



# Evaluation of Total Hydrocarbon Content and Polycyclic Aromatic Hydrocarbon in an Oil Spill Contaminated Soil in Rumuolukwu Community in Niger Delta

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## Abstract

This study assessed total hydrocarbon content (THC) and polycyclic aromatic hydrocarbon (PAH) in an oil spill contaminated soil in Rumuolukwu community in Niger Delta. The study was carried out between August 2013 to January 2014. THC and PAH were analyzed using standard procedure. PAH in the contaminated soil for both season were predicted using Diagnostic Ratios [Ant/(Ant+Phe), Flt/(Flt+Pyr), BaA/(BaA+Chr), Flt/Pyr and BaP/(BaP+Chr)]. PAH and THC concentration were higher in August 2013 (wet season) compared to January 2014 (dry season), indicating natural attenuation as the study period increases. Also, higher concentration of PAH and THC were observed at less depth (0-15cm) compared to higher depth (15cm – 60cm). Based on diagnostic ratio, PAH sources present in the oil contaminated soil depicted the predominance of mixed pyrogenic activities such as petroleum, biomass and coal combustion. Petrogenic sources were observed close to the point source.

**Keywords:** Diagnostic ratio, Oil spill, total hydrocarbon content, polycyclic aromatic hydrocarbon

## 1 Introduction

Environmental pollution affects the ecosystem and its biota. The environment is contaminated by human activities and to lesser extent by natural effects. Most environmental pollution resulting from natural effects are triggered by anthropogenic activities. For instance eutrophication in slow flowing surface water is mostly due to the effect of nutrient resulting from runoff after precipitation. Also, the discharge of effluents contain high nutrient could also cause eutrophication is addition to other contamination matrices. Some major activities that cause pollution to the environment include agricultural practices through the use of pesticides [1, 2], food processing such cassava and oil palm processing wastes [3], oil and gas exploration and its associated activities such as dredging [4-10].

Typically crude oil and natural gas account for over 50% of global energy sources [11]. Crude oil is a complex mixture containing several compounds which are fractionated into different products including gasoline of various grades, lubricating oils of various weights and grades, kerosene of various grades, jet fuel, diesel fuel, heating oil and other chemicals etc.

Exploration of crude oil is carried out in both offshore and onshore. For instance, Nigeria oil fields and offshore oil rigs have hundreds of wells with flow lines that carry crude oil to the lease tanks. The crude oil flows from the wells to the

unseen lease tanks through the flow lines, where it is accumulated, sampled and measured prior to further transportation through other connecting pipelines. The transportation of crude oil is carried out via flow/ trunk and pipeline depending on the destination.

Crude oil transportation lines could be damaged leading to oil spill. The destruction is caused by vandalism or rupture. Either way, it could cause attendant impact of the ecosystem. On soil it could lead to variation in microbial, physiochemical, heavy metal and hydrocarbon content of the soil. The change affects the various biota in such environment including microbes, insects, vegetation and wildlife. The effect can be direct leading to habitat alteration, and death and indirect leading to loss of food resources. However, crude oil is also source of energy to some lower organisms such as microbes especially hydrocarbon utilizing/degrading bacteria and fungi.

Petroleum is a complex mixture of hydrocarbons (aliphatic and aromatic) and organometallic complexes such as heavy metals (Vanadium, lead, chromium, nickel etc). Petroleum varies widely in composition and physical properties.

Even though the associated consequences of oil production and transportation in an environment has been well documented, especially on the adverse effects of oil spillage, which include soil, water and vegetation loss, a new

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trend which is yet receiving attention is the distribution and identification of Polycyclic Aromatic Hydrocarbons (PAH) sources using diagnostic PAH ratios [12-15] which is a fingerprinting technique to identify the type and source of hydrocarbons; whether petrogenic or pyrogenic.

PAHs can be classified as being of petrogenic (petroleum) or pyrogenic (combustion) origins; they can also be classified as being of natural and anthropogenic origins [13, 15]. According to Inengite et al. [15], United States Environmental Protection naphthalene (Naph); acenaphthene (Ace); acenaphthylene (Acen); fluorene (Flu); phenanthrene (Phe); anthracene (Ant); fluoranthene (Fluo); pyrene (Pyr); 1,2-benzanthracene (BaA); chrysene (Chry); benzo(b)fluorathene (benzo(b)); benzo(k)fluoranthene (benzo(k)); benzo(a)pyrene (BaP); 1,2,5,6-dibenzanthracene (Diben); indeno(1,2,3-cd) pyrene (Ind); 1,12 - benzopyrene (BghiP) as priority PAH constituents. PAH has the tendency to migrate to other region in the soil and are slow to degradation by indigenous microorganisms [15].

This study assessed the THC and PAH concentration in crude oil contaminated soil across a period of six months.

## 2 Materials and Methods

### 2.1 Study area description

Rumuolukwu is one of the major communities in Eneka within Port Harcourt metropolis, Rivers state, Nigeria. It is a developing area witnessing an urban sprawl of expansion of the Port Harcourt metropolis. Rumuolukwu community is located in Obio/Akpor Local Government Area of Rivers State. The area is fast developing. Like other major climatic conditions of the Niger Delta, the area is characterized by two distinct seasons viz: wet and dry season. The temperature and relative humidity of the area is  $30 \pm 7$  and 50 – 95% respectively all year round. A Shell Petroleum Development Company right of way passes through the community. Damage of the pipeline may have led to an oil spill within the right of way (Figure 1).



Figure 1: Faulty pipeline along the SPDC Right of way at Rumuolukwu

### 2.2 Sampling

Two sampling stations were established within the study area. The oil contaminated plot was located adjacent to the point source of oil spill, along the SPDC right of way and the control plot was 50 m from the affected plot. The control plot was an existing farmland with no history of oil spill contamination. Sampling covers a period of six months between August 2013 and January 2014 covering 3 month wet season (August – October) and 3 months dry season (October – January of the following year i.e. 2014). Prior to sample collection, a petroleum or oil sheen test as

recommended by the Minnesota Pollution Control Agency [16].

