EVALUATION OF POLYCYCLIC AROMATIC HYDROCARBONS AND TOTAL PETROLEUM HYDROCARBONS PROFILES IN SOME NIGERIAN CRUDE OILS

ABSTRACT

Crude oil samples were obtained from three locations (designated as Location 1, Location 2, and Location 3) in Niger Delta, Nigeria. The samples were subjected to liquid-liquid extraction using dichloromethane and analysed using GC-FID. The results of the analyses of the crude oils gave polycyclic aromatic hydrocarbons (PAHs) concentrations of 2.6089×10^4 ppm representing 60.06% and total petroleum hydrocarbon (TPH) concentration of 4.3201×10^4ppm at Location 1, PAHs concentration of 4.764×10^3ppm (62.8%) and TPH recording a concentration of 7.583×10^3ppm at Location 2, while Location 3 had PAHs concentration of 9.93×10^2 ppm (30.66%) and TPH concentration of 3.239×10^3ppm. The total concentrations of the high molecular weight PAHs were lower than those of the low molecular weight PAHs in the samples. Also the concentrations of the individual PAHs were higher in the low molecular weight PAHs. The mean PAHs concentrations of 2707.6ppm (location 1), 551.5ppm (location 2) and 90.7ppm (location 3) are different. The observed results show that all the sixteen polycyclic aromatic hydrocarbons listed as priority pollutants are present in the three crude oil samples with higher concentrations in the light crude oils than in the heavy crude oil and a strong correlation with the total petroleum hydrocarbon concentration.. It was also observed that though the ratios of the low molecular weight PAHs to high molecular weight PAHs of the crude oils indicate petrogenic, the unique diagnostic ratios suggest pyrogenic input. There is therefore the need to develop a method of PAHs removal from PAHs contaminated water based on locally available and cheap materials.

Keywords: polycyclic aromatic hydrocarbons , total petroleum hydrocarbon, gas chromatography, oil mining lease high molecular weight, low molecular weight,petrogenic.

INTRODUCTION

Polynuclear aromatic hydrocarbons (PAHs) are a category of compounds made of two or more fused aromatic rings. In their normal state they are un-substituted (Fetzer, 2000). They belong to the group also known as persistent organic pollutants (POPs), organic micro-pollutants (OMPs) or priority pollutants (USEPA, 1997). They are recalcitrant to biodegradation and can produce deleterious environmental effects.Polycyclic aromatic hydrocarbons are formed by incomplete combustion of organic matter containing fuels such as oil, wood, coal, diesel, fat, garbage and incense (Sorgi, 2007). PAHs also occur naturally in coal, crude oil, and gasoline and are present in products made from fossil fuels such as asphalt, creosote, coal tar. Natural sources of PAHs also include oil seeps, volcanic eruption, forest fires, decaying organic matter while anthropogenic sources include emission from petroleum refineries, gas flaring, power generation from fossil fuels, atmospheric fall out and inadvertent oil spill (ASTDR,1995; Aas*et al*,2007). There are sixteen priority PAHs (Figure 1). They can be grouped into low molecular weight polycyclic aromatic hydrocarbons (LMWPs) and high molecular weight polycyclic aromatic hydrocarbons (HMWPs) as shown in Table 1 below.

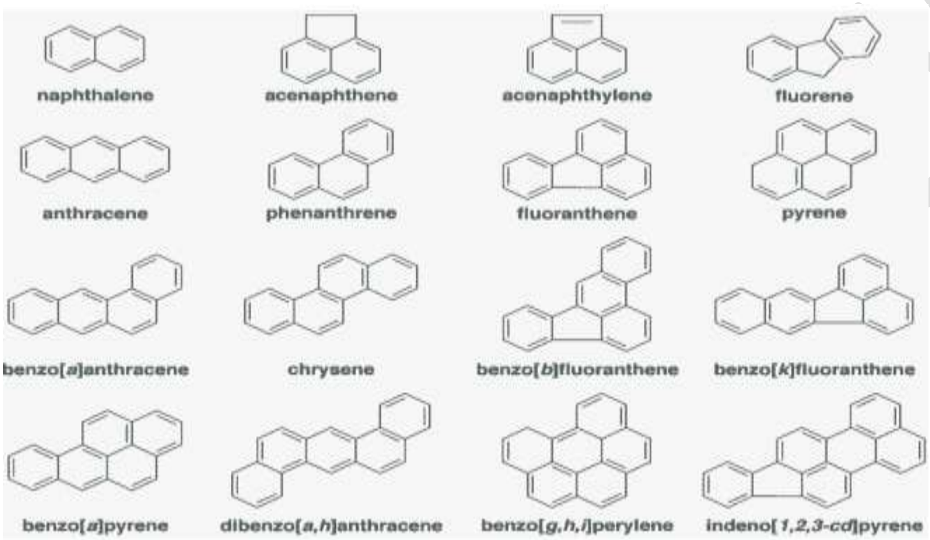

Figure 1: The sixteen most prominent PAHs: EPA 16 PAHs (Pampanin and Sydnes , 2013).

Table 1: The two main groups of the sixteen PAHs (CCME, 1999)

LMWPs	HMWPs
Naphthalene	Fluoranthene
Acenaphthene	Phenanthrene
Acenaphthylene	Benzo[a]anthracene
Fluorene	Benzo[b]Fluoranthene
Anthracene	Benzo[k]Fluoranthene
	Chrysene
	Pyrene
	Benzo[g,h,i]perylene
	Benzo[a]pyrene
	Dibenzo[a,h]anthracene
	Indeno[1,2,3-c,d]pyrene

HMWPs are of significant concern because of their toxic properties as well as their bioaccumulation in organic tissues due to their lipophilic character. Prolonged exposure to low levels of PAHs leads to adverse health effects due to their toxicity, carcinogenicity and mutagenicity (Wilke,2000;Zhang *et al*,2009).

Crude oil, known for its disparate physicochemical properties, provides 20% of Nigeria’s gross domestic product, 65% of its budgetary revenues and 95 % of the country’s export earnings (O’Neil, 2007). As a result, oil industry associated environmental damage largely resulting from oil spills (Table 1, Fig. 2) have affected communities around oil installations through interruption of socio-economic activities and potable water scarcity in rivers of the Niger Delta (Nwilo and Badejo, 2005).

Table2:OilspilldatainNigeriabetween2010and2016

Year	Number of Spills	Quantity Spilled (barrels)
2010	537	17,658.10
2011	673	66,960.84
2012	844	17,526.37
2013	522	4,066.20
2014	1087	10,302.16
2015	753	32,756.87
2016	434	1,658.98

Source: Department of Petroleum Resources (2016)

According to NOSDRA, about 6,600 spills occurred between 2005 and 2015. A recent study by Hodler and Breuderle (2017) revealed that of the 16,000 infants that didn’t survive their first month of life in 2012, about 11,000 infants representing 70%, should not have died if there were no spills. The study also pointed out that oil spills within 10km radius at any location prior to a child’s conception increases the death rate of infants below one month (neonatal mortality) by 38% for every 1000 live births (Hodler and Breuderle, 2017).

