Applied Science, Computing and Energy, 2026, 4(5), 847-862

Assessment of the levels of polycyclic aromatic hydrocarbons (PAHs) from effluents of petroleum tank farms at Calabar jetty, Nigeria

Blessing Udofia Ebong* and Mbuotidem Usen Ntinya
Received: 03 May 2026/Accepted: 18 July 2026/ Published: 28 July 2026

Abstract: *Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants of significant environmental and public health concern due to their toxicity, carcinogenicity, and resistance to degradation. This study assessed the occurrence, concentration, and possible sources of PAHs in soils collected from effluent channels of petroleum tank farms at Calabar Jetty, Cross River State, Nigeria. Soil samples were collected from six sampling locations associated with two petroleum storage facilities and analyzed for the sixteen United States Environmental Protection Agency (USEPA) priority PAHs. Extraction was carried out using Soxhlet extraction followed by clean-up and fractionation procedures, while identification and quantification were performed using an Agilent 7890A Gas Chromatography-Mass Spectrometry (GC-MS) system. The results showed that 11 out of the 16 priority PAHs were detected in the soil samples. Total PAH concentrations (∑PAHs) ranged from 8.0 × 10^4 ng/kg to 9.4 × 10^5 ng/kg dry weight, with a mean concentration of 4.23 × 10^5 ng/kg dry weight. Sample 1^O recorded the highest total PAH concentration (9.4 × 10^5 ng/kg), while sample 6^h exhibited the lowest concentration (8.0 × 10^4 ng/kg). Among the detected compounds, indeno(1,2,3-cd)pyrene recorded the highest individual concentration (5.4 × 10^5 ng/kg), followed by benzo(b)fluoranthene (1.6 × 10^5 ng/kg) and benzo(a)pyrene (1.5 × 10^5 ng/kg). Phenanthrene and benzo(b)fluoranthene were detected in all samples, indicating widespread contamination across the study area. The soils were generally neutral to slightly alkaline, with pH values ranging from 7.05 ± 0.01 to 7.79 ± 0.05, while organic matter content ranged from 11.19 ± 0.04% to 42.45 ± 0.19%. Diagnostic ratios including fluoranthene/pyrene (Fl/Pyr), fluoranthene/(fluoranthene + pyrene) [Fl/(Fl + Pyr)], and indeno(1,2,3-cd)pyrene /(indeno(1,2,3-cd)pyrene + benzo(ghi) perylene) [IcdP/(IcdP + BghiP)] indicated mixed PAH sources comprising petrogenic inputs, petroleum spills, liquid fossil fuel combustion, and biomass combustion from grass, wood, and coal. The detected concentrations exceeded several international environmental guideline values, suggesting significant ecological and human health risks. The study highlights the need for continuous environmental monitoring, improved effluent management practices, and implementation of effective pollution control measures to safeguard the Calabar Jetty ecosystem and surrounding communities.*

Keywords: *Polycyclic aromatic hydrocarbon, petroleum tank farms, Calabar jetty, Effluents, Assessment*

Blessing Udofia Ebong
Department of Chemistry, Western Illinois University, USA
Email: ; ebyblessingu@gmail.com

Mbuotidem Usen Ntinya
Department of Pure and Industrial Chemistry, University of Calabar, P.M.B. 1115, Calabar, Nigeria
Email: muntinyachem@gmail.com

1.0 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are major pollutants which are resistant to environmental degradation due to their highly hydrophobic nature (Akpanudo & Olabemiwo, 2024a, b; Udoetok *et al*., 2012). PAHs are large group of organic compounds with two or more fused aromatic rings. They are persistent

organic pollutants and can also be called polynuclear aromatic hydrocarbons. PAHs are generated from both natural and anthropogenic sources. Natural sources include volcanic eruptions and forest fires, while anthropogenic sources include petroleum exploration, refining, transportation, storage activities, fossil fuel combustion, industrial discharges, and accidental oil spills. Due to their persistence and tendency to accumulate in environmental matrices such as soil, sediments, water, and biota, PAHs have become contaminants of global environmental concern. One of the ways human can be exposed to PAHs is by incidental inhalation and ingestion of particles from soil contaminated by oil spills from petroleum derived products (Clark *et al.*, 2016; Aris *et al.* 2022), while Edu *et al.*(2016), Masato and Nobuo(2020) and Pooja, *et al. (*2023) described PAHs as the major pollutant with environmental concern in urban and industrial areas with low vapour pressure, very low aqueous solubility and highly lipophilic, Selvaraj et al. (2023) reported that the persistence and hydrophobic characteristics of PAHs facilitate their accumulation in environmental compartments, thereby they consist of carbon and hydrogen atoms with two or more fused aromatic rings without heteroatom or substituents. Although the health effects of individual PAHs are not exactly alike, the United States Environmental Protection Agency has listed about 16 PAHs as priority pollutants (USEPA, 2009). These are naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluorenthene, benzo(k) fluoranthene, benzo(a)pyrene, Dibenz(a,h) anthracene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene. Polycyclic aromatic hydrocarbons are lipophilic, the larger compounds are less H_2O soluble & less volatile (Essumang et al., 2009 and Bukowska *et al.* 2022). Petroleum tank farms are important facilities for the storage and distribution of refined petroleum products. However, operational activities such as product loading and unloading, leakages from storage facilities, accidental spills, and the discharge of untreated or poorly treated effluents can introduce substantial quantities of petroleum-derived contaminants into the surrounding environment. Such contamination may result in the accumulation of PAHs in nearby soils and water bodies, thereby posing ecological and public health concerns.