Soil samples were collected at various depth viz: 0 – 15 cm, 15 - 30 cm, 30 - 45 cm and 45 – 60 cm at contaminated and control soil. Also composite soil was collected at 0 - 15 cm and 15 – 30 cm. The soil sample was collected using a hand auger. The samples were collected and stored in aluminum foil packs and labeled accordingly. The samples were stored in ice coolers packed with ice chips before being transported to the laboratory for sample preparation and analysis.

### 2.3 Laboratory Analysis

#### 2.3.1 Total Hydrocarbon Content

The total hydrocarbon content was carried out following ASTM D 9071B – 7 (Soxhlet Extraction Method using Hexane Extractable Materials by American Society for Testing and Materials). During the analysis the soil sample were air-dried and sieved through a 2 mm mesh size sieve before being thoroughly mixed, especially the composited samples. Foreign objects like sticks, leaves and stones were discarded. About 10 grams of the sample was blended with 10 grams of anhydrous sodium sulphate, the homogenized sample was transferred to an extraction thimble and covered with glass wool. The extraction thimble was allowed to drain freely for the duration of the extraction period.

The soxhlet apparatus containing the extraction thimble and sample was set up with the attachment of a 250ml boiling flask containing 90 ml of n-hexane. The heating control on the heating mantle was adjusted so that a cycling rate of 20 cycles/h was obtained. Extraction was carried out for a period of 4 h. Afterwards, a clean 250 ml boiling flask was oven-dried at 105°C for 2 h, after which it was cooled in a desiccator at room temperature. With the use of tongs, the boiling flask was removed from the desiccator and weighed on a calibrated weighing balance.

At the end of the 4 h extraction period, the organic extract was filtered through grease-free cotton, into the pre-weighed boiling flask with the aid of hand gloves. The flask and cotton wool were then rinsed with n-hexane and added to the 250 ml boiling flask. The boiling flask was connected to the distilling head apparatus and the solvent was distilled by immersing the lower half of the flask in a heating mantle. The temperature of the heating device was adjusted to complete the distillation in less than 30 min. The solvent was disposed of in a glass bottle designated for storing organic waste before appropriate waste disposal.

On complete distillation, the distilling head was removed, followed by the immediate removal of the flask from heating mantle, before the flask was then cooled in a desiccator for 30 minutes and weighed. The gain in weight of the boiling flask was determined by subtracting the initial weight from the final weight of flask.

Calculation: The concentration of HEM (Hexane Extractable Material) in the soil sample as follows:

$$\text{HEM (mg/kg wet weight)} = \frac{\text{gain in weight of flask (mg)} \times 1000}{\text{weight of wet solid (g)}}$$

(ASTM D 9071B - 7. Hexane Extractable Materials using Soxhlet Extraction Method, American Society for Testing and Materials).

#### 2.3.2 Polycyclic aromatic hydrocarbon (PAH) by Gas Chromatography

Polycyclic aromatic hydrocarbons (PAHs) was analyzed with GC-FID methods. PAH analysis was carried out by employing the principle of gas chromatography by flame ionization detection as sample extracts in the mobile phase (helium gas) are being forced through an immobile, inert stationary phase (1,3-dimethyl siloxane) and components of

low solubility in the stationary phase take a shorter time to be transported through the column while components with high solubility in the stationary phase take a longer elution time leading to the differential mobilities of the fractional components of the polycyclic aromatic hydrocarbon (PAHs). Samples were automatically detected as they emerged from the column (at a constant flow rate) by the FID detector whose response was dependent upon the composition of the vapor and the area under each response peak was directly proportional to the concentration of the respective constituent fractions. Sample extraction methods, sample clean up and condition previously described by Inengite et al. [13, 15] was used for PAH analysis.

#### 2.4 Diagnostic ratios of PAHs

Diagnostic ratios of selected PAH concentrations are the most widely used technique for the identification and characterization of sources [17]. In order to identify sources of PAHs in the contaminated soil, the isomer ratios of Ant/(Ant+Phe), Flt/(Flt+Pyr), BaA/(BaA+Chr), Flt/Pyr and BaP/(BaP+Chr) were used to distinguish between petrogenic and pyrogenic sources [17, 18]. In this study, the applied PAHs DRs (Ant/(Ant + Phe), Flt/(Flt + Pyr), Flt/Pyr, BaP/(BaP + Chr), BaA/(BaA + Chr) as in (Table 1) were used for source identification of PAHs in the oil Contaminated and control plots.

### 3 Results and Discussion

PAH and THC properties of pipeline oil spill contaminated soil and control between August 2013 – January 2014 in Rumuolukwu, Eneka in Port Harcourt metropolis is presented in Table 2. The mean values from the various depth and composite soil were 361.8 mg/kg and 21.2 mg/kg for the control in August 2013. The concentration decline as the period of study increases. As such a mean value of 67.5 mg/kg and 37 mg/kg for the control at as January 2014. The concentration of both PAH and THC were higher in contaminated soil compared to the control. Also, the concentration were higher in the lower depth (i.e. 0 – 15cm) compared to 45 - 60cm depth. The occurrence of higher THC in top soil is in accordance with the findings of Osuji and Adesiyun [26], Osuji et al. [27].

Like THC, PAH concentration was higher during the month of August with mean value of 2.06mg/kg and 0.018 mg/kg at oil spill contaminated soil and control respectively. The PAH concentration decrease at the spill duration increases. However at as January 2014, the concentration of PAH were 0.21 and 0.005 mg/kg for oil spill contaminated soil and control respectively. Again the decline in concentration of PAH could be due to the activities of hydrocarbon utilizing microbes. The higher amount of PAHs detected in the oil contaminated soil may be an indication of the oil spillage that had occurred. The concentration of PAH at some instances especially the wet season in the oil spill contaminated soil is higher than 1 mg/kg recommended by DPR. Even though the PAH levels of the oil contaminated soil had exceeded this statutory limitation, it is worthy of note that the control site recorded values which were within limit.

