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Research Article

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Dibenzofurans and Methyldibenzofurans in Some Niger Delta Crude Oils.

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Abstract Dibenzofurans and methyldibenzofurans were examined in some Nigerian and UK oils, furans and their analogues are sensitive to and also indicates oxicity. Some oils were obtained and treated by dilution to 1uL/1µg of hexane/oil which was injected into the column of GC–MS equipment for whole oil analysis. The percent report and mass chromatograms for various samples were extracted for m/z 168 and 182. The values were obtained for the various peak areas and ratios and logs calculated. The different plots employed to delineate the data, show that most of the samples in distal offshore showed marine features, while some samples in the Greater Ughelli and Central Swamp depobelts which showed marine features had their depobelt deposited during eustatic high sea level which foster influxed and deposition of marine organic matter.

Keywords Dibenzofurans, Methyldibenzofurans, Crude Oils

1. Introduction

Furans and benzofurans are aromatic heterocyclics, they are aromatic compounds that contain oxygen atoms. They are also found in petroleum, in this context liquid petroleum (Crude Oils). Their precursors has been suggested to be polysaccharides, phenols (Born et al., 1989; 1999) lignin of woody plants (Fenton et al., 2007), and from biphenyls (Asif, 2010). Benzofurans and its alkylated series can be detected in petroleum crude oils and extracts of rocks especially source rocks (Fan et al., 1990, 1991; Radke et al., 2000; Nabbefeld, et al., 2010). Some C_2-DBF isomers including nine dimethyldibenzofurans (DMDBFs) and two ethyldibenzofurans (EDBFs) have been tentatively identified (Armstroff, 2004; Li et al., 2015).

Dibenzofurans (DBFs) are essential molecular markers in organic geochemistry in some cases diagonistic. The occurrence and distributions of DBFs in sedimentary rocks are related to depositional environment and organic matter type of the source rocks (Fan et al., 1990, 1991; Radke et al., 2000; Li et al., 2013; Li and Ellis, 2015). DBFs are generally more abundant in freshwater source rocks, coals and terrestrial/terrigenous crude oils, they generally occur in more oxic (more oxygen sufficient) environment than their sulfur-heterocyclic counterparts (dibenzothiophenes). Contemprory studies indicates that the presence of DBFs in oils can be controlled by subsurface secondary migration processes of oil (Li et al., 2011; Li and Ellis, 2015). Since they are attractive to the clay minerals on the inner walls of their migratory pathways. However, the application of DBFs in organic geochemistry is less common than their sulphur conterparts. Their migration can portray the form of geochromatography.

Oils from Liaohe and Beibuwan basins with terrigenous organic precursors and nearshore /coastal depositional environment were richer in 2–and 3–MDBF over 4–and 1– MDBF. The 4–and 1– MDBF are observed to be rich in marine samples. The plot of (1+4)/(2+3)–MDBF against pristane/phytane {(Pr)/(Ph)} has been suggested for delineating depositional environment/organic precursors and lithologies.

2. Geology of Niger Delta Basin

The Niger Delta Basin has been proposed to have been deposited in Mega Sequences between 5 to 10 millions years apart. The Niger Delta has the features of a continental slope, the sediment on a slope will slide down to rest and commence accumulation, once the angle of repose has been exceeded. The mega sequences are known as the depobelts (Reijers, 2011). Each depobelt is assumed to have had particular terrain that could have foster deposition of particular organic matter. Since the depositional environment is coastal in nature, near similar environment may always appear but with organic precursors that are different in composition as the opening of the Southern Atlantic fosters a wider demensions. The sedimentary mechanism of the Niger Delta is described by the Escalator regression Model (Knox & Omatsola, 1987), which is a function of rate of deposition and rate of subsidence resulting in the progradation of the Delta seaward (Evamy et al., 1978). Generally, the Niger Delta varies from Marine, into Paralic and into Continental Northwards (Oboh,1992a). However, the depobelt varies with the eustatic sea level changes of varied duration.

