

## Occurrence and sources of aliphatic hydrocarbons in anthropogenic impacted soils from petroleum tank-farms in the Niger Delta, Nigeria

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**Abstract.** The occurrence and compositional pattern of priority pollutants are vital in understanding the anthropogenic contributions, origin, and risks of these pollutants to the surrounding environment. Thus, the focus of this study was to determine the concentrations, compositional profiles, and sources of aliphatic hydrocarbons (AHCs) in anthropogenic impacted soils from petroleum tank-farms environment in the Niger Delta, Nigeria. Forty-five soil samples were collected from the vicinity of petroleum tank-farms at the top (0-15 cm), sub (15-30 cm), and bottom (30-45 cm) soil depths. The concentration of AHCs was determined using gas chromatography-mass spectrometer (GC-MS) after extraction by ultrasonication with hexane/dichloromethane and clean-up in silica gel/alumina packed column. The mean concentrations of AHCs in the samples ranged from  $0.52 \pm 0.90$  to  $35.26 \pm 35.69$  mg/kg. The AHCs results show that the equivalent carbon number index (ECn-) ECn-13-35 had the highest concentration when compared to ECn-8-12 and ECn-36-40. The linear regression and ANOVA indicate that there is no significant positive correlation between TOC and the total concentration of AHCs in the soil profiles, and a significant variation in AHCs levels between soil profiles respectively. Results also showed that soils from the tank-farms are moderately contaminated with AHCs when compared to the UNEP recommended limit. However, when compared to other regulatory thresholds, the observed concentrations of AHCs, human and environmental health risks are likely. Source apportionments depict that the principal sources of AHCs were petrogenic and plant diagenesis. Appropriate clean-up and mitigation measures and further study to determine the occurrence, composition, and exposure risks of other priority pollutants in water and sediment samples from the surrounding creeks should be determined.

**Keywords:** aliphatic hydrocarbons; occurrence profiles; source identification; soil pollution; exposure risk.

### 1. Introduction

Globally, considerable concerns have been devoted to the protection of soil and water resources around the industrial environment. Aliphatic hydrocarbons (AHCs) are components of total petroleum hydrocarbons (TPH), they are ubiquitous and are formed through diagenetic, biogenic, pyrolytic, and petrogenic pathways [1-3]. AHCs components ranged from gasoline to bitumen used as a source of energy in residential, commercial, industrial, and transportation operations. AHCs are also used as monomers in the synthesis of numerous chemicals and products used in industrial, commercial, domestic applications [4, 5]. The origins of TPH in the soil are through anthropogenic (equipment and facility breakdown, spills from drilling rigs and storage tanks, effluent discharges and spilled by-products) and natural (biogenic, oil seeps from the bottom of the sea and ocean which enters marine environment) sources [6, 7]. Generally, *n*-alkanes containing less than 20 carbon-atoms are related to ocean plankton such as algae and bacteria. The *n*-alkanes from oceanic low-plankton are depicted even carbon number predominance. The *n*-alkanes ranging from *n*-C<sub>10</sub> to *n*-C<sub>35</sub> are classified as fossil fuels and their combustion products [8]. Due to *n*-

alkanes non-polar and photo-catalytic stable characteristics, AHCs molecules are potential markers for the identification of hydrocarbon contamination and source apportionment [9].

Soil, sediment, and dust particles are significant components of the terrestrial ecosystem and act as a sink for several emerging contaminants such as AHCs, pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and heavy metals [10-12]. Soil physicochemical properties are significant in the fate and mobility of these contaminants in soil or sediments [13, 14]. Soil pollution with crude oil adversely affects both land and aquatic ecosystems through adsorption onto soil particles and the provision of excess carbon that might not be available for microbial use [15]. Also, due to the multiplier effects of soil not providing its traditional ecosystem support, soil contamination with priority pollutants has been reported to be the most life-threatening process [16 – 18].

Human and environmental health challenges associated with TPH pollution of aquatic and soil matrixes have drawn global attention. The World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA) classified

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total petroleum hydrocarbons (TPH) as persistence organic pollutants (POPs) in terrestrial and aquatic environments [1, 19-23]. AHCs are of a significant environmental and human health concern due to their ubiquitous, persistent and bioaccumulation properties. Several AHCs have toxic and carcinogenic properties [24]. AHCs are central nervous system (CNS) depressants and asphyxiants; severe toxic effects of AHCs are: cancer for 1,3-butadiene, asphyxia, and chemical pneumonitis for several kinds of paraffin and axonal neuropathy for *n*-hexane. AHCs of biogenic origin occur at lower concentrations in water and soil and are of the natural hydrocarbon baseline concentration [24].

The concentration of AHCs in unpolluted soil is  $\leq 10$  mg/kg dry weight [25]. Thus, the analysis of AHCs in soils may provide information on the origin of the hydrocarbon contamination, provided that environmental weathering is infinitesimal [26]. This allows for the fingerprinting of spilled AHCs, and the evaluation of the degradation levels of spilled oil [5, 27]. To classify the biogenic and anthropogenic origin of AHCs in soils, it is significant to examine the concentrations and composition of AHCs in soil profile samples. The knowledge of the occurrence, composition, and sources of AHCs in the soil is considerable for the partitioning of environmental matrixes where concentrations exceed the threshold limits, evaluation of exposure risks, and the development of soil quality management for AHCs polluted soils.

The study area sites are soils in the vicinity of petroleum products tank-farms located in Oghara, in the Niger Delta Nigeria. The non-compliance to standard guidelines in operation and maintenance of tank-farms will lead to spills and emission of AHCs during petroleum fractions discharge from ships, storage in the tank-farms, and loading into truck-tankers for distribution. The spilled petroleum products in soils from the tank-farms when washed into streams may expose hazardous risk to the immediate and adjacent soil, and nearby freshwater aquifer, and public health through the food chain. These can pose serious health hazards to humans. The knowledge of the occurrence, composition, sources, and potential health hazards of AHCs in soils in this study is critical to the strategic operations of petroleum product tank-farms and appropriate management of AHCs polluted adjacent soils and nearby aquatic environments. Therefore, the objective of this study was to determine the concentrations, composition, and evaluate the sources of AHCs in soils from the vicinity of petroleum tank-farms. Results from this study will provide information on the on-site human exposure risks and serve as an empirical tool for the evaluation of environmental quality management, and the location and management of petroleum fractions storage facilities.

## 2. Experimental

The study sites are located in Oghara town situate at  $5^{\circ} 35' N$ ,  $6^{\circ} 06' E$ . It has an average human population of 150,000 [28]. The study area plays host to the Nigerian

Naval Logistics Headquarters, Mopol 51, Delta State University Teaching Hospital, Delta State Polytechnic, and the local Government Council headquarter, Pan Ocean oil flow station, and a Gas Plant, about 300 million liters capacity petroleum products tank farms, and agricultural activities.

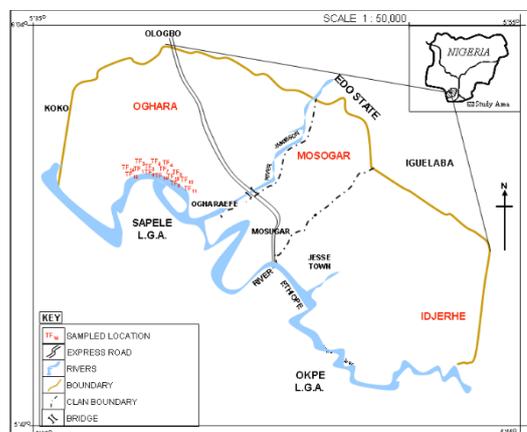


Figure 1. Map of Nigeria showing the study area and sample sites

The study sites are soils around the tank farms lying beside the River Ethiope that flows through River Koko and the Bight of Benin, Nigeria. The River Ethiope at Oghara is the major navigation channel for petroleum product laden ships that bring in products to the various tank-farms. The traditional occupation of the inhabitants along the River courses is fishing and timber logging.

