

CONTAMINATION OF MANGROVE ECOSYSTEM WITH PAHs AND BTEX AND IMPACT ASSESSMENT OF CAWTHORNE CHANNEL 2 AND 3 OIL FIELDS, RIVERS STATE

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ABSTRACT

Anthropogenic activities are the many causes of environmental crisis in the Niger Delta and this had led to ecological imbalance, particularly from crude oil exploration, production, transportation and uses. This research work considered the TPH toxic fractions of BETX and PAHs as major constituents of crude oil and their impacts on the river sediment and river water that had caused environmental hazards with the associated risk resulting from petroleum hydrocarbon contamination from crude oil spillages. This cause of contamination with the environmental effects necessitated the application of conceptual site model and it enabled me identified the possible receptors and developed source-pathway-receptors relationship model of the studied sites. River sediment samples were collected using amber wide-mouth and vial glass bottles with the aid of soil auger at 0-2m depths. Nkansah et al. (2017) sampling method was adopted as the study sites were divided into five zones – north, south, east, west and center. River water samples were also collected. Samples were collected in wet and dry seasons from coastal mangrove and GC-FID and GC-MSD analytical techniques were used. In the river sediment of Jacob kiri, TPH and PAHs decreased with depth while in Elem Kalabari it increases with depth. On application of CF and DC equations, Jacob kiri spill site was of low contamination while Elem Kalabari was moderately contaminated. EF equation applied on Jacob kiri river water shows no impact.

Keywords: BTEX, PAHs, pollution indices, ecological imbalance, source-pathway-receptor.

INTRODUCTION

Rivers State is part of the eastern Niger Delta region of Nigeria, and has a known geological environment with abundance of crude oil natural mineral deposits. It experienced daily occurrence of crude oil spillages caused both by the multinational companies and the sabotage acts. This daily occurrence causes both health and environmental risk with the associated diseases.

Assessment studies carried out in Rivers State revealed that there is relatively high quantities of crude oil in the mangroves of the Niger Delta environment as a result of spillages (UNEP, 2011). Udoetok and Osuji, 2007; Chukwujindeset *et al.*, 2008 and Osu and Asuoha, 2010 in their work on soil samples and profile studies examined for contamination revealed that all the samples were found to be contaminated with PAHs and BTEX. Riba *et al.* (2002a); Atta and Zakaria (2014); Popoola *et al.* (2015) and Hadiya and Vagif (2016) in their respective studies applied pollution indices and discovered that the anthropogenic sources contributed to heavy metal accumulation.

In 2011, 339 oil spills occurred and about 210 and 79 were sabotage and non-sabotage spills respectively. In 2012, 229 spills occurred and about 196 and 66 were sabotage and non-sabotage spills respectively. In 2015 second quarter, 27 spills occurred releasing 644 barrels of crude oil into the environment; 19 out of 27 spills were bunkery cases.

In this paper TPH, PAHs and BTEX fractions of the petroleum hydrocarbon of river water and sediment were studied.

MATERIAL AND METHOD

Materials

100ml glass beakers; 50ml, 100ml graduated cylinder, 500 ml/100ml Separatory funnels, Stainless steel Spatula, 250ml Erlenmeyer flasks; Glass funnels, Analytical balance capable of accurately weighing 0.0001g, Class ‘‘A’’ Volumetric flasks: 10, 25, 50 and 100ml; Class ‘‘A’’ Volumetric pipets: 1, 5ml, Microsyringe: 10 μ L, Whatman No. 41 Filter Paper and 2ml glass vials with Teflon-lined rubber caps.

Reagent water: organic free water, Solvents: hexane, methylene chloride, and acetone, Sodium Sulphate (anhydrous), Certified TPH reference standard and Surrogate spike standard (Ortho-terphenyl /OTP).

Method

Field trip to Cawthorne Channel 2 and 3 oil fields petroleum hydrocarbon spill sites at Jacob kiri and Elem Kalabari were made for both physical and empirical observations and samples were collected for laboratory analyses. Fig. 1 and 2 below show pictures of the spill sites visited, cause, and volume of spills determined.



Fig. 1: Cawthorne Channel 2 well 32 pipeline spill at Jacob kiri

The field visit to Cawthorne Channel 2 at Jacob kiri spill site (fig. 1) was on the 24th May, 2016 while the spill occurred on the 20th May, 2016. Quantity spilled was 2.47bbls of crude oil. Coordinates of the spill site was N04⁰ 32' 55.7" E007⁰ 00' 44.8" and the cause of the spill was hard saw cut on the pipeline.

Fig. 2 below is the field visit to Elem Kalabari spill site on the 14th May, 2017 while the spill occurred on the 7th May, 2017. Quantity spilled was not determined but that 52bbls was recovered. Coordinates of the spill site was N04⁰ 34' 30.75" E007⁰ 57' 17.47" and the cause of the spill was illegal bunkery activities that resulted to fire outbreak.





Fig 2: Cawthorne Channel 30” NCTL Spill at Elem Kalabari

Sampling, Preparation and Analysis

River Sediment: The impacted area was divided into 5 zones namely north (N), South (S), East (E), West (W) and Center (O). At each station, samples were collected at 0-2m depths using stainless steel soil auger. The samples were put in 60ml amber wide-mouth glass jars with Teflon-lined screw caps. Auto sampler 20ml vials were used to collect samples for BTEX parameters. The coordinates of spill sites and sample points were determined using GPS.

A total of 12 sediment samples were collected each from Jacob kiri and Elem Kalabari spill sites. The samples were cooled to $4 \pm 2^{\circ}\text{C}$ immediately after sample collection. A chain of custody form is used to log in the sample names and other relevant data. Control sample was also collected at the same depth.