Previous studies have reported elevated concentrations of PAHs in soils, sediments, and aquatic environments located near petroleum handling facilities. Essumang et al. (2009) observed significant PAH contamination in petroleum-impacted environments, while Mallah et al. (2021) reported that prolonged exposure to PAHs could result in serious ecological and human health consequences. Similarly, studies conducted in industrial and petroleum-producing regions have shown that petroleum storage and transportation activities are major contributors to environmental PAH contamination.

Due to their toxic, mutagenic, and carcinogenic properties, PAHs represent a significant environmental health concern. Long-term exposure to elevated concentrations of PAHs has been associated with adverse health effects, including respiratory disorders, skin diseases, liver dysfunction, kidney damage, reproductive abnormalities, and various forms of cancer.

etc. Mallah *et al.* (2021). It is therefore pertinent to check the level of PAHs in the chosen study area. Although numerous studies have investigated PAH contamination in petroleum-producing and industrial regions worldwide, limited information is available regarding the occurrence, distribution, and sources of PAHs in soils receiving effluents from petroleum tank farms at Calabar Jetty, Cross River State, Nigeria. Furthermore, there is a paucity of data on the potential environmental and public health implications

of PAH contamination in this strategic petroleum handling environment. Calabar Jetty serves as a major petroleum storage and distribution hub in southeastern Nigeria.

The continuous handling and movement of petroleum products within the facility increase the likelihood of hydrocarbon released into the surrounding environment. Consequently, assessing the levels of PAHs in effluent-impacted soils within the area is essential for evaluating environmental quality and potential ecological risks. This research looked at the levels and types of PAHs present in the chosen location, its health implications and suggest possible ways of eliminating them and avoid future pollution occurrences. Therefore, the aim of this study was to assess the concentrations, distribution patterns, and possible sources of polycyclic aromatic hydrocarbons in soils collected from effluent channels of petroleum tank farms at Calabar Jetty, Nigeria. The findings of this study will provide valuable baseline information on PAH contamination associated with petroleum tank farm activities at Calabar Jetty. The results will support environmental monitoring programmes, guide pollution control strategies, assist regulatory agencies in enforcing environmental standards, and contribute to the protection of aquatic ecosystems and human populations potentially exposed to petroleum-derived contaminants.

2.0 Materials and Methods

2.1 Study area

The study area is located at latitude 5°1′0″N and longitude 8°19′0″E of Calabar Highway, Harbour junction, Cross River State, Nigeria (Fig. 1). The study area lies within the humid tropical region of southern Nigeria and experiences a bimodal rainfall pattern with annual precipitation exceeding 2,500 mm.

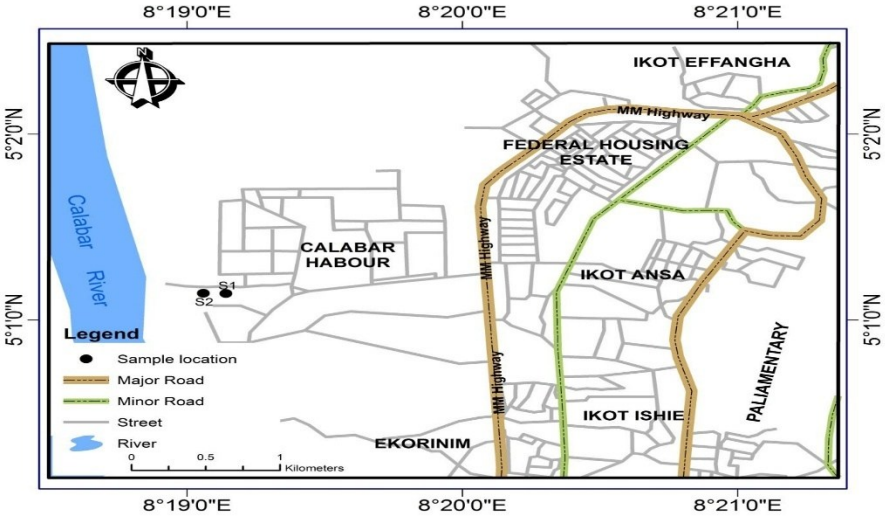

Fig 1: Map of the sampling location adapted from road network (Original map of the study area drawn by the lead author).

The area is characterized by high temperatures and relative humidity throughout the year. Calabar Jetty is situated along the Calabar River and serves as an important petroleum storage and distribution hub. Continuous petroleum handling activities within the area increase the likelihood of hydrocarbon contamination of surrounding soils and surface waters. These companies store petroleum products in 12-million-meter tones capacity tanks (Plates 1-5) and discharge to tankers for final delivery to fuel stations within the country. These companies are situated inside Calabar port which has jurisdiction over crude

oil terminals. They supply, source and distribute the oil and gas products needed by consumers, businesses and maritime operators

PLATE 1: Tank farms at Calabar jetty

PLATE 2: The pipes of the inlet lines where products are discharged from the vessels to the tank.

PLATE 3: The picture of the pump house, where products flow through from the tank farm to the gantry in Calabar jetty.

PLATE 4: Water and foam pumps used for washing the tanks in Calabar jetty.

PLATE 5: The picture showing the effluent discharge point after washing the tank in Calabar jetty.

2.2 Solvents

All chemicals and solvents used in this study were of analytical grade and were obtained from Merck (Germany). Solvents used included acetone, methanol, n-hexane, petroleum ether, dichloromethane, toluene, ethyl acetate, benzene, n-heptane, nitrobenzene, benzophenone, and benzenethiol. Silica gel (60–120 mesh) and activated alumina were used for sample clean-up and fractionation.