The Northern depobelt was deposited by sediments from the Abakaliki high and South of the Anambra Basin in the Middle –Late Eocene, characterized by falling sea level. Sediments of the Late Eocene to Middle Oligocene formed the Greater Ughelli depobelt during the rising sea level. In the Middle–Late Miocene the high hinterland was the source of sediment that accumulated into the Central Swamp and the Northern sector of the Coastal Swamp during low sea level. In the Late Miocene–Early Pliocene, the Coastal Swamp (partly low sea level) and Offshore were deposited during high sea level and eventual incession events caused the Agbada, Soku and Afam channels (Reijers, 2011).

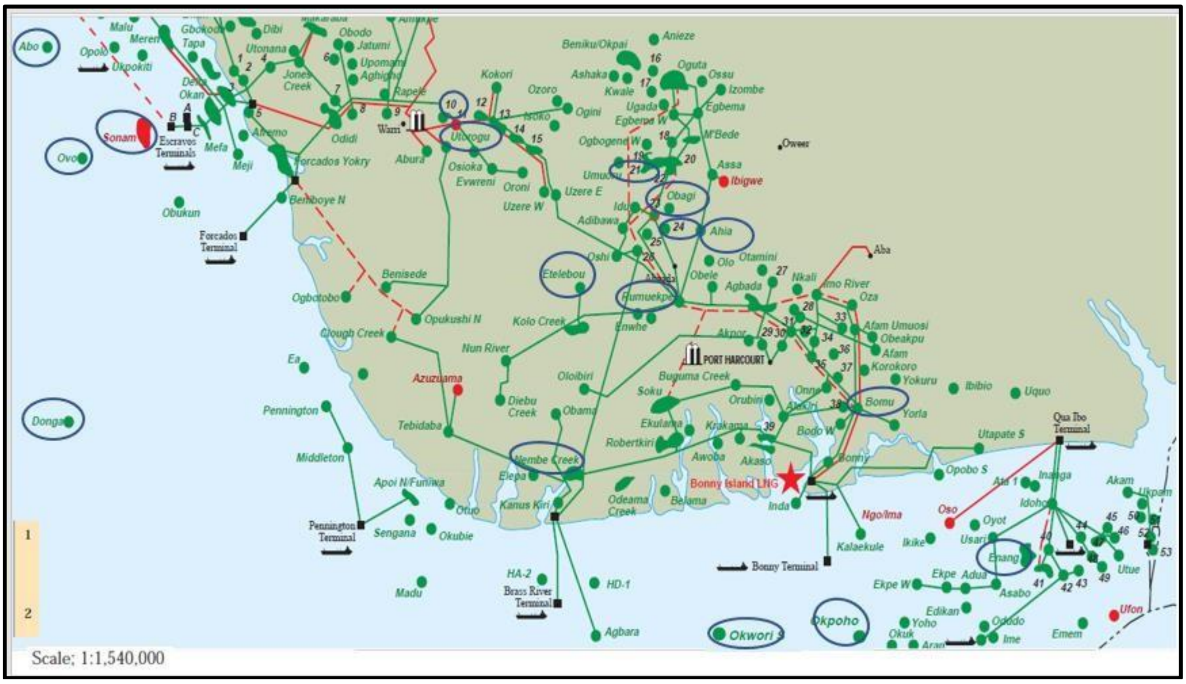

Figure 1: Map of Location of Oil fields from which samples were obtained. (Oil fields in blue circle).

