Geochemical Evaluation of the Source of Mystery Oil Spill Impacted at Imo-River, Niger Delta, Nigeria

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Abstract

Sediment samples contaminated with mystery oil spills at the Imo-River (South East, Nigeria) were collected and analyzed for biomarkers as well as Vanadium and Nickel metal contents using GC-FID and AAS respectively. Similar analyses where also carried out for three crude oil samples from three oil wells labelled A, B, and C. These wells are located near the study area. Geochemical evaluation on the data taken from the analyses revealed that samples from the study area have; the range of pristane and phythane ratios of 2.50-3.77, carbon preference index (CPI) of 1.15, range of Vanadium to Nickel ratio (V/Ni) of 0.035 - 0.103 and a positive rank correlation value with Total Petroleum Hydrocarbons (TPHs) of 0.30 with crude oil samples from well C. The information obtained from data gathered via analyses of samples from the study area proved positive correlation with crude oil source C.

Keywords: Biomarkers, Carbon preference Index, pristane / phythane ratio, Vanadium-Nickel ratio, Total Petroleum Hydrocarbons (TPHs)

1. Introduction

The problems of oil spillage constitute severe effects, not only to the environment of impacted oil spills, but also to the industry. Most communities in the Niger Delta region of Nigeria have had their sources of livelihood contaminated or polluted by spilled oil. There are cases of abandoned farmlands, fishing ponds, quality sources of drinking water and even ground water due to contamination as a result of seepage of spilled oil into the subsurface.

Consequently, oil companies have incurred so much financial lost cleaning up and maintaining damaged facilities that depict oil spills.

In cases of mystery spills, where the source of spillage is unknown, a prompt and accurate technique (petroleum fingerprinting) could be applied to identify the sources of petroleum contaminants (Osuji *et. al.* 2006). Identification of these parties is critical for owners of petroleum contaminated sites who are seeking to spread liability by identifying owners or operators of nearby facility which may be the source of the spill and thus be responsible for the petroleum contamination at these sites. This issue is also critical for those potential defendants who will seek to demonstrate that the petroleum products associated with their activities may not be the source of the contamination in question. It is also critical in situations where multiple parties seek to equitably allocate among themselves shares of contamination and associated clean-up costs. Petroleum fingerprinting technique involves the analysis of the released oil with a gas chromatography (GC) and measuring the hydrocarbon compounds it contains (Osuji *et al*., 2006). The objective is to obtain the less volatile and uneasily degraded fractions of crude oil called biomarkers such as n-paraffins, isopreniods, triterpanes, steranes , porphyrins as well as low and high molecular weight polycyclic aromatic hydrocarbons (PAHs) which are said to be source specific. From the chromatogram obtained, qualitative method (visual comparison of chromatograms) as well as quantitative techniques of calculating pristane-to-phytane (pr/ph) ratio, PAHs diagnostic ratio, carbon preference index (CPI) and correlation coefficient (statistical analysis) of data obtained from GC could be used for source identification (Tissot and Welte. 1984; Osuji *et al.,* 2006; Treibs, 1934).

Of the three stages of crude oil formation (diagenesis, catagenesis and metagenesis), the first and second stages have immense contribution to the bases of this work, as the carbon skeleton of the organic matter worked up on by microorganisms in the first stage of petroleum formation is stilled retained at the second stage after crude oil has been formed (Osuji, 2011and Meinschein, 1959). This could be seen from examples of biomarkers and precursors shown in the figure below:

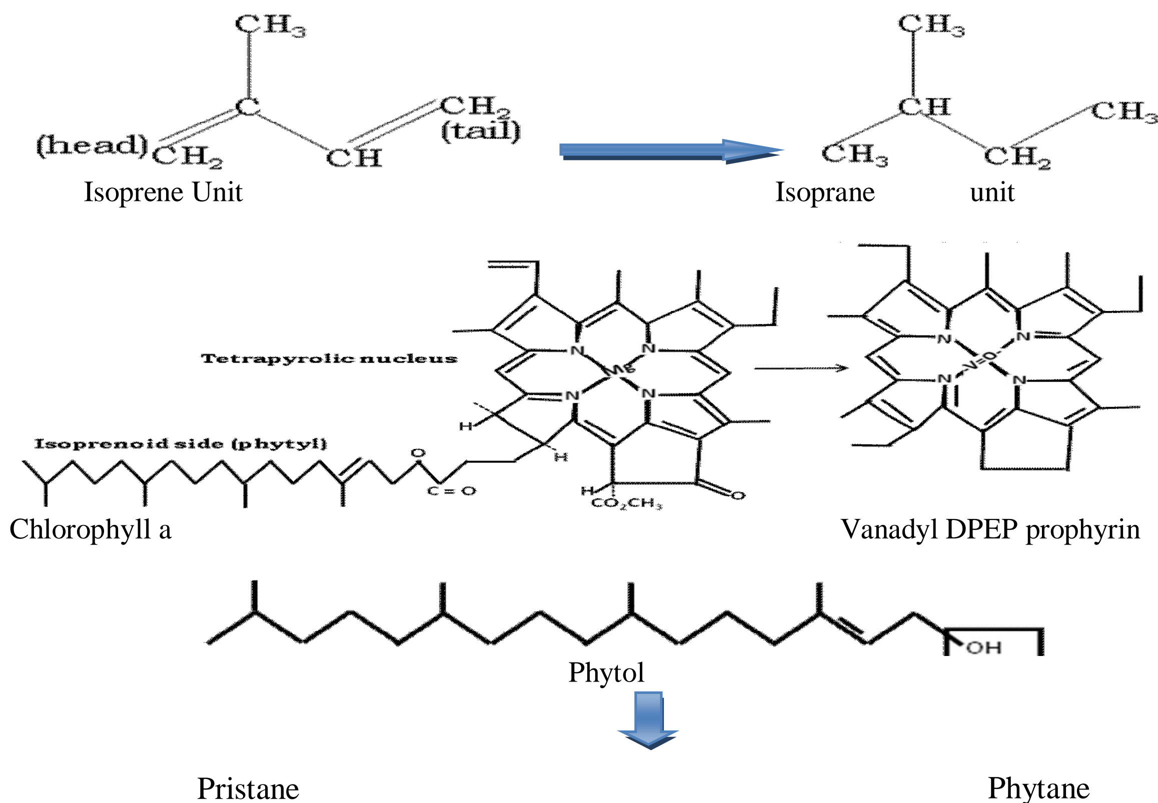

Figure 1: Relationship between Precursors and their resulting Biological or Geochemical Markers

Biological or geochemical markers are compounds and classes of compounds found in crude oil which are diagenetic alteration products of specific natural products and are structurally similar to the specific natural products of their origins (Hunt, 1975). They have their molecules being unchanged or having suffered only minor subsequent changes with preservation of the carbon skeleton (Tissot and Welte, 1984).

The precursors of biomarkers are mainly plant and animal sources. A wide range of linear or cyclic compounds, formally built up from several isoprene units is known in living plants and bacteria and to a smaller extent in animals. The double bonds of isoprene are lost and yield isoprene, the magnesium atom in chlorophyll a which is substituted for vanadium atom in vanadyl prophyrin as well as the carbon skelenton in phythol which are retained in compounds of pristane (2, 6, 10, 14-tetramethylpentadecane) and phythan(2, 6, 10, 14-tetramethylhexadecane) (Blumer *et al.* 1963; Treibs 1934; Brassell and Eglinton, 1986).

2. *Materials and Methods*

2.1 Sample Collection and Map of Study Area

Surface sediments of Imo River were collected on 15th December, 2009 at the located stations IRW_1,IRW_2,IRW_3,IRW_4, and IRW_5 (Tab.1,Fig.2 and, Fig. 3) along the Warife Community, Oruk-Anam Local Government Area of Akwa Ibom State, Nigeria; after the river system had been impacted by a mystery oil spillage on 12TH December, 2009. The sampling was done using the Van Veen grab sampler. This apparatus takes a sample of about 0.1 m^2 and penetrates a depth of 15 cm depending on the texture of the sediment.

It has two small trap doors in the top that was used to inspect the condition of the sample before the grab was open after visualizing to ensure that the sample was collected in an undisturbed state and to determine if water was present on top of the sample. The presence of water was siphoned off with a glass tube or slowly drained off so as not to wash the sample unduly (Loring and Rantala, 1992).

