

Evaluation of Levels of Persistent Organic Pollutants in Crude Oil Contaminated Soils at Omuigwe-Aluu Rivers State Nigeria

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Abstract: Following recent crude oil spill at Omuigwe-Aluu in Rivers State, Nigeria, the levels of polycyclic aromatic hydrocarbons, organochlorine compounds and total petroleum hydrocarbons in the crude oil contaminated soils were determined using gas chromatography-flame ionization detector and gas chromatography-mass spectrometer. The concentrations of toxic and carcinogenic polycyclic aromatic hydrocarbons which exceeded permissible limits in the soils were benz(a)anthracene 0.08 ± 0.01 ppm, chrysene 0.04 ± 0.01 ppm, benzo(b)fluoranthene 0.04 ± 0.007 ppm, benzo(k)fluoranthene 0.02 ± 0.00 ppm, benzo(a)pyrene 0.02 ± 0.01 ppm and dibenzo(a,h)anthracene, 0.04 ± 0.01 ppm. The concentrations of all the organochlorine compounds analysed were below detectable limits implying that the area is not polluted with organochlorine compounds. The highest concentration of total petroleum hydrocarbon (1016 ppm) was found at the spill site and is below intervention value of 5000 ppm. The exceedance of the toxic and carcinogenic polycyclic aromatic hydrocarbons could be due to oil exploitation activities. The area is contaminated with Total petroleum crude oil, soils, hydrocarbons. Regular monitoring of these pollutants in the study area is recommended.

Keywords: Polycyclic Aromatic Hydrocarbons, Organochlorine compounds, Total Petroleum Hydrocarbons, Crude oil, Soils

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I. Introduction

Crude oil is a primary raw material on earth and the greatest energy resource to human. Crude oil originates from the leftover of plants and animals over a long period [1].

Soil is an essential raw material supporting various parts of the ecosystem for human use [1]. Hence soil is a sink which absorbs or filters and could retain materials from infiltrating natural waters.

Environmental (mainly land and water) contamination with crude oil is called oil pollution and it has been estimated that 80% oil pollution comes from spillage [2]. Many communities in the Niger Delta region of Nigeria, including Omuigwe-Aluu have been contaminated with petroleum as a result of its production and exploration activities. The presence of artificial and natural contaminants in soils, sediments and ground water above the standard limits has impacted negatively on the ecosystems and raw materials, as well as the health of man [3].

Generally, Soils be may contaminated by the pilling up of heavy metals and polycyclic aromatic hydrocarbons from industrial emissions, mine tailings, wastes from metals, gasoline and paints containing lead, spraying of fertilizers, sewage sludge, pesticides, irrigation of wastewater, leftover of coal combustion, spilling of chemicals and rainfall [4] [5].

Globally, agricultural and industrial activities have increased the contamination of the ecosystem with organochlorines, products of petroleum and toxic metals [6]. These contaminants last very long and some remains in the area [7]. They are also harmful to plants and animals [8]. Organochlorines have been defined as highly toxic man made organic chemicals containing carbon used in industry and agriculture, as well as unintentional combustion processes of chlorine [9]. Organochlorine compounds (pesticides) are organic chemicals containing chlorine. Most of them are synthetic and they get into our surroundings through anthropogenic activities. Polycyclic aromatic hydrocarbons (PAHs) which are generally everywhere (soil, water and air) are group of different chemicals formed due to incomplete combustion of coal, oil and gas, garbage, tobacco. PAHs structures contain two or more benzene rings [10], [11], [12], [13], [14], [15], [16], [17] and have heteroatoms or substituents. PAHs with two to four rings are light PAHs while those with four rings and above are heavy PAHs. Heavy ones are usually harmful and stabilize better than the light PAHs [18], [19]. Exposure to PAHs has negative effects on humans, causing lungs cancer, DNA mutation and reproductive problems [20]. Some examples of PAHs are naphthalene, anthracene, phenanthrene, fluorine and pyrene. PAHs are either natural and synthetic and are usually colourless, white or pale yellow- green solids. PAHs are used in the production of coal tar, crude oil, creosote, roofing tar and with little used in medicines or for the production of dyes, plastics and pesticides [21].

Total petroleum hydrocarbons (TPH) are class of chemical compounds emanating from petroleum. They are found in the range of C₆ to C₄₀ as mixture containing hundreds to thousands of hydrocarbons including aliphatic and aromatic compounds [22].

Oil production in Nigeria has helped in the development of our society (socially, economically and politically) and also impacted negatively on the inhabitants and the environment due to crude oil spillage. Recently, there have been cases of crude oil spillage in some crude oil producing communities including Omuigwe-Aluu with its impact on land, water and air. Exposure to PAHs and heavy metals has negative effects on humans, causing lungs cancer, DNA mutation and reproductive problems [23]. In 2018 there was a tier 1 crude oil spill incident at Omuigwe-Aluu [24]. Omuigwe-Aluu is a land area where the inhabitants engage in medium scale farming of vegetables, cassava, maize farming, yam, plantain and palm oil plantation. Most harmful organochlorine pesticides are still used in most developing nations like Nigeria both at home and in agriculture. The continuous use of chlorinated compounds globally has been a thing of concern due to their movement and resistance to microbes [25]. It has been suggested that the reasons for the continual usage of organochlorine pesticides in developing countries like Nigeria, is due to their effectiveness and low cost [26]. Therefore, this study seeks to characterize and evaluate the levels of these organic pollutants.

II. Materials and Methods

Study Area

Omuigwe-Aluu (Fig. 1) is a town in Ikwerre Local Government Area of Rivers State in Nigeria. It is located in the Northern fringes of Port Harcourt metropolis on latitude 4.94403 and longitude 6.94226. Its boundaries are Imo State by the North, Obio/Akpor Local Government Area south, Etche Local Government East and Emohua Local Government Area of Rivers State West. People of Omuigwe-Aluu speak Igbo dialect. They are traditionally farmers, hunters and traders, but in recent times, contamination as a result of oil exploration and exploitation has caused reduction in the amount of farmland and forest available for their traditional occupations. The climate is tropical. Omuigwe-Aluu climate is affected by South Westerly wind coming from the Atlantic Ocean and dry North East Trade Winds coming from the Sahara desert.

The area has two seasons; the rainy season (April - October) and the dry season (November - March). Yearly rainfall in Omuigwe-Aluu is close to 240 cm with over 90% [27], relative humidity and average annual temperature of 27 °C [28]. It has tropical rainforest vegetation. The major tree species found in Omuigwe-Aluu include; *Elaeis guineensis* (oil palm tree), *Psidium guajava* (guava tree), *Theobroma cacao* (cocoa tree), *Chrysophyllum albidum* (African star apple tree or Agbalumo or Udara) and *Cocos nucifera* (coconut palm tree) [29].

Sample collection, preparation and analyses

Soil samples were taken using hand auger at six locations (4 at spill site 1 & 2, 4 at spill extension 1&2, 2 at 50 m away and 2 at about 200 m away as control site). Two random sampling points were selected at each of the six sampling locations. At the impacted area eight sampling points and two non-impacted (control) areas soil samples were collected. A total of twenty four soil samples including twelve top soils (0-15 cm) and twelve sub soils (15-30 cm) depths were taken with the aid of hand auger and stored in polyethylene bags. Twelve composite samples containing six top soils (0-15 cm) and six sub soils (15-30 cm) were made and taken to the laboratory for preparation and analyses. The composite samples were air – dried, grounded, sieved with 2 mm mesh and stored in labeled polythene bags under room temperature.

Analysis of Organochlorine compounds

Soil sample (1g) was weighed into a beaker and 40 ml of 1 M MgCl₂.6H₂O at pH 7 was added and agitated for 10 hrs using mechanical shaker, settled and filtered. The filtrate was analysed using GC-FID method 210918. The organochlorine standard having 17 organochlorine compounds was prepared at concentrations ranging from 0.100 to 2.000 ppm. Internal standards used were anthracene, PCB-153, and PF-38..

Extraction and analysis of polycyclic aromatic hydrocarbons

Prepared soil samples were extracted with US EPA modified ultrasonic oscillation extraction method [30]. Prepared soil samples (10 g) was weighed into a conical flask and 30 ml mixture solvents (acetone: dichloromethane) 1:1 ratio was added and agitated at 30 °C for 15 min with ultrasonic at 40 kHz frequency. The mixture was filtered with a funnel filled with anhydrous sodium sulphate. The extract was concentrated to 0.5 ml with a gentle stream of nitrogen (purity 99.999%) at 40 °C; cleaned up with a filled column (15 cm length × 10 mm id) having anhydrous sodium sulphate and silica gel. Lower part of the column had 10.0 g of activated silica gel at 100 °C for 24 hours) and 5.0 g anhydrous sodium sulfate (dryness for 10 h at 200 °C) in the upper part. Column was prewashed using of 30 ml acetone and 30 ml dichloromethane instantly. The extract was

passed through the column, which eluted 60 ml mixture of n-hexane and dichloromethane (volume (v: v), 1:1) at a flow rate of 0.5 ml·min⁻¹. PAHs elutions were collected and concentrated to 200 µl, reduced into n-hexane and just the volume to 1ml under a gentle stream of nitrogen. PAHs concentrations were analysed using GC/MS. Initially the column oven temperature was held at 60 °C for 2 min, then adjusted to 230 °C at a rate of 8 °C·min⁻¹ and held for 2 min, then adjusted to 290 °C at a rate of 2 °C·min⁻¹ and held for 2 min, and finally adjusted to 300 °C at a rate of 5 °C·min⁻¹ and held for 12 min. The injector temperature was maintained at 300 °C and the carrier gas helium (99.999%) at a constant flow rate of 1 mL·min⁻¹. The GC-MS was calibrated with 16 PAHs standard mixture. Extraction efficiencies calculation was done with deuterium labeled surrogate standards.