2.3 Equipment

The equipment used included a Soxhlet extraction apparatus, analytical balance (±0.001 g accuracy), glass chromatographic column, laboratory oven, muffle furnace, desiccator, beakers, crucibles, glass wool, and an Agilent 7890A Gas Chromatograph coupled with a 5975C Mass Selective Detector (GC-MS). Soil samples were collected in polythene bags which had never been used. The samples were collected from the waste channels of two different oil companies (H and O) using shovel, auger and spade at different depths ranging from 5-20cm. The samples were air-dried for about one month and then stored in air-tight container for further processing. One hundred grams (100 g) of each prepared soil sample was extracted using a Soxhlet apparatus with 150 mL of acetone:methanol:n-hexane (3:1:1, v/v/v). Extraction was carried out at 50°C for 15 h under continuous reflux conditions. The extracts obtained were concentrated using solvent evaporation and stored in clean amber bottles prior to clean-up and analysis.

2.4 Precipitation of Asphaltenes

Asphaltenes were separated from maltenes by precipitation using a petroleum ether:dichloromethane mixture (3:1, v/v). The solvent mixture was added to the concentrated extracts and thoroughly mixed. Following precipitation, the maltene fraction was separated and collected for subsequent chromatographic fractionation.

2.5 Characterization of Extracts

The extracts were characterized by resolution over silica gel and alumina (2:1) column. The column was developed with 10ml of n-hexane and each fraction was eluted with 50ml of the

solvents. The saturated hydrocarbon (SHC) fraction was eluted with n-hexane while the aromatic hydrocarbon (AHC) was eluted with methyl benzene. The vanadylporphyins were eluted with benzene/ethylacetate (3:1) mixture. The nickelporphyrins were eluted with a dichloromethane/n-heptane (2:3) mixture. The nitrogen compounds were eluted with nitrobenzene while the oxo compounds were eluted with benzoketone. Finally, the hetero components (NSO) were eluted from the column using a methanol/dichloromethane (2:1) mixture. Excess solvent was allowed to evaporate at room temperature under a fan to avoid denaturation of the fractions. All fractions were then weighed and their yields obtained by difference.

2.6 GC-MS analysis

The extracts of the sample were subjected to GC/MS analysis. The gas chromatographic model 7890A (GC) analysis was performed on an agilent technology interfaced with mass selective detector mode: 5975C (MSD). The electron ionization was at a 70V with an ion source temperature at 250ºC. Highly pure helium gas (99.9% purity) was used as a carrier gas while HP-5 (30mm X 0.25mm X 0.320mm) was used as the stationary phase. The oven temperature was at 80ºC held for 2 minutes and ramped to 280ºC while holding for 6 minutes at the rate of 10ºC/minute 1g/l was auto injected. The unknown samples were run against set of standards of 16 WHO prioritized PAHs and the identification of PAHs was confirmed by the retention time and abundance of quantification/confirmation ions in the authentic PAHs standards.

2.7 Determination of moisture content

The moisture content shows the amount of water in the soil. The moisture content was determined using the oven-drying method.50g of the soil sample crushed and poured into a clean, dried and weighed crucible. The weight of the container with the wet sample was taken using a weighing balance. The crucible was then placed in an oven for 24 hours at a temperature of 110± 5^0C, which was later removed and placed in a desiccator and the weight of the dry sample was taken. The measurement was done in duplicate. The moisture content in the soil is expressed as

$$Moisture\ (\%) = \frac{Wt_{moist} - Wt_{dried}}{Wtmoist_{\square}} \times \frac{100}{1} \quad (1)$$

where Wt_{moist} = weight of moist sample and Wt_{dried} = weight of dried sample

2.8 Determination of organic matter content

The organic content is the ratio expressed as percentage of the mass of organic matter in a given mass of soil to the mass of the dry soil. About 20g of the oven-dried test specimen from the moisture content experiment was placed in empty, clean and dry crucible and the mass was recorded. The crucible containing the sample was then placed in a muffle furnace overnight at a temperature of 440^0C. The crucible was then carefully removed from the furnace using tongs and allowed to cool to room temperature. The mass of the crucible containing the ash (burned soil) was recorded.

The organic content in the soil was calculated according to equation 2

$$Organic\ (\%) = \frac{Wt_{dried} - Wt_{ashed}}{Wt_{dried}} \quad (2)$$

where Wt_{ashed} = weight of ashed sample

3.0 Results and Discussions

3.1 Physicochemical Characteristics of Soils from Calabar Jetty

The physicochemical properties of the soil samples collected from the petroleum tank farm effluent channels at Calabar Jetty are presented in Table 1, while the sampling coordinates, conductivity, temperature, and colour characteristics are shown in Table 2. The results revealed noticeable variations in soil properties among the sampling locations. Sample 4^h recorded the highest pH value (7.79 ± 0.05) and moisture content (32.14 ± 0.10%), whereas the highest organic matter content was

observed in sample 6^h (42.45 ± 0.19%). These variations may reflect differences in the intensity of petroleum-related activities, waste discharge patterns, and local environmental conditions at the sampling points.

The colour of the soils ranged from dark grey to brownish-grey (Table 1), which may be associated with hydrocarbon contamination and the accumulation of organic materials. Darker soil colours have often been linked to elevated organic carbon and petroleum hydrocarbon contents in contaminated environments.

