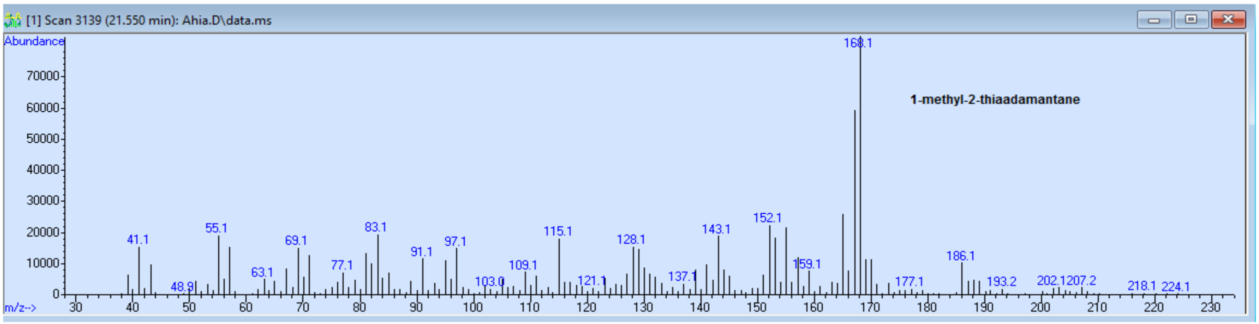


Figure 5: Mass spectra for 1-methyl–2–thiaadamanatane for Ahia oil

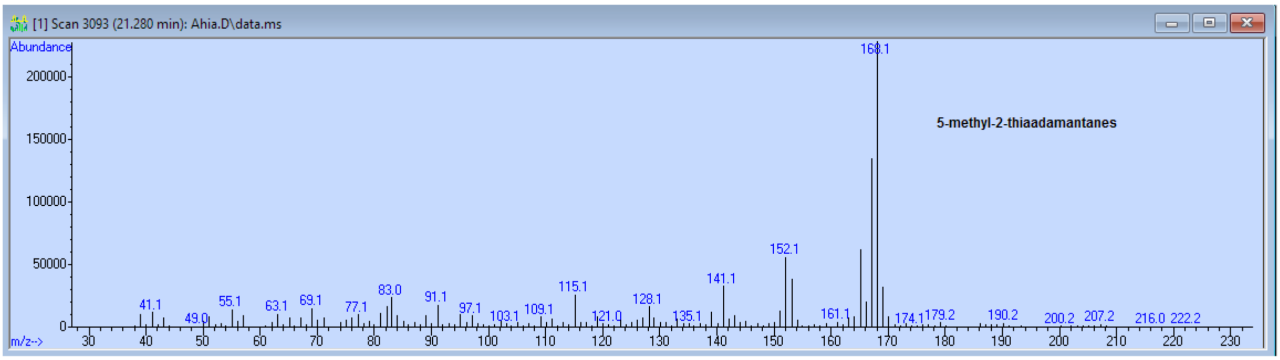


Figure 6: Mass spectra for 1-methyl–2–thiaadamanatane for Ahia oil

The results generated for this study is made up parametric ratios that have been obtained from the percentage report (Table 1).

Table 1: Parametric ratios generated from the percent report. 2-Thia=2-Thiaadamantane, AD=Adamantane, 1-Methyl =1-Methyl-2-thiaadamantane, 5-Methyl = 5-Methyl-2-thiaadamantane, DBT=Dibenzothiophene, P= Phenanthrene. Na= None applicable.