3. Results and Discussions

Table 1: logs ratios of dibenzofuran and dibenzothiophene and methyldibenzofuran

OILS	Log DBF	Log DBT	Pr/Ph	(1+4)/(2+3)	Log(1+4)	Log(2+3)
NEMBE 11	5.96	6.35	2.77	1.05	6.12	5.17
NEMBE 12	5.68	4.78	2.6	1.10	6.04	6
EGBEOMA	4.84	5.32	0.75	1.65	5.29	5.07
ETELBOU	4.63	4.31	2.01	1.77	5.12	4.87
GBARAN	3.67	4.46	2.08	2.09	4.38	4.06
OKPORHUI	5.15	4.52	1.9	1.97	5.69	5.39
OKWORI	3.47	3.7	4.61	1.96	4.48	4.16
OVHOR	4.54	4.02	1.76	2.92	5.29	4.82

SONAM-1	4.8	5.21	1.63	2.51	5.16	4.76
SONAM-2	3.63	4.27	2.85	1.60	4.87	4.47
SONAM-3	3.44	3.23	0.63	3.55	4.46	3.91
UGHELLI 1	4.13	4.74	1.04	1.58	5.06	4.86
UTOROGU 1	3.42	3.42	1.69	1.90	4.74	4.46
S-6	5.75	6.25	1.2	1.36	6.19	6.06
OBIAFU-2	5.18	4.1	3.12	2.13	5.05	4.73
OBIAFU-6.	5.1	4.14	3.4	2.26	4.99	4.43
OML 61-1.	5.11	4.38	3.88	2.00	4.93	4.63
OML 61-6.	5.1	4.39	2.93	2.19	4.96	4.62
OGBAGI 2	5.09	4.11	3.51	2.24	4.91	4.57
OGBAGI 6	5.34	4.17	2.97	1.90	5.21	4.93
BRENT 1	4.75	5.35	1.21	1.14	4.98	4.92
BONGA 1	4.71	4.19	2.16	1.26	5.15	5.05
ABO 1	4.28	4.55	2.62	2.48	4.63	4.24
USAN 1	4.27	3.93	1.73	1.87	4.73	4.46
RUMUEKPE 1	3.92	4.1	1.91	2.13	4.17	3.84
UTOROGU 2	5.16	4.01	1.32	1.60	5.64	5.43
NORTH SEA 1	4.75	5.35	1.4	1.14	4.98	4.92
MILLER 1	3.3	5.29	1.4	1.00	3.98	3.98
BOMU 1	4.83	5.37	2.04	0.95	5.05	5.07
AHIA	5.19	6.7	2.71	1.10	5.5	5.46
Deeper Offshore	4.89	6.67	1.94	1.28	5.43	5.32
Shallow Offshore	4.97	5.31	2.32	1.29	5.23	5.12

Table 1. presents the result of extractions from GC–MS (Gas Chromatography–Mass Spectrometry) percent reports of m/z 184 for dibenzothiophene and m/z 168 for dibenzofuran and 182 for methyldibenzofuran. These samples consist oils from different depobelts, the objective of this study is to examine potential differences in the distrubution of the dibenzofuran and methyldibenzofuran in oils of the Niger Delta Basin on the bases of its sedimentology, specifically its depositional pattern, using the depobelt concept.