Table 1: Physico-chemical characteristics of the soils

Parameters	1^O	2^O	3^O	4^h	5^h	6^h
P^H value	7.10±0.04	7.05±0.01	7.27±0.03	7.79±0.05	7.53±0.05	7.69±0.04
Moisture content %	17.51±0.09	20.04±0.04	15.00±0.06	32.14±0.10	23.36±0.05	28.20±0.09
Organic matter %	22.70±0.10	13.59±0.05	11.19±0.04	30.88±0.15	27.27±0.11	42.45±0.19

Table 2: Conductivity, temperature, coordinates, colour of samples

Sample code	Conductivity	Temperature	Coordinates	Colour
1^0	1.27	27.8 ± 0.03	$05^0$10'N$08^0$019'E	Dark grey
2^0	1.68	28.4 ± 0.02	$05^0$10'N$08^0$019'E	Dark grey
3^0	1.91	27.7 ± 0.04	$05^0$20'N$08^0$20'E	Dark grey
4^h	1.32	27.6 ± 0.01	$04^0$21'N$07^0$16'E	Brown
5^h	1.39	27.5 ± 0.03	$04^0$19'N$07^0$20'E	Brownish grey
6^h	1.62	26.9 ± 0.02	$04^0$20'N$07^0$21'E	Brownish grey

3.2 Soil pH

As shown in Table 1, soil pH values ranged from 7.05 ± 0.01 to 7.79 ± 0.05, with an overall mean value of 7.40 ± 0.03. The results indicate that the soils were generally neutral to slightly alkaline. Sample 4^h exhibited the highest pH value, while sample 2^O recorded the lowest.

The relatively narrow pH range observed suggests a similar geochemical environment across the study area. The slight alkalinity may be attributed to the presence of calcium carbonate ($CaCO_3$) and other alkaline constituents in the soil, as reported by Ali *et al*. (2021). Soil pH is an important environmental parameter because it influences nutrient availability, microbial activity, and the mobility and bioavailability of contaminants, including PAHs. According to Wang *et al*. (2023), soil pH significantly affects the solubility and chemical behaviour of various compounds within soil matrices. The near-neutral pH conditions observed in this study may favour the persistence of hydrophobic organic pollutants such as PAHs by reducing their degradation rates.

3.3 Soil Temperature, Conductivity and Organic Matter

The temperature and conductivity values of the soil samples are presented in **Table 1**. Soil temperatures ranged from 26.9 ± 0.02°C to 28.4 ± 0.02°C, with sample 2^O recording the highest temperature and sample 6H the lowest. The relatively uniform temperature distribution across the sampling locations reflects the tropical climatic conditions of the Calabar region.

Electrical conductivity values ranged from 1.27 to 1.91, with sample 3^{O} recording the highest conductivity. Elevated conductivity may indicate the presence of dissolved ions arising from petroleum residues, industrial discharges, and other anthropogenic inputs associated with tank farm operations.

Moisture content values ranged from 15.00 ± 0.06% to 32.14 ± 0.10%, while organic matter content varied from 11.19 ± 0.04% to 42.45 ± 0.19% (Table 1). Sample 6^{h} contained the highest organic matter content, suggesting a greater capacity for adsorption and retention of hydrophobic contaminants such as PAHs. Organic matter is a major controlling factor in the environmental fate of PAHs because these compounds strongly associate with organic carbon fractions in soil. The relatively high organic matter contents recorded in some locations may therefore contribute to the accumulation and persistence of PAHs in the study area.

3.4 Identification and Distribution of PAHs

The GC-MS retention times of the identified PAHs are presented in Table 3, while their concentrations are shown in Table 4. Among the sixteen United States Environmental Protection Agency (USEPA) priority PAHs investigated, eleven compounds were detected in the soil samples. These included acenaphthene, fluorene, phenanthrene, fluoranthene, pyrene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene, and benzo(ghi)perylene. However, naphthalene, acenaphthylene, anthracene, chrysene, and benzo(k)fluoranthene were not detected in any of the samples.

Table 3: GC-MS conditions under time scheduled selected ion monitoring

Compound	No. of Rings	Molecular mass	Retention time					
			1^{O}	2^{O}	3^{O}	4^{h}	5^{h}	6^{h}
Acenaphthene	3	153	9.301	9.370	9.267	-	9.667	-
Flourene	3	166	10.503	10.480	10.508	-	10.892	10.291
Phenanthrene	3	178	12.780	12.860	12.751	12.797	12.780	12.808
Fluoranthene	4	202	15.812	15.685	15.658	15.738	15.910	15.744
Pyrene	5	202	16.213	16.190	16.202	16.207	16.202	16.211
Benz(a)anthracene	5	252	19.223	19.240	19.240	19.332	19.234	19.240
Benzo(b) fluoranthene	5	252	22.164	21.649	21.871	21.432	21.563	22.055
Benzo (a) pyrene	5	276	22.164	21.649	21.781	21.432	21.964	22.055
Indeno (1, 2, 3-cd) pyrene	6	278	24.264	24.699	24.613	-	24.670	-
Dibenz(a,h) anthracene	6	276	24.865	24.682	24.613	-	24.653	-
Benzo(ghi) perylene	6	276	25.088	24.699	-	-	24.670	-