The river sediment samples were weighed and about 10g of a well mixed sample was put into solvent rinsed beaker and recorded the weight in the extraction log book and, 50ml of 1:1 Dichloromethane/acetone was added to the sample. After which, added 1mL of the surrogate spike standard to it and the beaker was covered with aluminium foil. Then, transfer the beaker to a mechanical shaker for about 1 hour. The sample was filtered through Whatman No.41 filter paper packed with 10g Na_2SO_4 and silica gel into Erlenmeyer flask, and concentrates the sample extract using a mechanical shaker to about 2 ml, then solvent exchange the extract with n-Hexane. Finally, re-concentrate the extract to 1 to 2mL and transfer by way of the pipette into the 2 ml auto sampler vial with Teflon lined caps.

The samples submitted for TPH analysis was extracted with methylene chloride, passed through sodium sulphate, solvent exchanged into hexane and concentrated in a mechanical shaker. The concentrated extract is then analyzed by a capillary column gas chromatograph equipped with a flame ionization detector (FID). The sample extracts from sediment samples were analyzed for

TPH and PAH using a Gas Chromatograph with a Flame Ionization Detector (GC-FID) (Agilent 6890 and 7890A GC System) and Gas Chromatograph with a Flame Ionization Detector (Agilent 7820 GC System and 5975 series, 7890A and 5975C Inert XL MSD) respectively, sample injection is done with auto sampler using a 10 µl syringe. While Gas Chromatograph/ Mass Selective Detector (GC/MSD) 7890A 5975C Inert XL MSD; 7697A Headspace GC-MS was used for BTEX analyses.

River Water: Eight river water samples were collected using 250ml amber glass bottles with Teflon-lined screw caps. The samples were collected below the river surface from Jacob kiri for TPH, PAHs and TPH. While auto sampler 20ml vials was used to collect samples for BTEX parameter. The sample bottles were filled with the water and were stored in a refrigerator temperature.

All samples after collection were stored in an ice-cooled box and taken to laboratory and stored at 4°C in a refrigerator before analysis with GC-FID and GC-MSD. pH and temperature were measured in-situ using Hanna HI 98125 instrument.

RESULTS AND DISCUSSION

Results

Table 1: CAWTHORNE CHANNEL 3 RIVER SEDIMENT AT ELEM KALABARI (mg/kg)

Rainy Season								Dry Season			
0-0.5m	0.5-1m	1-1.5m	1.5-2m	0-0.5m	0.5-1m	1-1.5m	1.5-2m	0-0.5m	0.5-1m	1-2m	0-0.5m

SN	Parameter	1	2	3	4	5	6	7	8	9	10	11	12
1	TPH	7,211.62	7,405.2	8,012.01	8,206.76	7,046.7	7,411.1	7,891.02	6,965.9	6,380.90	5,890.31	2,296.5	55.6
POLYCYCLIC AROMATIC HYDROCARBON (PAH) PROFILE													
1	Naphthalene	0.09	0.18	0.17	0.15	0.12	0.16	0.18	0.10	0.16	0.14	-	NT
2	Acenaphthylene	0.13	0.12	0.16	0.20	0.16	0.15	0.20	0.18	0.22	0.23	-	NT
3	Acenaphthene	0.21	0.22	0.23	0.26	0.20	0.19	0.27	0.21	0.23	0.21	-	NT
4	Fluorene	0.20	0.22	0.25	0.30	0.19	0.24	0.18	0.18	0.23	0.26	-	NT
5	Phenanthrene	0.63	0.72	0.73	0.68	0.66	0.70	0.72	0.60	0.70	0.66	-	NT
6	Anthracene	0.70	0.68	0.70	0.69	0.64	0.66	0.70	0.64	0.70	0.66	-	NT
7	Fluoranthene	0.11	0.09	0.12	0.14	0.10	0.09	0.14	0.12	0.13	0.11	-	NT
8	Pyrene	0.02	0.03	0.03	0.04	0.03	0.03	0.02	0.04	0.04	0.04	-	NT
9	Benz(a)anthracene	0.20	0.15	0.16	0.22	0.21	0.17	0.20	0.22	0.22	0.22	-	NT
10	Benzo(b)fluoranthene	0.04	0.06	0.06	0.05	0.04	0.06	0.06	0.05	0.06	0.07	10.2	NT
11	Chrysene	0.16	0.18	0.16	0.13	0.14	0.15	0.21	0.14	0.20	0.18	-	NT

12	Benzo(a)pyrene	0.12	0.10	0.11	0.14	0.10	0.09	0.10	0.12	0.12	0.12	-	NT
13	Benzo(k)fluoranthene	0.10	0.07	0.09	0.12	0.08	0.09	0.09	0.10	0.10	0.12	0.04	NT
14	1,2,3-benzofluoranthene	0.05	0.03	0.04	0.05	0.03	0.04	0.03	0.02	0.04	0.04	-	NT
15	Dibenz(a,h)anthracene	0.04	0.02	0.05	0.06	0.03	0.04	0.02	0.03	0.03	0.04	-	NT
16	Benzo(g,h,i)perylene	0.03	0.01	0.04	0.05	0.02	0.03	0.02	0.02	0.03	0.04	-	NT
	Total	2.83	2.88	3.10	3.28	2.75	2.89	3.14	2.75	3.21	3.14	0.26	-
	TOTAL PAH	1.88	1.92	2.07	2.18	1.83	1.92	2.09	1.83	2.14	2.09	0.17	-
BTEX PROFILE BTEX PROFILE													
1	Benzene	ND	ND	ND	ND	ND	NT	ND	ND	ND	ND	ND	NT
2	Toluene	0.02	0.03	0.03	0.02	0.04	NT	0.04	0.03	0.04	0.04	ND	NT
3	Ethylbenzene	0.09	0.11	0.10	0.12	0.12	NT	0.12	0.12	0.10	0.10	ND	NT
4	m,p-xylene	0.06	0.07	0.08	0.07	0.05	NT	0.07	0.08	0.06	0.06	ND	NT
5	o-xylene	0.06	0.07	0.06	0.07	0.06	NT	0.07	0.05	0.07	0.07	ND	NT
	Total BTEX	0.23	0.28	0.27	0.28	0.27	NT	0.30	0.28	0.27	0.27	-	-
	CF	1.442	1.481	1.602	1.641	1.409	1.482	1.578	1.393	1.276	1.178	0.459	0.011
	DC = 14.941												
	I-geo	-4.99	-4.84	-4.99	-4.19	-4.99	-5.05	-5.05	-4.85	-4.77	-4.84	-7.86	-