To ensure a representative sample, about 100g of the surface sediment was taken from five different locations or stations, with the five sample locations taken with a GPS reading as shown in table 1. The collected samples were placed in a labelled polyethylene vial (labelled IRW_1, IRW_2, IRW_3, IRW_4 and IRW_5), sealed and frozen for transportation to the laboratory, where they were air dried.

2.2 Gas Chromatography Analysis of PAHs and TPHs

The samples were dried, crushed and sieved using 0.5 mm sieve. 2.0±0.1 g of samples were weighed into a clean extraction container. 10 ml of extraction solvent (pentane) was added into the samples and mixed thoroughly and allowed to settle. The mixtures were carefully filtered into clean solvent rinsed extraction bottles using filter paper fitted into Buchner funnels. The extracts were concentrated to 2ml and then transferred for "clean up/separation".

1cm of moderately packed glass wool was placed at the bottom of 10 mm, ID x 250 mm long chromatographic column. Slurry of 2 g agitated silica gel in 10 ml methylene chloride was prepared and placed into the chromatographic column. To the top of the column was added 0.5 cm of sodium sulphate. The column was rinsed with addition of 10 ml methylene chloride. The column was pre-eluted with 20 ml pentane; this was allowed to flow through the column at a rate of about 2 minutes until the liquid in the column was just above the sulphate layer. Immediately, 1 ml of the extracted sample was transferred into the column, the extraction bottle was rinsed with 1 ml pentane and added to the column as well.

The stop-cock of the column was opened and the eluent was collected with a 10 ml graduated cylinder. Just prior to exposure of the sodium sulphate layer to air. Accurately measured volume of 8 – 10 ml of the eluant was collected and labelled "Aliphatic".

Following recovery of the aliphatic fractions and just prior to exposure of the sodium sulphate layer, the column was eluted with 1:1 mixture of acetone and methylene chloride in 1 – 2 ml increments. Another accurately measured 8 – 10 ml of the eluant was collected and was labelled "Aromatics". The "Aromatic" fraction was concentrated to 1 ml for PAHs analysis (Table 2) using Gas Chromatography.

The extracted organic matter (EOM) was analysed by capillary gas chromatography to afford gas chromatograms from which the values of the total petroleum hydrocarbons (TPHs) which serve as biomarker parameters were obtained (Figure 5 and Table 3).

The gas chromatography was conducted on a Varian 3400 GC fitted with 45 m x 0.25 mm fused silica column coated with a non-polar stationary phase (DB1). Both the injector and detector temperatures were set at 300^oC. The oven heating programme was set at 30^oC initial isothermal period of 2 minutes then heating up at the rate of 6^oC/min to 300^oC followed by final isothermal period of 13 minutes. The carrier gas was hydrogen set at a flow rate of 2ml/min. collection and processing of GC data was initially by Atlas software via a chromatographic server. This afforded the respective gas chromatograms as well as the corresponding injection reports containing peak heights, peak areas and concentrations (Ekpo, 2010).

2.3 Atomic Absorption Spectrometry Analysis of the Concentration of Nickel and Vanadium

A digital chemical balance was used to weigh 2.0±0.5 g of each of five air dried sediment samples into five different beakers. One millilitre (1 ml) perchloric acid ($HClO_4$) and 3 ml of conc. HNO_3 were added to each beaker, stirred and allowed to heat for 15 minutes until gases disappeared in a fume cupboard. The samples were allowed to cool and made up to 100 ml with demineralised water then an aliquot of 50 ml was taken for AAS analysis using a Perkin Elmer A Analyst 200 AAS, with prepared standard of the analysed heavy metals and their hollow cathode lamps, the values of their absorption was recorded (Ekpo, 2005). The concentration of heavy metals (table 5) was calculated in mg/kg from the equation:

$$conc.(mg/kg) = \frac{absorbance\ of\ solute}{absorbance\ of\ standard} x \frac{vol.\ of\ solvent}{weight\ of\ sediment} \ldots\ldots.(1)$$