Table 4: Concentrations of PAHs expressed in ng/kg

PAH Components	1^{O}	2^{O}	3^{O}	4^{h}	5^{h}	6^{h}
Naphthalene	-	-	-	-	-	-
Acenaphthene	1.0×10^4	-	1.0×10^4	-	-	-
Acenaphthylene	-	-	-	-	-	-
Fluorene	2.0×10^4	-	3.0×10^4	-	-	-
Anthracene	-	-	-	-	-	-
Phenanthrene	4.0×10^4	2.9×10^5	2.0×10^4	5.0×10^4	2.0×10^4	5.0×10^4
Fluoranthene	4.0×10^4	2.0×10^4	1.2×10^5	1.0×10^4	1.0×10^4	-
Pyrene	4.0×10^4	1.0×10^4	1.1×10^5	-	1.0×10^4	1.0×10^4
Benzo(a) anthracene	2.0×10^4	-	1.0×10^4	1.0×10^4	-	-
Chrysene	-	-	-	-	-	-
Benzo (b)floranthene	1.1×10^5	2.0×10^4	9.0×10^4	1.6×10^5	1.0×10^4	1.0×10^4
Benzo(k) fluoranthene	-	-	-	-	-	-
Benzo (a)pyrene	-	1.0×10^4	8.0×10^4	1.5×10^5	1.0×10^4	1.0×10^4
Indeno(1,2,3-cd) pyrene	5.4×10^5	1.0×10^4	6.0×10^4	-	1.0×10^4	-
Dibenz(a, h) anthracene	7.0×10^4	1.0×10^4	1.2×10^5	-	1.0×10^4	-
Benzo (ghi) perylene	5.0×10^4	1.0×10^4	-	-	1.0×10^4	-
Mean	9.4×10^5	3.8×10^5	6.7×10^5	3.8×10^5	9.0×10^4	8.0×10^4

The absence of several low-molecular-weight PAHs may be attributed to their relatively high volatility and greater susceptibility to dissolution and degradation during environmental exposure and sample processing. Similar observations were reported by Akash et al. (2023), who attributed the loss of lighter PAHs to volatilization processes. Xilin *et al*. (2024) also noted that prolonged environmental exposure can significantly reduce the concentrations of low-molecular-weight PAHs in contaminated soils.

The chromatographic identification of PAHs based on retention times is shown in **Table 3**. Phenanthrene, fluoranthene, pyrene, benzo(b)fluoranthene, and benzo(a)pyrene exhibited consistent retention times across the sampling locations, confirming their widespread occurrence within the study area.

A total of eleven PAHs were identified in sample 1^{O}, ten in sample 3^{O}, eight in samples 2^{O} and 5^{h}, five in sample 4^{h}, and four in sample 6^{h}. The variation in the number of detected compounds suggests differences in contamination sources, environmental conditions, and pollutant transport pathways within the jetty environment.

3.5 Concentrations of PAHs in Soil Samples

The concentrations of individual PAHs and total PAHs are presented in **Table 4**. Total PAH concentrations ranged from 8.0×10^4 ng/kg to 9.4×10^5 ng/kg, with an overall mean concentration of approximately 4.23×10^5 ng/kg. Sample 1^{O} recorded the highest total PAH concentration (9.4×10^5 ng/kg), followed by sample 3^{O} (6.7×10^5 ng/kg), whereas sample 6H recorded the lowest concentration (8.0×10^4 ng/kg).

The elevated PAH levels observed in samples 1^{O} and 3^{O} may be attributed to their proximity to active petroleum storage facilities and effluent discharge channels located close to the Calabar River. These locations are exposed to continuous petroleum handling activities, accidental spills, leakage from storage systems, tanker operations, and combustion emissions. Jun *et al*. (2022) similarly reported that

petroleum storage and transportation activities contribute substantially to elevated PAH concentrations in surrounding soils.

Among the individual PAHs, indeno(1,2,3-cd)pyrene recorded the highest concentration of 5.4 × 10^5 ng/kg in sample 1^O (Table 4). According to Tao *et al*. (2020) and Pradip *et al.* (2023), elevated concentrations of high-molecular-weight PAHs such as indeno(1,2,3-cd)pyrene are often associated with intense industrial activities, petroleum combustion, and pyrogenic sources. The dominance of this compound in sample 1^O therefore suggests significant anthropogenic influence.

Phenanthrene and benzo(b)fluoranthene were detected in all soil samples, indicating their widespread distribution within the study area. The persistence of high-molecular-weight PAHs such as benzo(a)pyrene, indeno(1,2,3-cd)pyrene, and benzo(b)fluoranthene may be related to their resistance to microbial degradation compared to lower molecular weight PAHs. Similar observations were reported by Zhang *et al*. (2020), who noted that biodegradation rates decrease with increasing molecular weight of PAHs.

3.6 Occurrence of Carcinogenic PAHs and Environmental Implications

Particular attention was given to benzo(a)pyrene because it is widely recognized as one of the most toxic and carcinogenic PAHs and is commonly used as an environmental contamination indicator (Ras et al., 2009). Benzo(a)pyrene was detected in five of the six samples and ranged from 1.0 × 10^4 ng/kg to 1.5 × 10^5 ng/kg (Table 4). The highest concentration occurred in sample 4H.

The elevated concentration of benzo(a)pyrene in sample 4^h may be associated with its relatively high organic matter content and the strong affinity of PAHs for humic substances. Sudipti *et al.* (2022) reported that soils rich in organic matter tend to accumulate greater quantities of hydrophobic contaminants because of their lipophilic nature.

The concentrations of benzo(a)pyrene recorded in this study were substantially higher than those reported by Samuel Sojinu *et al.* (2010) for soils and sediments in the Niger Delta, where concentrations ranged from 9.0 ng/kg to 2.05 × 10^3 ng/kg in soils and 1.7 × 10^2 ng/kg to 1.02 × 10^4 ng/kg in sediments. Similarly, the concentrations of several carcinogenic PAHs detected in this study exceeded values reported in other petroleum-impacted environments.