Information on the PAHs characteristics of most of the crude types, one of the most toxic and ubiquitous environmental pollutants in this part of the world is limited. Crude oil is composed of about 17000 substances and PAHs happen to be one group of them (Fingas, 2011a).

Neilson (1996) stated that PAHs are formed from natural products such as steroids, that overtime, has been transformed into aromatic compounds. Broadly speaking, two major sources of PAHs are recognizable: anthropogenic and lithogenic. Pyrogenic and petrogenic sources are classified as being anthropogenic. PAHs of pyrogenic origin are high molecular weight PAHs having 4–6 rings such as fluoranthene (Fla), pyrene (Py), benzo(a)anthracene (BaA), chrysene (Chy), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenzo(a,h)anthracene (DibA), benzo(g,h,i)perylen (BghiP) and

Indeno[1,2,3,(c,d)]pyrene (InP)(Liu *et al*.,2009, Riccardi *et al.*, 2013) and originates from incomplete combustion of fossil fuels and bush burning (Khairy *et al.*,2009 and Zakaria *et al.*,2002).The higher reactivity and toxicity associated with the pyrogenic PAHs compared to their petrogenic counterparts are believed to be due to their high content of non-alkylated PAHs (Beyer *et al.*, 2010). However, according to Pampanin and Sydnes(2013), the alkylated PAHs found in crude oil have been reported to be more toxic than their unsubstituted congeners. On the other hand,the petrogenic PAHs are comprised of the alkyl-substituted PAHs and are represented by naphthalene, acenaphthylene, acenaphthene, and fluorine. They are made up of 2-3 rings and hence are of the low molecular weight class.

Leaks from pipelines, discharge of used and new crankcase oil, crude and fuel oil, as well as wastes from factories and homes are thelikely sources of petrogenic PAHs (Saha *et al*,2009).The common occurrence and the natural environmental preponderance of PAHs in crude oil from other regions of the world (Table 3) have been well articulated by Pampanin and Sydnes (2013) and Menzie *et al.*, (1992).

Table 3: PAH concentrations in 48 different crude oils (Pampanin and Snydes,2013).

Crude oil	48 different crude oils (Kerr *et al.*,1999)			North Sea (Aas *et al.*,2000)	Goliat (Sundt *et al.*,2011)
PAH	Minimum mg/kg oil	Maximum mg/kg oil	Mean mg/kg oil	mg/kg oil	mg/kg oil
Naphthalene	1.2	3700	427	1169	1030
Acenaphthene	0	58	11.1	18	12
Acenaphthylene	0	0	0	11	*
Fluorene	1.4	380	70.34	265	75
Anthracene	0	17	4.3	1.3	*
Phenanthrene	0	400	146	238	175
Fluoranthene	0	15	1.98	10	6
Pyrene	0	9.2	-	20	*
Benzo[a]anthracene	0	16	2.88	11	Na
Chrysene	0	120	30.36	26	Na
Benzo[b]fluoranthene	0	14	4.08	4.2	Na
Benzo[k]fluoranthene	0	1.3	0.07	Nd	Na
Benzo[a]pyrene	0	7.7	1.25	1.3	Na
Dibenz[a,h]anthracene	0	7.7	1.5	Nd	Na
Benzo[g,h,j]perylene	0	1.7	0.08	1.0	Na
Indeno[1,2,3-cd]pyrene	0	1.7	0.08	Nd	Na

*Nd=not detected; Na= not analyzed

Most of the previous environmental toxicological studies on crude oil have focused on TPH, BTEX, and heavy metals. However, toxicological studies rank PAHs above the other parameters. This study was therefore designed to profile PAHs and provide information on some brands of crude oil produced from the Niger Delta, Nigeria.

Materials and Methods

Sample Source, Collection and Preparation

Locations 1 is within the Brass oilfield (**Coordinates4°18'44.32" N 6°14'27.28" E**) in Bayelsa State while and location 2 is within Okono oil field located in the South Eastern Niger Delta, approximately 50 kilometres offshore with coordinates of 3°58′60.00″N 7°16′60.00″E. Location 3 is located at Okwoibome in thickly forested terrain in the **northern** Niger Delta.

Marine sediment and mangrove mud were obtained from Bakana in Rivers State while the local bentonite was obtained from Nteje in Anambra State, Nigeria

Crude oil samples were collected with sampling thief from the ship composites during loading from the storage tanks of the different locations. The collected samples were placed in metal cans and transported to the laboratory.

GC-FID Analysis: PAHs concentration was determined using Varian 3800 chromatography as outlined in USEPA 8720D.Sample detection and identification were carried out using FID by taking advantage of the differences in retention time of the components while quantification was obtained from the corresponding areas of the respective chromatograms. Solvent blank was analysed and quantified with no PAHs found in these blanks. The GC was calibrated using dichloromethane-based standards. The coefficient of determination values (R^2) was greater than 0.95. Surrogate standards were introduced to the sample to attenuate abnormal matrix effect.

Results and Discussion

The results for the physicochemical parameters measured in the crude oil samples are presented in Table 4. The results are presented along with published specifications for light and heavy crude oil. The densities of Location 1 and Location 2 with values of 0.8448g/ml and 0.8227g/ml fall within the range of 0.78-0.88g/ml listed for light crude oils while the density of the co-mingled sample from Location 3 with a value of 0.9012 falls with the range (0.88g/ml-10g/ml) of crude oils designated as heavy. The density values recorded for these three crude samples agree with 0.8400g/ml and 0.9000g/ml reported by Wang *et a*l.,(2003) and Yang *et al.,(*2014).

The API gravity, for the crude oil samples ranged from 18^{o}– 40.41^{o} (Table 4). The API of crude oils, in general, range from 10^{o} – 50^{o}. API values greater than or equal to 33^{o} falls within the “light crude” category and API values less than or equal to 28^{o} falls within the heavy crude class (Tsaprailis, 2014). Location 1 and Location 2 had respective API values of 39.00^{o} and 40.41^{o}.Therefore they are classed as light crude oils since their API gravities are consistent with the values listed as light crude. On the other hand, the crude oil sample from Location 3 with an API value of 18^{o}which is below 28^{o} can be classed as heavy crude. The API range recorded for the three crude,18^{o}– 40.41^{o} oils is consistent with 18.2^{o} and 0.9012g/ml previously reported by Ofodile *et al*.,(2018) and Nmegbu (2014).

The viscosity for the crude oil samples ranged from 5.10 mPa.s– 40.41^{o}mPa (Table 4). The viscosity of crude range from 5mPa.s – 50,000mPa.s. Viscosity values within 5mPa.s -50mPa.s falls within the “light crude” category and viscosity values 50mPa.s-50,000mPa.s falls within the “heavy crude” class (Wang et al., 2003 and Hellebone, 2007). Location 1 and Location 2 had respective viscosity values of 5.10 mPa.s and 5.15 mPa.s Therefore they can be classed as light crude oil since their viscosity values are in line with the values listed as light crude. On the other hand, the crude oil sample from Location 3 with a viscosity value of 115mPa.s which is between 50 mPa.s-50000mPa.s can be classed as heavy crude. The viscosity range recorded for the three crudes, 5.10mPa.s^{-} 115 mPa.s (Table 4) is in agreement with 50 mPa.s and 112 mPa.s previously reported by Tsaprailis, (2014) and Wang *et al*. (2014).