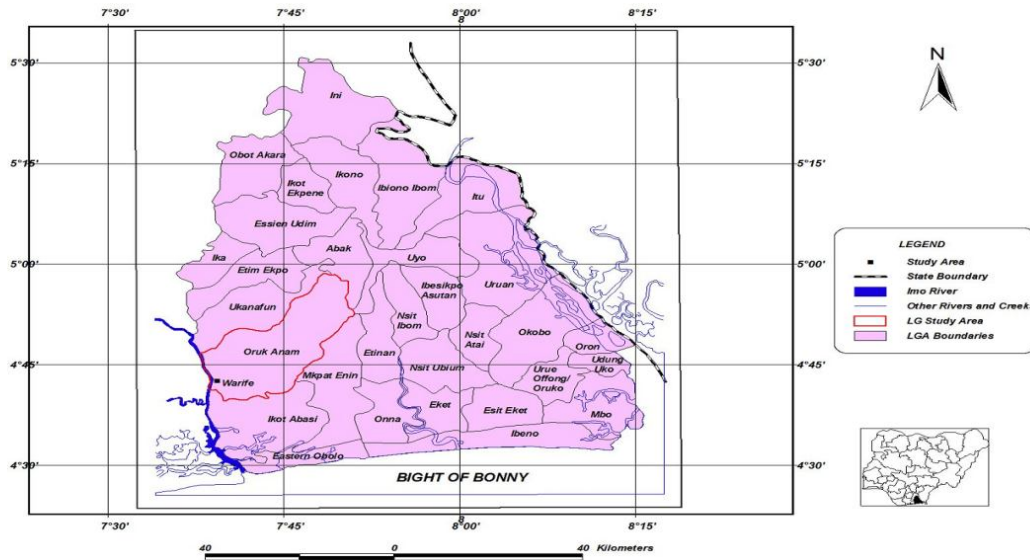

Figure 2: Map of Akwa Ibom State, Nigeria. Showing the study area Warife Community

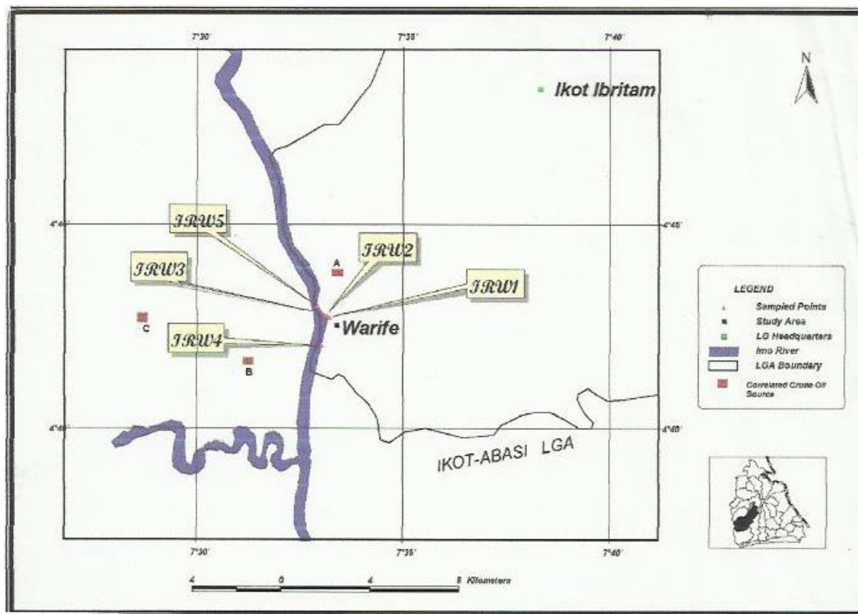

Figure 3: Enlarged Map of Study Area showing Sampling Points

3. *Result and Discussion*

Table1. Sampled Stations and Their Geographical Locations at the Imo River Study Site

Sampling location	GPS Reading
IRW_1	N04^0 42$'$ 44.3″ E004° 33$'$ 12.4″
IRW_2	N04^0 42$'$ 46.1″ E007° 33$'$ 02″
IRW_3	N04° 42$'$ 50″ E007° 33.01$'$ 02″
IRW_4	N04° 42′ 5.0″ E007° 32$'$ 52.7″
IRW_5	N04° 43$'$ 00.0″ E007° 32$'$ 55.5″