Total petroleum hydrocarbon (TPH): Prepared extract was used for this analysis. The extract was transferred into a labeled glass vials with Teflon. The sample was injected at the rate of 1 µl into the column of gas chromatography. The gas and liquid phases was separated and detected with GC-MS.

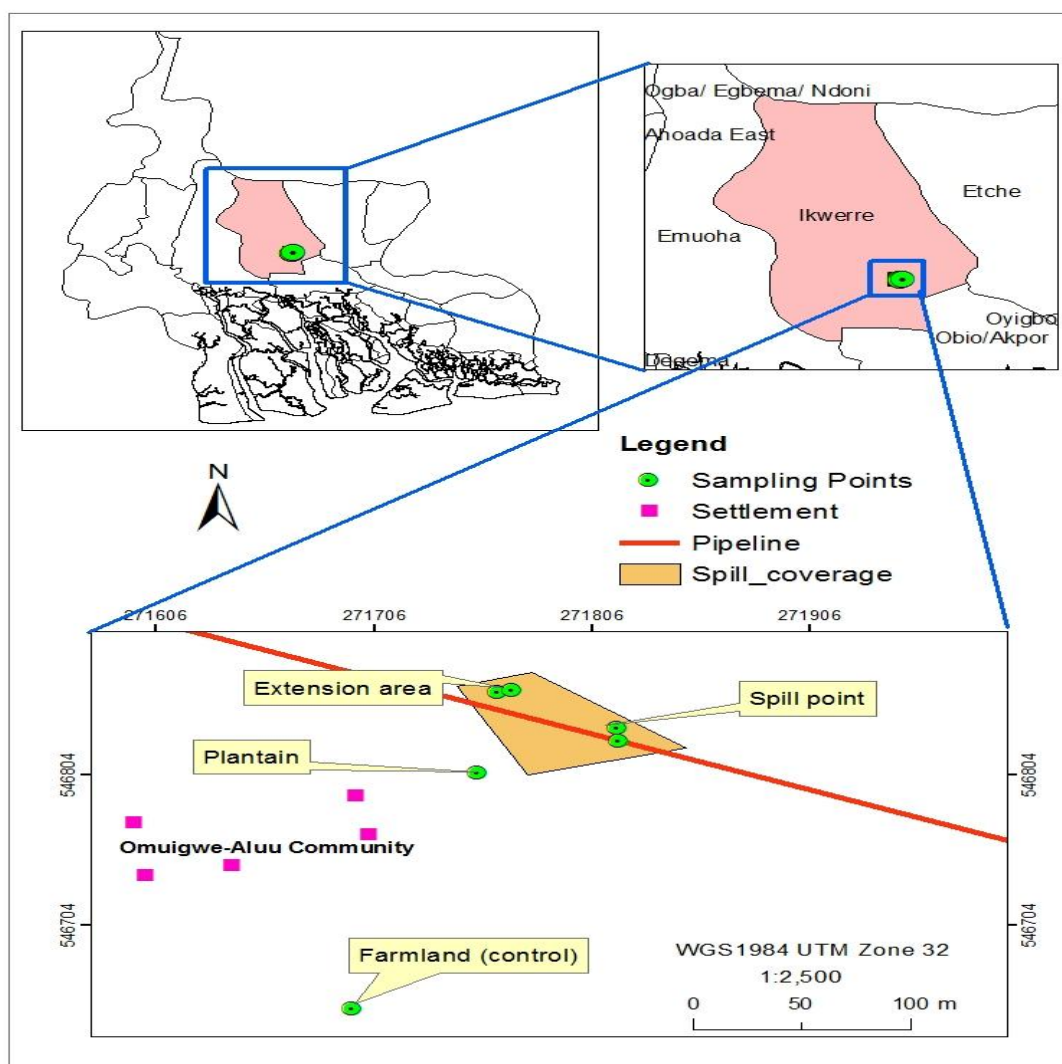


Fig.1: Rivers State Map indicating the area of Study and Sampling location

III. Results

Polycyclic Aromatic Hydrocarbons

Results of the analyses of Polycyclic Aromatic Hydrocarbons (PAHs) in soils at the study area are shown in Table 1 and Figs. 2 - 16. The individual PAH mean concentrations in soils in the study area ranged from 0.00±0.0 ppm to 0.01±0.01 ppm for naphthalene (top soil in control is highest), 0.00±0 ppm to 0.08±0.007 ppm for acenaphthylene (sub soil in spill site is higher), 0.00±0 ppm to 0.03±0.01 ppm for acenaphthene (top soil in 50m away is highest), 0.00±0 ppm to 0.11±0.01 ppm for Fluorene (top soil in spill point 1 is highest), 0.00±0 ppm to 0.08±0.01 ppm for anthracene (sub soil in 50m away is highest), 0.00±0 ppm to 0.19±0.01 ppm for phenanthrene (top soil in spill site 1 is highest), 0.00±0 ppm for O-Terphenyl in all the samples, 0.00±0 ppm to 0.16±0.01 ppm for fluoranthene (sub soil in spill site 2 is highest), 0.00±0 ppm to 0.02±0.01 ppm for Pyrene (sub soil in spill site 1 is highest), 0.00±0 ppm to 0.08±0.01 ppm for benz(a)anthracene (sub soil in spill site 1 is highest), 0.00±0 ppm to 0.04±0.01 ppm for Chrysene (spill site 1, spill site 2, and extension 1 are highest), 0.00±0 ppm to 0.04±0.01 ppm for benzo(b)fluoranthene (spill site 1 and extension 2 are highest), 0.00±0 ppm to 0.02±0.007 ppm for benzo(k)fluoranthene (sub soil in spill site 1 is highest), 0.00±0 ppm to 0.02±0.007 ppm for benzo(a)pyrene (spill sites 1 and 2 and extension 1 and 2 are highest), 0.00±0 ppm to 0.04±0.01 ppm for dibenzo(a,h)anthracene (sub soil in extension 2 is highest), 0.00±0 ppm for indeno(1,2,3-cd)pyrene in all samples and 0.00±0 ppm to 0.01±0.007 ppm for benzo(g,h i) perylene (spill sites 1 and 2 were highest).

Table 1: Mean Concentrations (ppm) of PAHs in Soils at Omuigwe-Aluu

S/ N	PAHs	Depth (cm)	Spill site 1	Spill site 2	Extension 1	Extension 2	50 m away	Control	USEPA
1	Naphthalene	0-15	0.00±0	0.00±0	0.00±0	0.00±0	0.00±0	0.01±0.01	0.04 d
		15-30	0.00±0	0.00±0	0.00±0	0.00±0	0.00±0	0.01±0	
2	Acenaphthylene	0-15	0.06±0.01	0.05±0	0.03±0.01	0.04±0	0.01±0.007	0.00±0	0.2c
		15-30	0.06±0.01	0.08±0.007	0.06±0	0.04±0	0.01±0	0.00±0	
3	Acenaphthene	0-15	0.01±0.007	0.02±0	0.01±0	0.01±0.007	0.03±0.01	0.00±0	0.2 c
		15-30	0.01±0.007	0.01±0.007	0.01±0	0.01±0.007	0.01±0.007	0.00±0	
4	Fluorene	0-15	0.11±0.01	0.07±0	0.04±0.01	0.05±0	0.00±0	0.00±0	0.2 c
		15-30	0.11±0	0.08±0.01	0.04±0.007	0.06±0	0.00±0	0.01±0.007	
5	Anthracene	0-15	0.03±0.01	0.01±0	0.03±0.007	0.03±0	0.06±0.01	0.00±0	0.2 c
		15-30	0.03±0	0.03±0	0.03±0.01	0.03±0.007	0.08±0.01	0.00±0	
6	Phenanthrene	0-15	0.19±0.01	0.11±0	0.08±0.007	0.07±0.01	0.00±0	0.01±0	0.2 c
		15-30	0.19±0.007	0.16±0.01	0.10±0	0.09±0.01	0.00±0	0.01±0.01	
7	O- Terphenyl	0-15	0.00±0	0.00±0	0.00±0	0.00±0	0.00±0	0.00±0	
		15-30	0.00±0	0.00±0	0.00±0	0.00±0	0.00±0	0.00±0	
8	Fluoranthene	0-15	0.12±0.01	0.11±0	0.10±0.007	0.10±0	0.01±0.007	0.01±0	0.2 c
		15-30	0.01±0	0.16±0.01	0.10±0	0.00±0	0.01±0.007	0.01±0	
9	Pyrene	0-15	0.01±0	0.01±0	0.01±0.007	0.01±0.007	0.00±0	0.00±0	0.2 c
		15-30	0.02±0.01	0.01±0	0.01±0	0.01±0.007	0.00±0	0.00±0	
10	Benz[a]anthracene	0-15	0.03±0.01	0.03±0.007	0.03±0	0.03±0.01	0.01±0	0.00±0	0.0001 b
		15-30	0.08±0.01	0.03±0.007	0.03±0.01	0.03±0	0.03±0.007	0.00±0	
11	Chrysene	0-15	0.04±0.01	0.04±0.007	0.03±0	0.02±0.01	0.00±0	0.00±0	0.0002 b
		15-30	0.04±0	0.04±0.01	0.04±0.01	0.02±0	0.00±0	0.00±0	
12	Benzo[b]fluoranthene	0-15	0.04±0.007	0.03±0	0.03±0.007	0.04±0.01	0.00±0	0.00±0	0.0002 b
		15-30	0.00±0	0.03±0.01	0.03±0	0.04±0.007	0.00±0	0.00±0	
13	Benzo[k]fluoranthene	0-15	0.00±0	0.00±0	0.00±0	0.00±0	0.00±0	0.00±0	0.0002 b
		15-30	0.02±0	0.00±0	0.00±0	0.00±0	0.00±0	0.00±0	
14	benzo[a]pyrene	0-15	0.02±0.007	0.02±0	0.02±0.007	0.02±0	0.01±0	0.00±0	0.0002 b
		15-30	0.02±0	0.02±0.01	0.02±0	0.02±0	0.01±0.007	0.00±0	