Table 2: CAWTHORNE CHANNEL 2 RIVER SEDIMENT AT JACOB KIRI (mg/kg)

SN	Parameter	Rainy Season								Dry season			
		0-0.5m	0.5-1m	1-1.5m	1.5-2m	0-0.5m	0.5-1m	1-1.5m	1.5-2m	0-0.5m	0.5-1m	1-2m	0-0.5m
1	TPH	5.50	5.44	5.33	5.28	5.38	4.81	4.52	4.47	4.35	4.28	2.60	2.82
POLYCYCLIC AROMATIC HYDROCARBON (PAH) PROFILE													
1	Naphthalene	-	1.101	1.098	-	1.011	1.028	-	-	0.991	-	-	NT
2	Acenaphthylene	1.901	-	1.578	1.863	1.900	1.900	-	-	-	1.676	-	NT
3	Acenaphthene	3.735	3.367	2.908	3.09873	4.011	3.325	-	-	3.912	3.722	-	NT
4	Fluorene	3.574	3.300	3.198	3.426	5.001	2.905	4.621	-	4.791	4.861	-	NT
5	Phenanthrene	5.161	5.001	4.980	5.092	5.010	4.853	4.771	4.721	5.120	5.200	-	NT
6	Anthracene	8.229	7.990	7.890	8.092	8.011	7.980	8.091	7.911	7.911	8.020	-	NT
7	Fluoranthene	9.614	9.142	8.905	9.087	9.261	8.987	9.002	-	8.711	9.260	-	NT
8	Pyrene	23.225	20.841	19.907	21.096	22.617	22.197	20.911	-	21.621	21.911	-	NT
9	Benz(a)anthracene	11.102	10.572	10.376	11.009	11.009	9.076	10.023	9.910	11.101	11.012	11.9	NT
10	Benzo(b)fluoranthene	28.570	27.091	25.789	27.009	26.612	21.237	20.151	21.161	25.991	26.106	13.2	NT
11	Chrysene	22.312	20.329	21.367	20.90876	20.953	17.905	18.661	18.211	19.616	21.010	9.9	NT
12	Benzo(a)pyrene	16.251	16.026	15.908	14.907	15.676	14.324	13.717	12.962	16.761	18.011	9.6	NT
13	Benzo(k)fluoranthene	21.318	21.001	20.908	21.097	20.911	19.907	18.901	19.101	21.202	21.302	15.8	NT
14	Indeno(1,2,3-cd)	14.577	14.025	13.908	14.245	14.461	13.654	12.611	11.611	12.671	13.111	-	NT

	pyrene												
15	Dibenz(a,h) anthracene	44.068	43.901	42.906	39.908	43.021	40.096	38.401	38.512	42.961	43.224	19.6	NT
16	Benzo(g,h,i) perylene	12.551	11.852	11.906	12.095	11.912	9.974	-	9.611	11.791	12.112	-	NT
	Total	226.194	215.539	213.541	212.941	221.377	199.357	179.861	153.711	215.151	220.538	80.0	-
	TOTAL PAH	150.796	143.693	142.361	141.961	147.585	132.905	119.907	102.474	143.434	147.025	53.33	-
BTEX PROFILE BTEX PROFILE													
1	Benzene	BDL	BDL	NT	NT	BDL	BDL	NT	BDL	NT	NT	BDL	NT
2	Toluene	BDL	BDL	NT	NT	BDL	BDL	NT	BDL	NT	NT	BDL	NT
3	Ethylbenzene	BDL	BDL	NT	NT	BDL	BDL	N	BDL	NT	NT	BDL	NT
4	M,p-xylene	BDL	BDL	NT	NT	BDL	BDL	NT	BDL	NT	NT	BDL	NT
5	o-xylene	BDL	BDL	NT	NT	BDL	BDL	NT	BDL	NT	NT	BDL	NT
	Total BTEX	-	-	-	-	-	-	-	-	-	-	-	-
	CF	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
	DC = 0.011												
	PLI = 0.00												
	I-geo	1.329	1.260	1.246	1.242	1.298	1.147	0.999	0.772	1.257	1.293	-0.017	-

Table 3: CAWTHORNE CHANNEL 2 RIVER WATER AT JACOB KIRI (mg/l)

SN	Parameters (mg/l)	CAWJW C	CAWJW 1	CAWJW 2	CAWJW 3	CAWJW4	CAWJW5	CAWJW6	CAWJW7
1	TPH	66.192	371.91	690.234	589.34	390.35	414.10	271.11	166.216
POLYCYCLIC AROMATIC HYDROCARBON (PAH) PROFILE									
1	Naphthalene	1.6716	3970.5274	3980.83742	4004.87459	4129.95278	4407.01850	1167.117	987.101
2	Acenaphthylene	2.2341	4004.8521	4409.25387	4502.13908	3897.03674	4357.43775	2653.980	-
3	Acenaphthene	-	5001.8620	5009.73542	4321.09634	3782.09521	4463.41973	1791.642	-