Table 2: Concentration of PAHs in Samples Measured in mg/kg

PAHs	IRW_1	IRW_2	IRW_3	IRW_4	IRW_5	MEAN	RANGE
Acenaphthene	BDL	BDL	BDL	0.72	BDL	0.72	0.00-0.72
Acenaphthylene	BDL	BDL	BDL	0.46	BDL	0.46	0.00-0.46
Anthracene	BDL	BDL	BDL	BDL	0.53	0.53	0.00-0.53
Benzo(a)pyrene	BDL	0.21	0.66	0.76	1.34	0.75	0.21-1.34
Benzo(b)flouranzthene	1.63	1.26	0.29	0.23	0.77	0.83	0.23-1.63
1,12-Benzoperylene	0.50	0.60	0.28	BDL	BDL	0.46	0.28-0.60
1,2,5,6Dibenzanthracene	0.31	1.26	1.09	BDL	0.23	0.72	0.23-1.26
Fluoranthene	BDL	BDL	BDL	BDL	1.81	1.81	0.00-1.81
Fluorene	BDL	BDL	BDL	0.84	0.44	0.64	0.44-0.84
Indeno(1,2,3)pyrene	0.29	1.96	1.56	BDL	1.42	1.31	0.29-1.96
Naphthalene	BDL	BDL	BDL	0.23	BDL	0.23	0.00-0.23
Phenanthrene	BDL	BDL	BDL	BDL	0.48	0.48	0.00-0.48
Pyrene	0.24	BDL	BDL	0.48	2.50	1.08	0.24-2.50
Benzo(k)flourathene	0.23	0.21	0.74	0.21	1.53	0.59	0.21-1.53

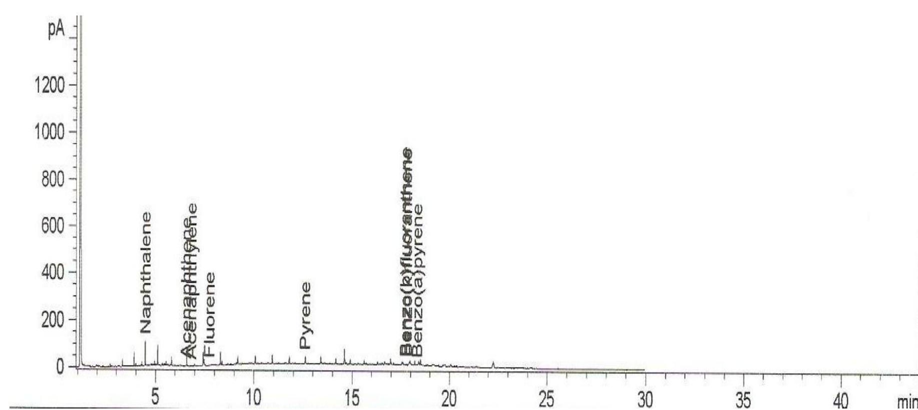

Figure 4: Chromatogram of PAHs at sampled Station IRW4

Table 3: Concentration of TPHs in Samples Measured in mg/kg

TPHs (mg/kg)	IRW_1	IRW_2	IRW_3	IRW_4	IRW_5	Mean	Range
C_{15}	0.0060	0.0130	0.0003	0.0070	0.0003	0.0053	0.0003-0.0130
C_{16}	BDL	0.1370	0.0183	BDL	0.0065	0.0539	0.0060-0.1370
C_{17}	0.1480	BDL	0.1305	BDL	0.0213	0.0999	0.0213-0.1480
Pristane	0.1218	2.0920	0.0100	0.3115	0.1198	0.5309	0.0100-2.0920
C_{18}	0.3200	1.1450	0.2935	0.1650	0.0260	0.3899	0.0260-1.1450
Phytane	BDL	0.6463	0.0031	0.0826	0.0479	0.2589	0.0479-0.6460
C_{19}	1.7480	0.9500	0.3960	0.2350	0.0258	0.6710	0.0258-1.7480
C_{20}	1.6860	1.5300	0.4319	0.2560	0.0209	0.7850	0.0209-1.6860
C_{21}	1.7100	1.7360	0.4204	0.3020	0.0280	0.8393	0.0280-1.7360
C_{22}	1.5910	1.9350	0.4257	0.3060	0.0292	0.8574	0.0292-1.9350
C_{23}	1.3930	2.0060	0.4062	0.2930	0.0315	0.8259	0.0315-1.3930
C_{24}	1.1830	1.7360	0.3678	0.2570	0.0280	0.7144	0.0280-1.7360
C_{25}	0.0330	1.3610	0.3051	0.2080	0.0230	0.3860	0.0230-1.3610
C_{26}	0.8110	1.1530	0.2340	0.1680	0.0195	0.4771	0.0195-1.1530
C_{27}	0.7070	1.0380	0.2142	0.1580	0.0180	0.4270	0.0180-1.038
C_{28}	1.120	0.682	1.1279	0.105	0.0109	0.4092	0.0109-1.120
C_{29}	0.7450	0.6180	BDL	0.0940	0.0098	0.3667	0.0098-0.7450
C_{30}	0.2260	0.3070	0.0137	0.0460	0.0044	0.1194	0.0044-0.3070
C_{31}	0.7570	0.5670	BDL	0.0840	0.0087	0.3542	0.0087-0.7570
C_{32}	0.4300	0.3270	0.0385	0.0510	0.0053	0.1704	0.0053-0.4300