The occurrence of high concentrations of carcinogenic PAHs poses potential ecological and human health risks to workers and residents within the vicinity of the jetty. Exposure may occur through inhalation of contaminated dust, dermal contact with contaminated soils, or indirect ingestion through the food chain following bioaccumulation.

3.7 Comparison with Previous Studies and International Standards

The PAH concentrations obtained in this study were compared with values reported from other regions worldwide. The concentration of benzo(a)pyrene (1.0 ×10^4 – 1.5 × 10^5 ng/kg) was lower than the values reported by Li *et al.* (2020) but higher than those reported by Samuel Sojinu *et al.* (2010) and several studies conducted in the Niger Delta region. Anyakora *et al.* (2005) reported concentrations of 5–6 ring PAHs ranging from 0 to 2.8 × 10^4 ng/kg in Niger Delta sediments. In contrast, the present study recorded concentrations ranging from 1.0 × 10^4 to 5.4 × 10^5 ng/kg for similar compounds, indicating a higher contamination burden within the Calabar Jetty environment.

The total PAH concentrations obtained in the present study were generally lower than the concentrations reported for heavily industrialized harbour and estuarine sediments in China (Libing *et al.,* 2023), Greece (Grigoriou *et al.,* 2022), and Korea (Yun-Hee *et*

al., 2023). Nevertheless, the concentrations remained sufficiently elevated to indicate substantial petroleum-related contamination.

Although some samples were below the Dutch intervention value (5.0×10^6 ng/kg) and the Polish standard (1.5×10^7 ng/kg), all detected PAHs exceeded the environmental exposure guideline of 2.0×10^2 ng/kg established by the USEPA (2009) and the American Conference of Governmental Industrial Hygienists. This suggests that the study area is contaminated with PAHs at levels capable of posing environmental and public health concerns.

The elevated concentrations observed may have originated from multiple sources including petroleum spills, tanker operations, fuel combustion, sewage deposition, irrigation inputs, and indiscriminate disposal of petroleum wastes. Similar source contributions have been reported by Rishikesh and Madhava (2022), Fernandez *et al.* (2002), and Lag *et al.* (2020).

Overall, the results demonstrate that soils around petroleum tank farms at Calabar Jetty are contaminated with significant concentrations of PAHs, particularly high-molecular-weight carcinogenic compounds. The findings underscore the need for regular environmental monitoring, improved effluent management practices, and implementation of pollution control measures to safeguard ecosystem integrity and public health.

4.0 Conclusion

This study assessed the occurrence and distribution of polycyclic aromatic hydrocarbons (PAHs) in soils collected from effluent channels of petroleum tank farms at Calabar Jetty, Cross River State, Nigeria. The results revealed significant PAH contamination within the study area, indicating the impact of petroleum storage, handling, and associated industrial activities on the surrounding environment.

Of the sixteen USEPA priority PAHs investigated, eleven were detected in the soil samples. The dominant compounds were indeno(1,2,3-cd)pyrene, benzo(b)fluoranthene, and benzo(a)pyrene, all of which are high-molecular-weight PAHs known for their persistence and potential toxicity. Total PAH concentrations ranged from 8.0×10^4 to 9.4×10^5 ng/kg dry weight, with a mean concentration of 4.23×10^5 ng/kg dry weight. These concentrations exceeded the recommended guideline value of 50 ng/kg, indicating substantial contamination and a potential risk to environmental and human health.

The distribution patterns and diagnostic assessments suggest that the detected PAHs originated from multiple sources, including petroleum spills, petroleum storage and transfer operations, fossil fuel combustion, sewage deposition, and other petrogenic and pyrogenic activities. The predominance of high-molecular-weight PAHs further indicates significant contributions from combustion-related processes and long-term accumulation in the soil.

The elevated concentrations of carcinogenic PAHs, particularly benzo(a)pyrene, raise concerns regarding possible ecological effects and human exposure through direct contact with contaminated soils, inhalation of contaminated particulates, and food-chain transfer. Continuous discharge of untreated or poorly managed effluents may further increase contamination levels in nearby terrestrial and aquatic ecosystems.

Therefore, regular environmental monitoring, effective effluent treatment, strict enforcement of environmental regulations, prompt remediation of contaminated sites, and improved petroleum handling practices are recommended to reduce PAH contamination and protect environmental quality and public health within the Calabar Jetty area.

5.0 References

Akash, S., Baskaran, S., Natarajan, R., & Thangaswamy, S. (2023). Biotransformation as a tool for remediation of polycyclic aromatic hydrocarbons from polluted environment - Review on toxicity and treatment technologies. *Environmental Pollution*, *318*, Article 120923. https://doi.org/10.1016/j.envpol.2022.120923

Akpanudo, N. W., & Olabemiwo, O. M. (2024a). Green synthesis and characterization of copper nanoparticles (CuNPs) and composites (CuC) using the *Echinochloa pyramidalis* extract and their application in the remediation of PAHs in water. *Water Practice & Technology*, *19*(2), 324–342. https://doi.org/10.2166/wpt.2024.012

Akpanudo, N. W., & Olabemiwo, O. M. (2024b). Synthesis and characterization of silver nanoparticles and nanocomposites using *Echinochloa pyramidalis* (Antelope grass) plant parts and the application of the nanocomposite in the remediation of polycyclic aromatic hydrocarbons (PAHs) contaminated water. *South African Journal of Chemical Engineering*, *47*, 98–110. https://doi.org/10.1016/j.sajce.2023.11.006

Ali, M., Song, X., Ding, D., Wang, Q., Zhang, Z., & Tang, Z. (2021). Bioremediation of PAHs and heavy metals co-contaminated soils: Challenges and enhancement strategies. *Environmental Pollution*, *295*, Article 118686. https://doi.org/10.1016/j.envpol.2021.118686