4	Fluorene	-	-	4537.90324	4652.09345	4231.09527	4889.02774	984.231	-
5	Phenanthrene	-	-	2.78833	1.27854	-	-	-	-
6	Anthracene	-	972.9012	4789.09367	897.07543	5289.07428	6136.62407	1061.985	721.854
7	Fluoranthene	6.4712	3390.2197	4452.90478	3289.04189	4526.72810	4665.79200	761.897	511.075
8	Pyrene	3.1165	4001.1905	3908.16732	4180.94720	3897.06132	4024.68116	521.231	-
9	Benz(a) anthracene	-	3782.0921	4871.09357	2898.04287	3678.06234	3334.22596	800.241	-
10	Benzo(b) fluoranthene	-	3318.0942	4005.94281	3980.07634	3217.96396	3576.45692	784.326	-
11	Chrysene	4.629	2091.8620	1987.29076	2589.95387	2178.95376	2609.90486	569.095	246.908
12	Benzo(a)pyrene	10.761	1350.9302	1345.09367	1249.07523	1622.91638	1588.11555	643.212	134.896
13	Benzo(k) fluoranthene	8.123	1789.0942	1905.52896	1789.53980	2001.28630	1886.90421	32.890	25.908
14	Indeno(1,2,3-cd) pyrene	-	1124.8032	1342.09638	1003.94328	1123.87293	1239.23193	42.412	3.708
15	Dibenz(a,h) anthracene	-	-	1298.08523	987.09356	1432.07593	1367.26741	12.674	-
16	Benzo(g,h,i) perylene	-	-	729.08537	589.09534	689.04267	662.32784	-	-
	Total	37.0064	3.4798e4	4.8574e4	4.0935e4	4.5697e4	4.91684e4	11826.933	2631.145
	Total PAH	1.85032	1,739.921	2,428.74	2,046.768	2,284.860	2,458.42	591.346	131.557
BTEX PROFILE									
1	Benzene	BDL	2.06	1.56	2.02	1.89	NT	NT	NT
2	Toluene	BDL	230.51	201.59	198.47	228.68	NT	NT	NT
3	Ethylbenzene	BDL	353.26	267.79	346.21	342.82	NT	NT	NT
4	M,p-xylene	BDL	715.94	573.12	689.93	709.25	NT	NT	NT
5	o-xylene	BDL	685.24	579.09	623.90	658.90	NT	NT	NT
	Total	-	1978.01	1623.15	1869.53	1941.54	-	-	-
		-	98.900	81.16	93.48	97.08	-	-	-

Applying Popoola *et al.*, 2015; Md Suhaimi *et al.*, 2014 contamination factor (Cf) expressed as:

$$Cf = \frac{C_n}{B_n} \quad \text{where } C_n = \text{measured concentration; } B_n = \text{background value}$$

$$\text{Jacob kiri Sample station 1: } Cf = \frac{5.5}{5000} = \mathbf{0.001}; \quad \text{Elem Kalabari sample station 4: } CF = \frac{8206.74}{5000} = \mathbf{1.641}$$

Applying Poopola *et al.*, 2015 and Tomlinson *et al.*, 1980 degree of contamination (Dc) expressed as

$$Dc = \sum Cf \quad 2$$

$$\text{Jacob kiri: } \sum Cf = (0.001 + 0.001 + 0.001 + 0.001 + 0.001 + \dots) = \mathbf{0.011}$$

$$\text{Elem Kalabari: } \sum Cf = (1.442 + 1.481 + 1.602 + 1.641 + 1.409 + \dots) = \mathbf{14.941}$$

Applying Muller (1969) index of geo-accumulation (I-geo) expressed as

$$I\text{-geo} = \log_2 \frac{C_n}{1.5 \times B_n} \quad 3$$

1.5 XBn

$$\begin{aligned} \text{Jacob kiri Sample station 1: } &= \log_2 \frac{150.796}{1.5 \times 40} = \log_2 2.5132 \\ &= \log \frac{1.5132}{\text{Log2}} = \frac{0.4002}{0.3010} = \mathbf{1.3296} \end{aligned}$$

$$\begin{aligned} \text{Elem Kalabari sample station 4: } &= \log_2 \frac{3.28}{1.5 \times 40} = \log_2 0.05466 \\ &= \log \frac{0.05466}{\text{Log2}} = \frac{-1.2623}{0.3010} = \mathbf{-4.1937} \end{aligned}$$

Applying Riba et al., 2002a enrichment factor (EF) expressed as:

$$EF = \frac{C_n - B_n}{B_n} \quad \text{-----} \quad 4$$

$$\text{Jacob kiri sample station 2} = \frac{690.234 - 5000}{5000} = -0.861$$

Discussion

Jacob kiri and Elem Kalabari oil spills: the pathway is through the river, affecting river water and river sediment through oral, inhalation and dermal of seafood then, to man. Also, through inhalation from the atmosphere to man (fig 3).