Table 1: Diagnostic Ratios of Individual PAH concentration for Source Diagnosis

PAH ratios	Value of ratios and indications					Reference
	Pyrogenic	Petrogenic	Gasoline, diesel	Petroleum comb.	Biomass, coal comb.	
Ant/(Ant + Phe)	>0.1	<0.1	-	-	-	[12, 19-22]
Flt/(Flt + Pyr)	≥0.4 - 0.5	<0.4	-	-	-	[12, 19]
	-	-	-	-	>0.5	[12, 23]
BaA/(BaA + Chr)	-	<0.2	-	-	-	[12, 17]
	-	<0.2	-	>0.35 (fuel combustion)	-	[20]
Flt/Pyr	-	<1.0	-	0.2 - 0.35	>0.35	[12, 19]
	-	<1.0	-	-	1.0 - 1.4	[12, 24]
BaP/(BaP + Chr)	-	-	0.49 (gasoline), 0.73 (diesel)	-	-	[12, 25]

Note: Phe phenanthrene, Ant anthracene, Flt fluoranthene, Pyr pyrene, BaA 1,2-Benzanthracene, Chr chrysene, BaP 1,2-Benzpyrene.

The apparent decline in THC and PAH concentration as the duration of spill increases could be due to natural degradation by indigenous hydrocarbon utilizing/degrading bacteria and fungi found in the soil. Furthermore, The sharp decline of THC and PAH at the top soil may have resulted from aerobic degradation of hydrocarbon while the slower decline in the bottom soil may have resulted from the anaerobic degradation of hydrocarbon as petroleum oil biodegradation by bacteria can occur under both aerobic and anaerobic conditions [28]. It is worthy of note that the control site had values which classified it as relatively uncontaminated, even though, the low amounts of THC that was recorded for the control site, may be indicative of the spread of oil contaminants to uncontaminated sites through cross-contamination in the form of volatilization, wind transport and deposition whether or not the site had any previous spill record.

The significant amount of hydrocarbons found in the oil contaminated soil as compared to the control soil may be an indication of the oil spillage that occurred on the oil contaminated site. At few instances higher concentration of crude oil was found in bottom soil i.e. high depth. This may have resulted from vertical delineation. Similar observation has been reported by Benka-Coker and Ekundayo [29] who observed an evidence of vertical delineation of oil up to depths of 7.2 m.

Comparing the THC and PAH levels from this study with another study in the Niger Delta reveal that Rumuolukwu oil contaminated soil had lower THC and PAH levels when compared to that of the oil contaminated soils of Owaza community in the Niger Delta as reported by Osuji and Nwoye [30].

The results obtained from this study, shows the predominance of pyrogenic PAHs, using diagnostic ratios of selected PAHs [31-33]. The cross plots showing the distribution of the PAHs to aid source identification is presented in Figure 2 – 9. The seasonal variation of the

various diagnostic ratio is presented in Table 3 and 4 for oil spill contaminated soil and non-contaminated soil respectively.

The PAH cross plots depict sampling points from top and bottom soil. Based on the four diagnostic ratios used to assess the oil contaminated and control soils (Figure 2 to 9); the Ant/(Ant + Phe) versus Flt/(Flt + Pyr) diagnostic ratios depicts the observed source distribution trend. These trends were in the order: pyrogenic > petrogenic = biomass, coal combustion and pyrogenic > petrogenic > biomass, coal combustion during the rainy and dry seasons respectively. The Flt/Pyr versus Flt/(Flt + Pyr) diagnostic ratios depicted the same trend (biomass, coal combustion > gasoline > petrogenic > pyrogenic) in both the rainy and dry seasons. BaP/(BaP + Chr) versus Flt/(Flt + Pyr) diagnostic ratios resulted in the trend (diesel > petrogenic = biomass, coal combustion > gasoline > pyrogenic) for both the rainy and dry seasons. Applying the BaA/(BaA + Chr) versus Flt/(Flt + Pyr) showed the trend (biomass, coal combustion > petrogenic > petroleum combustion > pyrogenic) in both the rainy and dry seasons. The seasonal differences in PAHs sources depicted an increasing petrogenicity with decreasing pyrogenicity during the dry season. The use of the Ant/(Ant + Phe) versus Flt/(Flt + Pyr) ratio and the Flt/Pyr versus Flt/(Flt + Pyr) ratio both depicted the dominance of pyrogenic PAHs. Based on the seasonality of the diagnostic ratio, BaP/(BaP + Chr) were recorded in the control, and at few instances BaA/(BaA + Chr) were also depicted. Contrary to the contaminated soil that the entire diagnostic ratios studied were reported.

Table 2: Total hydrocarbon and polycyclic aromatic hydrocarbon content in an oil spill soil