### 2.1. Soil sample collection and treatment

Forty-five soil samples were collected at the top (0-15 cm), sub (15-30 cm), and bottom (30-45 cm) soil profiles in the vicinity of petroleum product tank farms (TF). Using standard quality control and assurance measures, composite soil samples were derived from quadruplet samples for the quantification of AHCs with an equivalent carbon atom range of  $C_8$  to  $C_{40}$ . After the removal of the uppermost debris from the topsoil layer, soil samples were collected with a stainless-steel auger of 2.5 cm diameter probe. A stainless-steel container was used to transfer samples to the laboratory for analysis. Samples were air-dried in the laboratory, twigs, and stones removed and sieved using a 230-mesh ( $< 2$  mm).

### 2.2. Determination of some soil physicochemical properties

The soil electrical conductivity, pH, and total organic carbon (TOC) were determined using conductivity meter, pH meter (Lie-ci PXSJ-216F, lie-ci, Shanghai, China) in soil suspension (1:2 soil to water) and the dichromate-based wet oxidation digestion method of Walkley and Black (1954) as described in Radojevic and Bashkin [29].

### 2.3. Extraction and fractionation of AHCs in soils

The extraction and fractionation of AHCs were achieved using the USEPA 3550 method [30]. A 10 g fraction of a well-mixed sample was transferred into a solvent rinse beaker; 10 g of anhydrous sodium sulfate (purchased from Chengdu Kelong Chemical Reagent Company, Chengdu, China) was added until particles were loose. A 20 ml of the solvent mix of dichloromethane

(chromatographic-grade purity purchased from Water Company, Milford, MA, USA) and acetone  $\geq 99.5\%$  (Sigma-Aldrich, St. Louis, Missouri, USA) in ratio 3:1 was added and transferred to the vortex mixer and shaken for 5 minutes. This was sonicated for 10 minutes at 70 °C. The extract was then filtered through a glass funnel packed with glass wool and anhydrous sodium sulfate, and 1 ml of the fractionated sample was transferred to a Teflon screw-cap vial ready for GC analysis.

#### 2.4. Instrumental analysis and detection of AHCs

The fractionated samples were analyzed for AHCs with gas chromatography (GC; Varian CP 3800 series, Walnut Creek, CA, USA) equipped with a flame ionization detector (FID) as earlier described [10, 31, 32]. The separations were effected on Teknokroma capillary columns (30 m x 0.25 mm x 0.25  $\mu\text{m}$ , Ser: C12937). The instrument operating conditions were: the carrier gas, hydrogen was operated at 35 ml/minute with 350 ml/min for Air. Injector and Detector temperature were set at 250 °C and 300 °C with an equilibration time of 1 minute while the oven temperature was set at an initial temperature of 40 °C for 1 minute. This was then raised to 270 °C at the rate of 25 °C, and to 320 °C at the rate of 30 °C for 2 minutes. The alkanes were identified by comparing individual retention time to those obtained with the injected standard (1 mL) solution before the sample under the instrument conditions as that of the samples. The aliphatic hydrocarbons standard mixture containing  $n\text{-C}_8$  to  $n\text{-C}_{40}$  was purchased from AccuStandard (New Haven, CT, USA). For the quantification, working mixed standard solutions containing the aliphatic hydrocarbons ( $\text{C}_8\text{--C}_{40}$ ) were prepared by dilution of the stock solution (2000 mg/mL) with dichloromethane. These solutions were used to establish the external calibration line. Before analysis, batches of the samples were run with a solvent blank and analyzed in duplicate

#### 2.5. Source signature evaluation

Sources apportionment of AHCs was carried out using AHCs compound ratios such as low and high molecular weight AHCs (LAHCs/HAHCs), Carbon Preference Index (CPI), Natural  $n$ -Alkane Ratio (NAR),  $n$ -alkane proxy (Paq), Average carbon chain length (ACL), Terrigenous/aquatic  $n$ -alkane ratio (TAR), pristane/phytane,  $\text{C}_{31}/\text{C}_{19}$ ,  $n$ -alkane/isoprenoid,  $n$ -alkane/proxy, and  $n\text{-C}_{29}/n\text{-C}_{17}$ ,  $n\text{-C}_{17}/\text{Pr}$ ,  $n\text{-C}_{18}/\text{Ph}$  [3, 5, 14, 24, 31, 33-36].

2.5.1. Carbon Preference Index (CPI). The ratio of the sum of odd-numbered hydrocarbons to the sum of even-

numbered hydrocarbons is the CPI value, and it is used in evaluating the anthropogenic and biogenic origin of  $n$ -alkanes in environmental samples [5, 14]. In this study, the CPI evaluation was based on the range from  $n\text{-C}_{25}$  to  $n\text{-C}_{33}$ . The values of CPI less than 1.0 suggest the contribution of odd-numbered  $n$ -alkanes of biogenic origin [33].

$$\text{CPI}_{25-33} = 0.5 \times \left[ \frac{\text{C}_{25} + \text{C}_{27} + \text{C}_{29} + \text{C}_{31} + \text{C}_{33}}{\text{C}_{24} + \text{C}_{26} + \text{C}_{28} + \text{C}_{30} + \text{C}_{32}} \right] + \left[ \frac{\text{C}_{25} + \text{C}_{27} + \text{C}_{29} + \text{C}_{31} + \text{C}_{33}}{\text{C}_{26} + \text{C}_{28} + \text{C}_{30} + \text{C}_{32} + \text{C}_{34}} \right]$$

2.5.2. Natural  $n$ -Alkane Ratio (NAR) is defined as:

$$\text{NAR} = \frac{\sum n\text{-alkanes (C19 - C32)}}{[2 \times \frac{\sum n\text{-alkanes (C20 - C32)}}{\sum n\text{-alkanes (C19 - C32)}}]}$$

NAR close to 1 indicates higher terrestrial or marine plants.

2.5.3.  $n$ -Alkane proxy (Paq)

$$\text{Paq} = \frac{\text{C}_{23} + \text{C}_{25}}{\text{C}_{23} + \text{C}_{25} + \text{C}_{29} + \text{C}_{31}}$$

The Paq a value between 0.48 and 0.94 depicts submerged/floating species of macrophytes while values between 0.01 and 0.23 are associated to terrestrial plant waxes.

2.5.4. Terrigenous/aquatic  $n$ -alkane ratio (TAR)

$$\text{TAR} = \frac{\text{C}_{27} + \text{C}_{29} + \text{C}_{31}}{\text{C}_{15} + \text{C}_{17} + \text{C}_{19}}$$

The TAR ratio  $> 1$  and  $< 1$  are regarded as terrestrial and aquatic inputs respectively.

2.5.5. Average carbon chain length (ACL)

$$\text{ACL} = \frac{25(\text{C}_{25}) + 27(\text{C}_{27}) + 29(\text{C}_{29}) + 31(\text{C}_{31}) + 33(\text{C}_{33})}{\text{C}_{25} + \text{C}_{27} + \text{C}_{29} + \text{C}_{31} + \text{C}_{33}}$$

The ACL ratio is useful for the identification of environmental alterations in a particular ecosystem. A constant value for ACL indicates that little environmental changes are occurring in the system. ACL values are approximately constant for unpolluted environmental samples, and petrogenic  $n$ -alkanes decrease the ACL value to a lower number.

#### 2.6. Statistical analysis

All results were analyzed statistically with SPSS version 19 software.