Anyakora, C., Ogbeche, A., Palmer, P., Coker, H. A. B., & Ukpo, G. (2005). GC-MS analysis of polynuclear aromatic hydrocarbons in sediment samples from the Niger Delta Region. *Chemosphere*, *60*(7), 990–997. https://doi.org/10.1016/j.chemosphere.2005.01.030

Aris, I., Tony, H., Risky, K., Lilik, M., Novia, S., & Wulan, K. (2022). Endocrine disrupting chemicals (EDCs) in environmental matrices: Occurrence, fate, health impact, physio-chemical and bioremediation technology. *Environmental Pollution*, *302*, Article 119061. https://doi.org/10.1016/j.envpol.2022.119061

Bukowska, B., Mokra, K., & Michałowicz, J. (2022). Benzo[a]pyrene—Environmental occurrence, human exposure, and mechanisms of toxicity. *International Journal of Molecular Sciences*, *23*(11), Article 6348. https://doi.org/10.3390/ijms23116348

Choi, Y. H., Lee, J. Y., & Moon, K. W. (2023). Exposure to volatile organic compounds and polycyclic aromatic hydrocarbons is associated with the risk of non-alcoholic fatty liver disease in Korean adolescents: Korea National Environmental Health Survey (KoNEHS) 2015–2017. *Ecotoxicology and Environmental Safety*, *251*, Article 114508. https://doi.org/10.1016/j.ecoenv.2023.114508

Chormare, R., & Kumar, M. A. (2022). Environmental health and risk assessment metrics with special mention to biotransfer, bioaccumulation and biomagnification of environmental pollutants. *Chemosphere*, *302*, Article 134836. https://doi.org/10.1016/j.chemosphere.2022.134836

Clark, B. S., Pellon, S. T., Booker, B., Langston, M. A., & Hood, D. B. (2016). Validation of research trajectory of an exposure framework: Exposure to benzo(a)pyrene confers enhanced susceptibility to bacterial infection. *Environmental Research*, *146*, 173–184. https://doi.org/10.1016/j.envres.2015.12.023

Edu, I., Ntia, B., Nnaneke, O., & Joseph, E. (2016). Polycyclic aromatic hydrocarbons

loads and potential risks in freshwater ecosystem of the Ikpa River Basin, Niger Delta, Nigeria. *Environmental Monitoring and Assessment*, *188*, Article 681. https://doi.org/10.1007/s10661-016-5681-3

Essumang, D. K., Adokoh, C. K., Afriyie, J., & Mensah, E. (2009). Source, assessment and analysis of polycyclic aromatic hydrocarbon in the Oblogo waste disposal sites and some water bodies among the metropolis of Ghana. *Journal of Water Resource and Protection*, *1*(6), 456–468. https://doi.org/10.4236/jwarp.2009.16055

Eze, W. O., Chukwujindu, M. A. I., Francis, E. E., Godwin, E. N., & Bice, S. M. (2024). Distribution, sources, and risk of polycyclic aromatic hydrocarbons in soils from rural communities around gas flaring points in the Niger Delta of Nigeria. *Environmental Science: Processes & Impacts*, *26*(4), 721–733. https://doi.org/10. z1039/D3EM00481K

Fernández, P., Grimalt, J. O., & Vilanova, R. M. (2002). Atmospheric gas-particle partitioning of polycyclic aromatic hydrocarbons in high mountain regions of Europe. *Environmental Science & Technology*, *36*(6), 1162–1168. https://doi.org/10.1021/es0101859

Grigoriou, C., Costopoulou, D., Vassiliadou, I., Karavoltsos, S., Sakellari, A., Bakeas, E., & Leondiadis, L. (2022). Polycyclic aromatic hydrocarbons and trace elements dietary intake in inhabitants of Athens, Greece, based on a duplicate portion study. *Food and Chemical Toxicology*, *165*, Article 113087. https://doi.org/10.1016/j.fct.2022.113087

He, L., Sun, X., Li, S., Zhang, W., Chen, Z., & Bi, X. (2023). Ecotoxicological evaluation of oxidative stress-mediated neurotoxic effects, genetic toxicity, behavioral disorders, and the corresponding mechanisms induced by fluorene-contaminated soil targeted to earthworm (*Eisenia fetida*) brain. *Science of The Total Environment*, *871*, Article 162014. https://doi.org/10.1016/j.scitotenv.2023.162014

Joshi, P., Kumar, A., Pal, M., & Kothari, A. (2023). Roles of surfactant, oxidant and activator on enhanced electrokinetic-persulfate technique for the removal of hydrophobic organic compounds in soil: A review. *Journal of Environmental Chemical Engineering*, *11*(3), Article 109525. https://doi.org/10.1016/j.jece.2023.109525

Låg, M., Øvrevik, J., Refsnes, M., & Holme, J. A. (2020). Potential role of polycyclic aromatic hydrocarbons in air pollution-induced non-malignant respiratory diseases. *Respiratory Research*, *21*, Article 299. https://doi.org/10.1186/s12931-020-01563-1

Li, R., Cheng, M., Cui, Y., He, Q., Guo, X., & Chen, L. (2020). Distribution of the soil PAHs and health risk influenced by coal usage processes in Taiyuan city, northern China. *International Journal of Environmental Research and Public Health*, *17*(17), Article 6319. https://doi.org/10.3390/ijerph17176319

