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DETERMINATION AND RISK ASSESSMENT OF PAHs AND TOTAL HYDROCARBON CONTENT IN SURFACE WATER AND SEDIMENT OF EPIE CREEK, YENAGOA, BAYELSA STATE, NIGERIA.

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ABSTRACT: Petroleum and its by-products are major contributors of Poly-Aromatic Hydrocarbons (PAH) and Total Petroleum Hydrocarbons (THC) measured as total hydrocarbon content. These carcinogenic, mutagenic and toxic chemical substances can pollute water bodies and sediments. Hence the aim of this work was to determine the concentration of PAHs and THC of water and sediment samples collected from Epie Creek close to three petrol stations (Total, UnlessGod, and Barbizone). Extraction and clean-up of samples were carried out on the samples and consequently PAHs and THC were determined using Gas chromatography with flame ionization detector. THC (mg/l) in the Total, UnlessGod, and Barbizone Stations were respectively 117.358 ± 9.00, 189.334 ± 8.11, 259.045 ± 5.55; values were above permissible level of 10 mg/L. Also, the THC (mg/kg) values of the sediment's samples were; Total Station (3858.717 ± 10.21), UnlessGod Station (3522.389 ± 11.24) and Barbizone Station (2223.747 ± 13.44). These values were above the permissible level of 30 mg/kg. The molecular diagnostic ratios (Flt/pyr, Flt/flt + pyr, BaA/BaA + chry, Chry/BaA, Anth/178, Anth/anth + phen) indicated that the PAHs emanated from pyrogenic sources. High molecular weight PAHs (Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, and Chrysene) contributed about 98% to the toxicity equivalent quotient and mutagenic equivalent quotient. The incremental lifetime cancer risk for both children and adult were below 0.0001 indicating no dermal risk or negligible risk; reference PAHs were chrysene and benzo (a) anthracene. The average concentrations of the individual PAHs were higher than the effect-range low and effect range median values indicating a possible adverse effect on the ecosystem and consequently humans.

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Keywords: PAHs, Total hydrocarbon content, Toxicity equivalent quotient, Mutagenicity equivalent quotient, Carcinogenic, ecosystem

1. INTRODUCTION

Crude oil is a source of a family of several hundred chemical compounds called total petroleum hydrocarbons (TPH) (Aderinola *et al*., 2018). They are found as mixtures of aliphatic (straight carbon chain) and aromatic (carbon ring) compounds. Poly aromatic hydrocarbons (PAHs) are aromatic compounds that can have petrogenic or pyrogenic sources (Charriau *et al*., 2009). Thus, the bottom sediment being the habitat of many aquatic organisms is recognized as reservoir of petroleum hydrocarbons in the marine environments with high risk of bioaccumulation (Filho et al., 2013). These contaminants PAHs and straight chain hydrocarbons are known to cause some level of toxicity and mutagenicity in the ecosystem even at low concentrations (Ambade *et al.*, 2021). Adding to the hydro kinetic nature of river system, these toxicants could accumulate over time in the sediments and resumed along the water column, and this could be detrimental to the ecological community (Ambade *et al.*, 2021; Tanee *et al.*, 2016; Howard *et al.*, 2017). Furthermore, PAHS have been reported as persistent organic compounds (POCS) in an environmental medial (soil, water, sediments, air and biota (Ambade *et al.*, 2021; Stout *et al*., 2004; UNFPA 2003), which could pose ecological risk over time. Hence, this study was carried out to investigate the level PAHs and Total Hydrocarbon Content in Epie creek. Total Hydrocarbon Content means the combined mass of organic compounds measured by the specified procedure for measuring total hydrocarbon, expressed as a hydrocarbon.

2.0 MATERIALS AND METHODS

Study Area

Geographically, the Epie Creek is located between Latitude 4^0 55' 23" North, and Longitude 6^0 15' 28" East, in the Niger Delta Region, Bayelsa State. The Epie Creek is an important fresh water body located in

Yenagoa, Bayelsa State. The creek is aligning with the Yenagoa-Mbiama Road and it is connected to other rivers such as the Taylor, Ekole, Orashi River and River Nun. The Creek is used for fishing, agricultural and recreational activities, and is a major dump site for domestic, commercial and industrial wastes (Seiyaboh, 2018).

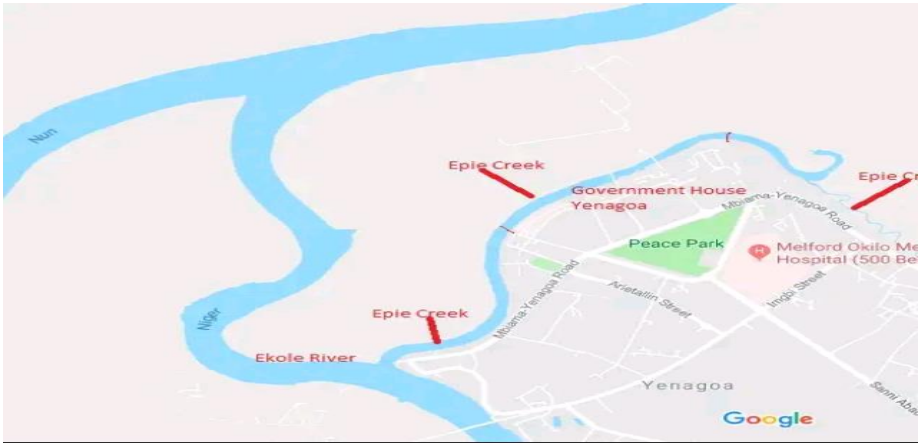


Fig. 1: Google map showing the Epie Creek in Yenagoa metropolis.
Source: Google Map, 2022.

Collection, Extraction and Clean-up of Samples

All reagents and chemicals were of chromatographic grade (Baker, Deventer, Netherlands). All glasswares were pre-washed and rinsed with distilled water and acetone before use.