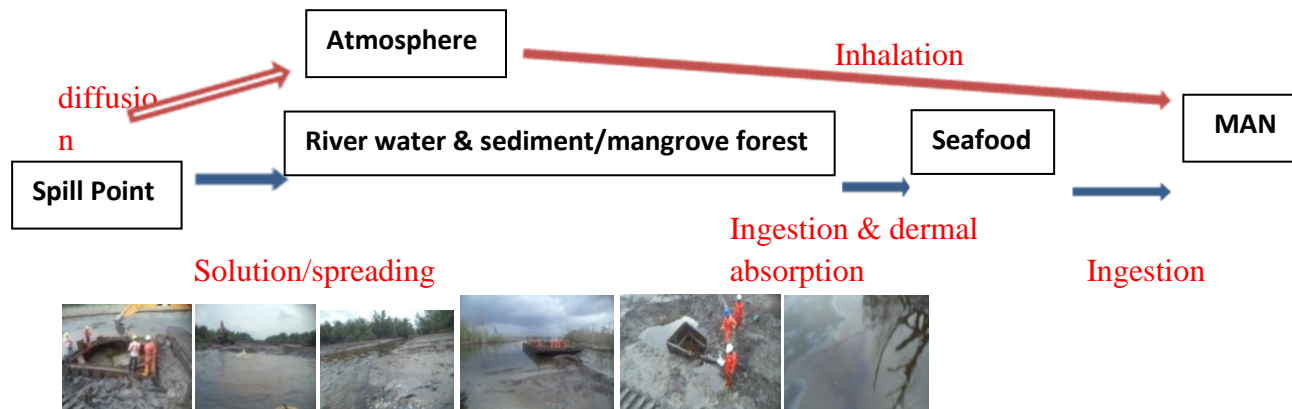


Fig. 3: Conceptual Site Model Pathways.

Fig. 4 and 5 below are the PAHs of river sediment fingerprints of Jacob kiri and Elem Kalabari samples while fig. 6 and 7 are their respective composition of PAHs. Fig 8 and 9 are the BTEX fingerprints of Elem Kalabari river sediment and Jacob kiri river water respectively. River sediment BTEX of Jacob kiri was below detective level (BDL).

River sediments have the capability to bio-accumulation and bio-availability. The maximum TPH level at Jacob kiri was 5.50mg/kg (table 1) which was far below the acceptable limit of 5000mg/kg (DPR, 2002). The maximum total PAHs level at Jacob kiri was 150.796mg/kg which was above DPR acceptable limit of 40mg/kg (DPR, 2002). Applying contamination indices of CF and DC (Popoola *et al.*, 2015), the river sediment of Jacob kiri shows no contamination with CF and DC equal to zero. Also, applying 1-geo (Muller, 1969), the river sediment was moderately contaminated with a maximum 1-geo of 1.32 (table 2). The maximum TPH at Elem Kalabari was 8,206.76mg/kg (table 1) which was above the DPR acceptable limit of 5000mg/kg while the maximum PAHs was 2.18mg/kg which was far below the DPR acceptable limit. Applying CF and DC, the sediment was of moderate contamination with a maximum CF of 1.641 and a DC of 14.941. The 1-geo values were less than zero indicating no contamination (table 1). The EF applied in Jacob kiri shows no impact. These indices were also applied by Hakanson (1980); Hadiya *et al.* (2016) and Md Suhami *et al.* (2014). UNEP (2011) reported that river sediment serves as a reservoir of crude oil pollutant once polluted.