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15	Dibenzo[a,h]anthracene	0-15	0.00±0	0.00±0	0.03±0.01	0.03±0	0.01±0.007	0.00±0	0.0003 b
		15-30	0.00±0	0.00±0	0.01±0	0.04±0.01	0.01±0	0.00±0	
16	Indeno[1,2,3-cd] Pyrene	0-15	0.00±0	0.00±0	0.00±0	0.00±0	0.00±0	0.00±0	0.0004 b
		15-30	0.00±0	0.00±0	0.00±0	0.00±0	0.00±0	0.00±0	
17	Benzo [g h i] perylene	0-15	0.01±0.007	0.01±0	0.00±0	0.00±0	0.00±0	0.00±0	0.2d
		15-30	0.01±0	0.01±0.007	0.00±0	0.00±0	0.00±0	0.00±0	

b= 2013, c= 2014, d= 1996

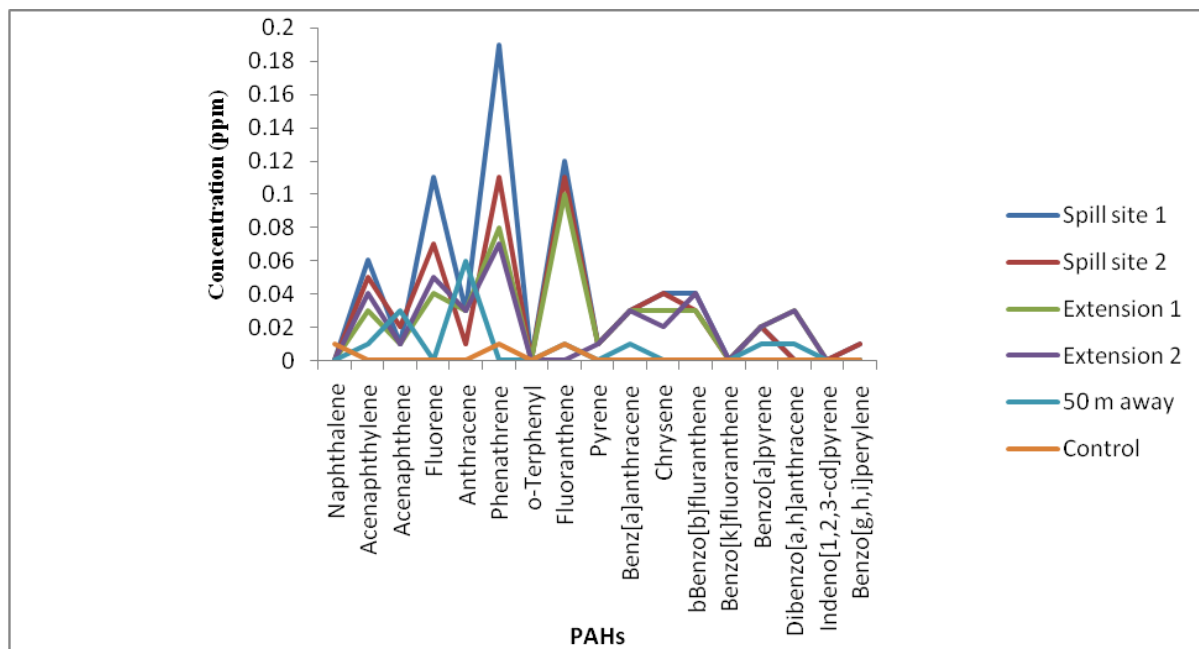


Fig. 2: Variations of concentrations of PAHs in soil at study sites (0-15 cm)

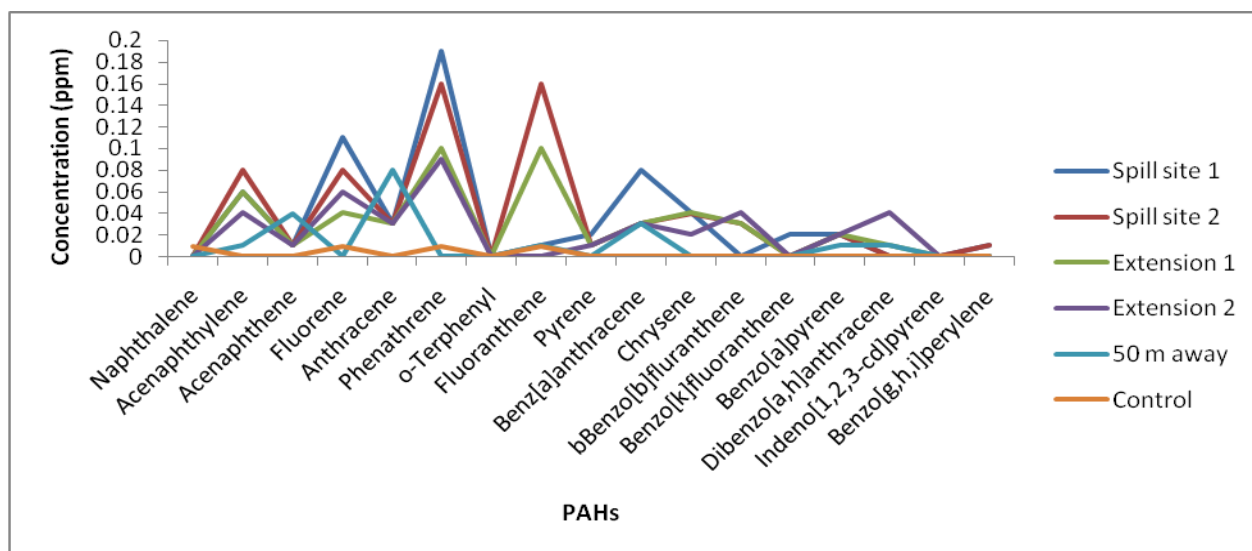


Fig. 3: Variations of concentrations of PAHs in soil at study sites (15- 30 cm)

Organochlorine Compounds

The results of organochlorine compounds in the soil at the study area are presented in Table 2.

Table 2: Concentrations (mg/kg) of Organochlorine Compounds in Soils at Omuigwe-Aluu

S/N	OCP	Depth (cm)	Spill site 1	Spill site 2	Extension 1	Extension 2	50 m away	Control
1	Aldrin	0-15	<0.01	<0.01	0.00	<0.01	<0.01	<0.01
		15-30	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

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2	alpha-BHC	0-15	0.00	0.00	0.00	<0.01	<0.01	<0.01
		15-30	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
3	beta-BHC	0-15	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
		15-30	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
4	delta-BHC	0-15	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
		15-30	0.00	<0.01	<0.01	<0.01	<0.01	<0.01
5	Gamma BHC	0-15	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
		15-30	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
6	DDD	0-15	<0.01	0.00	<0.01	<0.01	<0.01	<0.01
		15-30	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
7	DDE	0-15	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
		15-30	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
8	DDT	0-15	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
		15-30	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
9	Dieldrin	0-15	0.00	<0.01	<0.01	<0.01	<0.01	<0.01
		15-30	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
10	Endosulfan I	0-15	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
		15-30	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
11	Endosulfan II	0-15	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
		15-30	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
12	Endosulfan sulphate	0-15	<0.01	0.00	<0.01	<0.01	<0.01	<0.01
		15-30	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
13	Endrin	0-15	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
		15-30	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
14	Endrin aldehyde	0-15	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
		15-30	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
15	Heptachlor	0-15	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
		15-30	0.00	0.00	<0.01	<0.01	<0.01	<0.01
16	Heptachlor epoxide	0-15	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
		15-30	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
17	Methoxychlor	0-15	<0.01	<0.01	0.00	0.00	0.00	0.00
		15-30	0.00	0.00	<0.01	<0.01	<0.01	<0.01

Concentrations of the seventeen organochlorine compounds analysed ranged from <0.01 for alpha-benzene hexachloride (α -BHC), beta-Benzene hexachloride (β -BHC), delta-benzene hexachloride (δ -BHC), gamma-benzene hexachloride (γ -BHC), dichloro diphenyl dichloroethane (DDE), heptachlor-epoxide and endrin aldehyde at top and sub soils in spill site 1, extension 2 and control, aldrin, DDT and Endosulfan I in top and sub soils at spill site 1 and control to 0.00 mg/kg for heptachlor, dieldrin, endrin, endosulfan II, 1,1-dichloro-2,2-bis(p-chlorophenyl)ethane (DDD), DDT, methoxychlor, and endosulfan sulphate.

Total Petroleum Hydrocarbons

The results of Total Petroleum Hydrocarbons (TPHs) in the soils from the study area are shown in Table 3.