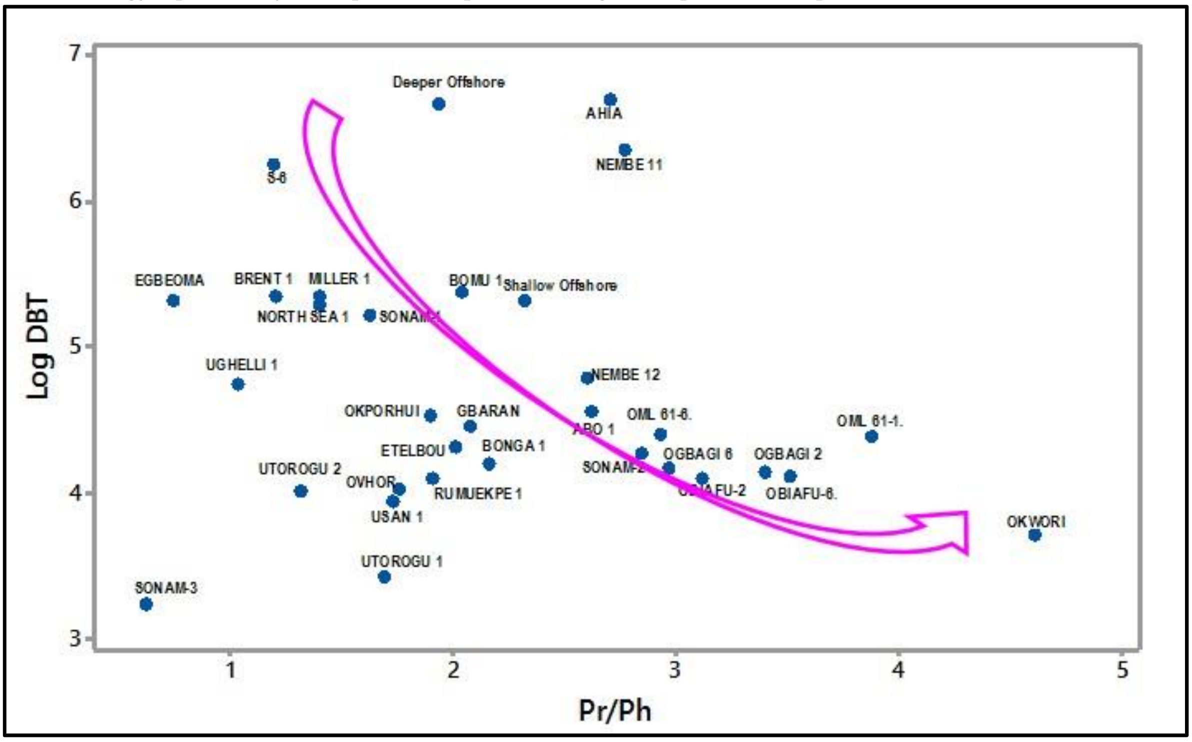

Figure 2: Plot of Log DBT against Pr/Ph

Figure 2 is a plot of log Dibenzothiophene (DBT) against Pr/Ph, dibenzothiophene is diagonistic for marine environments, higher values of DBT indicates higher degree of marine environments, sulpur will be high in near marine environments such as the Niger Delta continental where there are no enough Iron (Fe) in ferroginous soils that are runoffs into the continental slopes, the arrow indicates decreasing marine condition and increasing oxicity of the environment in the direction of the arrow. Samples such as Okwori may have more terrigenous matter due to the incisions that occur resulting in the formation of Qua Iboe Channel that provided sufficient supply of continental run offs towards the glacial eustacy, when there may be no current and marine flux that will ferry the marine organic precursors from the open sea.

Figure 3 is a plot of the sum of logs 1–Methyl and 4–Methyl dibenzofuran against Pristane/Phytane (Pr/Ph). The sum of logs 1–Methyl and 4–Methyl dibenzofuran is observed in other studies to be rich in marine samples the plot show a close similarity in terms of the distribution and discrimination of the samples relative to figure 2.