### 3. Results and discussion

#### 3.1. Physicochemical properties of soils

The results of some physicochemical parameters analyzed are presented in Table 1.

**Table 1.** Some physicochemical properties of soils in the vicinity of petroleum tank farms

	0-15 cm			15-30 cm			30-45 cm		
	pH	EC ( $\mu\text{s}/\text{cm}$ )	TOC (%)	pH	EC ( $\mu\text{s}/\text{cm}$ )	TOC (%)	pH	EC ( $\mu\text{s}/\text{cm}$ )	TOC (%)
TF1	6.72	83.77	0.51	6.31	52.81	0.42	5.21	43.59	0.39
TF2	6.21	53.81	2.51	6.31	50.30	1.96	4.61	39.68	1.80
TF3	5.81	123.25	2.56	4.71	79.06	2.19	4.31	53.21	1.66
TF4	5.61	63.43	1.26	5.31	48.50	1.23	4.91	47.70	1.04
TF5	6.41	42.38	2.22	5.61	38.48	1.54	5.71	40.38	1.43
TF6	4.71	39.88	4.56	4.41	39.68	3.85	4.31	32.57	3.24
TF7	6.31	76.35	2.59	6.51	59.72	2.24	5.11	54.71	1.99
TF8	4.91	66.83	1.80	4.21	43.19	1.60	4.31	42.38	1.40
TF9	7.62	96.39	0.87	6.41	66.63	0.59	6.31	49.90	0.48

	0-15 cm			15-30 cm			30-45 cm		
	pH	EC (µs/cm)	TOC (%)	pH	EC (µs/cm)	TOC (%)	pH	EC (µs/cm)	TOC (%)
TF10	6.41	106.21	2.84	5.91	81.46	2.65	5.11	89.58	2.47
TF11	5.81	49.00	3.57	4.71	42.38	3.35	4.31	28.66	3.10
TF12	6.21	56.71	2.93	5.71	38.28	2.70	5.31	33.37	2.65
TF13	5.61	63.63	3.01	5.01	59.02	2.54	4.51	50.40	2.19
TF14	6.81	57.92	1.43	6.41	39.78	1.15	6.21	31.26	0.98
TF15	5.71	57.72	4.22	5.31	44.79	3.80	5.11	46.49	3.40

The total organic carbon (TOC) in the soil profiles ranged from 0.39 to 4.56%, with the highest and lowest TOC levels occurring in the topsoil at site TF6 and bottom soil at site TF1 respectively. The electrical conductivity ranged between 28.6 and 123 µs cm<sup>-1</sup> in all sites and soil depths. The highest and lowest EC was observed in the topsoil at site TF3 and the bottom soil at TF11 respectively. The EC content depicts the presence of a high loading of inorganic mineral content [18]. The pH in the soil samples ranged from 4.20 to 7.60 for all sites and depths. The highest and lowest pH values were obtained in the topsoil at sites TF9 and subsoil at site TF8 respectively. The soil pH decreased with soil depth at all sites. The pH levels are slightly acidic and neutral; this is common to anaerobic soils of the Niger Delta [37, 38]. The range of pH, EC, and TOC values in this study

are favorable for the adsorption of HAHCs over LAHCs on active soil surfaces [39-41]. Similarly, several studies have revealed that high half-life, Log Kow > 4.0, and low solubility of priority organic pollutants such as AHCs with *n*-C<sub>13-35</sub> would be retained in soil surfaces and hence less susceptible to environmental degradation processes [37, 42]. The TOC, EC, and pH values in this study are significant to the compositional occurrence and fate of AHCs in the study area [43].

### 3.2. Occurrence and distribution profiles of AHCs in soils

The concentrations and summary statistics of AHCs congeners from the fifteen sample sites are presented in Table 2.

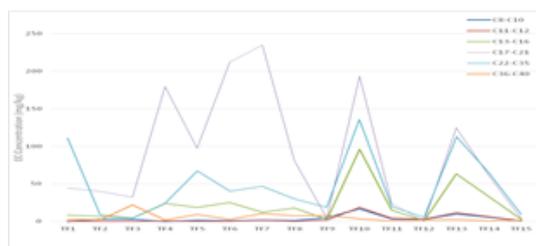
**Table 2.** Summary statistics of aliphatic concentrations (mg/kg) in soils in the vicinity of petroleum tank farms (*n* = 15)

	0-15 cm Depth					15 cm Depth					30 cm Depth				
	MEAN	SD	MEDIAN	MIN	MAX	MEAN	SD	MEDIAN	MIN	MAX	MEAN	SD	MEDIAN	MIN	MAX
C8	1.72	2.81	0.65	0.01	10.16	2.09	2.11	1.08	0.00	5.73	2.14	1.79	1.48	0.06	5.44
C9	1.36	1.48	1.24	0.01	5.75	1.54	1.35	1.51	0.01	4.00	1.48	1.36	1.40	0.03	3.75
C10	0.57	0.69	0.26	0.00	2.19	0.58	0.57	0.51	0.00	1.58	0.56	0.58	0.30	0.00	1.38
C11	1.20	1.66	0.23	0.00	5.65	1.39	1.55	0.50	0.00	4.07	1.46	1.49	0.68	0.00	3.64
C12	2.06	3.76	0.35	0.00	12.94	2.38	3.02	0.59	0.00	7.68	2.52	2.79	0.55	0.02	7.31
C13	3.13	5.59	0.47	0.18	18.52	3.88	4.24	1.73	0.21	10.81	3.82	3.91	1.33	0.16	10.15
C14	4.34	6.40	1.59	0.30	22.94	5.32	4.85	2.78	0.27	13.40	5.30	4.19	4.80	0.75	12.69
C15	6.05	7.93	3.51	0.01	28.63	8.56	5.92	7.09	0.45	16.42	10.01	5.12	9.88	0.76	21.37
C16	8.50	7.76	4.95	0.09	26.25	11.78	8.98	13.17	0.76	32.84	15.95	11.61	13.43	5.13	47.29
C17	14.21	14.13	7.77	0.01	43.10	25.16	23.82	11.62	0.03	66.34	23.23	22.40	11.60	4.87	73.78
Pr	13.09	15.16	5.97	0.03	48.13	18.76	13.13	23.04	0.20	43.90	20.50	12.64	18.93	5.19	49.56
C18	17.18	20.15	8.96	0.01	77.95	14.24	10.47	11.45	0.63	34.99	21.19	16.48	12.05	5.49	53.99
Ph	18.87	20.87	9.64	0.02	66.40	24.03	26.31	17.37	0.20	86.72	35.26	35.69	17.68	5.02	125.27
C19	8.98	7.71	7.28	0.11	28.99	11.18	10.52	8.85	0.58	39.17	11.34	7.56	9.11	3.46	30.01
C20	10.15	10.16	7.33	0.01	35.62	15.88	14.91	12.47	0.38	45.74	18.42	17.78	12.93	5.01	62.88
C21	6.32	6.15	4.39	0.01	22.43	9.24	7.57	9.30	0.21	29.01	14.77	11.67	11.17	1.43	36.73
C22	4.32	4.03	4.17	0.08	14.73	7.22	5.79	7.41	0.30	18.81	8.64	7.47	6.35	1.51	26.03
C23	3.22	3.03	2.16	0.04	11.75	7.65	11.02	3.44	0.50	43.17	4.08	2.18	3.96	0.45	7.97
C24	3.75	3.42	2.55	0.00	10.55	4.82	3.60	4.32	0.37	11.78	4.71	3.02	4.28	0.29	14.45
C25	2.63	3.18	0.93	0.00	8.33	3.75	3.37	4.16	0.00	11.84	4.04	2.82	3.65	0.37	9.55
C26	6.39	9.51	2.30	0.00	32.09	7.33	7.31	3.75	0.31	19.98	7.30	6.63	5.61	0.00	18.82
C27	2.10	3.02	0.74	0.00	9.05	6.13	16.68	1.22	0.00	66.12	1.97	1.39	1.68	0.00	4.23
C28	3.23	4.31	1.50	0.00	13.19	8.56	20.66	3.71	0.46	82.65	3.15	2.33	2.63	0.00	7.01
C29	2.75	3.40	1.22	0.00	11.31	8.75	22.84	2.92	0.44	90.90	2.59	1.49	2.39	0.00	5.13
C30	3.18	3.18	1.80	0.19	10.54	8.61	23.68	2.31	0.43	93.99	2.97	1.91	2.22	0.41	8.21
C31	3.30	3.44	1.36	0.24	10.80	7.73	18.92	2.74	0.96	75.85	3.07	1.86	3.09	0.33	7.02
C32	4.81	5.32	2.28	0.16	18.51	10.14	20.77	6.26	0.37	83.93	5.06	3.47	3.53	0.23	11.04
C33	2.38	2.11	2.22	0.25	8.52	6.60	16.82	1.66	0.26	66.71	2.11	1.24	1.70	0.00	5.06
C34	1.60	1.20	1.47	0.08	4.03	7.83	17.62	1.88	0.39	64.14	1.87	1.00	1.62	0.65	4.36
C35	2.95	6.60	0.75	0.00	26.45	3.48	3.85	1.34	0.31	12.90	1.22	0.87	0.99	0.00	3.20
C36	2.41	5.37	0.59	0.13	21.49	5.09	9.05	1.21	0.25	31.41	3.12	5.49	1.26	0.34	22.36
C37	1.17	1.16	0.66	0.12	3.71	1.14	0.83	0.88	0.00	2.85	0.88	0.40	0.73	0.00	1.38
C38	0.73	0.67	0.51	0.00	2.25	1.05	1.19	0.52	0.00	4.56	0.67	0.34	0.60	0.00	1.41
C39	0.52	0.56	0.32	0.00	1.91	0.64	0.50	0.46	0.00	1.59	0.70	0.74	0.46	0.00	2.77
C40	0.30	0.24	0.18	0.00	0.82	0.52	0.90	0.12	0.00	3.19	0.55	0.86	0.15	0.00	3.42
<b>TO-TAL</b>	<b>169</b>	<b>132</b>	<b>167</b>	<b>14.3</b>	<b>464</b>	<b>263</b>	<b>216</b>	<b>252</b>	<b>29.0</b>	<b>890</b>	<b>247</b>	<b>133</b>	<b>217</b>	<b>75.8</b>	<b>514</b>