Table 3: Concentrations (ppm) of TPHs in Soils at Omuigwe-Aluu

S/N	TPHs	Depths (cm)	Spill site	Extension	Control
1	n-C10	0-15	ND	ND	7.637×10^{-3}
		15-30	ND	ND	7.637×10^{-3}
2	n-C11	0-15	ND	6.598×10^{-3}	1.852×10^{-2}
		15-30	ND	1.195×10^{-2}	1.852×10^{-2}
3	n-C12	0-15	8.893×10^{-1}	ND	1.144×10^{-2}
		15-30	ND	ND	1.144×10^{-2}
4	n-C13	0-15	3.3801×10^{-1}	ND	5.525×10^{-2}
		15-30	2.999×10^{-1}	1.010×10^{-1}	5.525×10^{-2}
5	n-C14	0-15	5.1183	2.796×10^{-2}	2.512×10^{-2}
		15-30	3.6715	1.917×10^{-2}	2.512×10^{-2}
7	n-C15	0-15	6.8134	3.508×10^{-2}	6.222×10^{-1}
		15-30	5.0514	1.6438	6.622×10^{-1}
8	n-C16	0-15	38.065	2.752×10^{-2}	2.847×10^{-1}
		15-30	31.281	1.351×10^{-1}	2.847×10^{-1}
9	n-C17	0-15	141.62	3.809×10^{-2}	6.342×10^{-1}
		15-30	106.35	2.160×10^{-1}	6.342×10^{-1}
10	C17+	0-15	420.34	3.336×10^{-2}	4.352×10^{-1}
		15-30	318.75	1.123×10^{-1}	4.352×10^{-1}
11	C18+	0-15	240.87	ND	7.447×10^{-1}
		15-30	195.85	2.984×10^{-1}	7.447×10^{-1}
12	n-C18	0-15	102.99	9.459×10^{-2}	2.296×10^{-1}
		15-30	83.469	2.022×10^{-1}	2.296×10^{-1}

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13	n-C19	0-15	269.90	9.2373	5.6180
		15-30	198.85	9.3610	5.6180
14	n-C20	0-15	467.56	4.679 x10 ⁻¹	5.995 x 10 ⁻¹
		15-30	366.56	3.404x10 ⁻¹	5.995 x 10 ⁻¹
15	n-C21	0-15	348.62	8.792 x10 ⁻¹	8.019 x 10 ⁻¹
		15-30	141.71	2.696 x10 ⁻¹	8.019 x 10 ⁻¹
16	n-C22	0-15	365.86	5.161 x10 ⁻¹	8.849 x 10 ⁻¹
		15-30	279.98	5.2431	8.849 x 10 ⁻¹
17	n-C23	0-15	300.79	6.724 x10 ⁻¹	6.525 x 10 ⁻¹
		15-30	153.51	4.062 x10 ⁻¹	6.525 x 10 ⁻¹
18	n-C24	0-15	630.09	6.702 x10 ⁻¹	7.888 x 10 ⁻¹
		15-30	162.62	6.445 x10 ⁻¹	7.888 x 10 ⁻¹
19	n-C25	0-15	566.56	3.754 x10 ⁻¹	7.202 x 10 ⁻¹
		15-30	430.79	3.723 x10 ⁻¹	7.202 x 10 ⁻¹
20	n-C26	0-15	649.29	4.097 x10 ⁻¹	ND
		15-30	174.79	7.774 x10 ⁻¹	3.395 x 10 ⁻²
21	n-C27	0-15	441.96	3.720 x10 ⁻¹	ND
		15-30	345.71	1.278 x10 ⁻¹	2.452 x 10 ⁻²
22	n-C28	0-15	327.28	5.343 x10 ⁻¹	ND
		15-30	254.52	7.677 x10 ⁻¹	2.123 x 10 ⁻¹
23	n-C29	0-15	1016.43	9.661 x10 ⁻¹	ND
		15-30	551.73	4.772 x10 ⁻¹	6.288 x 10 ⁻¹
24	n-C30	0-15	474.97	3.981 x10 ⁻¹	ND
		15-30	384.29	9.398 x10 ⁻²	5.273 x 10 ⁻²
25	n-C31	0-15	282.22	1.1361	ND
		15-30	232.80	8.531 x10 ⁻¹	8.699 x 10 ⁻²
26	n-C32	0-15	254.76	4.982 x10 ⁻¹	ND
		15-30	205.16	9.806 x10 ⁻²	1.404 x 10 ⁻¹
27	n-C33	0-15	297.07	5.179 x10 ⁻¹	ND
		15-30	92.004	2.988 x10 ⁻¹	5.294 x 10 ⁻²
28	n-C34	0-15	178.09	1.363 x10 ⁻¹	6.242 x 10 ⁻²
		15-30	219.66	1.612 x10 ⁻²	7.781 x 10 ⁻²
29	n-C35	0-15	154.95	4.390 x10 ⁻²	1.626 x 10 ⁻¹
		15-30	203.79	6.741	1.626 x 10 ⁻¹
30	n-C36	0-15	77.510	1.349 x10 ⁻¹	1.589 x 10 ⁻¹
		15-30	54.457	1.643 x10 ⁻¹	1.589 x 10 ⁻¹
31	n-C37	0-15	82.036	1.103 x10 ⁻¹	7.609 x 10 ⁻²
		15-30	81.181	ND	7.610 x 10 ⁻²
32	n-C38	0-15	9.9675	3.977 x10 ⁻²	ND
		15-30	12.455	ND	ND
33	n-C39	0-15	7.1932 x 10 ⁻¹	ND	ND
		15-30	1.9086	ND	ND
34	n-C40	0-15	2.7369	ND	ND
		15-30	1.8321	ND	ND

ND: Not detected

TPHs concentrations in soils of the study area ranged from 7.637 x 10⁻³ ppm for n-C₁₀ (top and sub soils, control) to 1016.43 ppm for n-C₂₉ (top soil, spill site). Total concentrations of TPHs obtained for the locations were 8156.40 ppm (top soil, spill site), 5295.04 ppm (sub soil, sub site), 18.4100 ppm (top soil, extension), 23.0838 ppm (sub soil, extension), 13.5944 ppm (top soil, control) and 14.8424 ppm (sub soil, control).

The concentration of n-C₁₀ fraction in the study area was 7.637 x 10⁻³ ppm (top and sub soils) while it was not detected in other soil samples. The concentrations of n-C₁₁ fraction in the study area ranged from 6.598 x 10⁻³ ppm (top soil, extension) to 1.195 x 10⁻² ppm (sub soil, extension) while it was not detected in samples taken from the spill site. The concentrations of n-C₁₂ fraction in the area of study ranged from 1.1443 x 10⁻² ppm (top and sub soils, control) to 8.893 x 10⁻¹ ppm (top soil, spill site) while it was not detected in other soil samples.

The concentrations of n-C₁₃ fraction in the study area ranged from 5.525 x 10⁻² ppm (top and sub soils, control) to 3.3801 x 10⁻¹ ppm (top soil, spill site) while it was not detected in samples taken from the top soil, extension. The concentrations of n-C₁₄ fraction in the area of study ranged from 1.917 x 10⁻² ppm (sub soil, extension) to 5.1183ppm (top soil, spill site). The concentrations of n-C₁₅ fraction in the study area ranged from 3.508 x 10⁻² ppm (top soil, extension) to 6.8134 ppm (top soil, spill site). The concentrations of n-C₁₆ fraction in the study area ranged from 2.752 x 10⁻² ppm (top soil, extension) to 38.065 ppm (top soil, spill site). The concentrations of n-C₁₇ fraction in the study area ranged from 3.809 x 10⁻² ppm (top soil, extension) to 141.62 ppm (top soil, spill site). The concentrations of C₁₇⁺ fraction in the study area ranged from 3.336 x 10⁻² ppm (top soil, extension) to 420.34 ppm (top soil, spill site). The concentrations of n-C₁₈ fraction in the study area ranged

from 9.459×10^{-2} ppm (top soil, extension) to 102.99 ppm (top soil, spill site). The concentrations of C_{18}^{+} fraction in the study area ranged from 2.984×10^{-1} ppm (sub soil, extension) to 240.87 ppm (top soil, spill site), while it was not detected in top soil, extension. The concentrations of n- C_{19} fraction in the study area ranged from 5.6180 ppm (top and sub soils, control) to 269.90 ppm (top soil, spill site). The concentrations of n- C_{20} fraction in the study area ranged from 3.404×10^{-1} ppm (sub soil, extension) to 467.56 ppm (top soil, spill site). The concentrations of n- C_{21} fraction in the study area ranged from 2.696×10^{-1} ppm (sub soil, extension) to 348.62 ppm (top soil, spill site). The concentrations of n- C_{22} fraction in the study area ranged from 5.161×10^{-1} ppm (top soil, extension) to 365.86 ppm (top soil, spill site). The concentrations of n- C_{23} fraction in the study area ranged from 4.062×10^{-1} ppm (sub soil, extension) to 300.79 ppm (top soil, spill site). The concentrations of n- C_{24} fraction in the study area ranged from 6.445×10^{-1} ppm (sub soil, extension) to 630.09 ppm (top soil, spill site). The concentrations of n- C_{25} fraction in the study area ranged from 3.723×10^{-1} ppm (sub soil, extension) to 566.56 ppm (top soil, spill site).

The concentrations of n- C_{26} fraction in the study area ranged from 3.395×10^{-2} ppm (sub soil, control) to 649.29 ppm (top soil, spill site) while it was not detected in sample taken from the top soil, control. The concentrations of n- C_{27} fraction in the study area ranged from 2.452×10^{-2} ppm (sub soil, control) to 441.96 ppm (top soil, spill site) while it was not detected in sample taken from the top soil, control. The concentrations of n- C_{28} fraction in the study area ranged from 2.123×10^{-1} ppm (sub soil, control) to 327.28 ppm (top soil, spill site) while it was not detected in sample taken from the top soil, control. The concentrations of n- C_{29} fraction in the study area ranged from 4.772×10^{-1} ppm (sub soil, extension) to 1016.43 ppm (top soil, spill site) while it was not detected in sample taken from the top soil, control. The concentrations of n- C_{30} fraction in the study area ranged from 5.273×10^{-2} ppm (sub soil, control) to 474.97 ppm (top soil, spill site) while it was not detected in sample taken from the top soil, control. The concentrations of n- C_{31} fraction in the study area ranged from 8.531×10^{-1} ppm (sub soil, extension) to 282.22 ppm (top soil, spill site) while it was not detected in sample taken from the top soil, control. The concentrations of n- C_{32} fraction in the study area ranged from 9.806×10^{-2} ppm (sub soil, extension) to 254.76 ppm (top soil, spill site) while it was not detected in sample taken from the top soil, control.