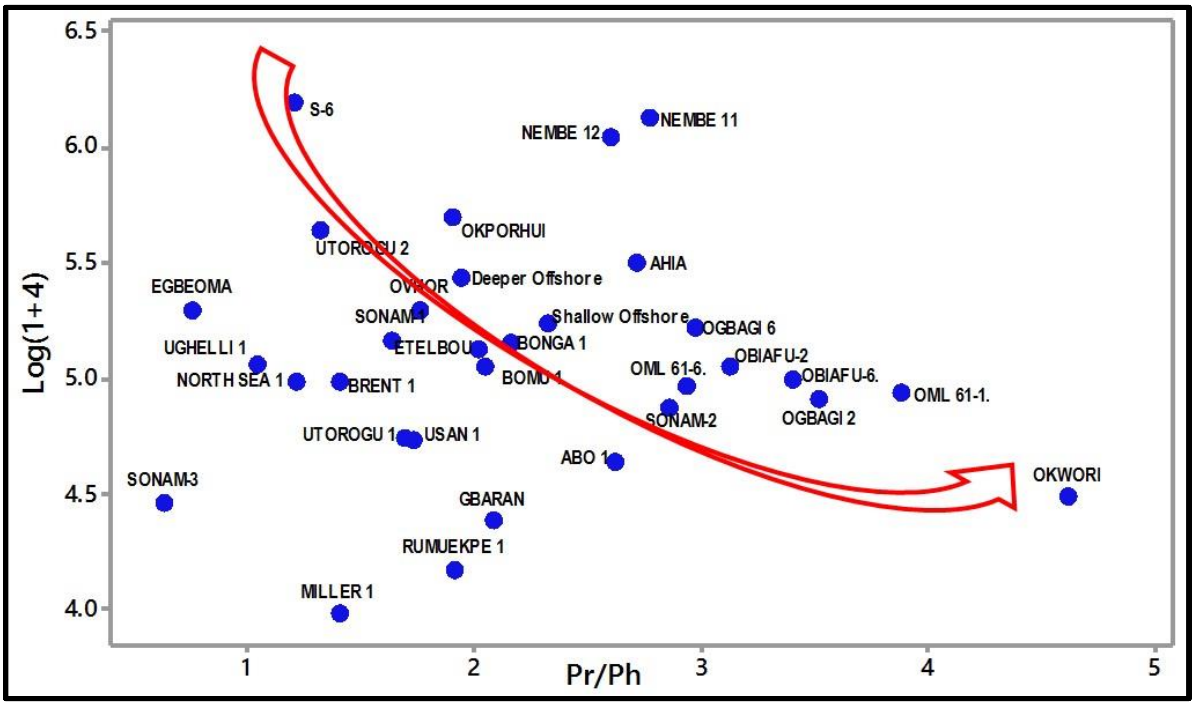

Figure 3: A plot of the log of the sum of 1–Methyl and 4–Methyl dibezofuran against Pristane/Phytane (Pr/Ph) ratio.

Sample such as Okwori could be explained with reference to its eailer elucidation in previous passage. The Nembe, Sonam, Ovhor, Brent, Miller, NorthSea are fairly consistent in both figures 1 and 2. Brent, Miller and NorthSea samples are from the United Kingdom where the environment of deposition is mainly marine to deep marine. Sonam, Ovhor, deep offshore, shallow offshore, and Usan are offshore samples which are located close to channels that supply terrigenous organic precursors, however their environment is marine and could be favoured by infux of marine organism driven by the coriolis force that fosters upwelling within the coastal, nearshore environment within the West African Coast.

Figure 4. is a plot of the log of the sum of 1–Methyl and 4–Methyl dibezofuran against log Dibenzothiophene both parameters are indicators of environment of deposition and are specifically sensetive for marine environment. Oils that have their origin from marine environment is rich in 1–methyl dibenzofuran and 4–methyl dibenzofuran and suphur from marine volcanoes. The high sulphur which is reflected on the dibenzothiophene is due to lack of supply of Iron via continental run offs as ferroginous sediments for scrubbing sulphur (Pepper and Corvi, 1995).