Surface waters were collected in triplicate from Epie creek close to three different petrol Stations namely; Total, UnlessGod and Barbizone petrol stations, located in Yenegwe-Epie, Yenizue-Epie and Agudama-Epie communities (all in Yenagoa metropolis). Samples were collected at 15cm depth of the river using amber-coloured 1Litre size glass bottles. Prior to collection of samples, the glass bottles were washed and sun-dried and at sampling points, the glass bottles were rinsed with the river water. Sediment samples were collected with soil auger at the same locations as the water sampling points. Samples were air-dried and homogenized.

Control water and sediment samples were obtained (in triplicate) to determine the background levels of petroleum hydrocarbons in the unaffected water and sediment for comparison with the contaminated site(s). all control samples were taken on the same day prior to actual field samples. Extraction was carried out on 10 g of sediment sample via solid-phase extraction using Soxhlet apparatus; extracting solvent was dichloromethane.

The sample extract (sediment and water) were transferred into a standard chromatographic column packed with activated silica gel slurry anhydrous sodium sulfate coating on topmost part. The hydrocarbon fraction was eluted with n-hexane. The eluate was concentrated to 1 mL by evaporation overnight in a fume hood and this concentrate was analyzed with GC-FID.

Sample Analysis

The separation and detection of PAHs and total hydrocarbon content in water samples and sediments were carried out using Varian model BV CP 3800 GC-FID.

Standard solutions of PAHs (1000 mg/L) were dissolved in acetone and stored at 4 ^{o}C. Working standards were prepared just before use.

Argon gas was used as carrier gas at a constant flow of about 1.0 mL/min. Split injection (3:1) was used with injection volume of 1 µL. Hydrogen (32 mL/min), air (380 mL/min) and nitrogen (auxiliary gas; 28 mL/min) were the gases used for the flame ionisation detector. The detailed GC-FID operating parameters were the ones used by Adetunj *et al*., 2020.

Risk assessment

Toxic equivalent quotient (TEQ) and mutagenic equivalent quotient (MEQ) were used to assess the Potential carcinogenic and mutagenic toxicities of the high molecular weight PAHs detected in the sediment samples; parameters are given in equations 1 and 2.

$$TEQ = \sum C_n \times TEF_n$$

$$MEQ = \sum C_n \times MEF_n$$

Where C_n = concentration of each PAH congener (n) in the mixture

TEF_n = Toxic equivalence factor (TEF) for each PAH congener (n)

MEF_n = Mutagenic equivalent factor (MEF) for each PAH congener (n)

The TEF values used for Chry, BbF, BkF, BaP in these calculations were 0.01, 0.1, 0.1, 1 and corresponding

MEF values were 0.017, 0.25, 0.11, 1.0. (Adeniji *et al.*, 2019; Durant, 1996).

Dermal Lifetime Cancer Risk

The dermal incremental lifetime cancer risk was calculated using the equation below

$$ILCR_{derm} = \frac{C_{sed} \times SA \times AF_{sed} \times ABS \times EF \times ED \times CF \times SFO \times GIABS}{BW \times AT}$$

C_{sed} is the concentration of the pollutant in the sediment (mg/kg)

$ILCR_{derm}$ is the incremental lifetime cancer risk via dermal contact of sediment particles; SA is the surface area of the skin that is in contact with sediment (cm^2/day); AF is the skin adherence factor for dust/sediment (mg/cm^2); and ABS is the dermal absorption factor (chemical specific).

The SFO values ($mg^{-1}kg^{-1}day^{-1}$)$^{-1}$ for the contaminants were Chry = 7.3 x 10^{-3}, BbF = 7.3 x 10^{-1}, BbK = 7.3 x 10^{-2}, and BaP = 7.3 (USEPA, 2009).

The other variables used for the calculations are given in Table 1

Table 1: Variables for calculating incremental lifetime cancer risk

Exposure variables	Age	
	Child	Adult
Body weight, BW (kg)	15	60
Exposure duration, ED (year)	6	24
Exposure frequency, EF (days/year)	313	313
Average time, AT (days)	52 x 365 = 18,980	52 x 365 = 18,980
Adherence factor, AF (mg/cm2)	0.2	0.07
Absorption fraction, ABS (unitless)	0.13	0.13
Exposure skin area, SA (cm2)	2800	5700
Average time, AT in h	52 years x 365 days/yr x 24 hrs/day = 455520	52 years x 365 days/yr x 24 hrs/day = 455520
Gastrointestinal absorption factor, GIABS	1	1 (
Conversion factor, CF	1 X 10^{-6}	1 X 10^{-6}
Exposure time, ET (hr/day)	8	8

Source: (USEPA, 2001; Ferreira and Miguel, 2005; USEPA, 2012; Man *et al.*, 2013; Iwegbu and Obi, 2016; Onyedikachi *et al.*, 2019)

3. RESULTS AND DISCUSSION

3.1. PAHs in water samples

A. TOTAL STATION

The analysis of the water samples gave the results in Figures 2 – 3 and Tables 2 – 4; Figures 2, 3 4 are chromatograms identifying the PAHs respectively in the Total, UnlessGod, and Barbizone filling stations while Tables 2, 3, and 4 show the concentrations of PAHs in same order. The concentrations of PAHs in mg/L ranged from 1.20 – 2.66 (Table 2), 2.21 - 13.95 (Table 3) and 1.40 - 4.57 (Table 4).