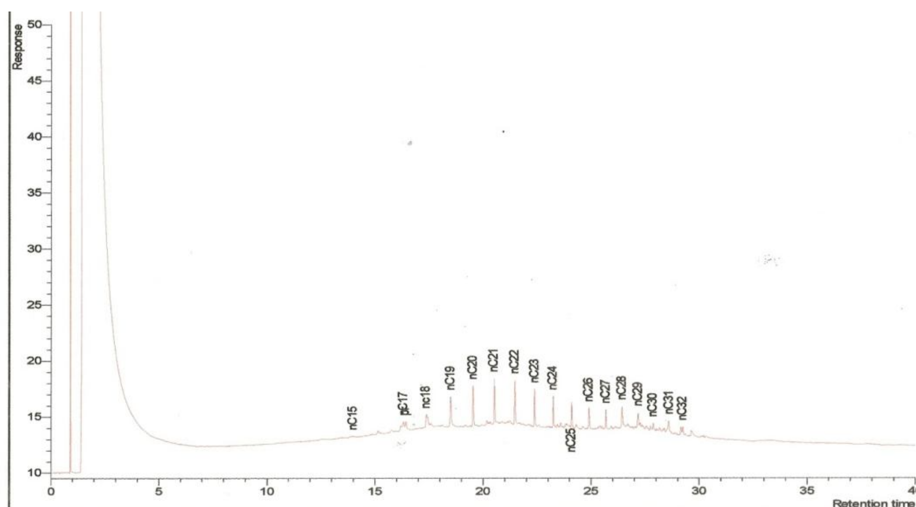

Figure 5: Chromatogram of TPHs at Sampled Station IRW_1.