The distribution of the individual AHCs ranged from ND to 48.13 mg/kg with a mean concentration range of 0.57 ± 0.69 to 18.87 ± 20.87 mg/kg in topsoil. In subsoil samples, the AHCs concentrations ranged from ND to 93.99 mg/kg with a mean concentration range of 0.52 ±

0.90 to 25.16 ± 23.82 mg/kg, while the AHCs concentrations ranged from ND to 125.27 mg/kg with a mean concentration range of 0.55 ± 0.86 to 35.26 ± 35.69 mg/kg in the bottom soil samples. The

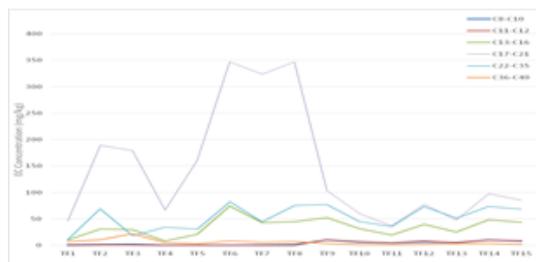
concentrations of the equivalent carbon number index (EC<sub>n</sub>) are presented in Figures 2-4.



**Figure 2.** Concentration distribution of equivalent carbon number index (EC) in topsoil

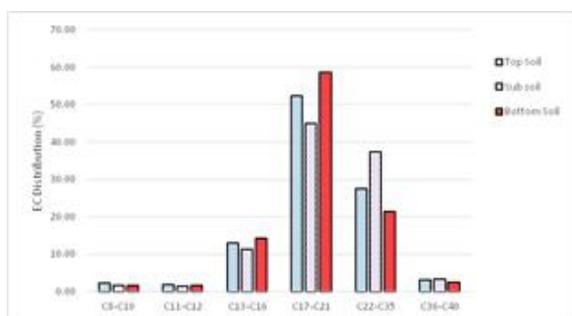


**Figure 3.** Concentration distribution of equivalent carbon number index (EC) in subsoil



**Figure 4.** Concentration distribution of equivalent carbon number index (EC) in bottom soil

The total concentrations of EC<sub>n</sub>-8-10 and EC<sub>n</sub>-11-12 congeners ranged from 0.03 to 16.88 mg/kg and ND to 18.60 mg/kg respectively. Similarly, the total concentrations of the EC<sub>n</sub>-13-16 and EC<sub>n</sub>-17-21 congeners range from 1.93 to 96.34 mg/kg, and 0.33 to 346.96 mg/kg respectively. The total concentrations of EC<sub>n</sub>-22-35 and EC<sub>n</sub>-36-40 AHCs ranged from 4.53 to 715.72 mg/kg and 0.59 to 34.34 mg/kg respectively.

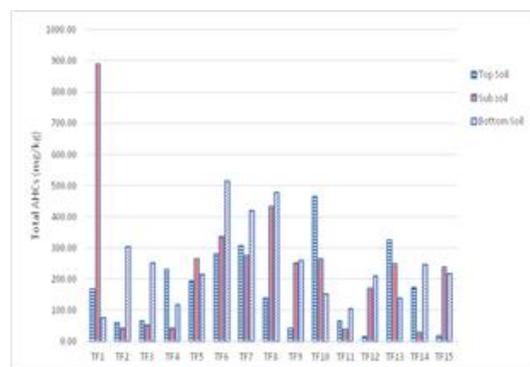


**Figure 5.** Percentage distribution of equivalent carbon number index in soils

Across all sites (Figure 5), the percentage distribution of EC in the top soil is in the order of EC<sub>n</sub>-17-21 > EC<sub>n</sub>-22-35 > EC<sub>n</sub>-13-16 > EC<sub>n</sub>-36-40 > EC<sub>n</sub>-8-10 > EC<sub>n</sub>-11-12. Also the percentage distribution of EC in the sub and bottom soils is in the order of EC<sub>n</sub>-17-21 > EC<sub>n</sub>-22-35 > EC<sub>n</sub>-13-16 > EC<sub>n</sub>-36-40 > EC<sub>n</sub>-8-10 >

EC<sub>n</sub>-11-12 and EC<sub>n</sub>-17-21 > EC<sub>n</sub>-22-35 > EC<sub>n</sub>-13-16 > EC<sub>n</sub>-36-40 > EC<sub>n</sub>-8-10 > EC<sub>n</sub>-11-12 respectively.

The percentage distribution shows that EC<sub>13-35</sub> species contributed a significant ratio of the total AHCs in this study. As presented in Table 2 and Figure 2, the soil samples contained variable concentrations of both LAHCs and HAHCs, but the HAHCs were found in a higher proportion. The presence of AHCs of higher carbon atoms shows several sources of AHCs in the study area [44]. The high concentrations of EC<sub>n</sub>-13-16, 17-21, and EC<sub>n</sub>-22-35 in the top, sub, and bottom soils, Figure 5, depicts that the origin of AHCs is from microbial biogenic and terrestrial vascular plants. The occurrence of EC<sub>n</sub>-15, 17 and 19 shows that AHCs are from algae and marine phytoplankton, and the presence of EC<sub>n</sub>-20 and 21 in samples from some samples indicates that AHCs are from petroleum origin [45, 46].