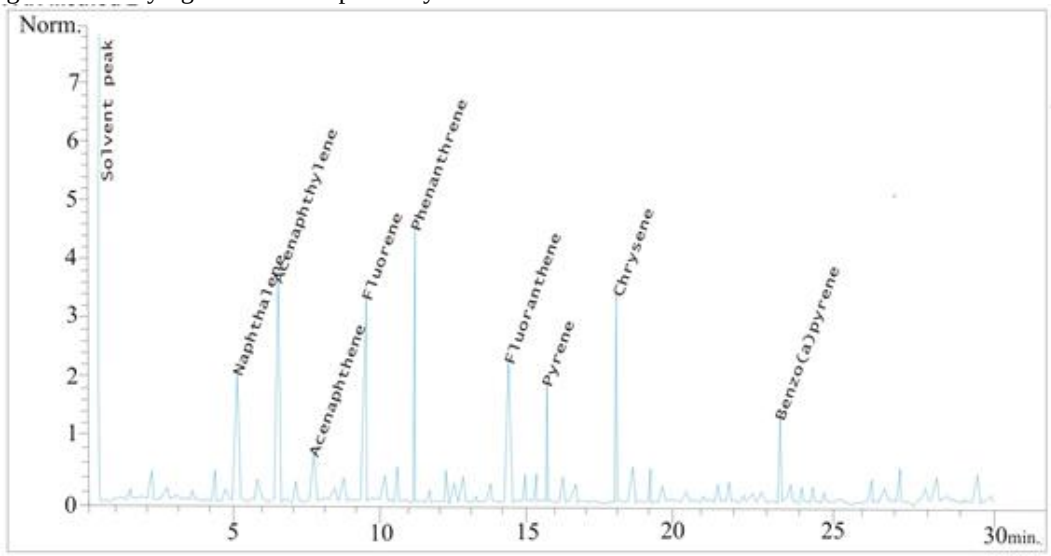


Figure 2: GC-FID Results of PAHs in Total Water samples.

Table 2: PAHs concentration in “Total” water samples

PAH	Amount (ppm)
Solvent peak	-
Naphthalene	1.20 ± 0.01
Acenaphthylene	2.22 ± 0.02
Acenaphthene	1.97 ± 0.01
Fluorene	1.21 ± 0.04
Phenanthrene	2.66 ± 0.21
Fluoranthene	1.75 ± 0.04
Pyrene	1.32 ± 0.02
Chrysene	2.31 ± 0.24
Benzo(a)pyrene	1.97 ± 0.01

B. UNLESSGOD STATION

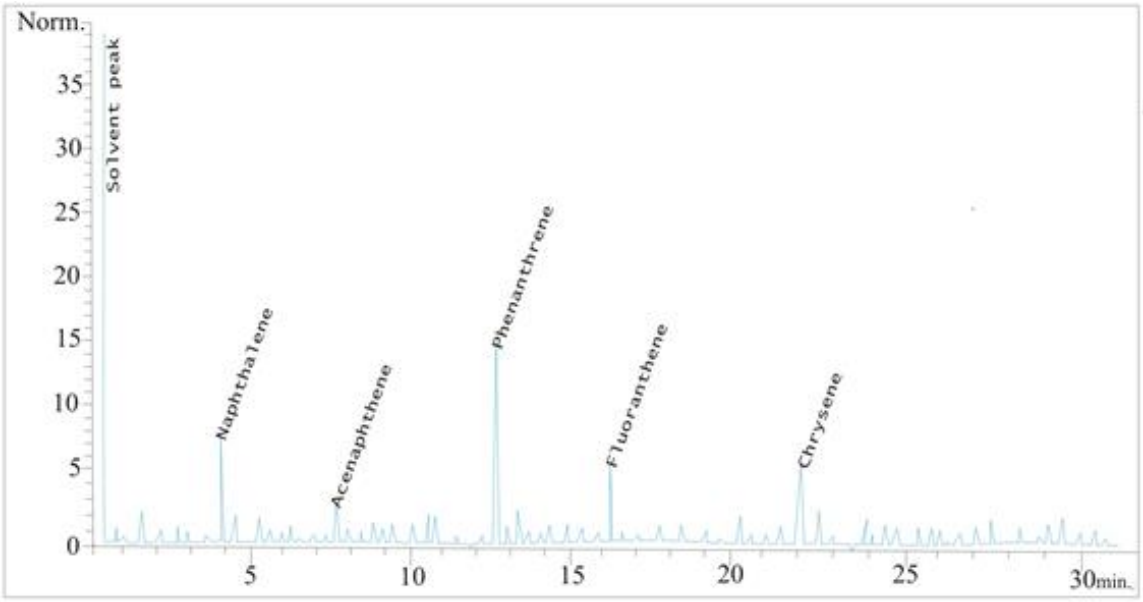


Figure 3: GC-FID Results of PAHs in UnlessGod Water samples.

Table 3: PAHs in UnlessGod Water samples

PAH	Amount (ppm)
Solvent peak	
Naphthalene	7.83 ± 0.08
Acenaphthene	2.22 ± 0.01
Phenanthrene	13.95 ± 0.09
Fluoranthene	2.21 ± 0.02
Chrysene	4.21 ± 0.01

C. BARBIZON

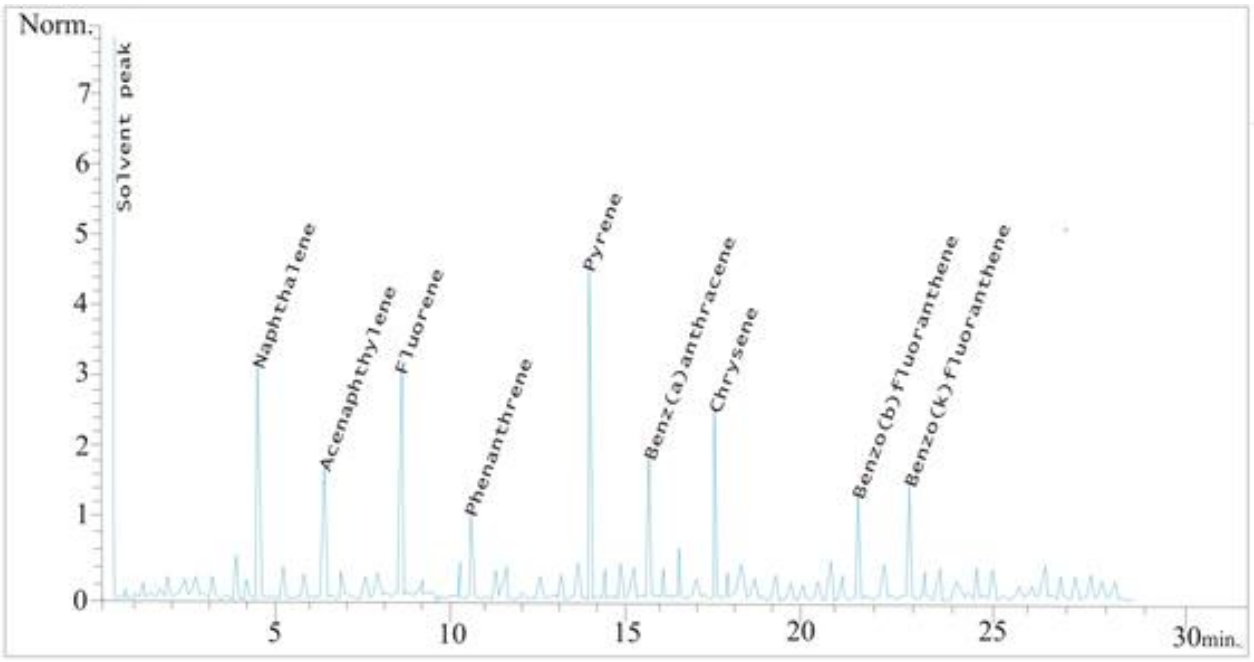


Figure 4: GC-FID Results of PAHs in Barbizon Water samples.