The concentrations of n- C_{33} fraction in the study area ranged from 5.294×10^{-2} ppm (sub soil, control) to 297.07 ppm (top soil, spill site) while it was not detected in (top soil, control). The concentrations of n- C_{34} fraction in the area of study ranged from 1.612×10^{-2} ppm (sub soil, extension) to 219.66 ppm (sub soil, spill site). The concentrations of n- C_{35} fraction in the study area ranged from 4.390×10^{-2} ppm (top soil, extension) to 203.79 ppm (sub soil, spill site). The concentrations of n- C_{36} fraction in the area of study ranged from 1.349×10^{-1} ppm (top soil, extension) to 77.510 ppm (top soil, spill site). The concentrations of n- C_{37} fraction in the study area ranged from 7.609×10^{-2} ppm (top and sub soils, control) to 82.036 ppm (top soil, spill site) while it was not detected in sub soil, extension. The concentrations of n- C_{38} fraction in the study area ranged from 3.977×10^{-2} ppm (top soil, extension) to 12.455 ppm (sub soil, spill site) while it was not detected in other soil samples. The concentrations of n- C_{39} fraction in the study area ranged from 7.1932×10^{-1} ppm (top soil, spill site) to 1.90885 ppm (sub soil, spill site) while it was not detected in other soil samples.. The concentrations of n- C_{40} fraction in the study area ranged from 1.8321 ppm (sub soil, spill site) to 2.7369 ppm (top soil, spill site), while it was not detected in other soil samples.

IV. Discussion

Polycyclic Aromatic Hydrocarbons

Mean concentrations of PAHs ranged from 0.00 ± 0 ppm – 0.19 ± 0.01 ppm. acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, except pyrene, were above their standard limits of 0.2 ppm [31] as shown in Table 1. According to [32],[33] the above listed are all classified as non carcinogenic. These PAHs may not pose threat to the health of inhabitants in the area.

Naphthalene: Naphthalene concentration ranged from 0.00 ± 0.0 ppm to 0.01 ± 0.01 ppm, which is below [34] standard limit (0.04 ppm). It is classified as non carcinogenic to human. Naphthalene was not a threat in the soils of the study area.

Benz(a)anthracene: Benz(a)anthracene is a carcinogenic, mutagenic and toxic PAHs [35]. Benz(a)anthracene concentrations in soils in the study area ranged from 0.00 ± 0 ppm to 0.08 ± 0.01 ppm in all the samples and it exceeded the permissible limit of 0.0001 ppm set by [35]. Hence, benz(a)anthracene may pose health problems in the study area.

Benzo(a)pyrene: Benzo(a)pyrene is one of the PAHs considered to be carcinogenic, mutagenic and toxic [35]. The concentrations of benzo(a)pyrene in soils ranged from 0.00 ± 0 ppm to 0.02 ± 0.007 ppm. The result was

above [35] standard limit of 0.0002 ppm. Benzo(a)pyrene concentrations may be a threat to man's health in the area.

Benzo(b)fluoranthene and Chrysene: These PAHs are carcinogenic, mutagenic and toxic [35]. Mean concentrations of chrysene and benzo(b)fluoranthene ranged from 0.00±0 ppm to 0.04±0.01 ppm and 0.00±0 ppm to 0.04±0.01 ppm respectively. Benzo(b)fluoranthene at spill 1 and extension 2 exceeded the standard limit of 0.0002 mg/kg [35]. Lives in the area may be at risk. The high concentrations could be attributed to crude oil pollution in that area.

Indeno(1,2,3-c,d)pyrene and Dibenzo(a,h)anthracene: Indeno(1,2,3-cd)pyrene and dibenzo(a,h)anthracene are carcinogenic, mutagenic and toxic PAHs [35]. The mean concentrations of dibenzo(a,h)anthracene in soils ranged from 0.00±0 ppm to 0.04±0.01 ppm. The concentrations of dibenzo(a,h)anthracene in spill site 1 and 2 exceeded the permissible limits 0.0003 ppm [35]. Indeno(1,2,3-Cd) pyrene was 0.00±0 ppm. Therefore this may pose threat to the health of inhabitants in that area.

o-Terphenyl : o-Terphenyl concentration was 0.00 ppm in all the samples analyzed.

Benzo (k) fluoranthene concentration in soils ranged from 0.00±0 ppm to 0.02±0 ppm. This is within the permissible limits. Therefore it might not pose health problems to inhabitants in the study area. Results in this study were higher than that of [16]. The peaks of PAHs were shown in Figs. 4-15.

Organochlorine compounds (OCPs)

Concentrations of seventeen OCPs were all below limits [37]. The soils are not polluted with OCPs, hence it may be due to no or little use of OCPs by farmers in Omuigwe-Aluu. The results of alpha-BHC, beta-BHC, delta-BHC, gamma BHC, heptachlor, aldrin, heptachlor-epoxide were same as the one reported by [41], while alpha-BHC, beta-BHC, delta-BHC, gamma BHC, heptachlor, aldrin, heptachlor-epoxide while alpha-BHC, beta-BHC, delta-BHC, gamma BHC, heptachlor, aldrin, dieldrin, DDT, endrin, endosulfan I are same and endosulfan II, DDD, heptachlor-epoxide, DDE, methoxychlor, endrin aldehyde and endosulfan sulphate. Results were above the reports of [38].

Total Petroleum Hydrocarbons

TPHs concentrations in this study ranged from 6.598 x 10⁻³ ppm (n-C₁₁, top soil, extension) to 1016.43 ppm (n-C₂₉, top soil, spill site) (Table 3). The highest TPH concentration was found at the spill site (top soil) due to crude oil spillage. Concentrations of TPHs were below target value of 50 ppm [39] with the exception of n-C₁₇:141.62 ppm (top soil, spill site), C₁₇₊: 420.34 ppm (top soil, spill site), C₁₈:102.99 ppm (top soil, spill site), C₁₈₊: 240.87 ppm (top soil, spill site), n-C₁₉: 269.90 ppm (top soil, spill site), n-C₂₀: 467.56 ppm (top soil, spill site), n- C₂₁: 348.62 ppm (top soil, spill site), n-C₂₂: 365.86 ppm (top soil, spill site), n-C₂₃:300.79 ppm (top soil, spill site), n- C₂₄: 630.09 ppm (top soil, spill site), n-C₂₅: 566.56 ppm (top soil, spill site), n- C₂₆: 649.29 ppm (top soil, spill site), n-C₂₇: 441.96 ppm (top soil, spill site), n-C₂₈: 327.28 ppm (top soil, spill site), n-C₂₉: 1016.43 ppm (top soil, spill site), control, n-C₃₀: 474.97 ppm (top soil, spill site), n-C₃₁: 282.228 ppm (top soil, spill site), control, n-C₃₂:254.76 ppm (top soil, spill site), n-C₃₃: 297.07 ppm (top soil, spill site) , n-C₃₄:219.66 ppm (sub soil, spill site), n-C₃₅: 203.79 ppm (sub soil, spill site), n-C₃₆:77.10 ppm (top soil, spill site) and n-C₃₇: 82.036 ppm (top soil, spill site) which are high but, are below the intervention value of 5000 ppm [37]. The concentrations of n-C₁₁ (spill site), n-C₁₂ (extension), n-C₁₃ (top soil, extension), n-C₁₈⁺ (top soil, extension), n-C₂₆, n-C₂₇, n-C₂₈, n-C₃₀, n-C₃₁, n-C₃₂, n-C₃₃ and n-C₃₈ (top soil, control) and n-C₃₇ (sub soil, extension) were not detected. These observations could be attributed to either slow seepage of the spill oil to that depth or the detectable limit of the analytical instrument. The non detection of concentrations of n-C₁₀ (spill site and extension), n-C₁₂ (sub soil, spill site and extension), n-C₃₈ (sub soil, extension and control), n-C₃₉ and n-C₄₀ (extension and control) could be attributed to the detection limits of the analytical instrument. The soils in the study area, though contaminated, are not polluted with TPHs. Hence, the inhabitants are not threatened by TPHs. The observed concentrations are below what was reported by previous researchers [38], [39], [19]; but above that reported in [40].TPH concentrations of top and sub soils showed that the extension and control sites were low compared to the spill site which could be attributed to the crude oil spill in the area.

V. Conclusion

This study has shown that the concentrations of benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a) pyrene and dibenz(a,h) anthracene in the soils exceeded standard limits. The exceedance of these toxic and carcinogenic PAHs could be due to oil exploitation activities and which could pose health and environmental hazards in the area. The area is not polluted with organochlorine compounds as

their concentrations were below limits. However the area is contaminated with total petroleum hydrocarbons as their concentrations in some sites are above target value but below intervention value. It is recommended that the levels of pollutants in the area should be regularly monitored.