The pour point of the three crude oil samples ranged from -36^{o}C– 18^{o}C. The recommended pour point range for crude oils, irrespective of the type, is from -40^{o}C– 30^{o}C. The observed pour point values for Location 1, Location 2 and the co-mingled sample from Location 3 with respective pour point values of -36^{o}C, 18^{o}C and 15^{o}C are within the required specification for the crude oils classed as :”light crude” and “heavy crude”(Table 4). The pour point range recorded for the three crudes,-36^{o}C– 18^{o}C is in tandem with -80^{o}C– 30^{o}C previously reported by in *Engineeing ToolBox*(2017) and Nmegbu (2014).

The Total Acid Number (TAN) for the crude oil samples ranged from 0.236mgKOH/g-0.313 mgKOH/g (Table 4). The specified TAN range for crude is 0.01mgKOH/g-3.00mgKOH/g (*Engineering ToolBox*, 2017). The observed TAN values of 0.236mgKOH/g, 0.282mgKOH/g and 0.313mgKOH/g for Location 1, Location 2 and the co-mingled sample from Location 3 respectively are within the specified range. *Easternunion* (2016), an oil industry commercial bulletin had reported a range of 0.27mgKOH/g-0.53mgKOH/g for four different Nigerian crudes. These numbers are consistent with the TAN values obtained for the three crudes. The elevated value of 0.313mgKOH/g for TAN in sample from the co-mingled Location 3 compared to that of Location 1 and Location 2, agrees with the report in *The Engineering ToolBox* (2017), of a possible relationship between TAN and specific gravity/density.

The nickel (Ni) concentration for the crude oil samples ranged from 1.24ppm- 2.81ppm $^{(}$Table 4). The specified Ni range for crude oils is 0-50ppm (*Engineering ToolBox*, 2017). The observed Ni concentration of 1.76ppm, 1.24 and 2.81ppm for Location 1, Location 2 and the co-mingled sample from Location 3 respectively are within the specified range. *Easternunion* (2016), an oil industry commercial bulletin had reported a range of 2.0ppm- 4.8ppm for four different Nigerian crudes. These concentrations are comparable to the trace metal concentrations obtained for the three crudes that ranged from 1.24pp-2.81ppm.

The Vanadium (V) concentration for the crude oil samples were all <2.0 (Table 4). The specified Ni range for crude oils is 0.0-150ppm (*Engineering ToolBox*, 2017). The observed V concentrations of <2.0 for Location 1, Location 2 and the co-mingled sample from Location 3 respectively are within the specified range. *Easternunion* (2016), an oil industry commercial bulletin had reported a range of 0.4ppm- <2.0 ppm for four different Nigerian crudes. These concentrations are comparable to the trace metal concentrations for V obtained for the three crudes with respective values of <2.0 ppm each.

Table 4: Levels of Physicochemical Properties of the three crude oil samples

Property	Unit	Location 1	Location 2	Location 3	Light Crude	Heavy crude
Density@15 °C	g/mL	0.8448	0.8227	0.9012	0.78-0.88	0.88-1.0
API gravity	°	39.00	40.41	18.00	30-50	10-30
Viscosity @ 15°C	mPa.s	5.15	5.10	115	5-50	50-50,000
Pour Point	°C	-36	18	15	-40 to 30	-40 to 30
TAN	mgKOH/g	0.282	0.236	0.313	Na	Na
Nickel	ppm	1.76	1.24	2.61	Na	Na
Vanadium	ppm	< 2	< 2	< 2	Na	Na

PAHs: The chromatograms resulting from the analysis of the three crude oil samples indicated that all the sixteen PAHs regarded as priority pollutants, were present, but at different concentrations as represented by the peaks (Figures 2-4)