Table 4: PAHs in Barbizon Water samples

PAH	Amount (ppm)
Solvent peak	-
Naphthalene	3.94 ± 0.02
Acenaphthylene	1.51 ± 0.01
Fluorene	2.74 ± 0.04
Phenanathrene	1.94 ± 0.06
Pyrene	4.57 ± 0.10
Benzo (a)anthracene	1.40 ± 0.02
Chrysene	2.76 ± 0.01
Benzo(b)fluorine	1.97 ± 0.02
Benzo(k)fluoranthene	2.42 ± 0.08

PAHs IN SEDIMENT SAMPLES

Sediment samples were also analyzed for PAHs and the results are shown in Figures 5 – 7 and Tables 5 – 7. The figures are chromatograms identifying the presence of PAHs in the respectively samples while the tables contain the concentrations of PAHs (mg/kg) in the samples. The average concentrations of PAHs in mg/kg ranged from 98.970 - 427.100 (Table 5), 108.215 - 398.215 (Table 6) and 168.02 - 434.22 (Table 7).

The toxicity of PAHs have also been assessed in sediments by using effect-based guidelines–effect range median (ER-M) and effect range low (ERL) developed by environmental professionals (Wang et al., 2018; King et al., 2007). The individual PAH concentrations were higher than the effect-range low and effect-range median values (Table 8). This abnormal values indicates that the sediments can be toxic to aquatic resources (Kingsley and Witthayawirasak, 2020).

A. TOTAL STATION

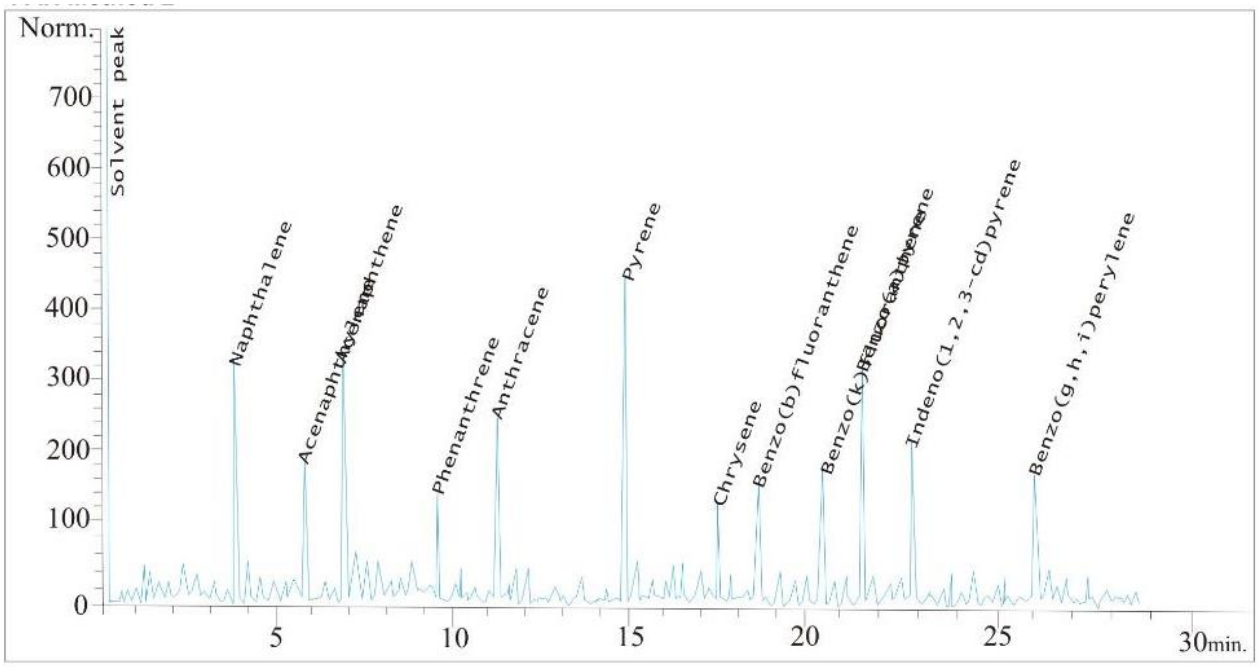


Figure 5: GC-FID Results of PAHs in Total Station Sediment samples.

Table 5: PAHs in Total Station Sediment samples

PAH	Amount (mg/kg)
Solvent peak	--
Acenaphthene	324.20 ± 0.78
Acenaphthylene	186.22 ± 0.35
Anthracene	218.94 ± 1.25
Benzo(a)pyrene	273.72 ± 2.58
Benzo(b)fluoranthene	134.71 ± 0.06
Benzo(g,h,i)perylene	128.94 ± 0.09
Benzo(k)fluoranthene	148.56 ± 0.65
Chrysene	98.97 ± 0.09
Dibenz(a,h)anthracene	-
Indeno(1.2,3-cd)pyrene	156.12 ± 0.18
Naphthalene	339.19 ± 0.33
Phenanthrene	133.32 ± 0.44
Pyrene	427.10 ± 0.58