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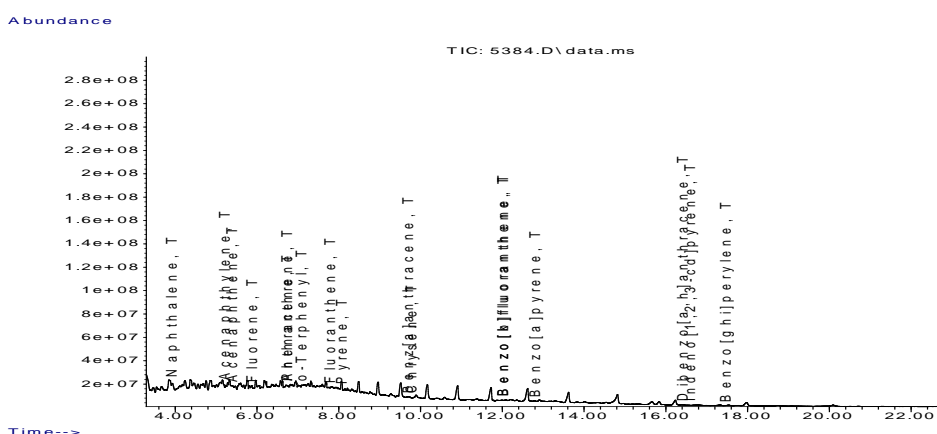


Fig. 4 PAHs chromatogram for spill site 1 (0-15 cm)

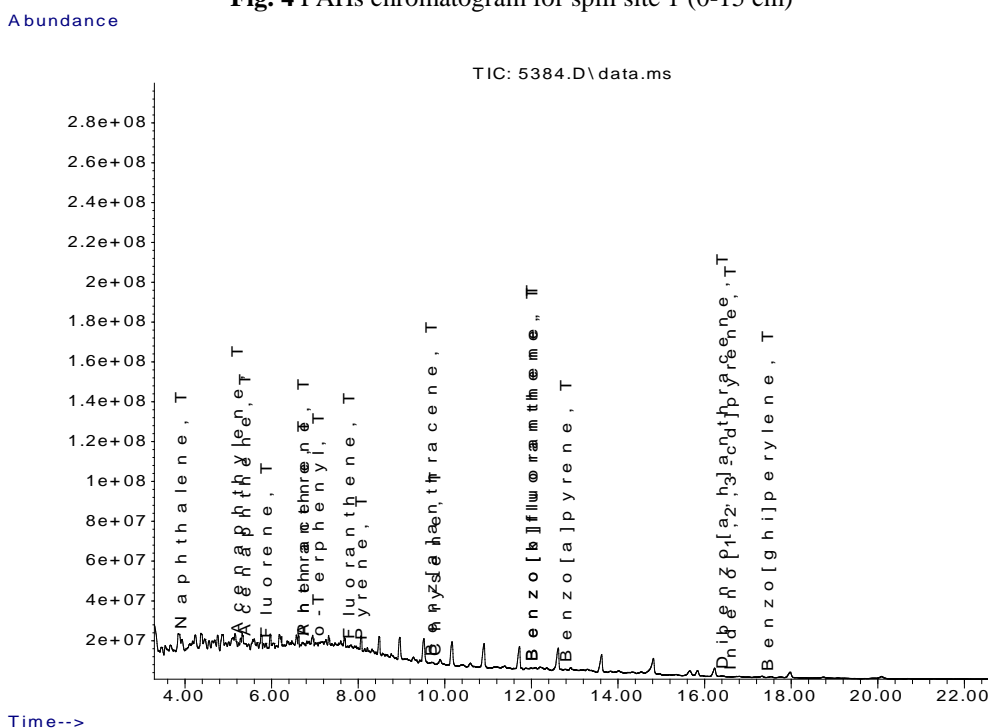


Fig. 5 PAHs chromatogram for spill site 1 (15 -30 cm)

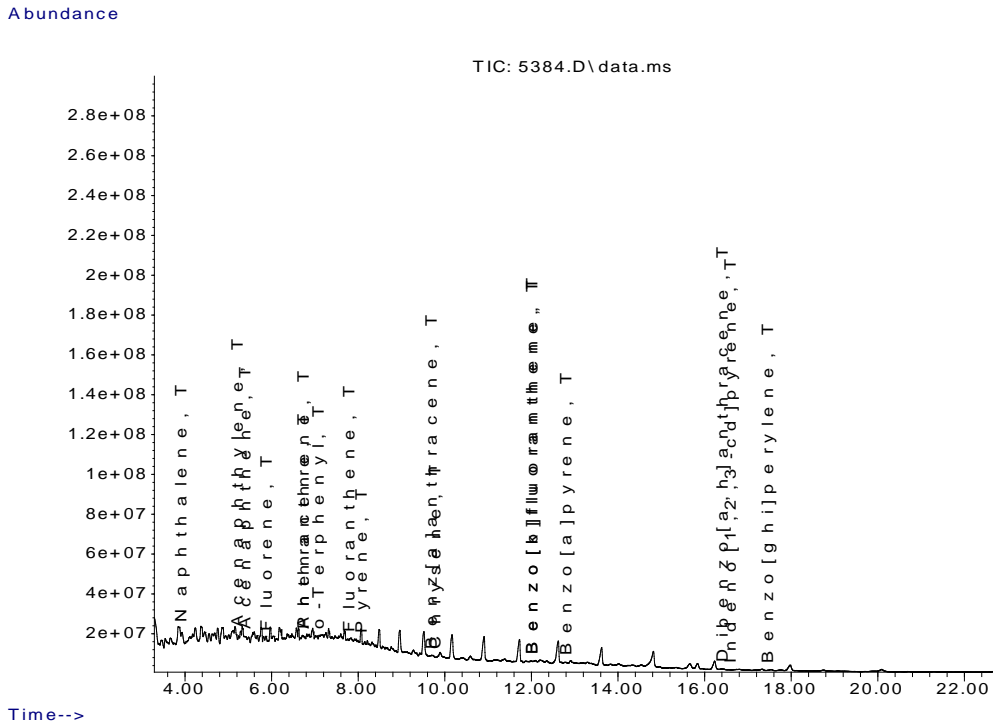


Fig. 6 PAHs chromatogram for spill site 2 (0-15 cm)

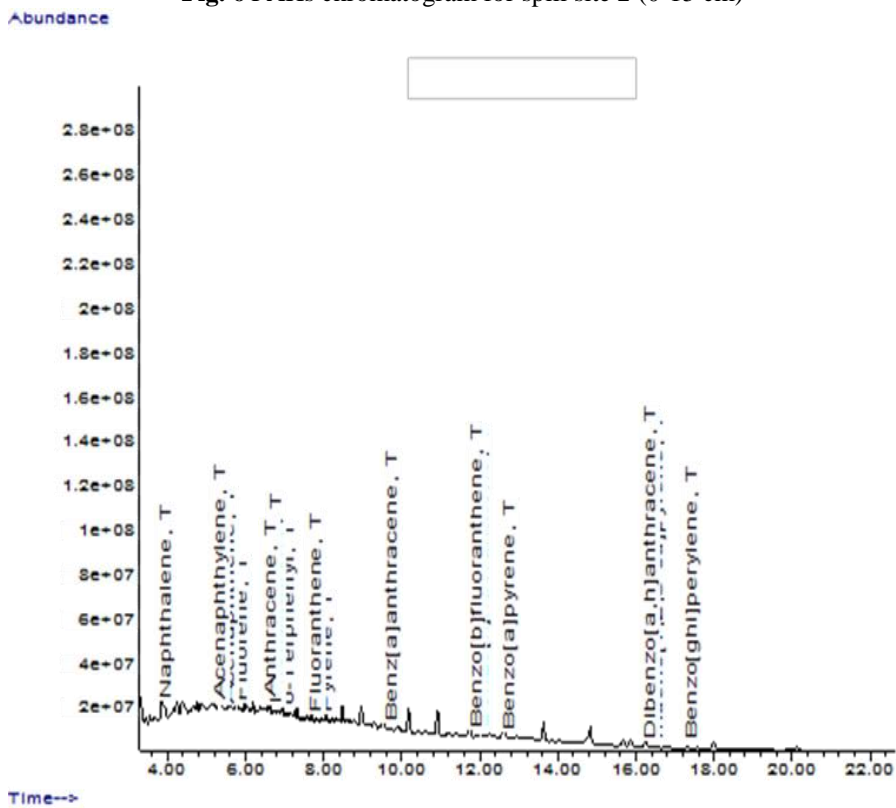


Fig. 7 PAHs chromatogram for spill site 2 (15 -30cm)

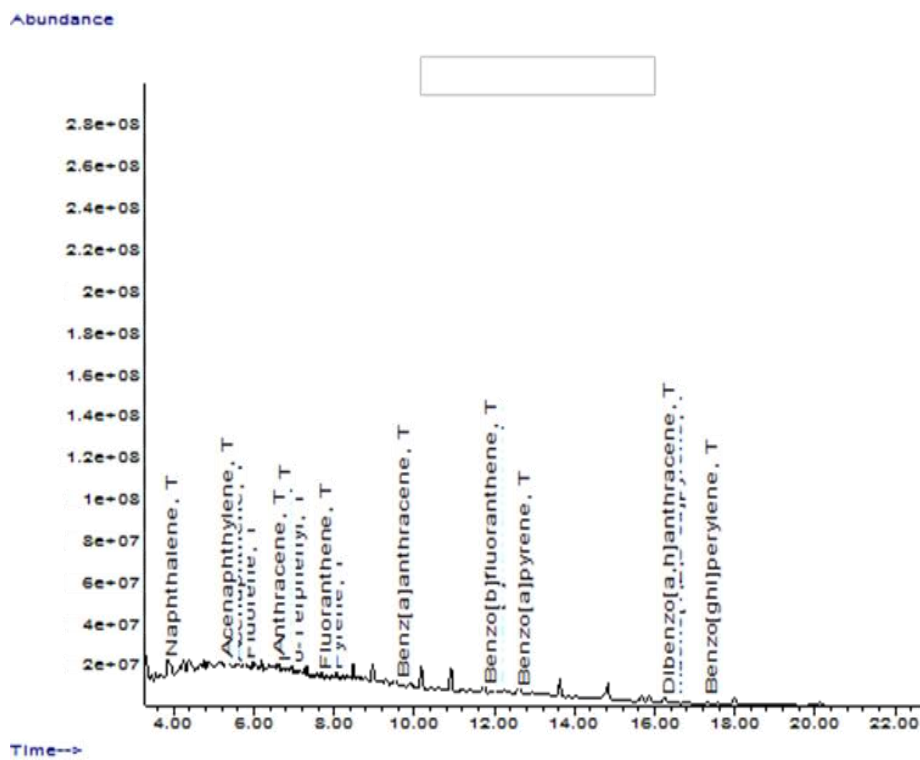


Fig. 8: PAHs chromatogram for Extension 1 (0- 15 cm)