Wells	2-Thia/AD	5-Methyl/AD	1-Methyl/AD	DBT/P
Ahia	19.46	31.62	10.76	0.19
Nembe	8.12	12.79	4.93	0.82
Kolo Creek	0.11	0.16	0.07	9.14
Obagi	20.38	na	na	0.04
Oluma	9.34	3.22	2.37	na
Utorugu	8.89	15.59	5.83	0.01
Soku	2.29	3.27	2.28	na
Abo	na	8.01	2.63	0.64
Escravos	1.11	1.59	0.50	2.36
Afam	na	na	na	5.68
Umutu	na	na	na	46.88

The DBT/P values showed that Umutu had the highest value. Earlier studies had postulated that high values of DBT/P ratios are potential indictors of reservoir souring [8-9]. However, the ranges of values above 0.7 had been used as a reference for reservoir souring [9]. The study showed that soured oils had very high organic sulphur compounds with Dibenzothiophene bearing the highest percentage [8]. Values of DBT/P for soured oils were in the range of 6.6.

Niger Delta oils in this study have variable values of DBT/P, values ranges from 0.01 to 46.88. oil samples for which the DPT/P is higher than 0.80 are Nembe Creek, Kolo Creek, Escravos, Afam and Umutu. By the values of DBT/P ratios, the named oil samples are the ones that have undergone souring for the suite of samples used for this study.

Possible Proxies for Reservoir Souring

Proxies for reservoir souring infers possible parametric ratios of biomarkers that could be applied as indicators of reservoir souring in Nigeria oils. Adamantane which occurs in oils are highly stable against most in–reservoir processes including biodegradation, water washing, and evaporative fractionation [13]. However, studies have shown that 2–thiaadamanatane increases with TSR occurrence (souring process) in the reservoir, in their study demonstrated that there was increase in thiaadamantane concentration resulting from the reaction of elemental sulphur with adamantane, under to TSR conditions [3]. In this study the Dibenzothiophene, 2–thiaadamanatane, 5–Methyl-2-thiaadamantane and 1–Methyl-2-thiaadamanatane were related to each other on a 2D–plots.

Figure 7 is a plot of Dibenzothiophene/Phenanthrene and Dibenzothiophene/Adamanatane, the shows a fair correlation between the two ratios. Despite the source the possible source contribution effect on the Dibenzothiophene/Phenanthrene ratios it bears a fair relationship with the Dibenzothiophene/Adamanatane ratios which expresses the possible effect of souring which contributes to the presence of Dibenzothiophene in oils relative to the fact that Adamanatane are fairly stable in oils [8]. Hence increases in the ratio of Dibenzothiophene/Adamanatane of should indicate a souring process that produces H_2S which in turn generates Dibenzothiophene possibly from biphenyls [9]. There is a greater susceptibility to generation of Dibenzothiophene relative to the used up of Adamantane for generation of thiaadamantane.