B. UNLESSGOD

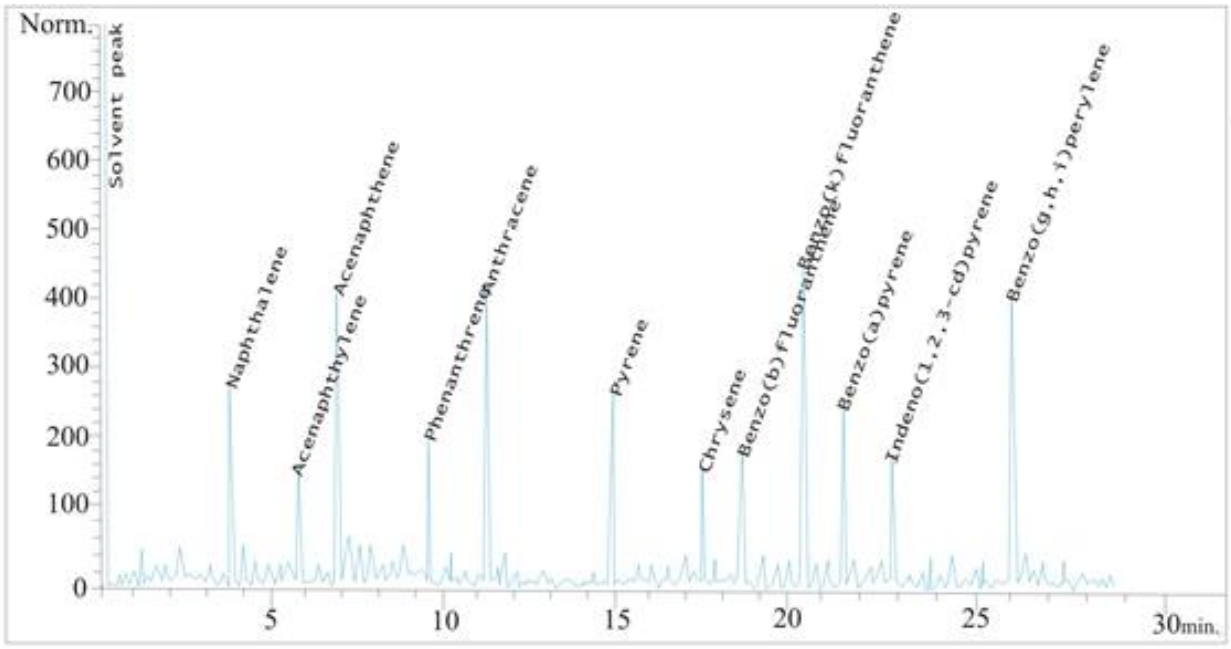


Figure 6: GC-FID Results of PAHs in UnlessGod Sediment samples.

Table 6: PAHs in UnlessGod Sediment samples

PAH	Amount (mg/kg)
Solvent peak	-
Acenaphthene	391.642 ± 2.54
Acenaphthylene	108.215 ± 0.57
Anthracene	398.101 ± 0.09
Benzo(a)pyrene	228.978 ± 1.28
Benzo(b)fluoranthene	172.089 ± 0.09
Benzo(g,h,i)perylene	352.157 ± 0.45
Benzo(k)fluoranthene	398.215 ± 0.01
Chrysene	129.157 ± 0.14
Indeno(1.2,3-cd)pyrene	146.543 ± 0.35
Naphthalene	235.541 ± 0.45
Phenanthrene	133.644 ± 0.58
Pyrene	241.948 ± 0.07

C. BARBIZON

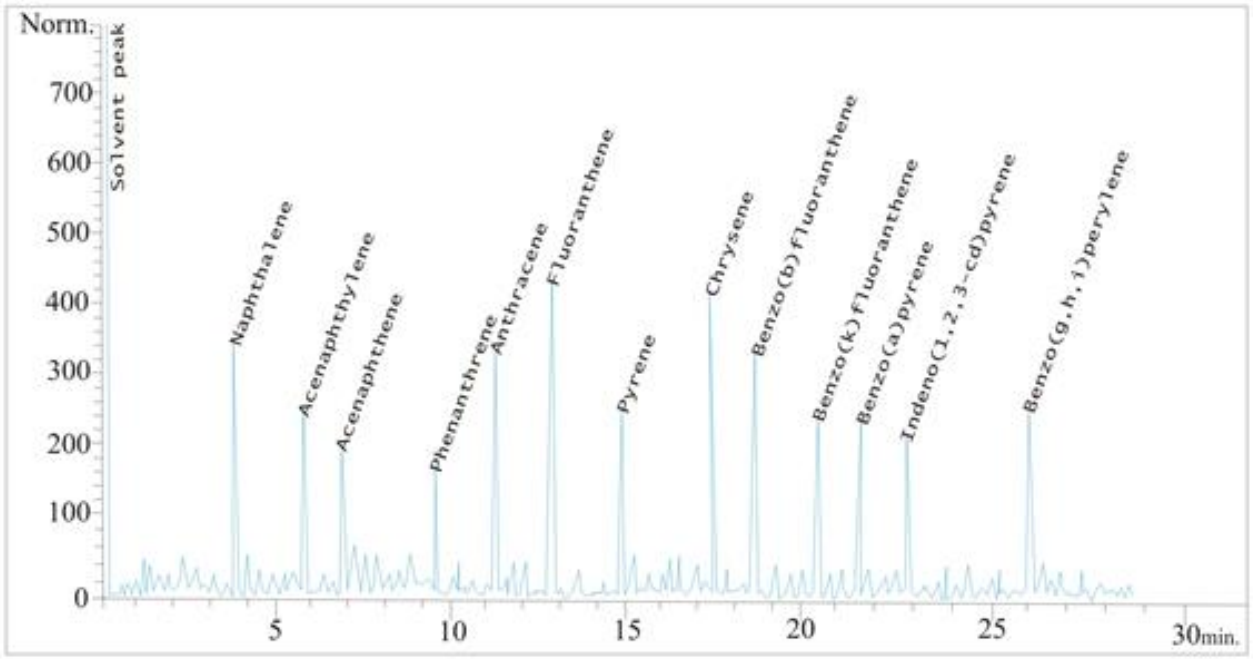


Figure 7: GC-FID Results of PAHs in Barbizone Sediment samples.