Months of the Year	Parameter(s)	CPS (0-15)	CPS (15-30)	CPS (30-45)	CPS (45-60)	COMPS (0-15)	COMPS (15-30)	Mean	SD	CCS (0-15)	CCS (15-30)	CCS (30-45)	CCS (45-60)	COMCS (0-15)	COMCS (15-30)	Mean	SD
August 2013	THC(mg/kg)	954.9	277.9	180.3	50.97	508.9	198.0	361.8	327.7	33.93	25.10	16.27	12.80	22.65	16.46	21.2	7.7
	PAH(mg/kg)	6.366	2.120	0.883	0.345	1.705	0.913	2.06	2.21	0.093	0.046	0.007	0.016	0.023	0.018	0.033	0.032
September 2013	THC(mg/kg)	264.4	228.3	116.1	44.5	330.9	170.4	192.4	103.8	27.3	11.3	9.1	8.0	16.3	11.2	13.9	7.2
	PAH(mg/kg)	1.659	1.452	0.434	0.187	1.682	0.906	1.05	0.64	0.033	0.012	0.005	0.003	0.024	0.010	0.015	0.012
October 2013	THC(mg/kg)	233.3	127.8	136.2	110.9	244.3	293.1	190.9	75.5	NM	NM	NM	NM	NM	NM	NM	NM
	PAH(mg/kg)	1.276	0.933	0.951	0.480	1.437	1.504	1.1	0.39	NM	NM	NM	NM	NM	NM	NM	NM
November 2013	THC(mg/kg)	151.4	170.2	192.3	117.8	195.8	65.7	148.9	49.9	NM	NM	NM	NM	NM	NM	NM	NM
	PAH(mg/kg)	0.985	1.019	1.495	1.567	1.588	0.269	0.99	0.51	NM	NM	NM	NM	NM	NM	NM	NM
December 2013	THC(mg/kg)	133.5	71.2	89.8	83.6	159.7	69.4	101.2	36.9	0.68	0.52	0.30	0.23	1.42	1.88	0.8	0.7
	PAH(mg/kg)	0.625	0.422	0.453	0.417	0.733	0.233	0.48	0.18	0.021	0.007	0.003	<0.001	0.013	0.010	0.009	0.008
January 2014	THC(mg/kg)	108.5	59.3	62.5	57.4	65.8	51.3	67.5	20.7	0.50	0.35	<0.01	<0.01	1.06	1.37	0.5	0.6
	PAH(mg/kg)	0.271	0.320	0.226	0.154	0.133	0.179	0.21	0.07	0.013	0.004	0.002	0.001	0.004	0.004	0.005	0.004

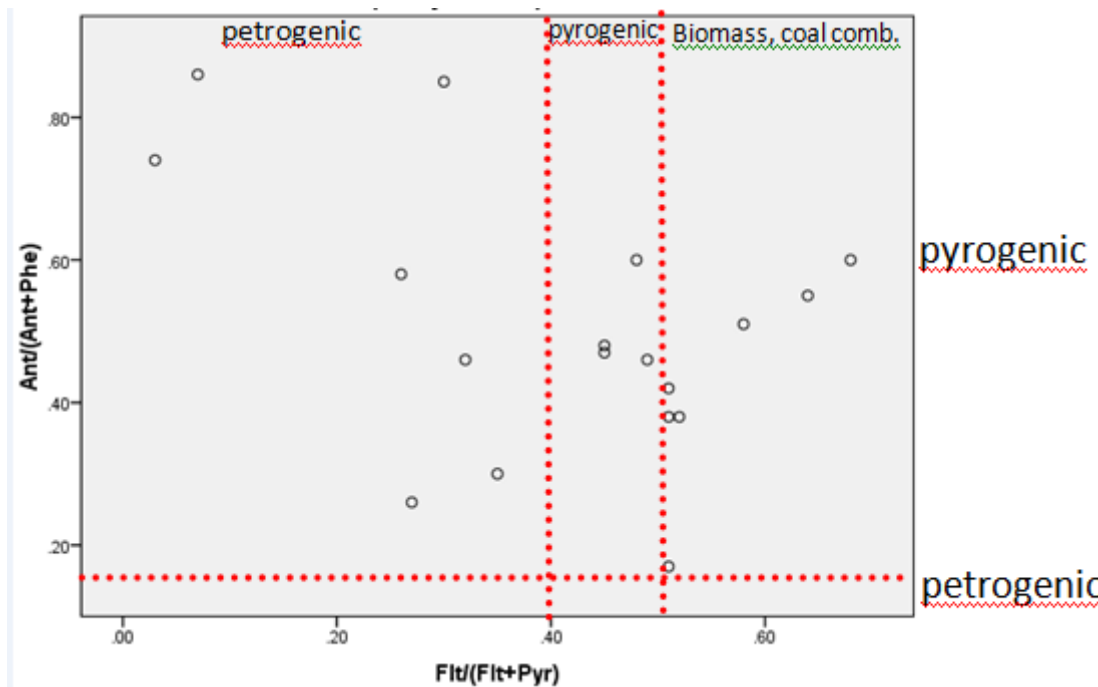


Figure 2: Scattered plot for Ant/(Ant+Phe) vs flt(flt+pyr) for oil contaminated plot during raining season

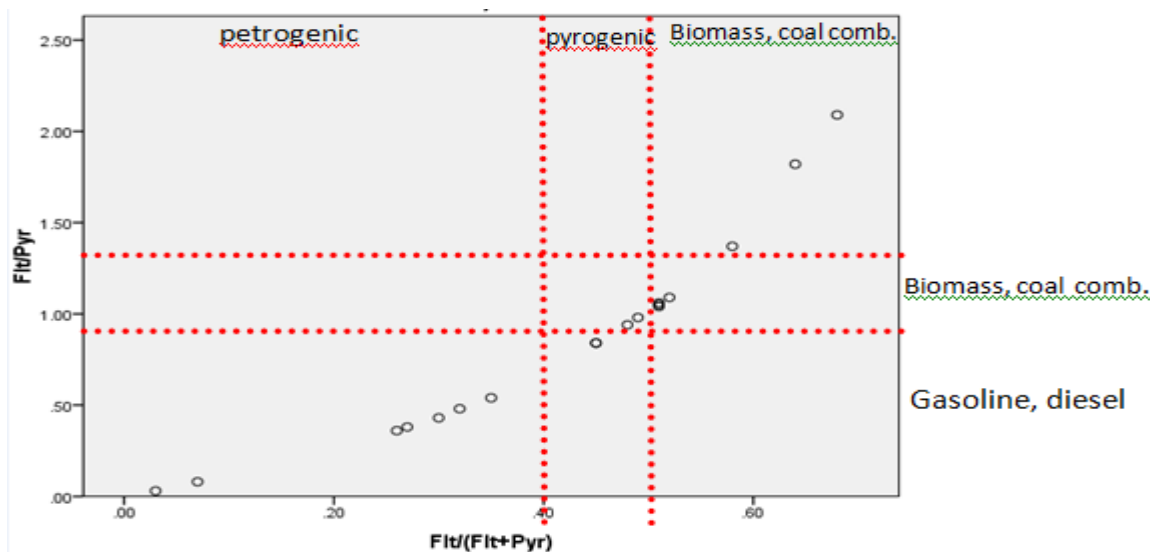


Figure 3: Scattered plot for Flt/Pyr vs flt(flt+pyr) for oil contaminated plot during raining season