**Figure 6.** ΣAHCs in soil profiles and sites

This study shows that 47% of the tank-farms were relatively polluted with AHCs (Figure 6); this depicts incessant petroleum products spills arising from the loading and offloading of products, equipment failure, onsite cleaning, and repair of haulage-trucks. The spilled petroleum products constitute the effluents that are discarded through drains and directed into the nearby river. This could significantly contribute to a total AHCs pollution load and accumulate in the sediment of the adjacent aquatic environment. Across soil profiles, Table 2, the AHCs occurrence pattern depicts the odd over even carbon number predominance; this suggests that phytoplankton/algae and terrestrial vascular plants contributed to the sources of AHCs.

The total AHCs concentrations are presented in Figure 6. The total AHCs results ranged from 14.26 to 464.49 mg/kg in the topsoil, 29.05 to 889.68 mg/kg in the subsoil, and 104.63 to 513.74 mg/kg in the bottom soil. This shows that at topsoil, TF10 had the highest concentrations, and TF12 had the lowest in the topsoil, TF1 had the highest concentrations and TF14 had the lowest in the subsoil, and at the bottom soil, TF6 had the highest concentrations and TF1 had the lowest concentrations in the subsoil, depicting the concentrations of AHCs in the order of bottom soil > subsoil > topsoil. This shows irregular and varied concentrations of AHCs in soils around the tank farms. The observed relatively low concentrations of AHCs in the top and subsoils when compared to the bottom soil could be related to the observed soil physicochemical properties. Also, the environmental processes such as

hydrolysis, leaching, volatilization, weathering, and photolysis that could influence AHCs distribution are comparably higher at top and subsoil than bottom soil. Similarly, the intense anthropogenic activities and observed soil physicochemical properties in the tank farms may have influenced the topsoil disturbances, hence AHCs infiltration to bottom soil. This could have contributed to the irregular and variable concentrations of AHCs congeners in this study. The observed concentrations of total AHCs were lower than the UNEP recommended limit of 10,000 mg/kg, suggesting moderate AHCs contamination. Generally, the concentration of HAHCs is higher than LAHCs, depicting a significant degradation profile of LAHCs and the relatively high persistence and resistance of HAHCs to environmental degradation processes of hydrolysis, volatilization, biodegradation, photolysis, and oxidation. This may be responsible for their accumulation in the soil samples [47, 48]. Also, the obtained average values TOC, EC, and pH could have significantly determined the concentrations and composition of AHCs in this study [43].

### 3.3. Occurrence and distribution profiles of AHCs in soils

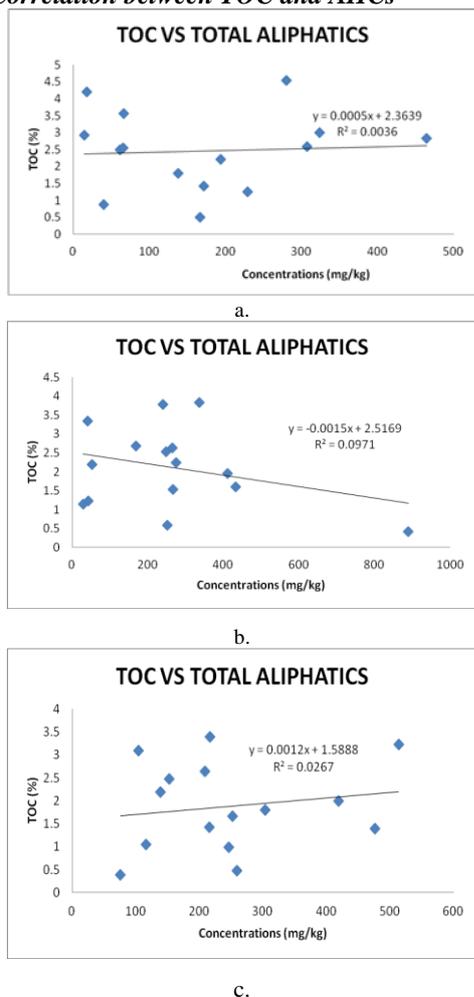
The concentrations and summary statistics of AHCs congeners from the fifteen sample sites are presented in Table 2. The distribution of the individual AHCs ranged from ND to 48.13 mg/kg with a mean concentration range of  $0.57 \pm 0.69$  to  $18.87 \pm 20.87$  mg/kg in topsoil. In subsoil samples, the AHCs concentrations ranged from ND to 93.99 mg/kg with a mean concentration range of  $0.52 \pm 0.90$  to  $25.16 \pm 23.82$  mg/kg, while the AHCs concentrations ranged from ND to 125.27 mg/kg with a mean concentration range of  $0.55 \pm 0.86$  to  $35.26 \pm 35.69$  mg/kg in the bottom soil samples. The concentrations of the equivalent carbon number index (EC<sub>n</sub>-) are presented in Figure 2-4. The concentrations of the equivalent carbon number index (EC<sub>n</sub>-) in the sample sites are presented in Figure 2-4. The total concentrations of EC<sub>n</sub>-8-10 and EC<sub>n</sub>-11-12 congeners ranged from 0.03 to 16.88 mg/kg and ND to 18.60 mg/kg respectively. Similarly, the total concentrations of EC<sub>n</sub>-13-16 and EC<sub>n</sub>-17-21 congeners range from 1.93 to 96.34 mg/kg, and 0.33 to 346.96 mg/kg respectively. The total concentrations of EC<sub>n</sub>-22-35 and EC<sub>n</sub>-36-40 ranged from 4.53 to 715.72 mg/kg and 0.59 to 34.34 mg/kg respectively. Across all sample sites Figure 5, the percentage distribution of equivalent carbon number index in the topsoil is in the order of EC<sub>n</sub>-17-21 > EC<sub>n</sub>-22-35 > EC<sub>n</sub>-13-16 > EC<sub>n</sub>-36-40 > EC<sub>n</sub>-8-10 > EC<sub>n</sub>-11-12. Also the percentage distribution of EC in the sub and bottom soil depths is in the order of EC<sub>n</sub>-17-21 > EC<sub>n</sub>-22-35 > EC<sub>n</sub>-13-16 > EC<sub>n</sub>-36-40 > EC<sub>n</sub>-8-10 > EC<sub>n</sub>-11-12, and EC<sub>n</sub>-17-21 > EC<sub>n</sub>-22-35 > EC<sub>n</sub>-13-16 > EC<sub>n</sub>-36-40 > EC<sub>n</sub>-8-10 > EC<sub>n</sub>-11-12 respectively.

The percentage distribution shows that EC<sub>n</sub>-13-35 species contributed a significant ratio of the total AHCs in this study. As presented in Table 2 and Figure 2, the soil samples contained variable concentrations of both LAHCs and HAHCs, but the HAHCs were found in a higher proportion. The presence of AHCs of higher carbon atoms shows several sources of AHCs in the

study area [44]. The high concentrations of EC<sub>n</sub>-13-16, 17-21, 22-35 in the top, sub, and bottom soils (Figure 5) depicts that the origin of AHCs is from microbial biogenic and terrestrial vascular plants. The occurrence of EC<sub>n</sub>-15, 17, and 19 shows that AHCs are from algae and marine phytoplankton, and the presence of *n*-C<sub>20</sub> and *n*-C<sub>21</sub> in samples from some tank-farms indicates that AHCs are from petroleum origin [45, 46]. This study shows that 47% of the tank-farms were relatively polluted with AHCs (Figure 6); this depicts incessant petroleum products spills arising from the loading and offloading of products, equipment failure, onsite cleaning, and repair of haulage-trucks. The spilled petroleum products constitute the effluents that are discarded through drains and directed into the nearby river. This could significantly contribute to a total AHCs pollution load and accumulate in the sediment of the adjacent aquatic environment. Across soil profiles (Table 2), the AHCs occurrence pattern depicts the odd over even carbon number predominance; this suggests that phytoplankton/algae and terrestrial vascular plants contributed to the sources of AHCs.