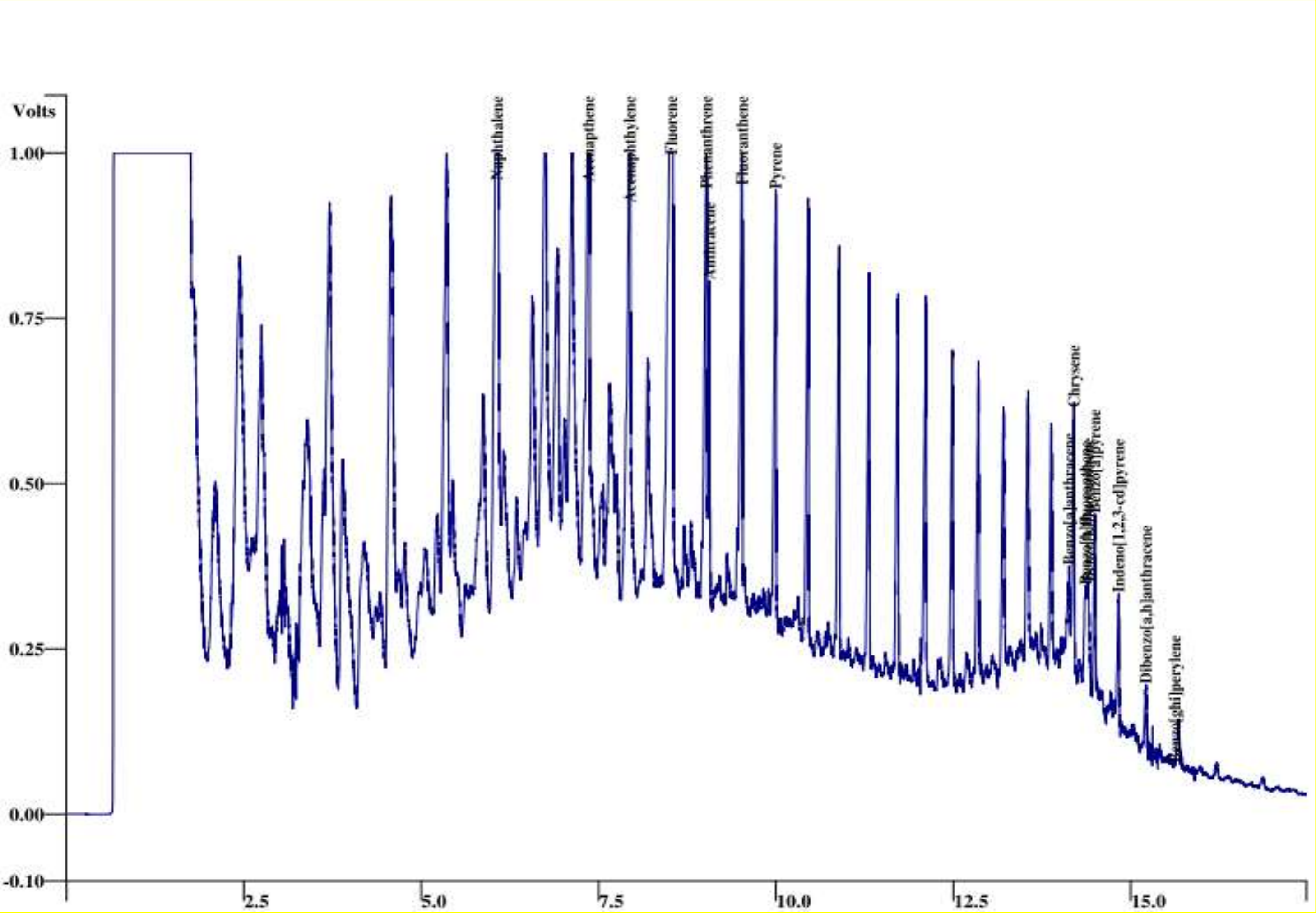

Figure 2: PAHs Chromatogram of crude oil from Location 1

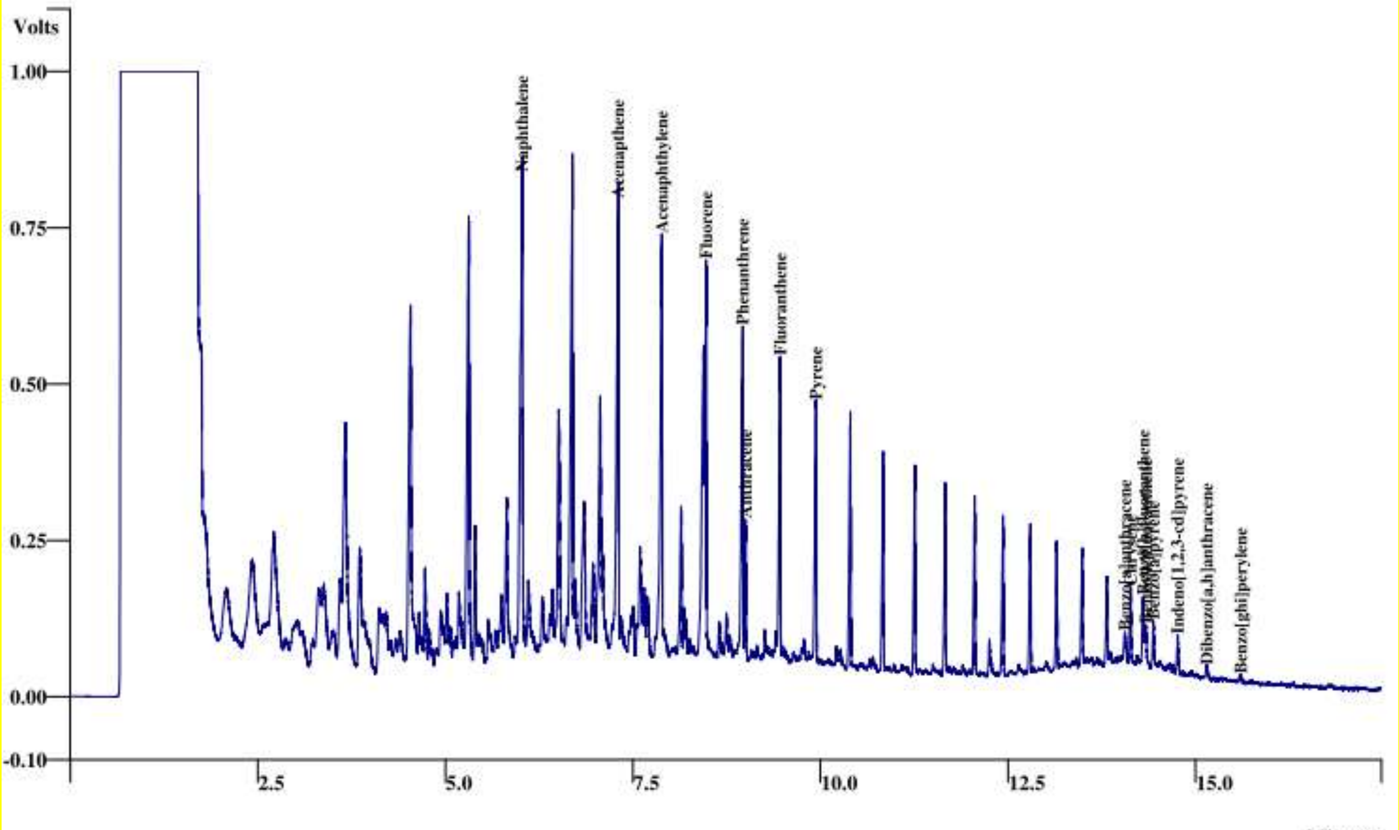

Figure 3:Chromatogram of PAH from Location 2

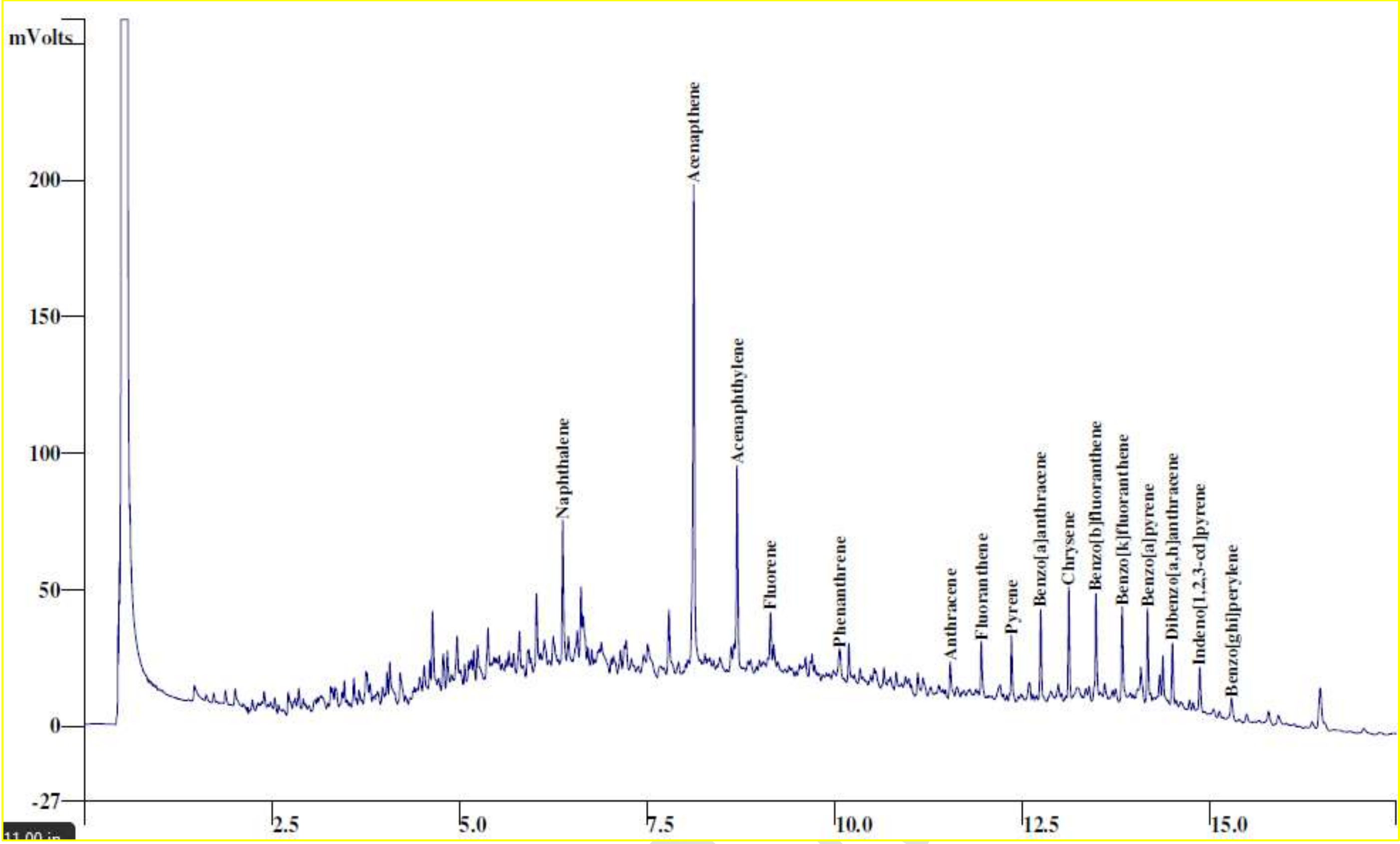

Figure 4:Chromatogram of PAH from Location 3

The total concentrations of the PAHs in the crude samples ranged from 992.76ppm-26089.35ppm (Table 5). While Location 1 and Location 2 had PAHs concentrations of 26089.35ppm and 4764.07ppm respectively, the co-mingled sample from Location 3 had a PAHs concentration of 992.76 ppm. The results indicated that the total PAHs concentrations in the light crude oils (Location1 and location 2 with respective API gravities of 39^o and 40.41^o) are higher than that in the heavy crude oil (Location 3 having API gravity of 18^o). These results are in line with those reported in the literature of some Nigerian crude oils (Table 6) with total PAHs values that ranged from 3236.60ppm-4190ppm (Mark *et al*., 2015).

Table 5: Concentrations of PAHs in Crude Oils from the Study Areas

		Concentration, ppm		
S/N	Name of PAH	Location 1	Location 2	Location 3
1	Naphthalene	2752.1516	807.8830	71.1764
2	Acenaphthene	2310.9417	595.1026	286.5304
3	Acenaphthalene	4550.9194	864.4487	71.5936
4	Fluorene	3651.2429	385.9713	35.9264
5	Phenanathrene	1648.0137	458.7422	46.3639
6	Anthracene	1332.1754	196.6523	33.9607
7	Fluoranthene	1644.7887	395.1564	30.4360
8	Pyrene	1791.9515	363.7250	27.6489
9	Benzo(a)anthracene	454.2253	84.2905	43.6241
10	Chrysene	1031.4888	108.7293	45.1513
11	Benz(b)fluoranthene	890.3987	151.0388	73.9764
12	Benz(k)fluoranthene	950.1061	93.4174	62.7025
13	Benz(a)pyrene	1377.0304	104.6393	60.7151
14	Indeno(1,2,3,c,d)pyrene	987.5146	81.8951	45.1758
15	Dibenz(a,h)anthracene	698.0814	49.7820	35.6755

16	Benz(g,h,i)perylene	18.3161	22.5919	22.1054
	Total	26089.3457	4764.07	992.7623

Also the total concentrations of the LMWPs were higher than the total concentrations of the HMWPs in all the three crude oil samples (Table 7). This observation is in agreement with that reported by Mark *et al.*,(2015) and Magi *et al.,* (2002). The same trend in concentration and occurrence of PAHs in crude oil from different parts of the world have been reported in studies by Kerr *et al.*, (1999) and Faksness *et al.*,(2008).