Generally, more petrogenic sources were identified during the dry season as this may have resulted from soil erosion which followed the incessant rainfall and flooding that characterized the sampling period. Even though a mixed petrogenic and pyrogenic source was identified in this study like earlier studies, there was an observed contrast in relation to earlier findings of Inengite et al. [14], where a combination of petroleum and combustion sources were identified during the wet season, with the predominance of

combustion sources during the same dry season. Similar studies by Inengite et al. [14] while applying cross plots of diagnostic ratios revealed that the Kolo creek sediment depicted pyrogenic PAHs except in the rainy season that showed PAHs of petrogenic origin. Further diagnostic PAH ratios study on roadside soils of Delhi, India showed a mixed pyrogenic activities such as petroleum, biomass and coal combustion which may have resulted because of vehicular emissions [12].

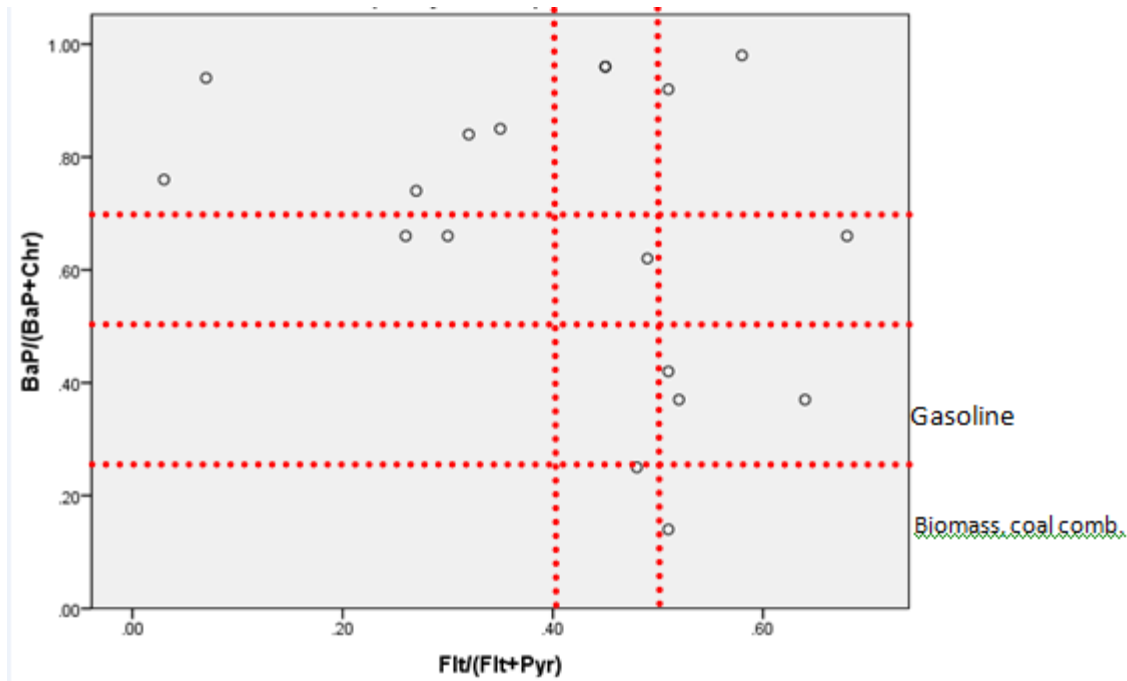


Figure 4: Scattered plot for BaP/(BaP+Chr) vs flt/(flt+pyr) for oil contaminated plot during raining season

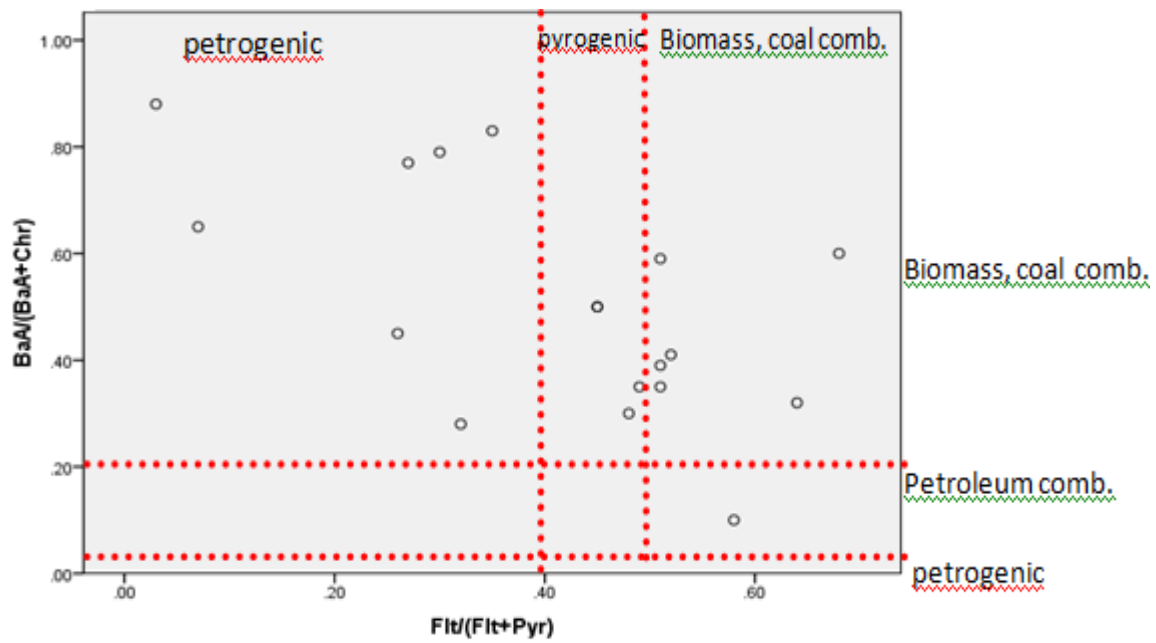


Figure 5: Scattered plot for BaA/(BaA+Chr) vs flt/(flt+pyr) for oil contaminated plot during raining season