The total AHCs concentrations are presented in Figure 6. The total AHCs results ranged from 14.26 to 464.49 mg/kg in the topsoil, 29.05 to 889.68 mg/kg in the subsoil, and 104.63 to 513.74 mg/kg in the bottom soil. This shows that at topsoil, TF10 had the highest concentrations, and TF12 had the lowest in the topsoil, TF1 had the highest concentrations and TF14 had the lowest in the subsoil, and at the bottom soil, TF6 had the highest concentrations and TF1 had the lowest concentrations in the subsoil, depicting the concentrations of AHCs in the order of bottom soil > subsoil > topsoil. This shows irregular and varied concentrations of AHCs in soils around the tank farms. The observed relatively low concentrations of AHCs in the top and subsoil when compared to the bottom soil could be related to the observed soil physicochemical properties. Also, the environmental processes such as hydrolysis, leaching, volatilization, weathering, and photolysis that could influence AHCs distribution are comparably higher at top and subsoil than bottom soil. Similarly, the intense anthropogenic activities and observed soil physicochemical properties in the tank farms may have influenced the topsoil disturbances, hence AHCs infiltration to bottom soil. This could have contributed to the irregular and variable concentrations of AHCs congeners in this study. The observed concentrations of total AHCs were lower than the UNEP recommended limit of 10,000 mg/kg, suggesting moderate AHCs contamination. Generally, the concentration of HAHCs is higher than LAHCs, depicting a significant degradation profile of LAHCs and the relatively high persistence and resistance of HAHCs to environmental degradation processes of hydrolysis, volatilization, biodegradation, photolysis, and oxidation. This may be responsible for their accumulation in the soil samples [47, 48]. Also, the obtained average values TOC, EC, and pH could have significantly determined the concentrations and composition of AHCs in this study [43].

### 3.4. Correlation between TOC and AHCs



**Figure 7.** Plot of TOC vs total aliphatic concentrations in top, sub and bottom soil profile samples: a. topsoil; b. subsoil; c. bottom soil.

The linear regression between TOC and AHCs for soil profiles (Figure 7) indicates a weak correlation between the soil depths ( $R^2$  value varied from 0.0036 to 0.0971).

The results show that the correlation between TOC and AHCs was highest at the subsoil ( $R^2 = 0.0971$ ), followed by bottom soil ( $R^2 = 0.0267$ ) and the topsoil ( $R^2 = 0.0036$ ). From the calculated  $R^2$  values, it is evident that there is no significant positive correlation between TOC and total AHCs concentrations in the soil profiles. The low correlation between TOC and AHCs in the soil profiles suggests fresh pollution occurrence and non-equilibrium adsorption behavior between AHCs and TOC. Also, it shows the dominance of anthropogenic input over natural attenuation processes and also showed that the fate of AHCs in these soils is not determined by organic matter contents, the presence of dissimilar and multiple sources of AHCs profiles, and the degradation behavior of AHCs concerning observed soil physicochemical properties at different soil layer.

A number of studies have demonstrated a poor correlation of TOC with organic pollutants having similar characteristics with AHCs [49-53].

### 3.5. ANOVA

The one-way ANOVA (0.05 level of significance) of the total concentrations in the top, sub, and bottom soil profile samples are presented in Table 3.

The results show that the values of  $F_{cal}$  are greater than  $F_{crit}$  in the soil profiles. Therefore, the impact of soil depth variation on the concentration levels of AHCs changes considerably. These imply a significant  $P < 0.05$  variation in AHCs levels among the soil profiles. This could be related to the soil physicochemical properties, biological and chemical reactions within the soil profile, AHCs properties, and mechanical disturbances within the soil profile [18].

**Table 3.** Results of ANOVA for the investigation of variation in concentration PM10 and PM2.5 among different monitoring stations in the study area ANOVA of aliphatic petroleum hydrocarbons in tank farm soil

(0-15 cm)

Source of variation	SS	df	MS	Fcal	P-value	F crit
Between Groups	6986.828	14	499.0592	7.852445	3.48E-15	1.711199
Within Groups	32412.86	510	63.55462			
Total	39399.68	524				

(15-30 cm)

Source of variation	SS	df	MS	Fcal	P-value	F crit
Between Groups	18728.38	14	1337.741	8.615135	6.96E-17	1.711199
Within Groups	79191.79	510	155.278			
Total	97920.16	524				

(30-45 cm)

Source of variation	SS	df	MS	Fcal	P-value	F crit
Between Groups	7064.247	14	504.5891	3.638933	8.55E-06	1.711199
Within Groups	70718.65	510	138.664			
Total	77782.9	524				

### 3.6. Sources of AHCs in soils

The challenges of evaluating the origins of AHCs in all environmental matrixes are associated with the complex and multiple sources arising from post-deposition and

environmental modification of the parent compounds. However, compositional evaluation is a vital tool in pollutant source evaluation. The results of source apportionment in this study are presented in Table 4.