Table 6::Comparison of PAHs from this study and others

PAHs Total	Crude oil type	Designation	Country
26089.35ppm	Light	This study	Nigeria
4764.07ppm	Light	This study	Nigeria
992.76 ppm	heavy	This study	Nigeria
3530.3 ppm	Light	Mark *et al*.,2015	Nigeria
3236.6ppm	Light	Mark et al.,2015	Nigeria
4019.0ppm	blend	Mark *et al*.,2015	Nigeria
3388.6ppm	Light	Mark *et al*.,2015	Nigeria
139.0ppm	Ligh3	NACEM, 2016	USA
501.1ppm	heavy	Yang *et al*.,2014	China
218.0ppm	heavy	Wang *et al*.,2003	China

The crude sample from Location 2 had a total LMWPs concentration of 3,308.8 ppm while that from Location 1 and Location 3 had respective total LMWPs concentration of 16,245.5 ppm and 545.6ppm. The differences between the PAHs concentration means with values of 2707.6ppm, 551.5ppm and 90.7ppm respectively is significant ($p>0.05$) suggesting regional differences (Table 7).

Table 7: Total and mean concentrations of PAHs and TPH for the thee crude oil samples

PAHs	Location 1	Location 2	Location 3
Total PAH	26089.3457	4764.07	992.7623
Mean	2707.6	551.5	90.7
LMWPs	16,245.5	3,308.8	545.5
HMWPs	9843.8457	1455.27	447.2623
LMWPs/HMWPs	1.65	2.27	1.22 *
TPH			
Total TPH	43,201	7,583	3,239
Mean	1234.305	216.664	92.555

Higher concentrations of LMWPs compared to the HMWPs as observed in this study is typical of hydrocarbons of petrogenic origin. This is in agreement with studies reported by Soclo *et al*., (2000).

The ratios between the LMWPs and the HMWPs in the crude oils (*) were greater than one (>1) in all the samples (Table 7) which indicated petrogenic source for the crude samples. A similar observation was reported by Magi *et al*., 2002 in which the ratios of LMWPs/HMWPs were <1 and typically represented pollution of pyrogenic origin.

It was also observed that irrespective of the location and the geological setting, the relative abundance of the PAHs in the three crude oil samples from different locations were consistent (Table 6). The same consistency in compositional and distribution pattern as well as relative abundance (Figure 5) has been reported by other workers (NRC, 2003; Fingas.2011a).