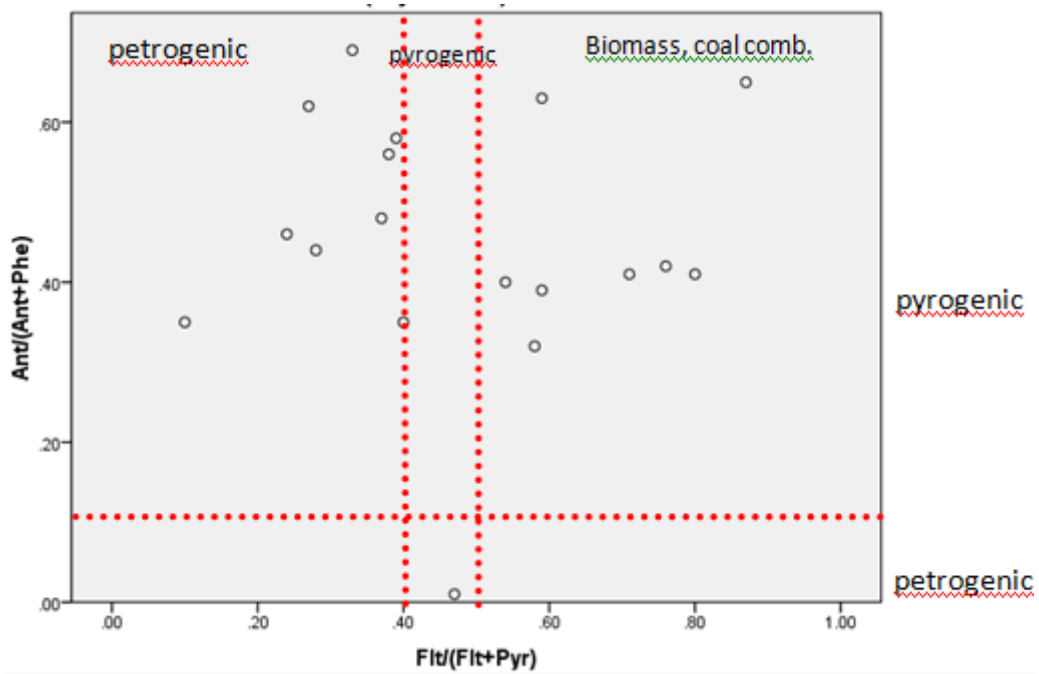


Figure 6: Scattered plot for Ant/(Ant+Phe) vs flt(flt+pyr) for oil contaminated plot during dry season

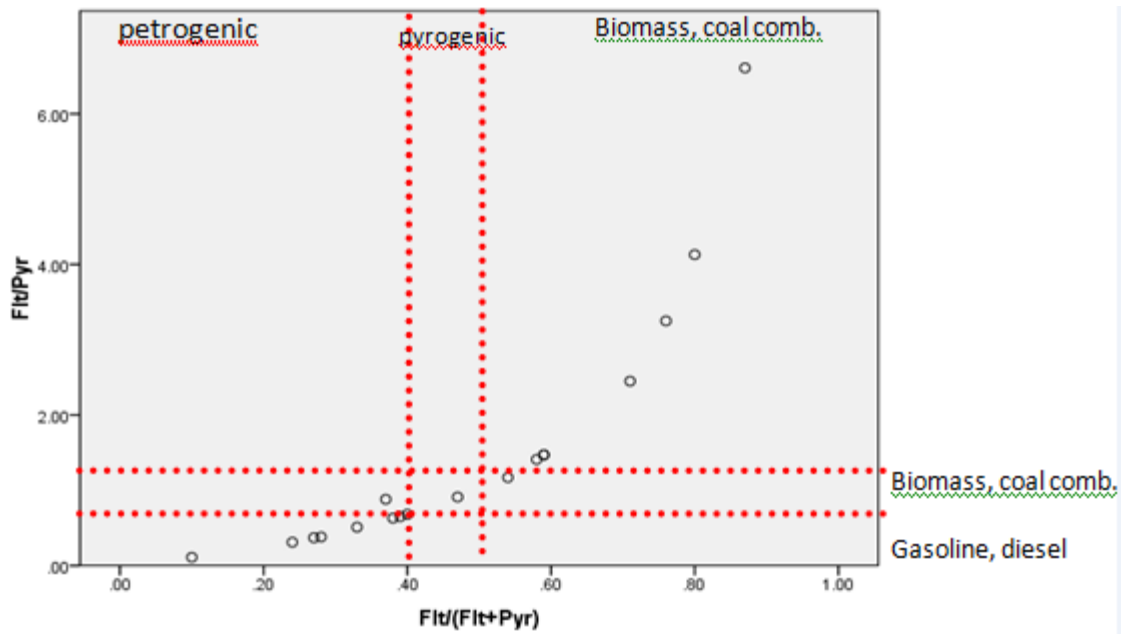


Figure 7: Scattered plot for Flt/Pyr vs flt(flt+pyr) for oil contaminated plot during dry season