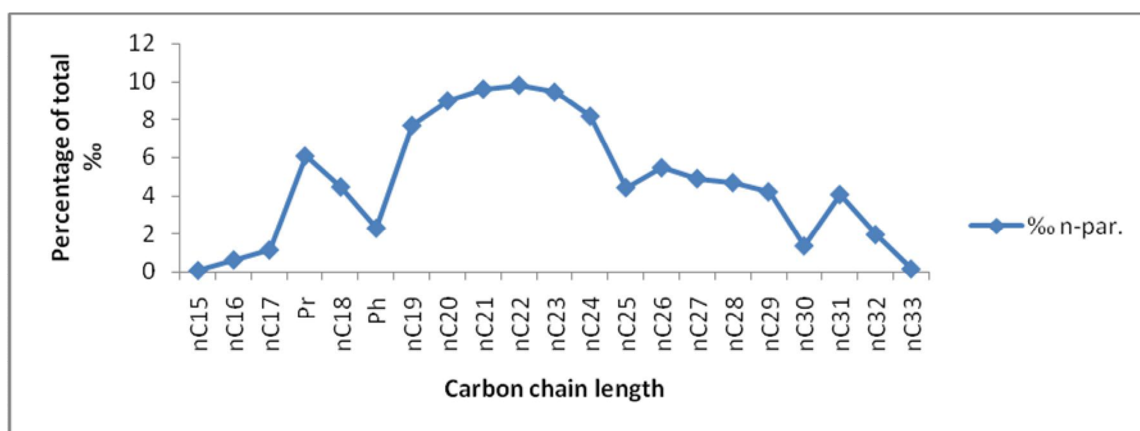

Figure 6: % n-paraffin of different Carbon Chain Length in the Five Samples

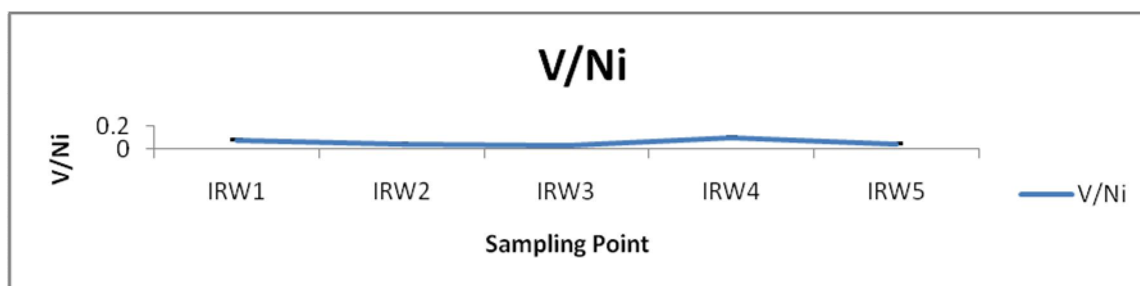

Figure 7: Vanadium-Nickel ratio for Different Sampling Point Showing % Errors

Table 4: Pristane and Phytane Ratios of Samples from Study Area

Sample Location	IRW_1	IRW_2	IRW_3	IRW_4	IRW_5
Pr/Ph	BDL	3.24	3.20	3.77	2.50

Table5. Analyzed Concentration of Nickel and Vanadium in Samples

Heavy Metal	IRW_1	IRW_2	IRW_3	IRW_4	IRW_5	Mean	Range	Mean±S.E at 95%C.L
Ni	5.71	9.01	17.12	2.42	7.26	8.30	2.42-17.12	8.30±4.80
V	0.45	0.42	0.59	0.25	0.36	0.41	0.25-0.59	0.41± 0.11

Table 6: Vanadium and Nickel Ratios of Samples from Sampling Area

Sample Stations	IRW_1	IRW_2	IRW_3	IRW_4	IRW_5
V/Ni	0.079	0.047	0.035	0.103	0.050

Table 7: Linear Rank Correlation Data (R_{xy}) of Crude Oil Samples Which Oil Facilities are Close to the Study Area

Correlating Oil Sources	A	B	C
R_{xy}	-0.41	-0.65	0.30

Figure 8: Study Area Showing Stains of Crude Oil on Fishing Trap at Low Tide

The source of the mystery spill might be determined either by quantitative or qualitative method, via evaluation of data obtained from TPHCs analysis (Table: 3). Quantitative method involves evaluation of PAHs and TPHCs (hydrocarbons fingerprinting) through correlation with other crude oil samples (Uhler, 1997).

3.1 Quantitative Method of Tracing the Source of the Mystery Spill

The correlative data of PAHs diagnostic ratio , pristane and phytane ratio, carbon preference index (CPI), correlation coefficient (r_{xy}) and Vanadium to Nickel ratio (V/Ni) were used for quantitative studies .

From table 2 and figure 4 , the predominance of high molecular weight PAHs; 1,2,5,6-dibenzanthracene 0.23-1.26ppm, flouranthene 0.00-1.81ppm, indeno(1,2,3) pyrene 0.29-1.96ppm and benzo(k) flouranthene 0.21-1.53ppm as compared to the low molecular weight PAHs; anthracene 0.00-0.53, acenaphthene 0.00-0.72, acenaphthylene 0.00-0.46, flourene 0.44-0.84 and phenanthrene0.00-0.48 indicate that the PAHs are likely to be originated from pyrogenic sources than petrogenic sources (Boll *et al.*, 2009).

From table 4, the pristane and phytane ratios (Pr/Ph) of samples with range of 2.50-3.77 indicates that the impacted crude oil could be sourced from an oxic environment as well as terrestrial organic matter, according to Hunt (1997) the oil is derived mostly from a marine plant Syringodium as shown in figure 6. On correlating the TPHs values to three other crude oils sources (A, B and C), which oil facilities are close to the study area. As shown in table 7, it is likely that the impacted crude oil is related to oil sample from crude oil source C.