**Table 4.** Source indices of aliphatic hydrocarbons in soils in the vicinity of petroleum tank farms

Site	Depths	ACL	<i>n</i> -C17/Pr	C18/Ph	CPI	Pr/Ph	C31/C19	MH	LAHCs/HAHCs	<i>n</i> -C29/ <i>n</i> -C17	TAR	Paq	NAR
TF1	0-15	29.1	3.23	0.52	37.9	0.25	1.76	C28	1.0	1.47	1.50	0.39	-0.01
	15-30	29.9	3.4	0.77	285.8	2.03	5.34	C30	0.35	1.93	2.04	0.23	0.01
	30-45	30.9	1.16	2.79	0.0	1.03	0.09	C18	4.8	0.06	0.54	0.41	0.06
TF2	0-15	31.4	0.8	2.38	0.0	2.34	0.20	C18	6.5	0.09	0.60	0.24	0.20
	15-30	27.6	1.51	0.56	9.7	0.76	0.27	C17	6.3	0.01	0.09	0.89	-0.03
	30-45	27.6	1.74	0.55	13.6	0.30	0.25	Ph	10.5	0.07	0.32	0.73	0.04
TF3	0-15	32.3	0.9	1.38	2.0	0.80	0.09	C36	1.6	0.00	0.36	0.86	0.25
	15-30	30.5	1.54	1.38	4.3	0.46	3.16	C36	0.68	0.36	0.57	0.38	0.12
	30-45	27.5	2.26	1.75	3.5	0.44	0.07	C18	7.39	0.00	0.19	0.89	0.25
TF4	0-15	28.3	0.75	0.33	4.4	0.50	0.06	Ph	27.53	0.05	0.32	0.70	0.01
	15-30	30.3	1.49	8.01	4.6	2.20	0.40	C18	3.0	0.13	0.61	0.28	0.22
	30-45	30.4	0.74	0.81	8.7	0.54	0.66	Ph	4.30	0.15	0.93	0.59	0.22
TF5	0-15	29.6	1.8	1.00	12.2	0.58	0.05	C35	2.4	0.19	0.38	0.53	-0.19
	15-30	30.1	2.43	0.51	6.7	0.45	0.04	C17	9.4	0.03	0.45	0.54	0.11
	30-45	27.9	2.09	0.46	7.0	0.54	0.03	C17	15.94	0.04	0.19	0.82	-0.24
TF6	0-15	28.7	1.4	1.01	14.2	0.80	0.30	C17	11.0	0.03	0.29	0.58	-0.18
	15-30	27.5	1.9	0.41	10.3	0.43	0.13	Ph	16.1	0.05	0.26	0.61	-0.20
	30-45	29.8	0.65	0.43	18.5	0.40	0.23	Ph	10.6	0.11	0.47	0.50	0.14
TF7	0-15	30.5	7.2	1.42	14.0	0.11	0.20	C18	8.1	0.01	0.46	0.50	0.23
	15-30	31.4	1.62	1.78	31.0	2.44	0.20	C17	2.36	0.07	0.32	0.65	-0.15
	30-45	27.3	1.9	0.45	12.4	0.44	0.10	Ph	18.6	0.03	0.24	0.74	-0.05
TF8	0-15	30.5	4.6	3.12	6.9	0.38	0.09	C18	5.5	0.13	0.49	0.62	-0.14
	15-30	27.9	1.66	0.40	21.8	0.42	0.17	Ph	7.9	0.15	0.36	0.68	0.02
	30-45	28.1	1.80	0.42	17.9	0.47	0.08	Ph	12.19	0.06	0.25	0.64	-0.26
TF9	0-15	31.8	0.41	55.78	3.1	8.50	0.82	C26	1.21	8.48	1.72	0.08	-0.64
	15-30	28.5	0.48	0.65	18.3	1.37	0.44	Pr	4.22	0.30	0.50	0.57	-0.20
	30-45	28.4	0.52	0.63	18.6	1.28	0.43	Pr	4.45	0.29	0.48	0.58	-0.18
TF10	0-15	28.1	0.48	0.62	33.5	1.36	0.41	Pr	4.80	0.28	0.47	0.59	-0.17
	15-30	28.3	0.55	0.61	19.0	1.21	0.42	Pr	4.68	0.27	0.47	0.59	-0.16
	30-45	28.6	0.62	0.60	11.2	1.09	0.46	Pr	4.31	0.27	0.47	0.57	-0.16
TF11	0-15	29.6	2.79	0.54	4.7	0.26	0.51	Ph	3.95	0.20	0.43	0.55	-0.14
	15-30	30.1	2.83	0.54	3.6	0.26	0.71	Ph	2.54	0.27	0.48	0.47	-0.16
	30-45	28.9	0.62	0.77	9.9	1.10	0.54	Pr	2.98	0.49	0.50	0.44	-0.26
TF12	0-15	31.4	4.79	0.34	10.5	1.50	5.62	C11	0.12	2.16	1.76	0.06	-0.30
	15-30	28.7	0.51	0.83	16.3	1.31	0.50	Pr	3.08	0.55	0.50	0.43	-0.28
	30-45	28.8	0.50	0.79	20.3	1.32	0.68	Pr	3.13	0.54	0.55	0.43	-0.22
TF13	0-15	28.6	0.51	0.83	30.4	1.31	0.44	Pr	3.36	0.54	0.49	0.45	-0.28
	15-30	28.9	0.49	0.76	24.4	1.33	0.80	Pr	3.16	0.53	0.58	0.43	-0.18
	30-45	29.0	0.49	0.79	13.7	1.32	0.81	Pr	2.88	0.57	0.63	0.42	-0.20
TF14	0-15	29.3	0.47	0.63	18.4	1.35	1.45	Pr	2.83	0.53	0.74	0.40	-0.01
	15-30	30.2	0.16	3.15	3.1	1.02	0.89	C26	1.35	13.72	1.77	0.37	-0.35
	30-45	28.4	0.48	0.63	18.0	1.36	0.44	Pr	4.31	0.30	0.49	0.57	-0.19
TF15	0-15	28.4	0.02	0.85	3.7	0.69	0.98	C19	1.67	73.07	1.81	0.53	0.07
	15-30	28.3	0.48	0.62	17.8	1.36	0.44	Pr	4.41	0.29	0.48	0.58	-0.17
	30-45	28.5	0.54	0.69	17.6	1.24	0.45	Pr	3.93	0.37	0.48	0.53	-0.21

**Average carbon chain length (ACL).** As presented in Table 4, the ACL ratios ranged from 27.3 to 31.4, this shows a difference of 4.1 units. This wide difference depicts severe disturbances in the ecosystem as a result of intense anthropogenic input related to petroleum hydrocarbons and its derivatives interfering with ACL balance [24].

***n*-Alkane/isoprenoid ratio.** The *n*-alkanes ratio is a significant marker that provides useful information about the origin, fate, and mechanism of aquatic and terrestrial organic materials since they have minor biodegradation ability [54]. Therefore, EC<sub>n</sub>-17/Pr and EC<sub>n</sub>-18/Ph ratios are important indexes for the classification of the sources and levels of the degradation of petroleum hydrocarbons [55]. During biodegradation, microorganisms utilize *n*-alkanes as an energy source, values less than 1 are indicative of biodegraded petroleum, and values greater than 1 depicts recent inputs [56]. The EC<sub>n</sub>-17/Pr and EC<sub>n</sub>-18/Ph ratios ranged from 0.02 to 4.79 and 0.33 to 55.78 respectively. The EC<sub>n</sub>-17/Pr and EC<sub>n</sub>-18/Ph ratios correspond to recent inputs i.e., non-heavily degraded petroleum [55]. However, EC<sub>n</sub>-17/Pr and EC<sub>n</sub>-18/Ph

showed distinctive ratios in 33% of the samples, this suggests a mixture of recent inputs and highly degraded hydrocarbon.

**Carbon preference index (CPI).** The CPI is useful in identifying the anthropogenic and biogenic contributions to AHCs in soil. The CPI value greater than 1 is suggestive of the presence of odd-numbered AHCs of biogenic origin. The contribution of vascular plants to AHCs in the environment usually shows as CPI values between 3 and 6 [14, 33]. The even-numbered *n*-alkane preference is normally characterized by a CPI value less than 1, and CPI equal to 1 when the total numbers of even and an odd number of AHCs are abundant, which indicates that the origin of AHCs in the sites is of petroleum origin [46, 57]. The CPI evaluation was based on the EC<sub>n</sub>-25-33 range. The CPI values were greater than 1 (Table 4). This depicts that the AHCs are from biogenic, terrestrial higher plant waxes, and petroleum origin [58, 59].

**Pristane/phytane ratio.** Pristane and phytane hydrocarbons are not basic components of several terrestrial biotas but are of organisms and petroleum produced from the diagenesis of phytol and other

isoprenoidyl [60]. Some uncertainties that are associated with pristane/phytane ratio used as a signature of petroleum hydrocarbon sources are that pristane can be produced from zooplankton, marine animals, and pristane and phytane presence in crude oils may be natural hydrocarbons of post-depositional transformation involving oxidation reactions of the phytol side chain or catalytic hydrogenation of phytadiene [61]. Pristane/phytane value is usually higher in biogenic samples [25, 62], and in soils, without hydrocarbon input, it is usually 3–5. The Pr/Phy ratio ranged from 0.11 to 2.44 in 93% of the samples depicts petroleum inputs.

**ECn-31/ECn-19 ratio.** An ECn-31 is a marker for terrestrial biogenic *n*-alkanes, and ECn-19 indicates marine biogenic origin [63]. The value of ECn-31/ECn-19 ratio < 0.4 and > 0.4 depicts the presence of marine biogenic origins and land-derived hydrocarbons [63, 64]. The ratio of ECn-31/ECn-19 in this study is in the boundary of 0.4 in 89%. This shows that the sources of these aliphatics are through anthropogenic pathways as reported in Commendatore and Esteves [65].