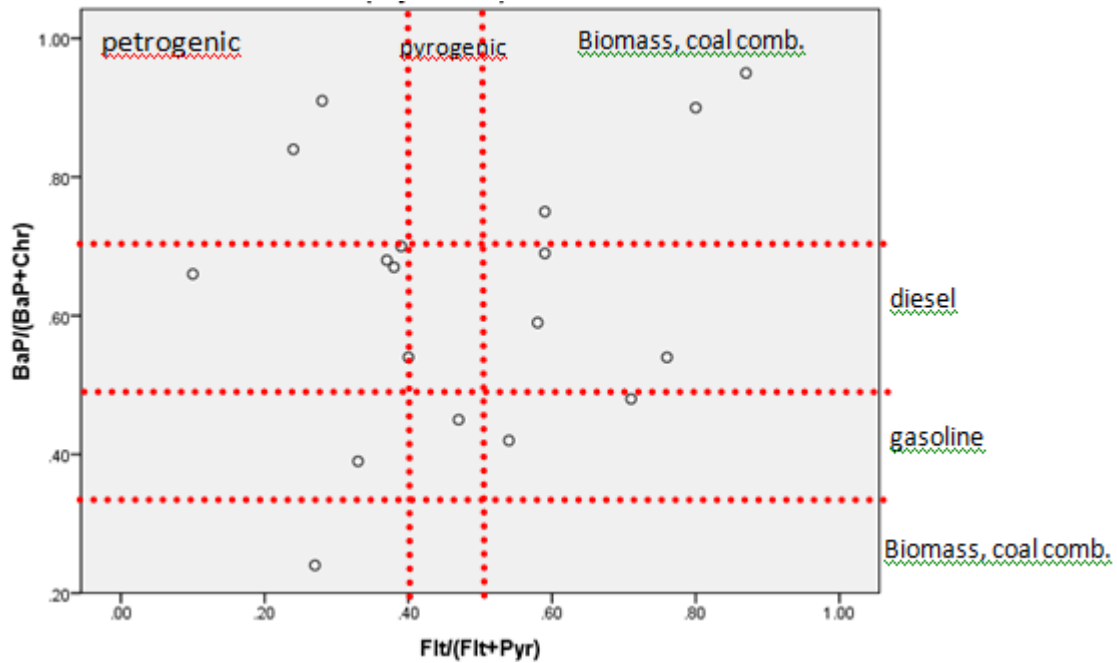


Figure 8: Scattered plot for  $BaP/(BaP+Chr)$  vs  $flt/(flt+pyr)$  for oil contaminated plot during dry season

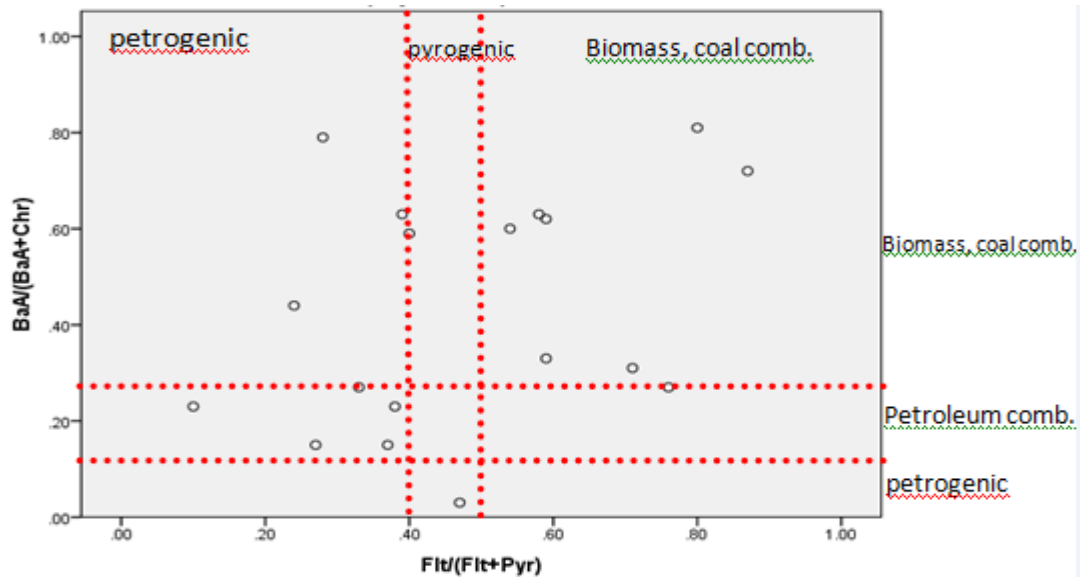


Figure 9: Scattered plot for  $BaA/(BaA+Chr)$  vs  $flt/(flt+pyr)$  for oil contaminated plot during dry season

Table 3: Diagnostic PAHs Ratios for Source Diagnosis at contaminated soil for both seasons