Table 7: PAHs in Barbizone Sediment samples

PAH	Amount (mg/kg)
Solvent peak	--
Acenaphthene	193.79 ± 0.25
Acenaphthylene	226.22 ± 0.06
Anthracene	327.97 ± 0.65
Benzo(a)pyrene	196.22 ± 0.08
Benzo(b)fluoranthene	294.62 ± 0.17
Benzo(g,h,i)perylene	254.17 ± 0.14
Benzo(k)fluoranthene	201.90 ± 0.21
Chrysene	401.16 ± 0.25
Fluoranthene	434.22 ± 1.25
Indeno(1.2,3-cd)pyrene	182.58 ± 1.05
Naphthalene	339.62 ± 0.09
Phenanthrene	168.02 ± 1.25
Pyrene	242.30 ± 0.72

PAHs and ER-L and ER-M

Table 8: Descriptive statistics, ER-L and ER-M values of PAHs contents in the sediment

			Average concentration of PAHs in mg/kg		
PAHs	ER-L (mg/kg)	ER-M *(mg*/kg)	TOTAL	UNLESSGOD	BARBIZONE
Nap	0.16	2.1	339.19	235.541	339.62
Acy	0.044	0.64	186.22	108.215	226.22
Ace	0.016	0.5	324.2	391.642	193.79
Flu	0.019	0.54	-	-	434.22
Phe	0.24	1.5	133.32	133.644	168.02
Ant	0.085	1.1	218.94	398.101	327.97
Flt	0.6	5.1	-	-	-
Pyr	0.665	2.6	427.1	241.948	242.3
BaA	0.261	1.6	-	-	-
Chry	0.384	2.8	98.97	129.157	401.16
BbF	0.32	1.8	134.71	172.089	294.62
BkF	0.28	1.62	148.56	398.215	201.9
BaP	0.43	1.6	273.72	228.978	196.22
InP	0.24	-	156.12	146.543	182.58
DahA	0.063	0.26	-	-	-
BghiP	0.085	1.6	128.94	352.157	254.17

PAHs and molecular diagnostic ratio

The calculated diagnostic ratios (Table 9) traced the sources of PAHs to pyrogenic sources as they are categorized in Table 9 (Tongo et al., 2017; Xiao et al., 2014).

Table 9: PAHs and Molecular diagnostic ratios and possible sources of PAHs in the water and sediment samples

WATER				
	Ratio	Petrogenic	Pyrogenic	
Flt/pyr	1.33	< 1.0	> 1.0	Total
Flt/flt + pyr	0.57	< 0.4	> 0.4	
BaA/BaA + chry	0.34	< 0.2	0.2 – 0.35	Barbizone
Chry/BaA	1.97	< 0.4	> 0.9	
SEDIMENT				
Anth/178	1.25	< 0.1	≥0.1	Total
Anth/anth + phen	0.62	< 0.1	>0.1	
Anth/178	2.24	< 0.1	≥0.1	UnlessGod
Anth/anth + phen	0.75	< 0.1	>0.1	
Anth/178	1.84	< 0.1	≥0.1	Barbizone
Anth/anth + phen	0.66	< 0.1	>0.1	

Risk Assessments

High molecular weight PAHs (Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Chrysene) contribute about 90% to the toxic equivalent quotient (TEQ) and mutagenic equivalent quotient (MEQ) (Table 10). Research show that bioavailability is influenced by the molecular structure and size of PAHs. LMW PAHs are removed faster by physico-chemical and biological processes due to their higher solubility, volatility and the ability of many microorganisms to use them as sole carbon sources in comparison to the HMW PAHs (Adeniji et al., 2019; Jiries et al., 2000).

Table 10: The Risk Assessment of PAHs In The Sediment: Toxicity And Mutagenicity

	TOTAL STATION			
	TEQ	%	MEQ	%
Benzo(a)pyrene	273.72	90.33	273.72	84
Benzo(b)fluoranthene	13.47	4.45	33.68	10
Benzo(k)fluoranthene	14.86	4.90	16.34	5
Chrysene	0.99	0.33	1.68	0.5
TOTAL	303.04		325.42	
	UnlessGod			
	TEQ	%	MEQ	%
Benzo(a)pyrene	228.98	79.70	228.98	72
Benzo(b)fluoranthene	17.21	5.99	43.02	14
Benzo(k)fluoranthene	39.82	13.86	43.80	14
Chrysene	1.292	0.45	2.20	0.7
	Barbizone			
Benzo(a)pyrene	196.22	78.52	196.22	66
Benzo(b)fluoranthene	29.46	11.79	73.65	25
Benzo(k)fluoranthene	20.19	8.08	22.21	7
Chrysene	4.01	1.61	6.82	2
TOTAL	249.88		298.90	

Dermal Incremental Lifetime Cancer Risk ($ILCR_{DERMAL}$) for PAHs in water samples

In this study, only ($ILCR_{DERMAL}$) was calculated because the creek is only used for swimming and other recreational activities**.** Dermal Incremental Lifetime Cancer Risk values (Table 11) for chrysene and benzo (a) anthracene are at safe levels according to Table 12 (Adeniji et al., 2019; Jiries et al., 2000).

Table 11: Dermal Incremental Lifetime Cancer Risk ($ILCR_{DERMAL}$)

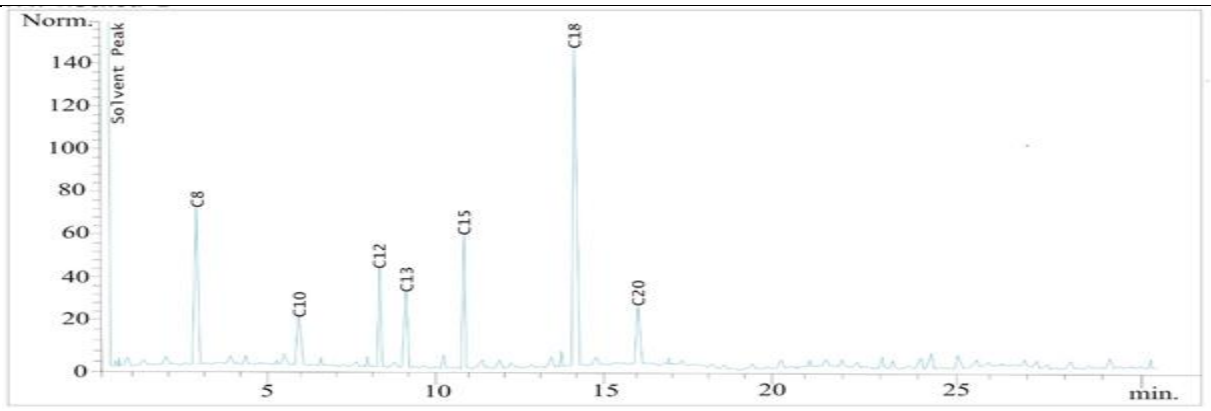
	ILCR		Sampling sites
	Child	Adult	
Chrysene	3.37E-10	2.4E-10	TOTAL
BaA	2.88E-08	2.05E-08	
Chrysene	6.16E-10	4.39E-10	UnlessGod
BaA	4.03E-10	2.87E-10	
BaA	2.04E-08	1.46E-08	Barbizone