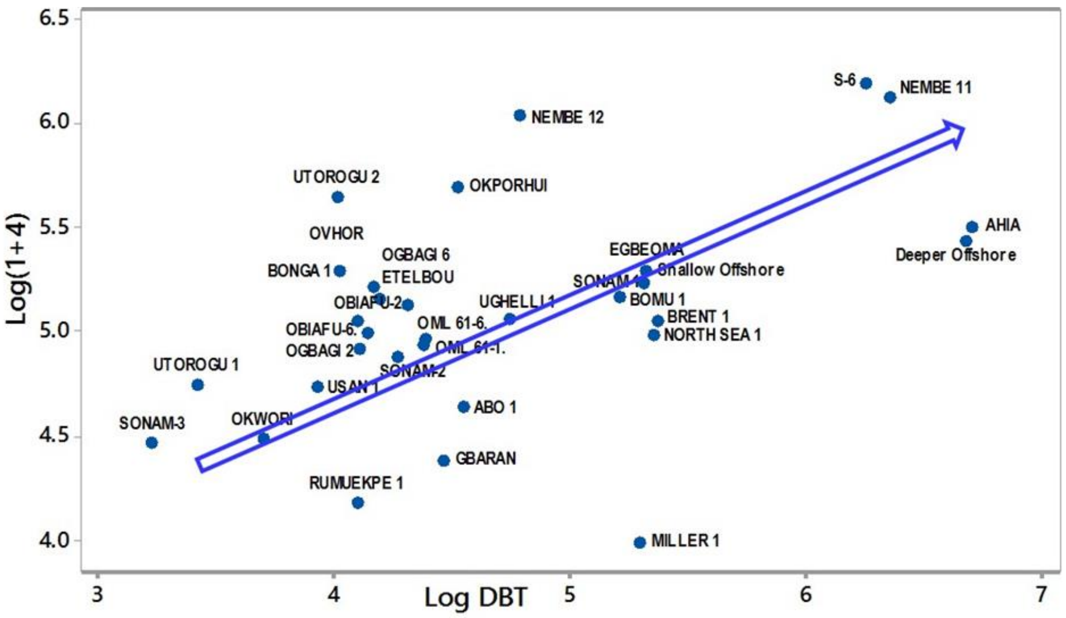

Figure 4: A plot of the log of the sum of 1–Methyl and 4–Methyl dibezofuran against Dibenzothiophene

Thus, samples with high dibenzothiophene had their organic precusors deposited in distal environment from nearshore/coastal environment. In figure 4, Samples from the Greater Ughelli and and Lower Central Swamp depobelt such Bomu, Ughelli, Obiafu, Gbaran, Egbeoma normally show abit marine features because their organic precursors were deposited during eustatic high sea levels in the Middle– Late Miocene and Late Miocene–Early Pliocene respectively which fosters influx and deposition of marine organic precursors for the suite of oil studied. Figure 5 is the plot of the ratio of the sum of 1 and 4 methydibenzofuran to the sum of 2 and 3 methyl dibenzofuran against Pr/Ph ratio. The plot shows that for all samples the the sum of the 1 and 4 methyl dibenzofuran is higher than the sum of 2 and 3 methyl dibenzofuran implying greater marine contributions from the stand point of the isomers of methyl dibenzofuran for the suite of oils studied. The factors to this observations may vary from high eustatic sea levels to distal environments of deposition. Samples such as Sonam 1, Ovhor, Abo1 may be due to distal environment of deposition, where there is less contributions of terrigenous materials, while samples such as Rumuekpe, OML 61s Ogbagi, Obiafu, Gbaran, Etelebou may be due to high eustatic sea levels during the depositions of the corresponding depobelts/megasequences.