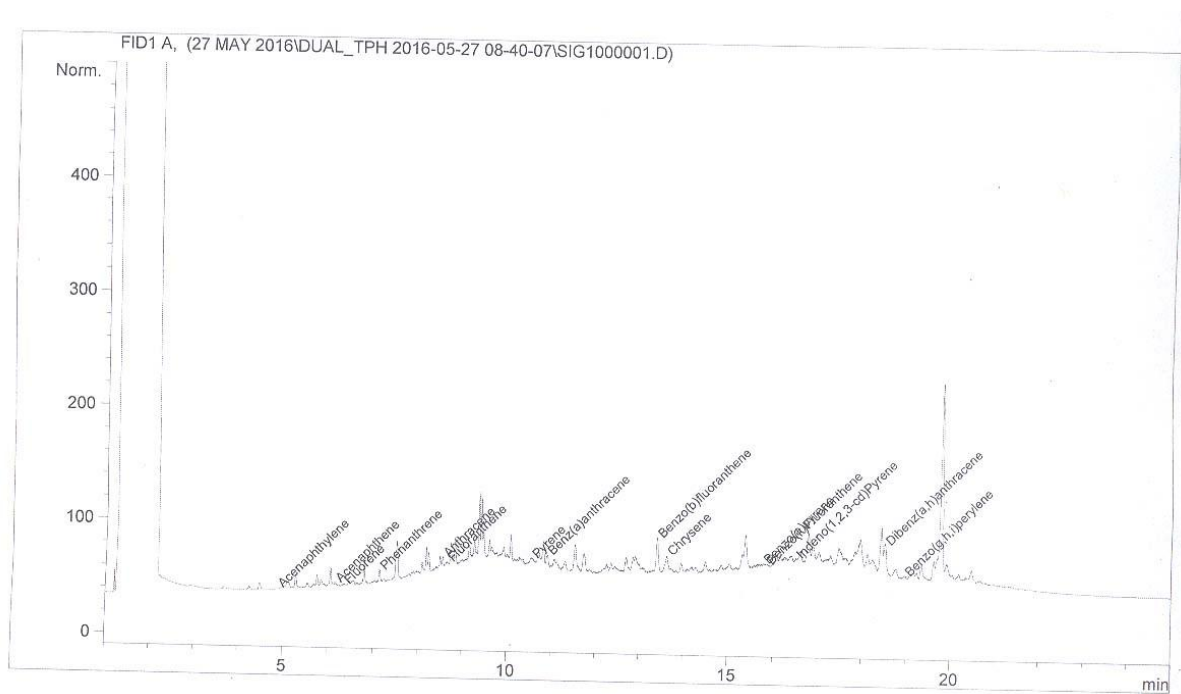


Fig. 4: GC-FID of PAHs in Jacob kiri River sediment