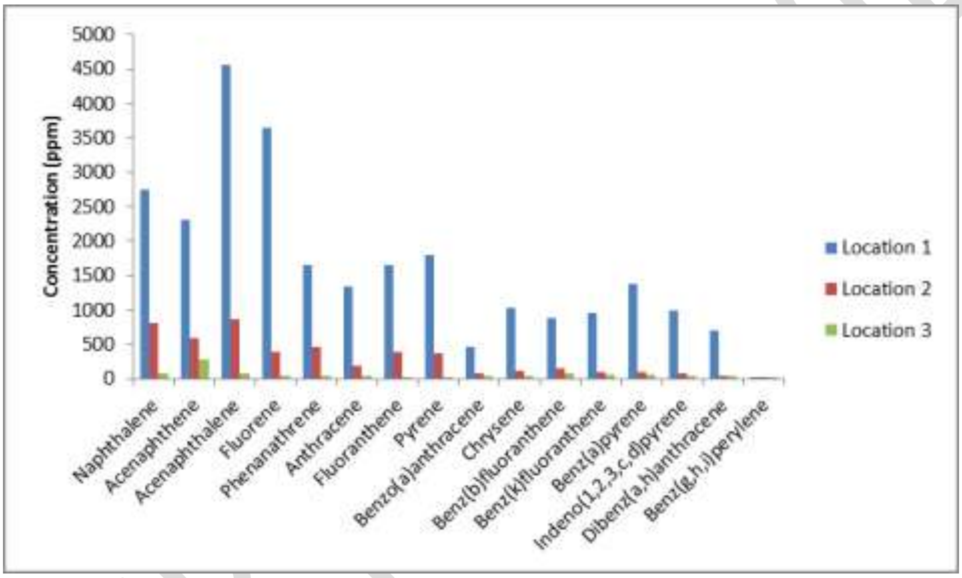

Figure 5: Relative Abundance of PAHs in the three Crude Oil Samples

Such compositional and distribution pattern in the distribution of hydrocarbons in crude oils has given rise to unique ratios that researchers have employed as diagnostic tool for PAHs source identification and characterisation. (Table 8).

Table 8: Unique PAHs ratios of the three crude samples

PAH Unique ratio	Location 1	Location 2	Location 3	Petrogenic	Pyrogenic
ANT/(PHE+ANT)	0.45	0.30	0.01	≤ 0.10	>0.10
FLR/(PYR+FLR)	0.48	0.52	0.01	≥ 0.50	>0.50
FLR/PYR	0.92	1.09	1.1	<1	>1
PHE/ANT	1.24	2.33	1.37	>10	<10

From the results obtained, the crude oil samples indicated mixed sources in the crude oil formation with pyrolysis predominating. Results of unique ratios that do not point to a single source due to a mix of petrogenic and pyrogenic diagnosis has been reported by Yunker *et al*., (2002) and Pampanin and Snydnes, (2009).

The percentages of PAHs in the three crude oil samples were calculated to be 60.06%, 62.8% and 30.66% for Location 1, Location 2 and Location 3 respectively. This is consistent with values reported by Fingas (2003); Aas *et al*., (2009); and Deepthike *et al*., 2009) in studies of crude oils from the North Sea and the Exxon Valdez Oil Spill.

It also highlights the toxic potential of the crude samples based on their respective PAHs concentrations. Wilke (2000) and Zhang *et al.*(2009) reported that prolonged exposure to low levels of PAHs leads to adverse health effects due to their toxicity, carcinogenicity and mutagenicity.

The PAHs concentration profiles were also compared with the total petroleum hydrocarbons (TPH) profiles (Figures 6-9, and Table 9) of the respective crude oil samples in order to investigate, possible relationship between the PAHs and the TPH in crude oils.