Mallah, M. A., Liu, Y., Xi, H., Wang, W., Feng, F., & Zhang, Q. (2021). Relationship between polycyclic aromatic hydrocarbons and cardiovascular diseases: A systematic review. *Frontiers in Public Health*, *9*, Article 649372. https://doi.org/10.3389/fpubh.2021.649372

Ma, J., Yu, C., Zhao, S., Mei, L., Zhang, B., Tang, H., Mutai, B., & Chen, Q. (2022). Effect of terminal electron acceptors on the anaerobic biodegradation of PAHs in marine sediments. *Journal of Hazardous Materials*, *438*, Article 129569. https://doi.org/10.1016/j.jhazmat.2022.129569

Nawa, M., & Suzuki, N. (2020). Toxicities of polycyclic aromatic hydrocarbons for aquatic animals. *International Journal of Environmental Research and Public Health*, *17*(4), Article 1363. https://doi.org/10.3390/ijerph17041363

Okoye, E. A., Bocca, B., Ruggieri, F., Ezejiofor, A. N., Nwaogazie, I. L., Domingo, J. L., Rovira, J., Frazzoli, C., & Orisakwe, O. E. (2021). Concentrations of polycyclic aromatic hydrocarbons in samples of soil, feed and food collected in the Niger Delta region, Nigeria: A probabilistic human health risk assessment. *Environmental Research*, *202*, Article 111619. https://doi.org/10.1016/j.envres.2021.111619

Pooja, C., Arfin, I., Pankaj, K., & Sunil, K. (2023). Nano-bioremediation: An eco-friendly and effective step towards petroleum hydrocarbon removal from environment. *Environmental Research*, *231*(Pt 2), Article 116224. https://doi.org/10.1016/j.envres.2023.116224

Ras, M. R., Marcé, R. M., Cuadras, A., Marí, M., Nadal, M., & Borrull, F. (2009). Atmospheric levels of polycyclic aromatic hydrocarbons in gas and particulate phases of atmospheric samples. *International Journal of Environmental Analytical Chemistry*, *89*(8–12), 543–556. https://doi.org/10.1080/03067310802610276

Samuel, S. O., Wang, J., Sonibare, O. O., & Zhao, E. (2010). Polycyclic aromatic hydrocarbons in soils and sediments from oil exploration areas of the Niger Delta, Nigeria. *Journal of Hazardous Materials*, *174*(1–3), 641–647. https://doi.org/10.1016/j.jhazmat.2009.09.099

Selvaraj, B., Gitanjali, J., Gandhimathi, R., Nadana, S., Aruljothi, K. N., Lee, J., & Sabariswaran, K. (2023). Recent trends in polycyclic aromatic hydrocarbons pollution distribution and counteracting bio-remediation strategies. *Chemosphere*, *337*, Article 139396. https://doi.org/10.1016/j.chemosphere.2023.139396

Sudipti, A., Sonika, S., Devanshi, S., & Jasmine, S. (2022). Bioremediation: An ecofriendly approach for the treatment of oil spills. In *Advances in oil-water separation* (pp. 353–373). Elsevier.

Tao, W., Lin, J., Wang, W., Huang, H., & Li, S. (2020). Biodegradation of aliphatic and polycyclic aromatic hydrocarbons by the thermophilic bioemulsifier-producing *Aeribacillus pallidus* strain SL1. *Ecotoxicology and Environmental Safety*, *189*, Article 109994. https://doi.org/10.1016/j.ecoenv.2019.109994

Udoetok, I. A., Akpanudo, N. W., Ubuo, E. E., & Ukpong, E. J. (2012). Effect of potassium aluminium sulphate on the total petroleum hydrocarbon of diesel oil. *International Journal of Materials and Chemistry*, *2*(3), 101–104. https://doi.org/10.5923/j.ijmc.20120203.03

United States Environmental Protection Agency. (2009). *Determination of PAHs in ambient air using gas chromatography/mass spectrometry (GC/MS)* (Compendium Method TO-13A; EPA/625/R-96/010b). Center for Environmental Research Information.

Wang, S., Shao, Z., Xu, W., & Zhao, X. (2023). Insights into electro-bioremediation of PAH-contaminated soil under polarity reversal conditions: Effect of effective current intensity and soil properties on microbial function. *Chemical Engineering Journal*, *478*, Article 147493. https://doi.org/10.1016/j.cej.2023.147493

Wang, X., Chen, Y., Chen, T., Gao, L., Yu, Z., Chen, Y., Yu, Z., Liu, X., & Wang, H. (2024). Lagging pollution of polycyclic aromatic hydrocarbons in the rebuilt e-waste site: From the perspective of

characteristics, sources, and risk assessment. *Science of The Total Environment*, *929*, Article 172406. https://doi.org/10.1016/j.scitotenv.2024.172406

Zhang, H., Zhang, X., & Geng, A. (2020). Expression of a novel manganese peroxidase from *Cerrena unicolor* BBP6 in *Pichia pastoris* and its application in dye decolorization and PAH degradation. *Biochemical Engineering Journal*, *153*, Article 107402. https://doi.org/10.1016/j.bej.2019.107402

Declarations

Funding

The authors received no financial support for the research, authorship, and/or publication of this article.

Ethical Approval

Not applicable

Informed Consent

Not applicable.

Consent for Publication

Not applicable.

Declaration of Competing Interests

The authors declared no competing interests

Data Availability Statement

Data shall be made available upon request

Conflict of Interest

The authors declared no conflict of interest

Author Contributions

The work was designed by Blessing Udofia Ebong . Other components of the work were jointly carried out with Mbuotidem Usen Ntinya. Blessing developed the first draft of the manuscript, while the other author joined in the corrections