With the evaluation of odd and even-carbon-numbered n-alkanes measured by the carbon preference index (CPI), showing the ratio by weight of odd to even molecules in crude oils.

$$CPI = \frac{1}{2}\left[\frac{C_{25}+C_{27}+C_{29}+C_{31}+C_{33}}{C_{24}+C_{26}+C_{28}+C_{30}+C_{32}} + \frac{C_{25}+C_{24}+C_{29}+C_{31}+C_{33}}{C_{26}+C_{28}+C_{30}+C_{32}+C_{34}}\right] \quad \text{............(1)}$$

The high molecular weight n-alkanes inherited from terrestrial plants are normally diluted by hydrocarbons from kerogen degradation having CPI value of about 1. However some oils, probably derived mainly or solely from terrestrial organic materials having been reworked by bacteria and other microbes, still show large amount of high molecular weight n-alkanes with a moderate odd predominance.

CPI < 1 signifies the predominance of even-carbon-numbered n-alkane molecules over odd molecules, while the predominance of odd-carbon-numbered n-alkanes molecules is signified by CPI > 1(Tissot and Welte, 1984).
CPI value for this work is calculated from $nC_{25} - nC_{33}$ using equation 1 as shown above, which gives a CPI of 1.15. This value signifies an odd-even carbon predominant and it is similar to the value of crude oil sample C.

By statistical analysis using the correlation data obtained from linear rank correlation coefficient (r_{xy}) of the number of carbon atoms(C_n) in the TPHs analyzed in the study area and correlated samples;

$$r_{xy} = \frac{N\sum xy - \sum x \sum y}{\sqrt{N\sum x^2 - (\sum x)^2}\sqrt{N\sum y^2 - (\sum y)^2}} \quad \text{.............(2)}$$

Unrelated measurement x and y have $r_{xy} = 0$, strongly related measurement have positive values of r_{xy} and negatively related quantities have negative r_{xy} values (Frank *et al.,* 1995); from this result , the positive linear correlation coefficient value for sample C and sample from the study area (table 7) could indicates a strong relationship existing between their biomarkers, unlike the negative values shown by crude oil sources A and B.

The intrinsic Vanadium-Nickel ratios (V/Ni) measured in table 6 is also used as a potential diagnostic parameter. This is because the ratio do not change with the biodegradation or weathering of the released oil (Hunt, 1997).The (V/Ni) ratio at the study area ranges from 0.035 to 0.103, which is not related to that of the correlating source A which concentration of vanadium was below detected limit as well as correlating source B with a range of 1.1-7.6.

3.1.2 Qualitative Method of Tracing the Source of the Oil Spillage

By this method, chromatogram of hydrocarbons from crude oil fingerprint are usually observed and compared visually.

For this work, chromatogram of petroleum hydrocarbons in figure 5 was compared with those of crude oil samples A, B, and C. The result showed positive relationship between samples from the study area and the correlating sample C.

However, assessing the geographical location of the study area and locations of positioned facilities owned by these companies (where samples A , B , and C are taken from) through maps of the study area at figure 2 and 3; it could be deduced that the impacted oil spill could come from any of these facilities as the Warife river system is said to be flowing in both directions.

4. *Conclusion*

Quantitative analysis of hydrocarbon fingerprints could provide a more accurate method of evaluating and investigating crude oils impacted source. This is because of the stability of high molecular weight biological or geochemical markers. This is noticed in this work as the source of the mystery oil spills is likely to be attributed to the crude oil source C as noticed from the evaluation of pristane - phytane ratios, CPI, rank correlation coefficient and V/Ni ratio of the sampling station which matches with correlated crude oil source C and not with correlated crude oil sources A and B.

Qualitative or visual method may not be very accurate as is the case of this work where nearest suspected oil facilities did not turn out to give positive correlation with the impacted crude oil sample.

Acknowledgement

The authors are grateful to all those who facilitated the field program and laboratory processes, some of which are Akwa Ibom State Ministry of Environment, Eleme (INDORAMA) Petrochemicals Nigeria, Getammen Nigerian Limited, Technological Partners International Nigeria Limited, Department of Pure and Industrial Chemistry University of Port Harcourt. We also extend our gratitude to the Nigerian Sao Tome and Principe Joint Development Authority for their scholarship fund which contributed to the success of this work.

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