**Major hydrocarbon (MH) ratio.** Major hydrocarbon (MH) is the carbon number with the highest concentration that contributes significantly to the total AHCs concentration [66]. The ratio can be used to determine the direction of the hydrocarbon load, and it varies in environmental samples. Forty percent, 46% and 20% of the samples are odd carbon numbers, even carbon numbers and Pr and Ph AHCs respectively. (Table 4). However, all samples had MHs between *n*-C<sub>11</sub> and *n*-C<sub>36</sub>, this depicts that the MHs are from phytoplankton, microbial marine biogenic, and petroleum origin [67].

**LMW/HMW AHCs ratio.** The ratio of LMW/HMW AHCs is a marker of AHCs that differentiate between terrestrial and macrophytes plant inputs. HMW-AHCs are the sum of concentrations of AHCs from ECn-27 to 36, while LMW-AHCs are the sum of concentrations of AHCs from ECn-16 to 26. LMW-AHCs are from marine biogenic sources and HMW-AHCs are from terrestrial vascular plants [45]. The ratio greater than 1 is indicative of a natural input from marine biogenic sources, a value less than 1 is suggestive of a natural input from terrestrial biogenic reactions, and the value close to 1 is related to petroleum source. The LAHCs/HAHCs ratios in this study ranged from 0.12 to 27.53 (Table 4). This suggests that the origin of AHCs in the tank-farms is of petroleum and terrestrial biogenic and considerable contributions from marine biogenic.

**ECn-29/ECn-17 ratio.** The ECn-29/ECn-17 ratio provides important information on the inputs of allochthonous and autochthonous hydrocarbons in environmental samples since *n*-C<sub>29</sub> and *n*-C<sub>17</sub> are associated with land plants and marine organisms respectively [14]. The values of ECn-29/ECn-17 ranged from 0.01 to 73.07. The ECn-29/ECn-17 values in 93% of the samples were less than 1 suggesting the predominance of autochthonous inputs of AHCs, and 7% of the samples were greater than 1 suggesting the predominance of allochthonous inputs.

**Terrigenous/aquatic *n*-alkane ratio (TAR).** The terrigenous/aquatic *n*-alkanes ratio is an index to

determine the contributions of aquatic and terrigenous AHCs origin. In this study, the TAR ratio ranged from 0.09 to 2.04 with TF1 having the highest value of 2.04. The high TAR shows that the short-chain *n*-alkanes are susceptible to degradation when compared to *n*-alkanes with longer chains [47, 57]. However, the TAR values in this study are in agreement with the reported TAR ratios in Aly-Salem and Morsy [31].

***n*-Alkane proxy (Paq).** The Paq index range from 0.01 and 0.23 are associated with terrestrial plant waxes, and values between 0.48 and 0.94 are related to submerged/floating species of macrophytes [34]. The Paq ratios obtained ranged from 0.06 to 0.89; this indicates a combination of terrestrial plant waxes and submerged/floating species of macrophytes as sources of AHCs.

**Natural *n*-alkane (NAR) ratio.** The NAR close to 1 indicates higher marine or terrestrial plants of the *Posidonia* specie [31]. The NAR values in this study ranged from – 0.01 to 0.25 suggesting a broad range of terrestrial input of AHCs.

### 3.7. Implications for environment and human occupational exposure risk of AHCs in soils

The anthropogenic contamination of soil with variable concentrations of AHCs usually results from the accidental breakdown of equipment and operational defects. Even at low concentrations, AHCs may exhibit temporary effects on the ecosystem and humans upon exposure. Due to the movement of organic contaminants, the observed AHCs concentrations could contaminate ground and surface water of the immediate environment through the mass transfer process between the solid and liquid phases and chemical reactions of dissolved species from one form to another.

The regulatory limits of the Baltic, Nordic and Western countries, Canada, and the Agency for Toxic Substances and Disease Registry (ATSDR) were used to estimate the human and environmental health hazard through oral, dermal and inhalation arising from observed concentrations of AHCs [68, 69]. The total concentrations of ECn-8-10 could be classified as very bad according to AHCs limit values in Norway soils [70]. The constituents of the ECn-8-10 are *n*-nonane, *n*-decane, *n*-pentane, *n*-heptane, cyclohexane, and *n*-hexane. The isomer *n*-hexane is the most potent and is associated with peripheral neuropathy in humans through occupational exposure [71]. The toxicological effects of *n*-hexane are predicated through 2,5-hexanedione isomer which interferes with microtubules and spindle fiber formation, inhibiting meiosis, and resulting in testicular atrophy [72]. The total concentration of ECn-11-12 could be classified as good according to AHCs limit values in Norway soils [70]. The constituents of this group are *n*-undecane, *n*-dodecane, and pentylcyclopentane. The health hazards that are likely in humans through occupational exposure when concentrations exceed the threshold limit are toxic, mutagenic, and carcinogenic effects [71, 73, 74]. The total concentration of the ECn-13-35 fractions could be classified as very bad according to AHCs limit values in Norway soils [70]. This group are characterize with *n*-tri-, tetr-, penta- and hexadecane, *n*-hepta, *n*-octa, *n*-

nonadecane and *n*-eicosadecane, *n*-heneicosane, *n*-docosane, *n*-tetracosane and *n*-hexacosane. Hepatic lipid granulomas in humans have been observed through diet and ingestion [71].

Generally, due to their frequent usage and show of environmental and human toxic effects, the exposure of humans and animals to EC<sub>n</sub>-8-40 could have probable multiple health challenges, therefore, AHCs increasing contamination levels in soil and aquatic environment is of considerable health concern [19]. Their long half-life, ubiquitous, highly lipid solubility, and bioaccumulation from the environment to the gastrointestinal tract of mammals in the food chain and the potential for toxicity to humans, some AHCs have been banned by health authorities [75, 76].

#### 4. Conclusions and recommendations

The mean concentrations of AHCs ranged from  $0.52 \pm 0.90$  to  $35.26 \pm 35.69$  mg/kg respectively. Across soil profiles, EC<sub>n</sub>-13-35 had the highest concentration when compared to EC<sub>n</sub>-8-12 and EC<sub>n</sub>-36-40. Results show that the range of soil pH, EC, and TOC are favorable for the adsorption of HAHCs with EC<sub>n</sub>-13-40 on active soil surfaces. The linear regression and ANOVA levels depict that, there is no significant positive correlation between TOC and AHCs concentrations in the soil profiles; however, there is significant variation in AHCs levels among the soil profiles, respectively. The results reveal that soils within the vicinity of the petroleum tank-farms are moderately polluted when compared to the UNEP 10,000 mg/kg recommended limit in soils. However, human and environmental health hazards are likely through oral, dermal, and inhalation exposures from the observed concentration of AHCs when compared to the Baltic, Nordic and Western countries, Canada, and the ATSDR regulatory limits. Source apportionment showed that the principal sources of AHCs were petrogenic and plant diagenesis. The occurrence and composition of AHCs are significantly dependent on the anthropogenic origin of these compounds. To avoid AHCs concentrations in the soil exceed the recommended limit, necessary precautions of clean-up and mitigation is taken. Also, further study should be carried out to determine the occurrence and compositional patterns of priority pollutant sources and environmental and on-spot human exposure risks in soils/sediments and water samples from the surrounding creeks.

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provided resources, collected, prepared, and analyzed the samples for the determination of AHCs; Onoriode O. Emoyan, Chiedu C. Ikechukwu and Godswill O. Tesi compiled the results and statistically analyzed the data; Onoriode O. Emoyan - writing, review and editing supervision.

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