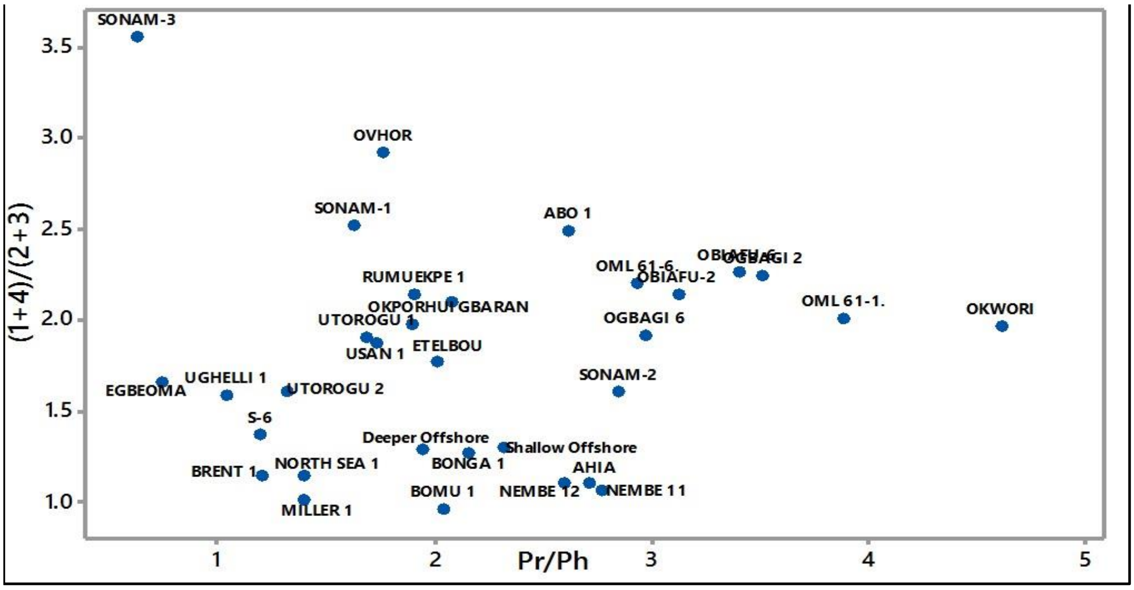

Figure 5: A plot of the ratio of th sum of 1and 4 methydibenzofuram to the sum of 2 and 3 methyl dibenzofuran against Pr/Ph ratio.

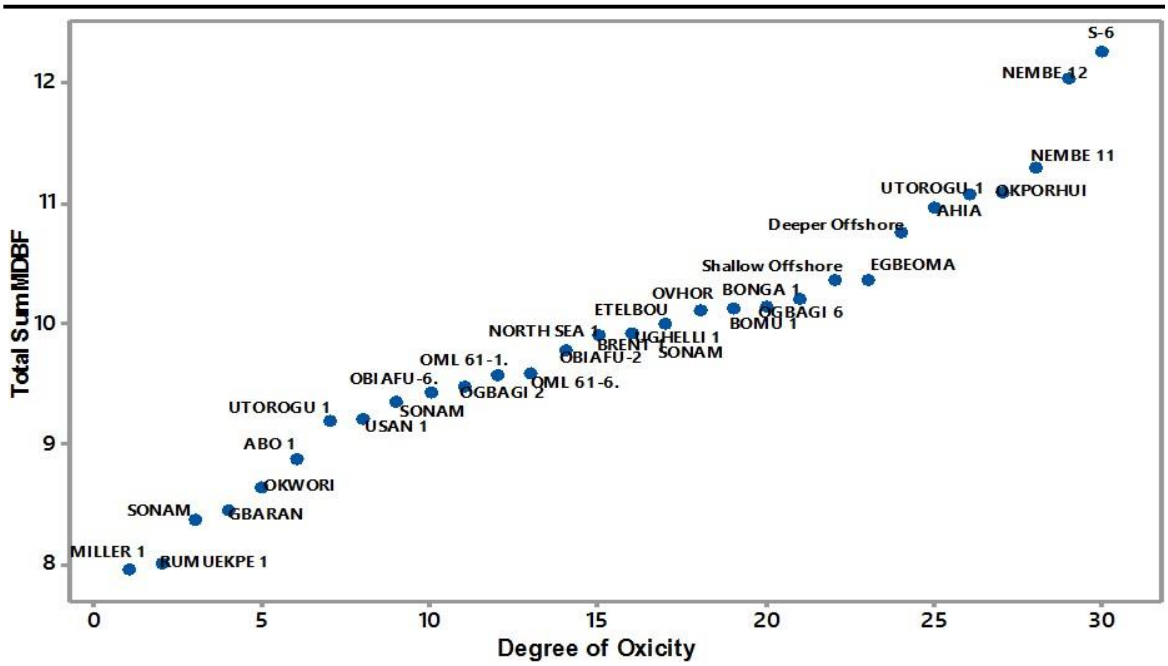

Figure 6: A plot of the sum of Methyl Dibenzofuran aganist Degree of Oxicity

Figure 6 is a plot of the sum of Methyl Dibenzofuran and Degree of Oxicity. it should be noted that methyl dibenzofuran indicates oxicity however, the 1 and the 4 isomers are more in marine environments relative to nearshore, coastal or shallow marine environment. The total which is the sum of 1+4+2+3 isomer are in increasing value reflecting oxicity. From figure 6, it can be observed that samples such as Sonam, Abo1, Okwori, and Usan1 are offshore samples in distal environments and clusters with Miller which is a UK sample known to be Marine this confirms to an extend their partly marine nature while samples such as Rumuekpe, Gbaran, Utorogu1 could have marine feature due to the deposition of the Greater Ughelli megasequence during eustatic high sea level which could have ferried marine organism for deposition in the Middle–Late Miocene for the suite of oils studied.