Table 12: classification of ILCR

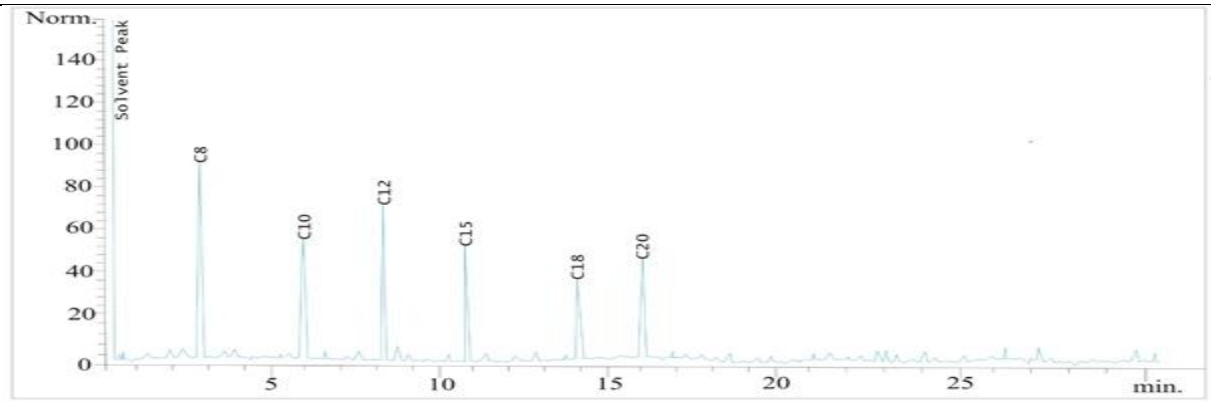
ILCR	INDICATION
≤ 10-6	No risk or neglible risks
≥10-4	High risk with adverse health such as cancer

TOTAL HYDROCARBON CONTENT IN WATER AND SEDIMENT SAMPLES

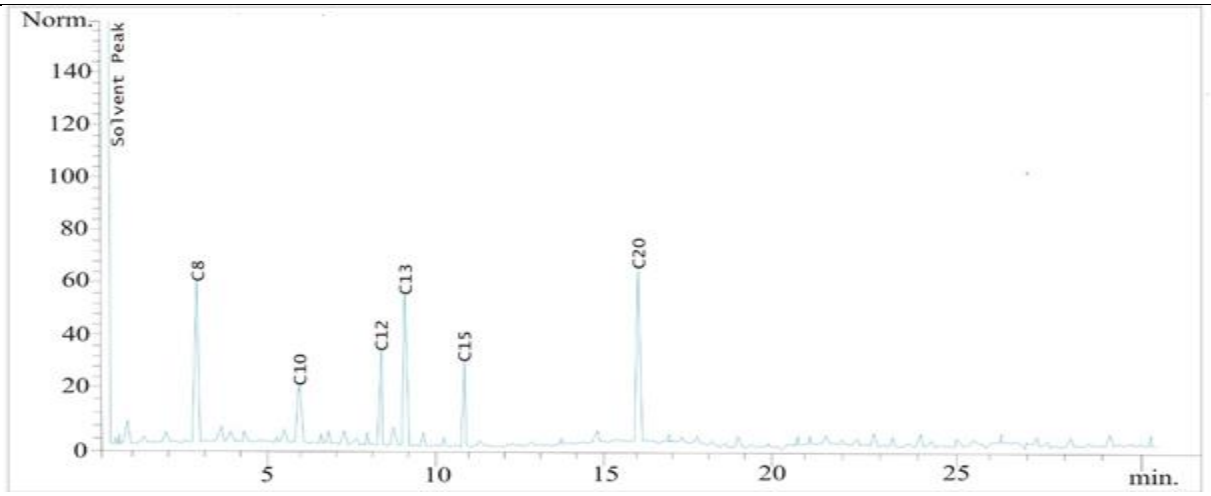
The analysis of water and sediment samples gave the results shown in Figures 8 and 9; the figures show that only C8 – C20 contributed to the total hydrocarbon content (THC) and no contributions from C22 – C40. Table 13 shows the total hydrocarbon content of water samples and sediment samples for the different stations under study. The THC values of the water samples are all above 10 mg/L (permissible level) and the THC values of the sediment samples were all above 30 mg/kg (permissible level) (DPR, 2002).