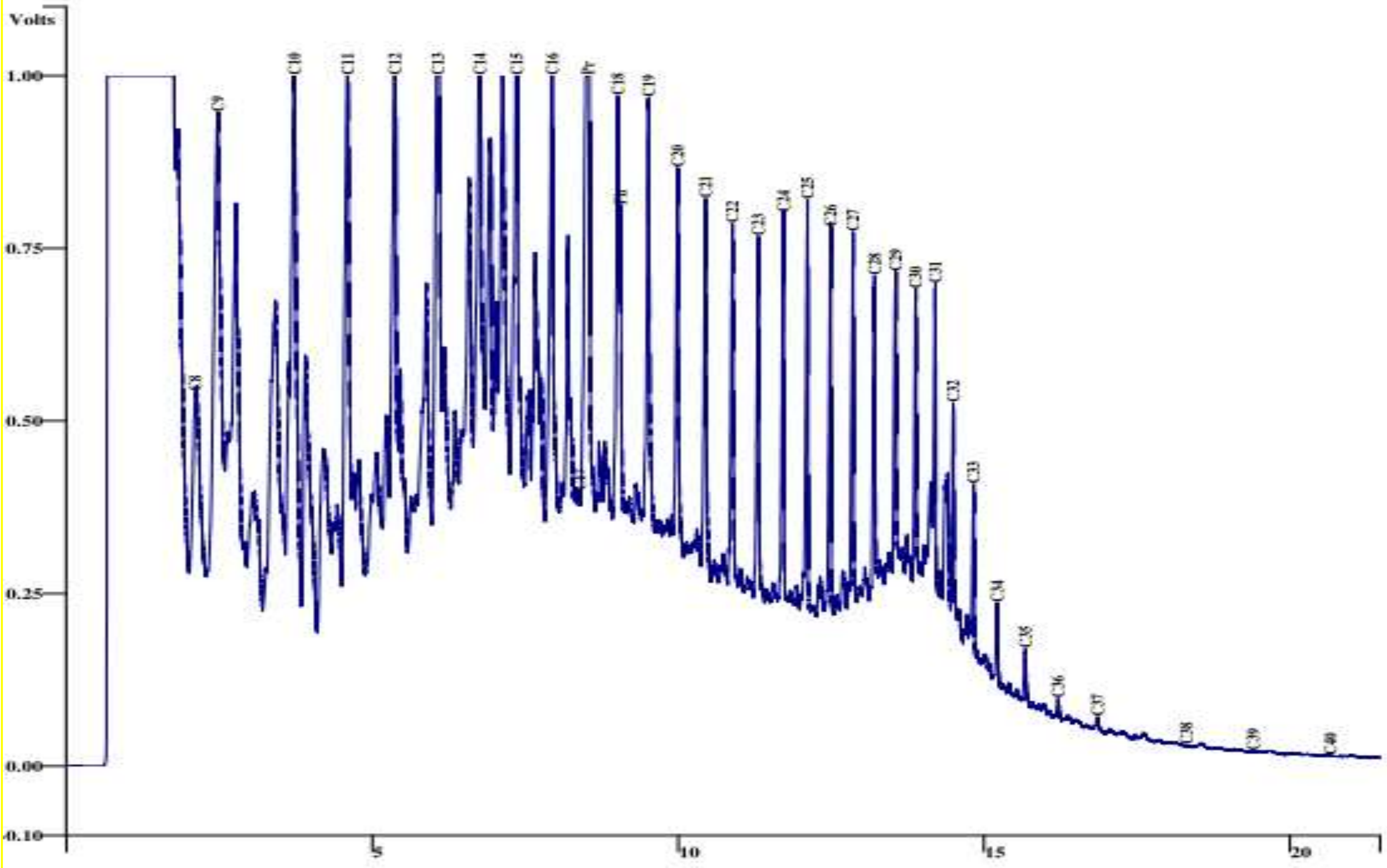

Figure 6: TPH Chromatogram of crude oil from Location 1

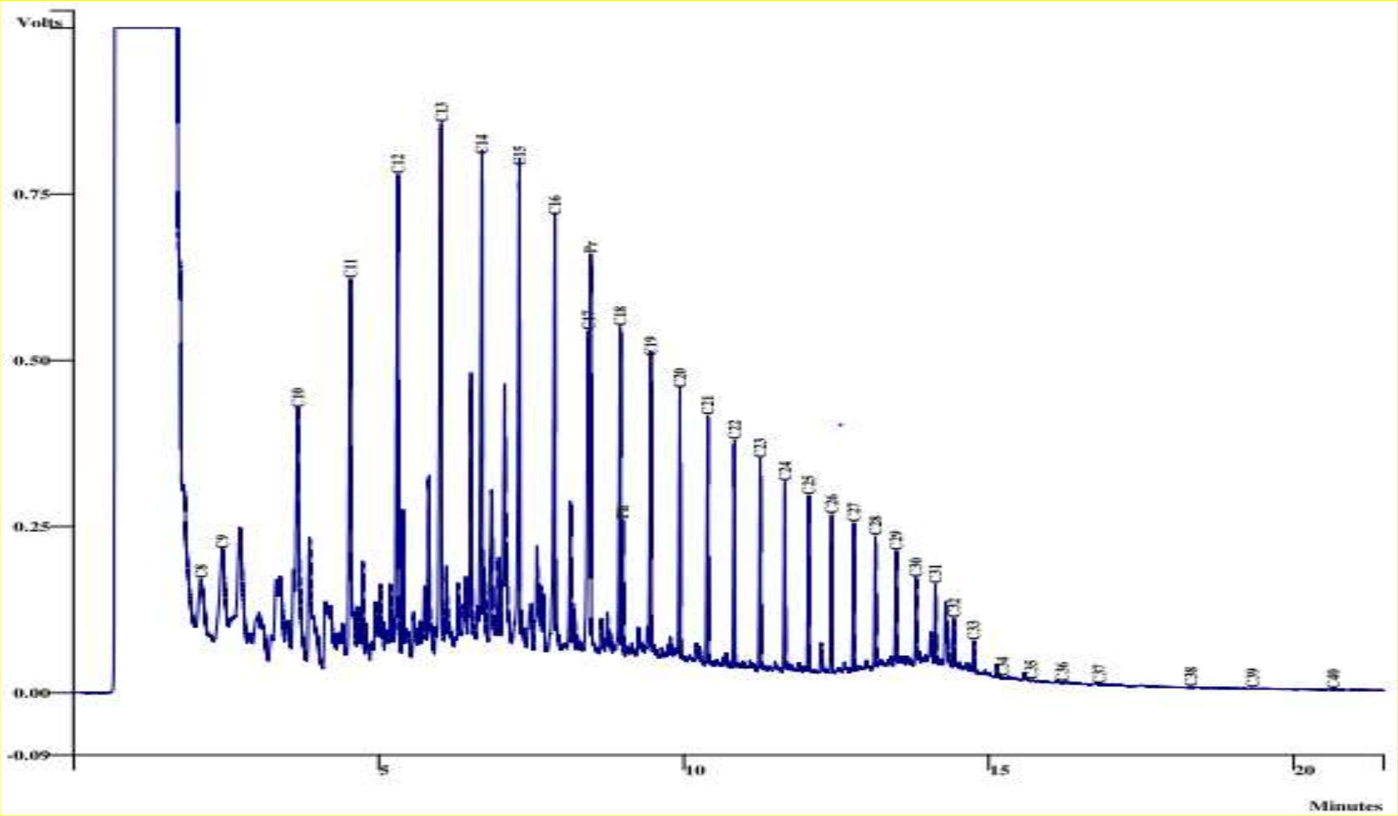

Figure 7:Chromatogram of TPH from Location 2

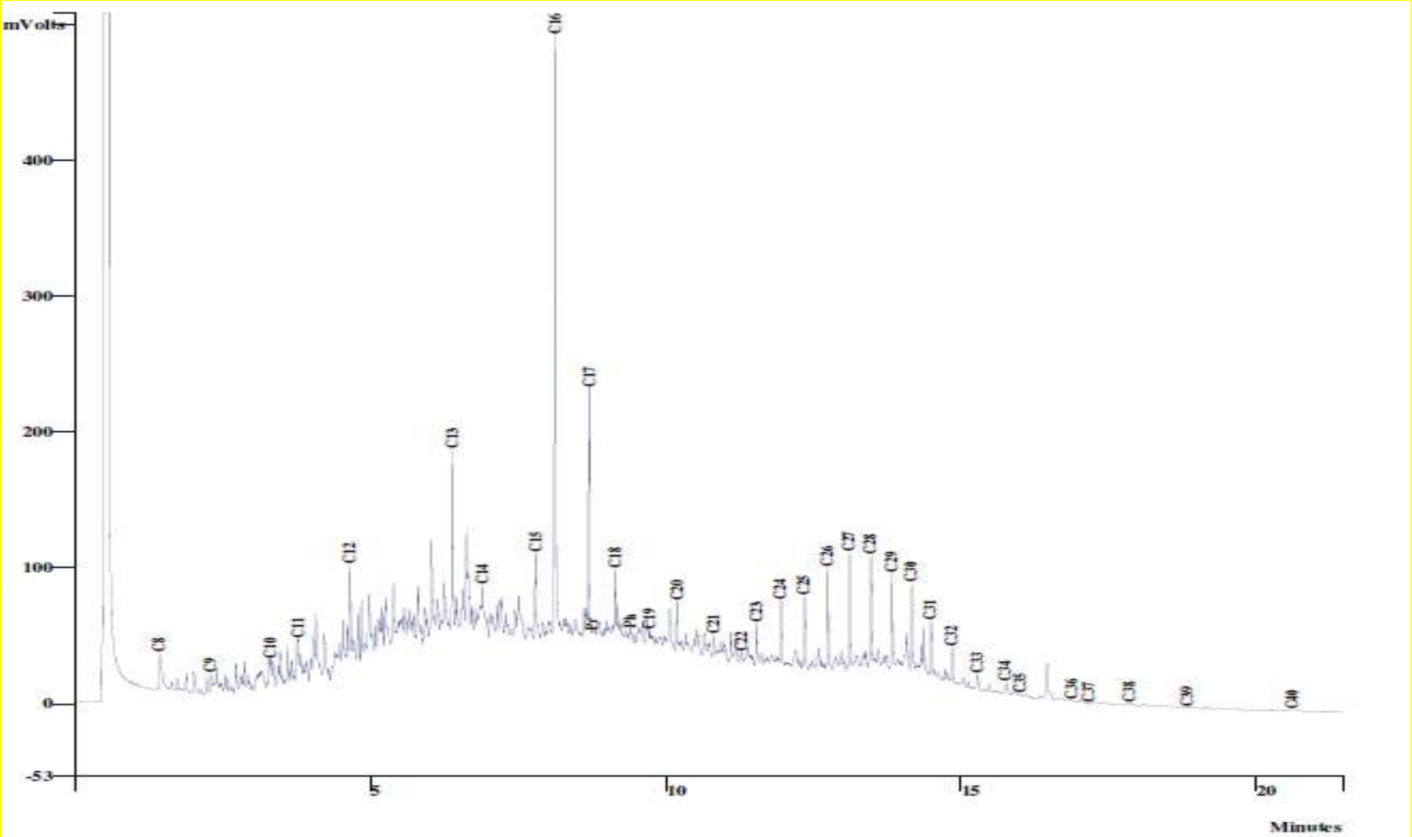

Figure 8:Chromatogram of TPH from Location 3

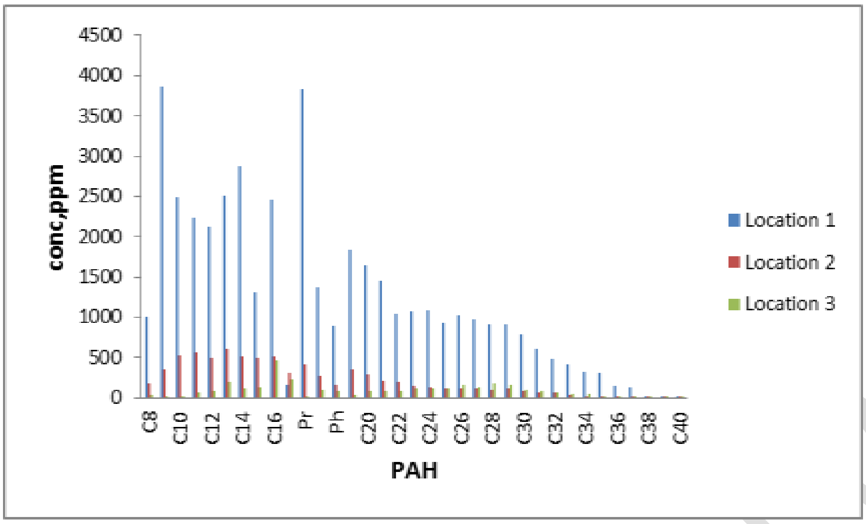

Figure 9: Relative Abundance of TPH in the three Crude Oil Samples

Table 9: Concentrations of TPH in crude oils from the study locations

		Concentration, ppm		
S/N	Hydrocarbon	Location 1	Location 2	Location 3
1	C8	1006.668	178.0411	44.1908
2	C9	3854.684	347.7734	14.477
3	C10	2494.321	528.8795	19.4569
4	C11	2237.048	563.2609	61.3427
5	C12	2124.772	506.0682	91.4833
6	C13	2499.705	608.5251	203.1366
7	C14	2875.903	519.1251	122.1494
8	C15	1315.322	494.2538	128.6315
9	C16	2456.023	520.2319	468.7405
10	C17	160.6039	313.4565	234.7897
11	Pr	3823.687	426.8178	26.9776
12	C18	1371.946	278.0484	100.5874
13	Ph	903.0316	166.5952	77.3108
14	C19	1830.883	349.029	42.2802
15	C20	1638.828	287.9901	85.4236
16	C21	1447.638	217.2082	78.2152
17	C22	1037.735	192.8407	82.2765
18	C23	1069.432	155.253	111.8668
19	C24	1093.887	132.4769	116.6021
20	C25	924.4124	121.8283	114.7974
21	C26	1025.763	108.7458	162.1111
22	C27	983.9706	108.8237	134.3216
23	C28	908.1005	97.4949	181.3757
24	C29	907.1578	109.7828	156.5651
25	C30	784.6279	84.8713	101.9263
26	C31	605.7593	68.9735	78.8809
27	C32	477.3135	60.7109	65.5927
28	C33	415.0035	33.4994	58.7802
29	C34	319.588	0.8863	60.2272
30	C35	302.6475	0.3213	0.7025
31	C36	153.3584	0.1986	0.9844
32	C37	131.7359	0.0655	0.0739
33	C38	9.8099	0.1716	2.4583
34	C39	7.981	0.5439	0.1891
35	C40	1.3439	0.4293	10.4827
		43,201	**7,583**	**3,239**