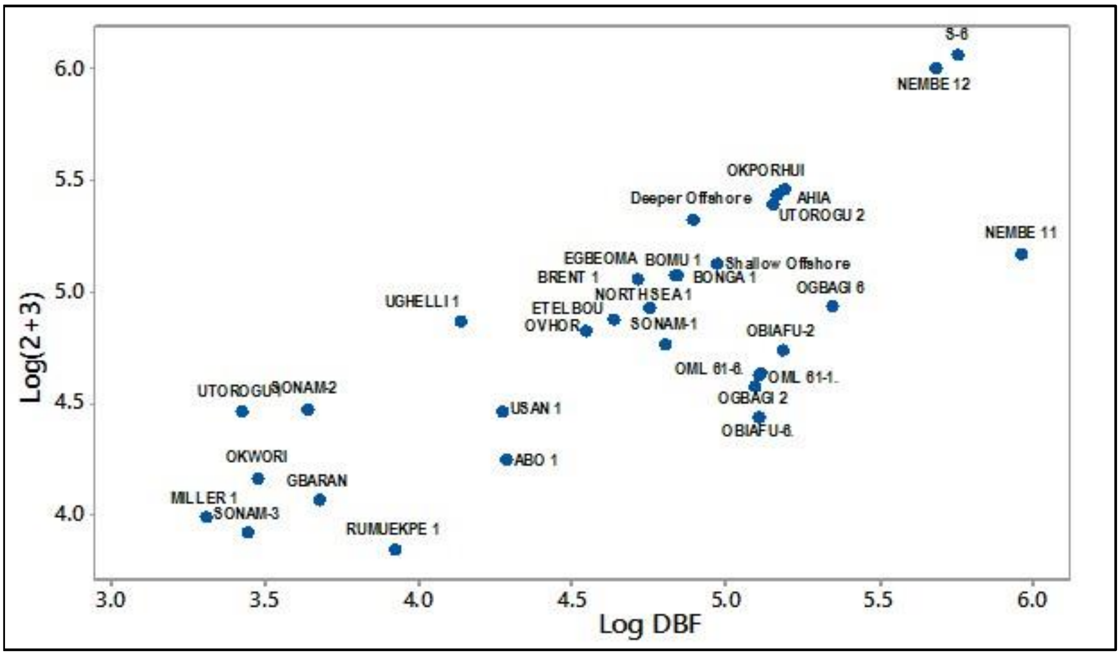

Figure 7: The log of the sum of 2–Methyl and 3–Methyldibenzofuran and log of dibenzofuran

Dibenzofuran and Methyl dibenzofuran are sensitive to Oxicity of the media or environment in which the organic precursors were deposited. Both parameters in figure 5 indicates oxicity, the cluster of samples in the lower left corner of figure 7 indicates more marine than oxic samples, while samples in the upper right corner indicates more oxic than marine samples. The cluster in the middle together with the non Nigerian samples such Northsea1, Brent1 and Miller show samples with terrigenous contributions but in Marine environments. The plot of figure 7 looks scattered, but, intricately maintains the order as in figure 6.

Conclusion:

The study on the distribution of dibenzofuran and methyldibenzofuran in some Niger delta oils shows some confirmity with ealier studies on the fact that the parameters are sensistive to oxicity. The mixed with marine oils from United kingdom help to recognize that some samples from the hinterland of the Niger Delta Basin that had marine charcteristics were due to the deposition of the depobelt during eustatic high sea level that fostered influx and deposition of marine organic matter.

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