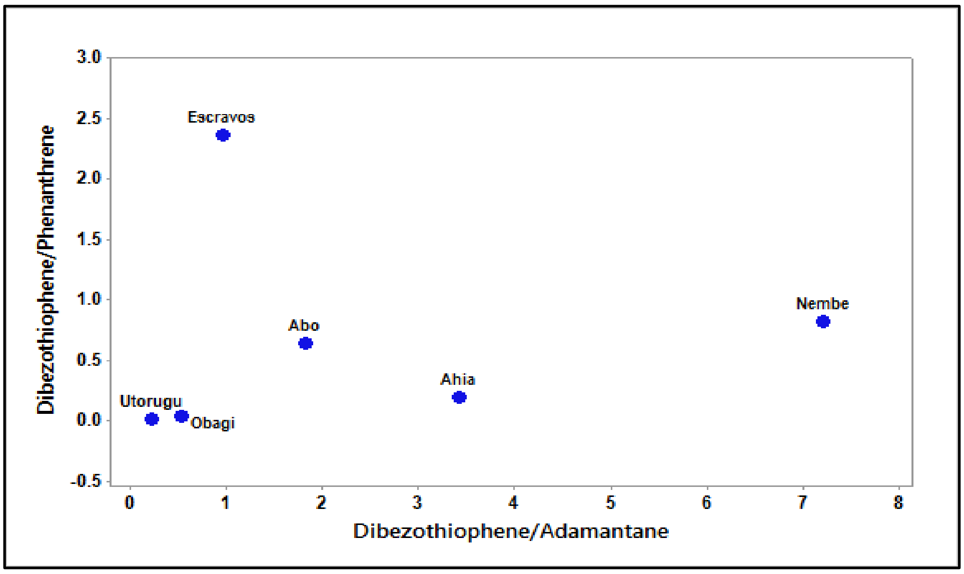


Figure 7: Plot of Dibenzothiophene/Phenanthrene and Dibenzothiophene/Adamanatane

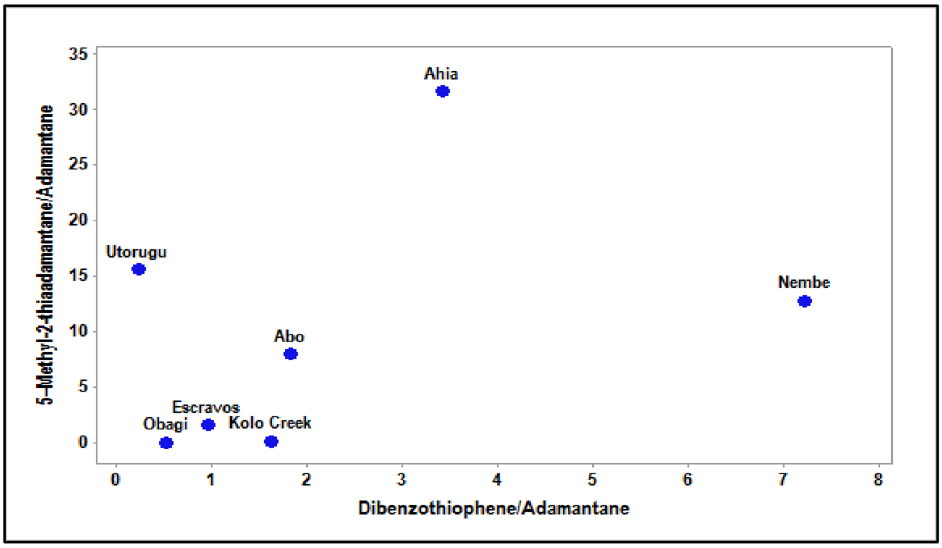


Figure 8: Plot of 5–Methyl-2-thiaadamantane/Adamantane and Dibenzothiophene/Adamanatane

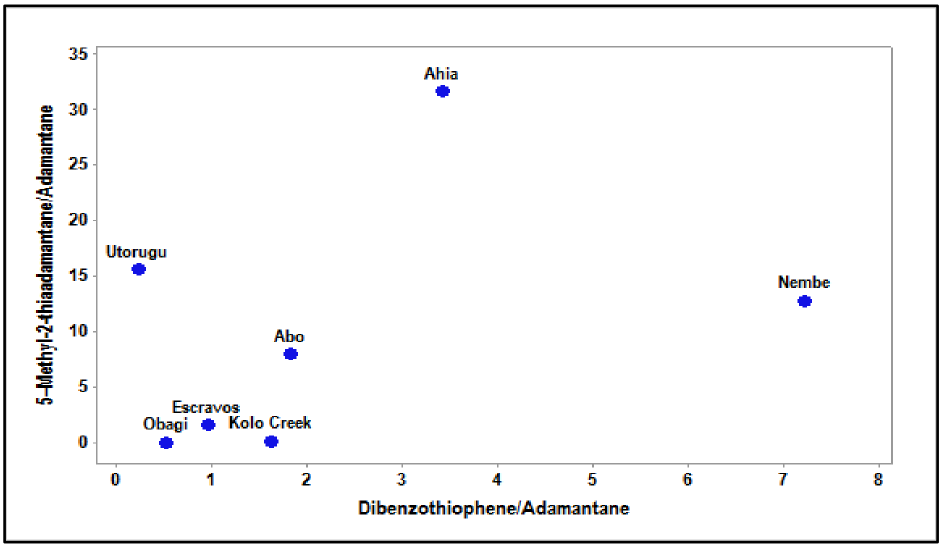


Figure 8: Plot of 5–Methyl-2-thiaadamantane/Adamantane and Dibenzothiophene/Adamanatane