The total PAHs and TPH, as well as the mean PAHs and TPH were calculated (Table 7). There was high correlation coefficient (r=0.9992) between the total values of PAHs and TPH (Fig. 10). This shows that there is a strong correlation between PAHs and TPH in a crude sample and this could suggest pristine co-existence. This is in line with the concentrations of non- aromatics that ranged from 363.4pm-439.6ppm reported by Mark *et al*.,(2015) It is therefore possible to have an estimate of the PAHs concentration of a crude oil sample from the TPH and vice versa.

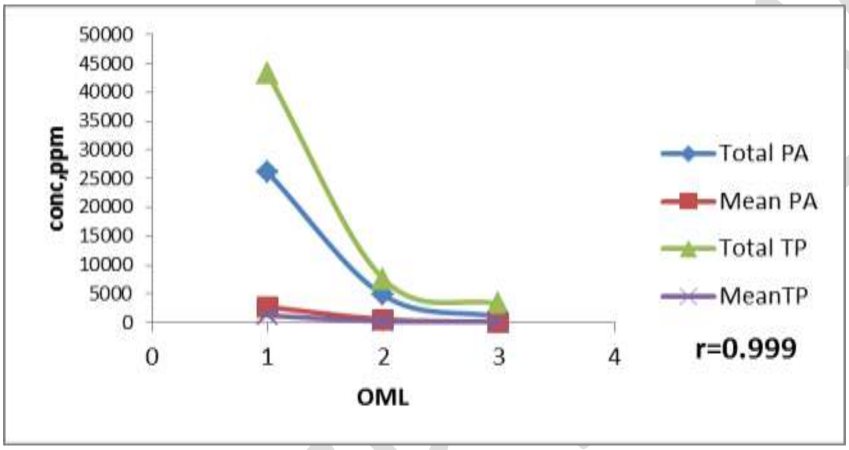

Figure 10: Relationship between PAHs and TPH Concentrations in the three crude oil samples

Conclusion

The results of the crude oil analysis indicate that samples from Location 1 and Location 2 are light crude oil while the sample from Location 3 is heavy crude. All the sixteen priority PAHs are present in all the three samples. Light crude oils contain higher PAHs concentrations than the heavy crude oil. The concentrations of the LMWPs were higher than the concentrations of the HMWPs irrespective of the location. The ratio of the LMWPs/HMWPs indicated that all the crude oil samples are of petrogenic source. The unique compositional and distribution pattern of PAHs in the study samples favours mixed sources with evidence of 'pyrolytic' input which may suggest some geothermal-mediated processes. The positive correlation (r=0.9992) between the PAHs and TPH as observed in this study suggest they are both petrogenic. The implication of our findings suggests that future risk evaluations of crude oil impacted sites may need to include PAHs.

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