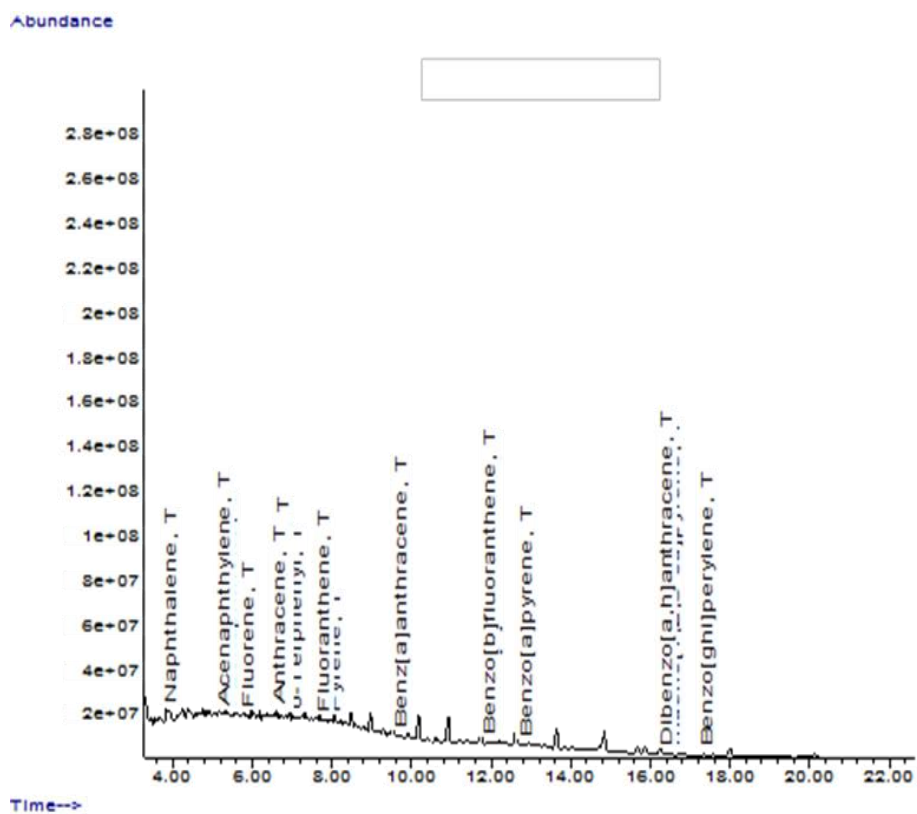


Fig. 9: PAHs chromatogram for Extension 1 (15-30 cm)

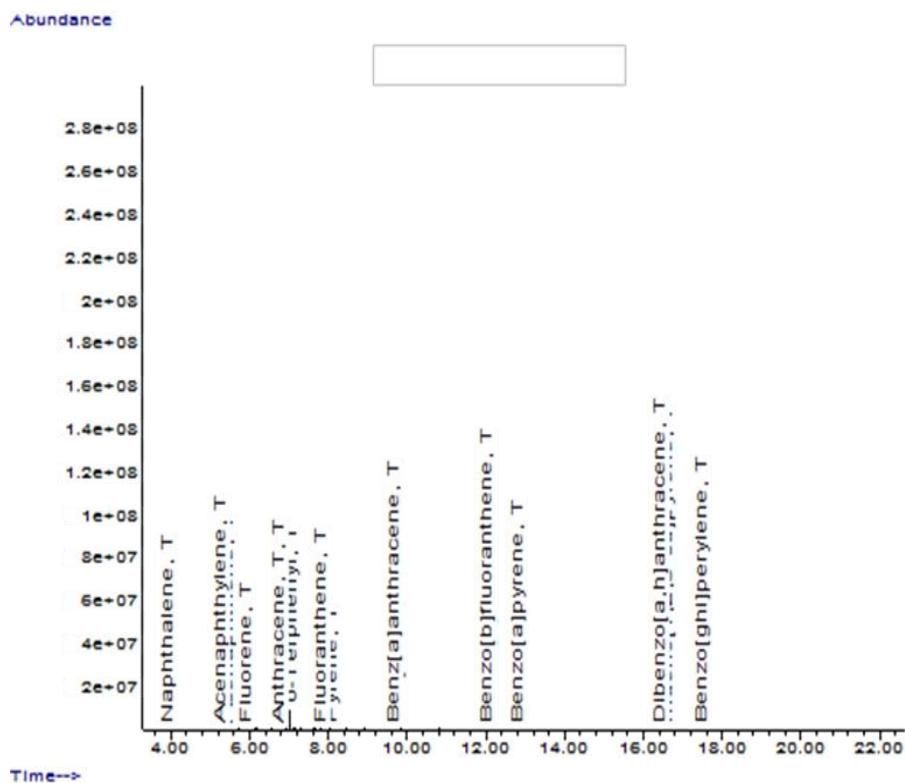


Fig. 10: PAHs chromatogram for Extension 2 (0- 15 cm)

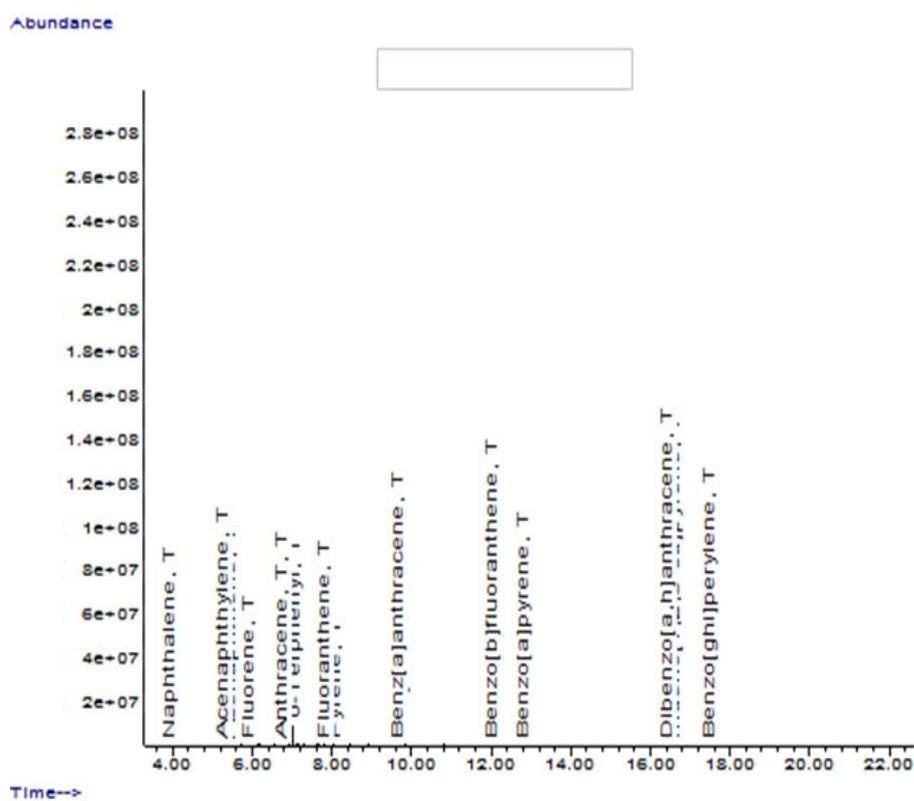


Fig. 11: PAHs chromatogram for 50 m away (0-15 cm)

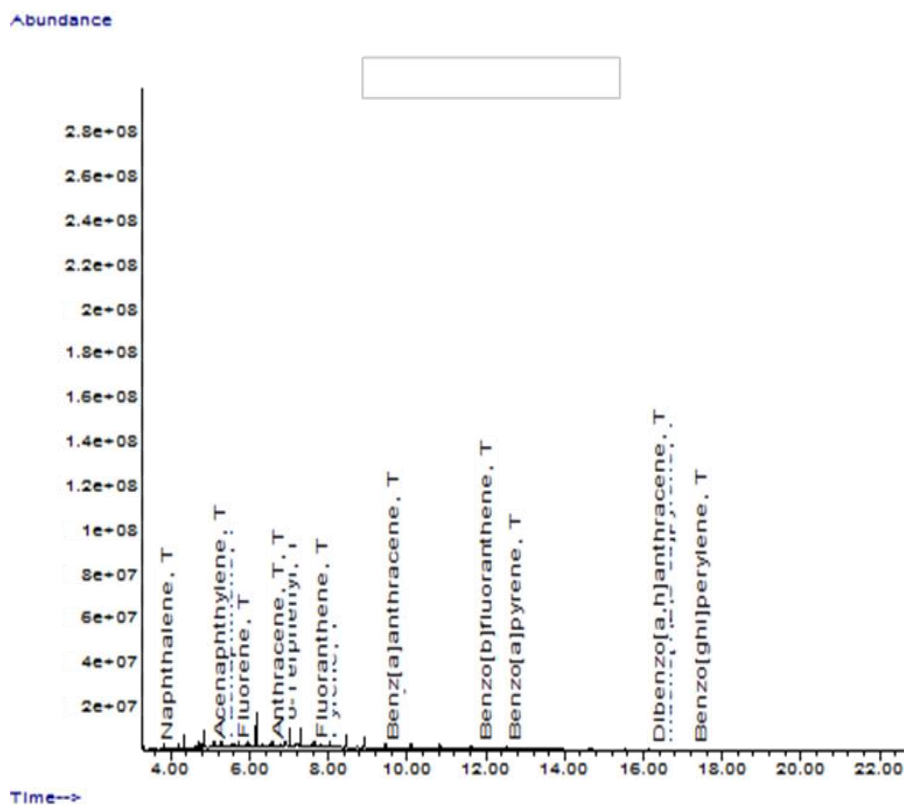


Fig. 12: PAHs chromatogram for Extension (15-30 cm)