Figure 8 is a plot of 5–Methyl-2-thiaadamantane/Adamantane and Dibenzothiophene/Adamanatane, the shows a fair correlation between the two ratios. The plot rationally corroborates the presence of 5–Methyl-2-thiaadamantane relative to Dibenzothiophene in the oils. the presence of 2–thiaadamantane in oils has been used as TSR indicator or molecular fingerprint for souring processes [14].

5–Methyl-2-thiaadamantane in oils has been attributed to modification of diamondoidthiols and they are only present in TSR altered oils while Dibenzothiophene is postulated to be generated from Biphenyls and occurs in elevated amounts in TSR alter oils [4,8,9]. Since both compounds are products of reservoir souring, though produced via different mechanism and rates, may correlate fairly. Figure 8 shows a fair correlation between 5–Methyl-2-thiaadamantane and Dibenzothiophene. This may serve as a tool for confirming that the high occurrence Dibenzothiophene in Nigeria oils could be indicator for reservoir souring if it has a fair to excellent correction in a 2D plot as in figure 7. The trend of the plot shows that Ahia and Nembe Creek samples are the most soured while Obagi is the least soured.

Figure 9. is a plot of 2-thiaadamantane/Adamantane and 5–Methyl -2-Thiaadamantane/Adamantane. Essentially it's a tool for corroborating 2-thiaadamantane and 5–Methyl -2-Thiaadamantane.

2-thiaadamantane is formed by the replacement of a carbon atom by a sulphur atom, while the 5–Methyl -2-Thiaadamantane is formed by bridgehead-alkylation of 2-thiaadamantane. The occurrences of 2-thiaadamantane in oils has been accepted as an indication of reservoir souring [14]. However, the occurrence 5–Methyl -2-Thiaadamantane which has been postulated to be derived from alkylation of 2-thiaadamantane, which should bear some degree of corroboration between the two compounds, inbid to exam this possibility, figure 9 is considered.

Figure 9 showed a significant correlation between 2-thiaadamantane and 5–Methyl -2-Thiaadamantane. The trend in figure 8, shows that Ahia oil sample is the most soured, while Kolo Creek oil sample is the least soured sample.

Conclusion

Potential mechanisms for the reservoir within the Niger delta are thermochemical sulphate reduction for reservoir with temperature regime at 100ºC and bacterial sulphate reduction potentially for reservoirs with temperature at less than 100ºC. the fact that Niger delta has ferrogenious materials which scrub marine sulphur into pyrites, which could be a source of H_2S, the initial presence of H_2S would initiate and foster reservoir souring.

The GC–MS result show the presence of 2-thiaadamantane which has be accepted as an indicator of reservoir souring, however, earlier studies have shown increase Dibenzothiophene/Phenanthrene ratios which may indicate souring. The detected 2-thiaadamantane was identified by the extracted spectra which was confirmed by comparison with literature. Similarly, 5–Methyl -2-Thiaadamantane and 1–Methyl -2-Thiaadamantane were detected by m/z= 168 ion and identified via extracted spectra. Plot of 5–Methyl-2-thiaadamantane/Adamantane and Dibenzothiophene/Adamanatane correlated fairly for the suite of oils studied. This observation infers that the dibenzothiophene and 5–Methyl-2-thiaadamantane corresponding to indicating souring in the reservoirs for the corresponding oils. 5–Methyl-2-thiaadamantane and 2-thiaadamantane can only be found in reservoirs where souring occurs.

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