S/N	SAMPLE ID	Ant /(Ant + Phe)	Flt/Pyr	BaP /(BaP + Chr)	BaA /(BaA + Chr)	Flt /(Flt + Pyr)
1.	CPS (0-15cm)Aug	0.38	1.04	0.14	0.39	0.51
2.	CPS (15-30cm)Aug	0.38	1.09	0.37	0.41	0.52
3.	CPS (30-45cm)Aug	0.26	0.38	0.74	0.77	0.27
4.	CPS (45-60cm)Aug	0.30	0.54	0.85	0.83	0.35
5.	COMPS (0-15cm)Aug	0.85	0.43	0.66	0.79	0.30
6.	COMPS (15-30cm)Aug	0.74	0.03	0.76	0.88	0.03
7.	CPS (0-15cm)Sept	0.46	0.98	0.62	0.35	0.49
8.	CPS (15-30cm)Sept	0.60	2.09	0.66	0.60	0.68
9.	CPS (30-45cm)Sept	0.17	1.05	0.42	0.35	0.51
10.	CPS (45-60cm)Sept	0.58	0.36	0.66	0.45	0.26
11.	COMPS (0-15cm)Sept	0.60	0.94	0.25	0.30	0.48
12.	COMPS (15-30cm)Sept	0.55	1.82	0.37	0.32	0.64
13.	CPS (0-15cm)Oct	0.42	1.06	0.92	0.59	0.51
14.	CPS (15-30cm)Oct	0.46	0.48	0.84	0.28	0.32
15.	CPS (30-45cm)Oct	0.86	0.08	0.94	0.65	0.07
16.	CPS (45-60cm)Oct	0.47	0.84	0.96	0.50	0.45
17.	COMPS(0-15cm)Oct	0.51	1.37	0.98	0.10	0.58
18.	COMPS(15-30cm)Oct	0.48	0.84	0.96	0.50	0.45
19.	CPS (0-15cm)Nov	0.41	2.45	0.48	0.31	0.71
20.	CPS (15-30cm)Nov	0.35	0.11	0.66	0.23	0.10
21.	CPS (30-45cm)Nov	0.40	1.17	0.42	0.60	0.54
22.	CPS (45-60cm)Nov	0.32	1.41	0.59	0.63	0.58
23.	COMPS (0-15cm)Nov	0.01	0.91	0.45	0.03	0.47
24.	COMPS (15-30cm)Nov	0.42	3.25	0.54	0.27	0.76
25.	CPS (0-15cm)Dec	0.39	1.47	0.75	0.62	0.59
26.	CPS (15-30cm)Dec	0.46	0.31	0.84	0.44	0.24
27.	CPS (30-45cm)Dec	0.41	4.13	0.90	0.81	0.80
28.	CPS (45-60cm)Dec	0.65	6.61	0.95	0.72	0.87
29.	COMPS (0-15cm)Dec	0.48	0.88	0.68	0.15	0.37
30.	COMPS (15-30cm)Dec	0.63	1.47	0.69	0.33	0.59
31.	CPS (0-15cm)Jan	0.35	0.68	0.54	0.59	0.40
32.	CPS (15-30cm)Jan	0.58	0.65	0.70	0.63	0.39
33.	CPS (30-45cm)Jan	0.56	0.63	0.67	0.23	0.38
34.	CPS (45-60cm)Jan	0.44	0.38	0.91	0.79	0.28
35.	COMPS(0-15cm)Jan	0.69	0.51	0.39	0.27	0.33
36.	COMPS(15-30cm)Jan	0.62	0.37	0.24	0.15	0.27
	Gasoline	-	<1.0	0.49	-	-
	Diesel	-	-	0.73	-	-
	Biomass, Coal comb.	-	1.0 - 1.4	0.07 - 0.24	>0.35	>0.50
	Petroleum comb.	-	-	-	0.2 - 0.35	-
	Petrogenic	<0.10	-	-	<0.20	<0.40
	Pyrogenic	>0.10	-	-	>0.35	>0.50

Table 4: Diagnostic PAHs Ratios for Source Diagnosis at non-contaminated soil for both seasons

S/N	SAMPLE ID	Ant /(Ant + Phe)	Flt/Pyr	BaP /(BaP + Chr)	BaA /(BaA + Chr)	Flt /(Flt + Pyr)
1.	CCS (0-15cm)Aug	ND	ND	1.00	ND	ND
2.	CCS (15-30cm)Aug	ND	ND	0.73	0.38	ND
3.	CCS (30-45cm)Aug	ND	ND	1.00	ND	ND
4.	CCS (45-60cm)Aug	ND	ND	0.66	0.68	ND
5.	COMCS (0-15cm)Aug	ND	ND	0.68	0.89	ND
6.	COMCS (15-30cm)Aug	ND	ND	0.79	0.47	ND
7.	CCS (0-15cm)Sept	ND	ND	1.00	ND	ND
8.	CCS (15-30cm)Sept	ND	ND	1.00	ND	ND
9.	CCS (30-45cm)Sept	ND	ND	1.00	ND	ND
10.	CCS (45-60cm)Sept	ND	ND	1.00	ND	ND
11.	COMCS (0-15cm)Sept	ND	ND	0.63	0.31	ND
12.	COMCS (15-30cm)Sept	ND	ND	0.56	0.34	ND
13.	CCS (0-15cm)Dec	ND	ND	1.00	ND	ND
14.	CCS (15-30cm)Dec	ND	ND	1.00	ND	ND
15.	CCS (30-45cm)Dec	ND	ND	1.00	ND	ND
16.	CCS (45-60cm)Dec	ND	ND	ND	ND	ND
17.	COMCS (0-15cm)Dec	ND	ND	1.00	ND	ND
18.	COMCS (15-30cm)Dec	ND	ND	1.00	ND	ND
19.	CCS (0-15cm)Jan	ND	ND	0.57	0.21	ND
20.	CCS (15-30cm)Jan	ND	ND	0.44	0.20	ND
21.	CCS (30-45cm)Jan	ND	ND	0.89	0.52	ND
22.	CCS (45-60cm)Jan	ND	ND	0.62	ND	ND
23.	COMCS(0-15cm)Jan	ND	ND	0.57	0.14	ND
24.	COMCS(15-30cm)Jan	ND	ND	0.75	0.36	ND
	Petrogenic	<0.1	-	-	<0.20	<0.40
	Pyrogenic	>0.1	-	-	-	≥0.4 - 0.5
	Gasoline	-	<1.0	0.49	-	-
	Diesel	-	-	0.73	-	-
	Biomass, Coal comb.	-	1.0 - 1.4	0.07 - 0.24	>0.35	>0.50
	Petroleum comb.	-	-	-	0.2 - 0.35	-
	Petrogenic	<0.10	-	-	<0.20	<0.40
	Pyrogenic	>0.10	-	-	>0.35	>0.50

NOTE: ND stands for "Non Detection". CPS - Centre of polluted Site, COMPS - Composite of polluted site, CCS - Centre of control site, COMCS - Composite of control site.

#### 4 Conclusion

This study assessed THC and PAH in an oil spill contaminated soil in Rumuolukwu community in Niger Delta. Findings showed that THC had substantial reduction suggesting natural attenuation of contaminate soil. The evaluation of PAH sources present in the oil contaminated soil depicted the predominance of mixed pyrogenic activities such as petroleum, biomass and coal combustion. Petrogenic sources were observed close to the point source (that is, within close proximity to the faulty oil pipeline), the predominance of mixed pyrogenic PAHs may in part, have been due to the presence of high molecular weight PAHs, resulting from the littering of study site with dead remains of wood and plants which could have diffused into the sources, as well as the resultant effect of the old farm practice of bush burning which has persisted in this region.

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