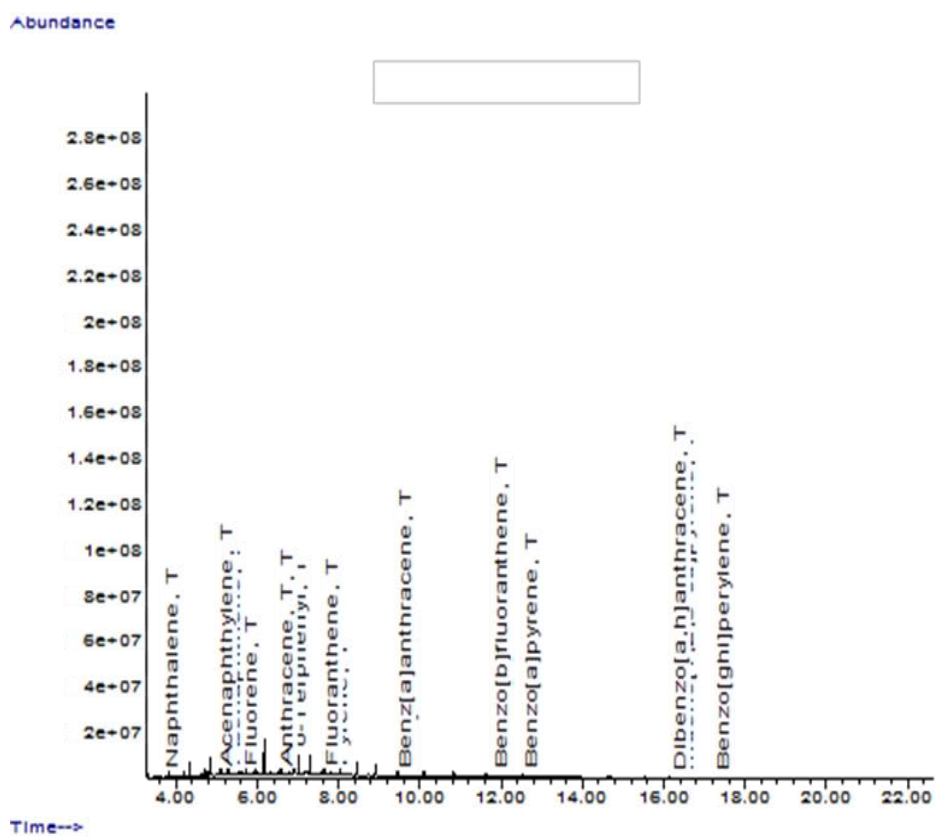


Fig. 13: PAHs chromatogram for 50 m away (15-30 cm)

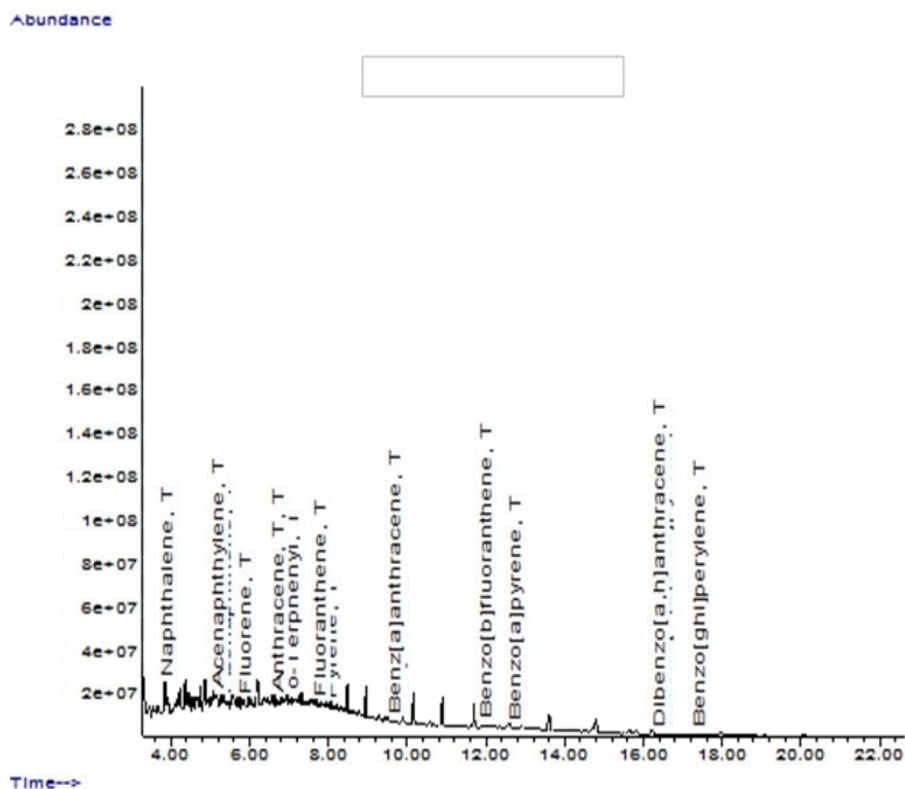


Fig. 14: PAHs chromatogram for control (0-15 cm)

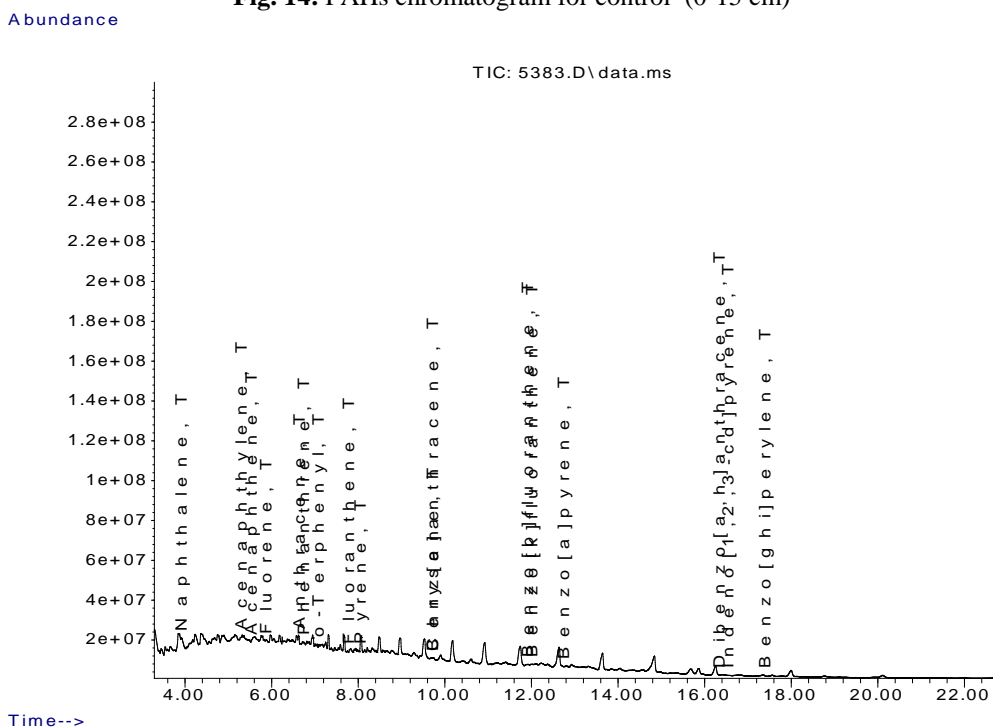


Fig. 15: PAHs chromatogram for Extension (15-30 cm)

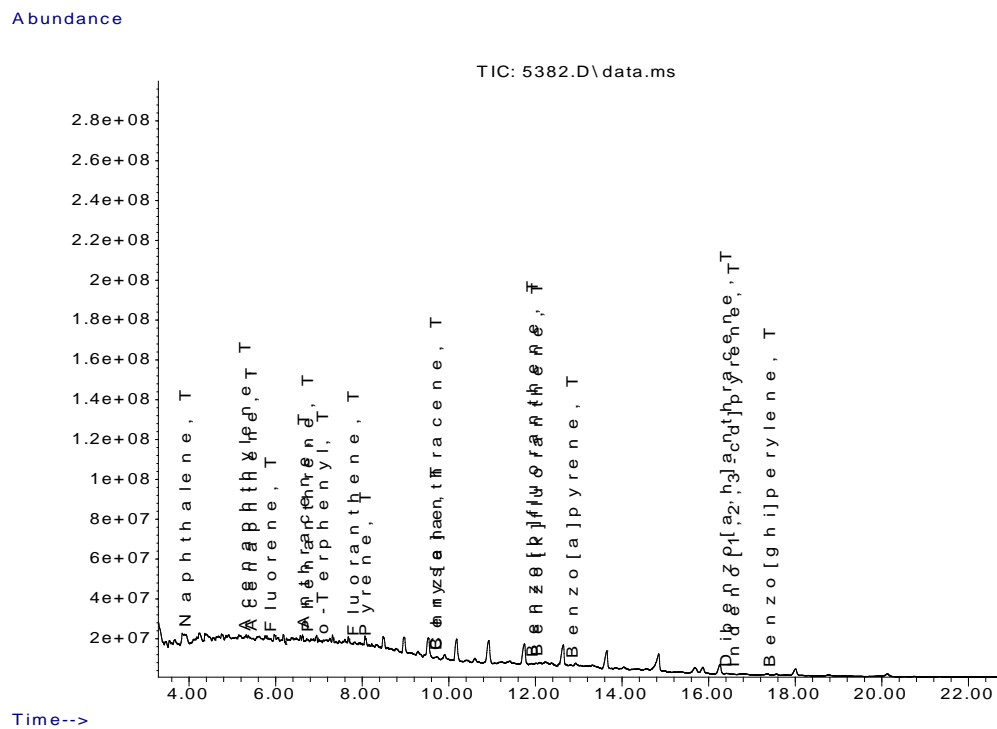


Fig. 16: PAHs chromatogram for control (15-30 cm)

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