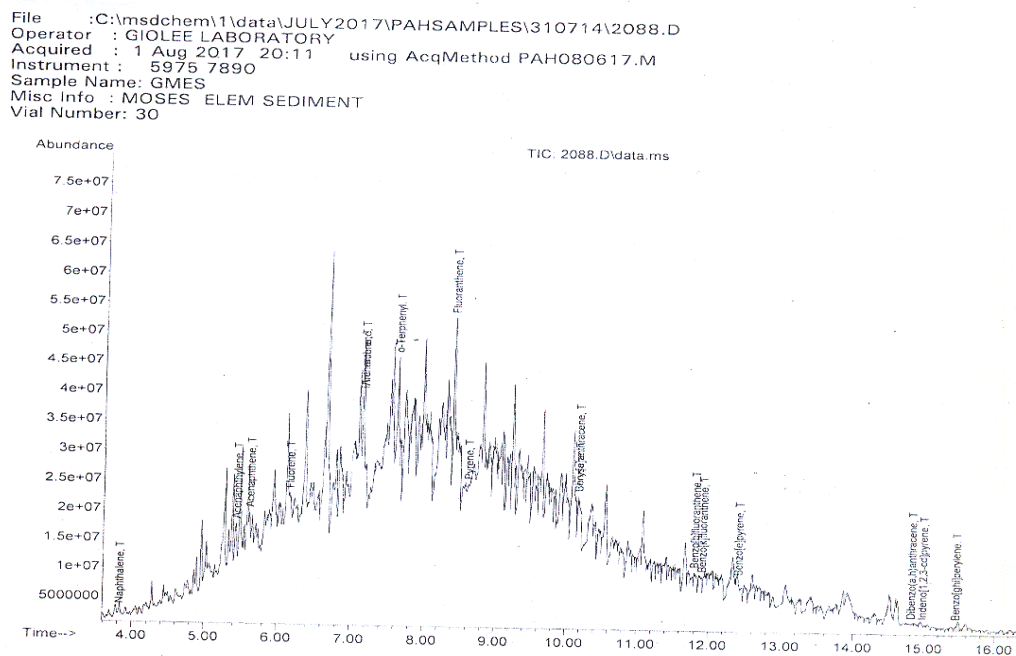
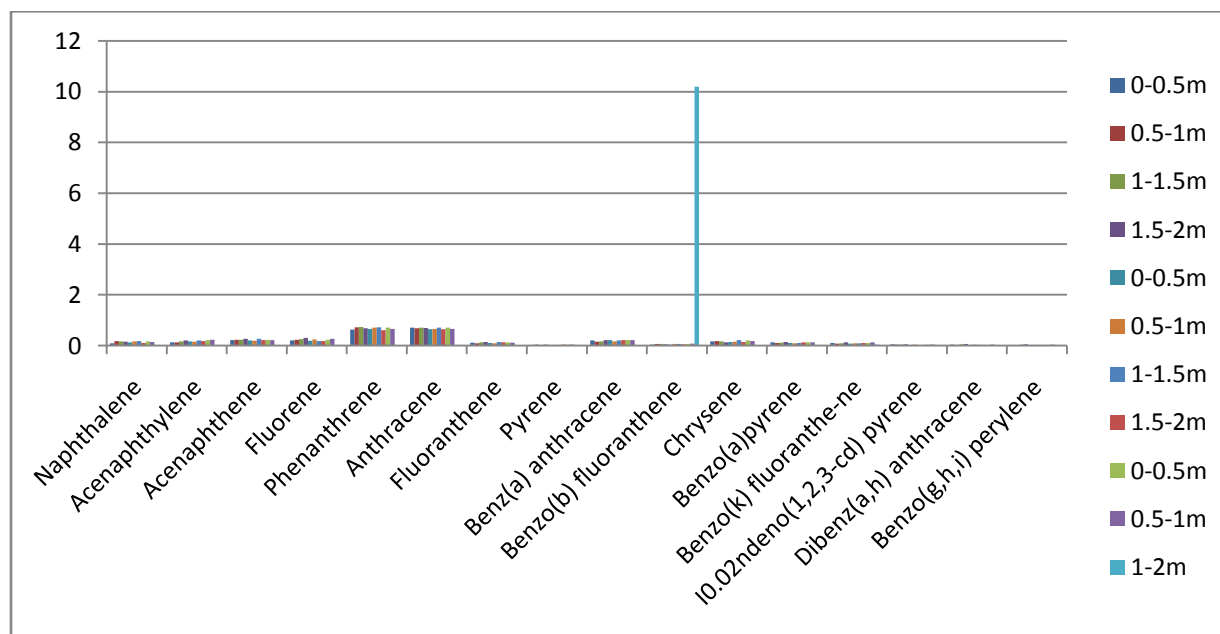
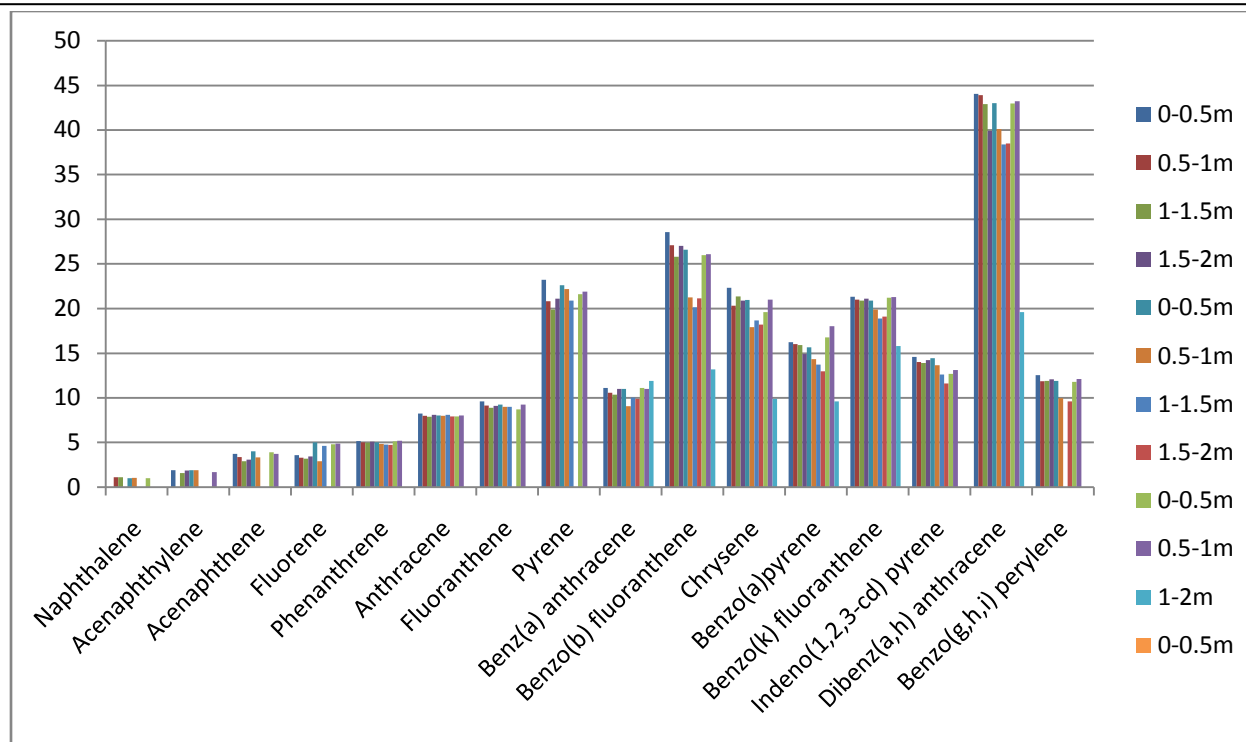