A: TOTAL FILLING STATION

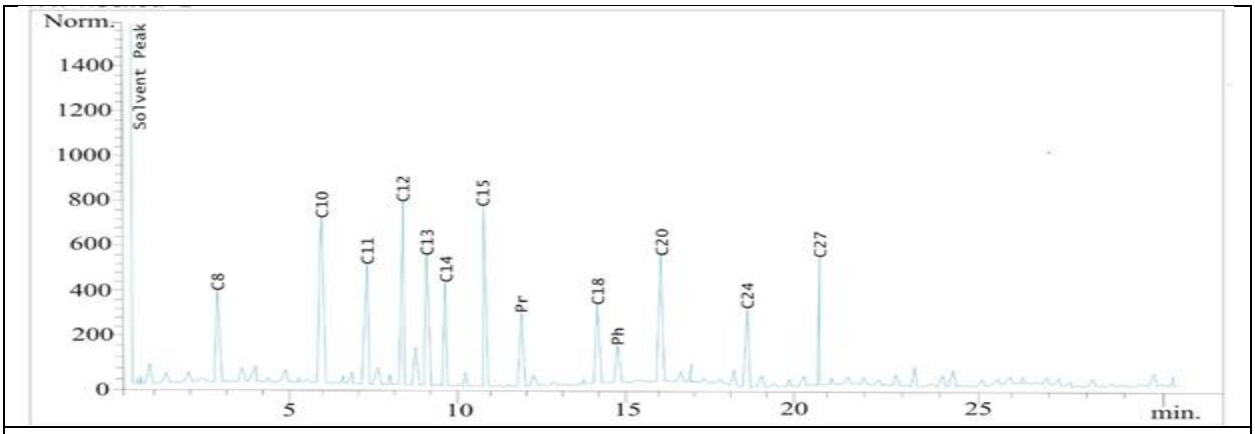


B: UNLESSGOD STATION

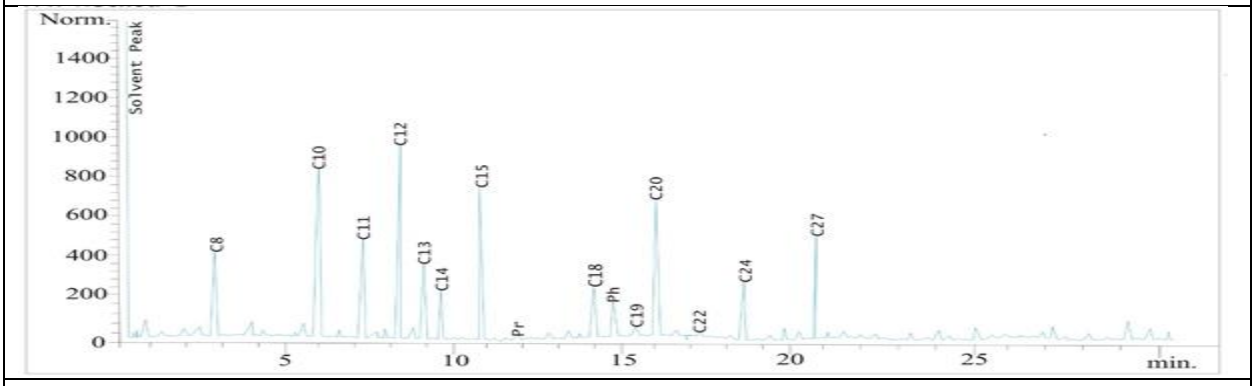


C: BARBIZONE STATION

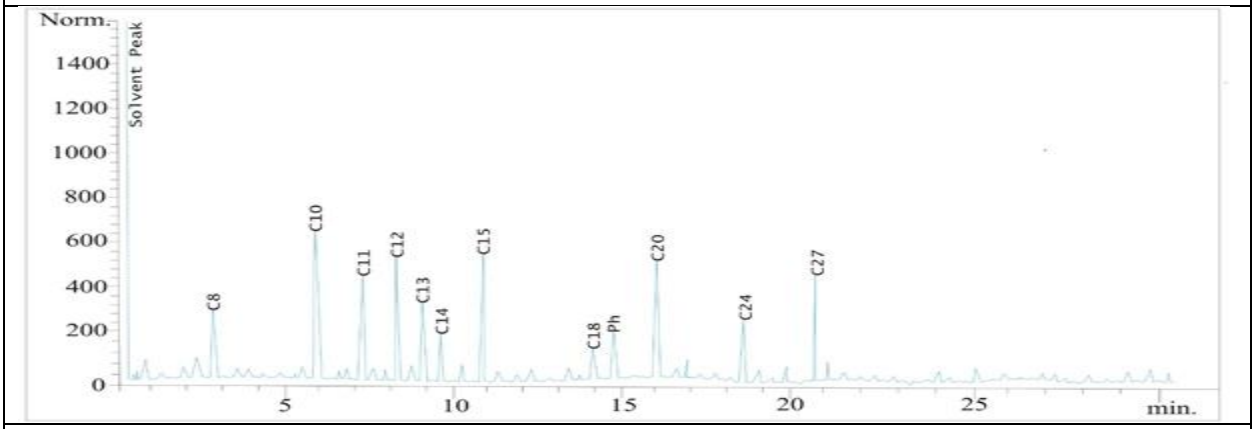
Figure 8: Chromatograms of Total Hydrocarbon Content Analyses Of Water Samples



A: TOTAL FILLING STATION



B: UNLESSGOD STATION



C: BARBIZONE STATION

Figure 9: Chromatograms of Total Hydrocarbon Content Analyses of Sediment Samples

Table 13: Summary of total hydrocarbon content analyses

	THC (mg/kg)	
	WATER	SEDIMENT
TOTAL STATION	117.358 ± 9.00	3858.717 ± 10.21
UNLESSGOD STATION	189.334 ± 8.11	3522.389 ± 11.24
BARBIZON STATION	259.045 ± 5.55	2223.747 ± 13.44

Note: ONLY C8 – C20 contributed to the THC; no contributions from C22 – C40

4. Conclusions

The activities of the filling stations may have impacted negatively on the waters and sediments because the total hydrocarbon contents of water samples were above the permissible level of 10 mg/L and those of the sediments were also above the permissible level of 30 mg/kg

High molecular weight PAHs (Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, and Chrysene) contributed about 98% to the toxicity equivalent quotient and mutagenic equivalent quotient.

The incremental lifetime cancer risk for both children and adult were below 0.0001 indicating no dermal risk or negligible risk; reference PAHs were chrysene and benzo (a) anthracene.

The average concentrations of the individual PAHs were higher than the effect-range low and effect range median values indicating a possible adverse effect on the ecosystem and consequently humans.

The molecular diagnostic ratios (Flt/pyr, Flt/flt + pyr, BaA/BaA + chry, Chry/BaA, Anth/178, Anth/anth + phen) indicated that the detected PAHs emanated from pyrogenic sources.

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Conflict of interest

None declared.

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