Fig. 5: GC-FID of PAHs in Elem Kalabari River Sediment



File :C:\msdchem\1\data\AUGUST 2017\BTEX SAMPLES\030817\2088.D
Operator : GIOLEE LABORATORY
Acquired : 3 Aug 2017 14:42 using AcqMethod BTEX280617.M
Instrument : 5975 7890
Sample Name: GMES
Misc Info : MOSES ELEM SEDIMENT
Vial Number: 1

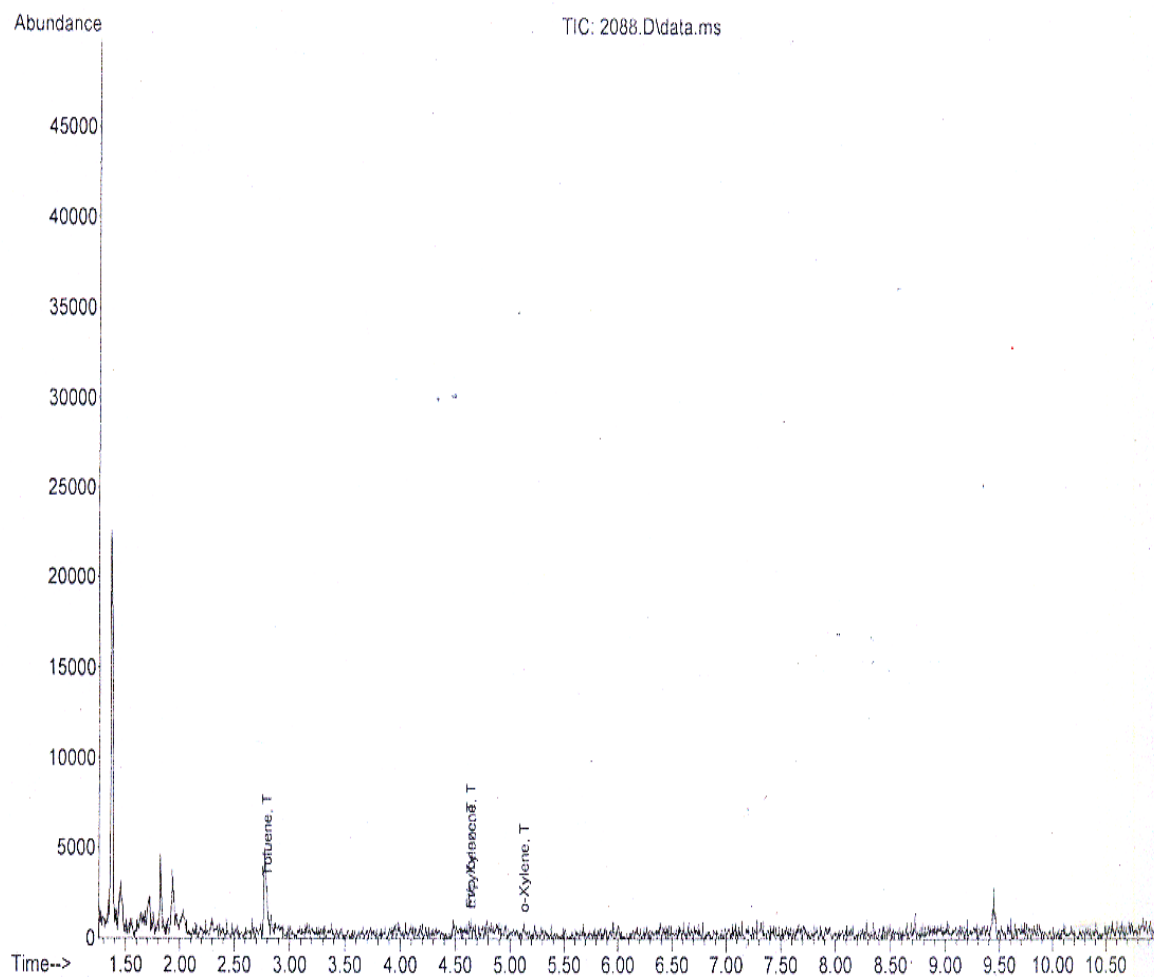


FIG. 8: GC-MS of BTEX in Elem Kalabari River Sediment

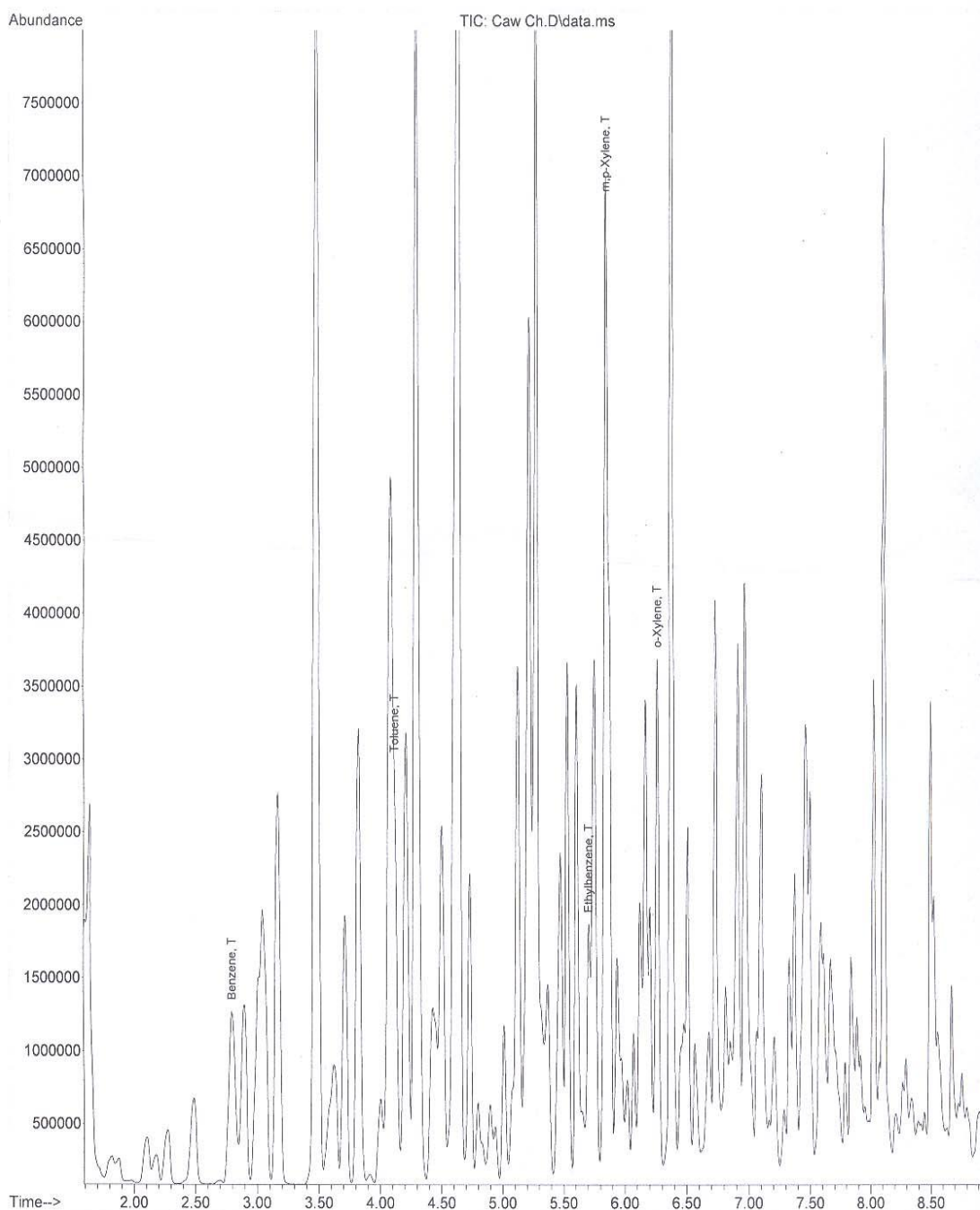


FIG. 9: GC-MS of BTEX in Jacob kiri River Water

The TPH in Elem Kalabari sediment was above the acceptable limit while in Jacob kiri sediment, TPH in all the samples were within the acceptable limit. The Elem Kalabari river sediment and Jacob kiri river water contains some significant level of BTEX.

Conclusion

In Jacob kiri, the TPH and PAHs decreased with depth while in Elem Kalabari, the TPH and PAHs increased with depth. The increase with depth in Elem Kalabari could be attributed to the fire outbreak that must have burnt or evaporated virtually all the free-phase crude oil at the surface. The Elem Kalabari sediment samples were moderately polluted based on contamination factor calculations while Jacob kiri sediment samples were of low contamination judging from the index of geo-accumulation calculation.

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Conflict of Interest

This paper is an extract from my Ph.D research work which was carried out in the Geology department of Federal University of Technology, Owerri, Nigeria. The content, field work and laboratory analysis, results and interpretations were all my original work.

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