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Levels, Source Apportionment, and Health Risk Assessment of Polycyclic Aromatic Hydrocarbons in Soils Around Selected Petrol Filling Stations in Kogi State, Nigeria

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ABSTRACT
Soils around petrol filling stations are exposed to polycyclic aromatic hydrocarbons (PAHs) from fuel spillage, storage tank leakage, and incomplete combustion of petroleum products. This study assessed the levels, distribution, sources and health risk of the 16 USEPA priority PAHs in soils around petrol filling stations in Kogi Central (Zone 1: Ajaokuta, Okene) and Kogi West (Zone 2: Obajana, Lokoja), Kogi State, Nigeria. Twelve soil samples from filling stations and four controls were analyzed using Gas Chromatography-Mass Spectrometry (GC-MS). Surrogate (o-terphenyl) recoveries ranged from 94.0 to 101.6%. Total PAH (Σ16PAHs) concentrations ranged from 0.540 to 5.90 µg/kg, with mean values of 2.55 µg/kg in Zone 1 and 3.45 µg/kg in Zone 2 (combined mean 3.00 µg/kg). A two-sample t-test showed significantly higher PAH concentrations at filling stations than controls ($t = -2.30$, $p = 0.038$), with no significant difference among the four towns ($p = 0.094$). Low molecular weight (2-3 ring) PAHs dominated the distribution (65.7%), followed by 4-ring (30.2%) and 5-6 ring PAHs (4.12%). All individual and total PAH concentrations were below the Dutch maximum permissible concentrations, indicating unpolluted soils. Diagnostic ratios (LMW/HMW = 1.91; Ant/(Ant+Phe) = 0.77; Flt/(Flt+Pyr) = 0.90; BaA/(BaA+Chr) = 0.68) revealed a predominantly pyrolytic origin for the PAHs, with a minor petrogenic contribution. The mean benzo[a]pyrene equivalent concentration (BaPeq) was 0.0595 µg/kg, far below the 600 µg/kg Canadian soil quality guideline, denoting low carcinogenic potential. The results supply baseline data for PAH monitoring in the study area and complement previously published data for Kogi East.

Keywords: Polycyclic Aromatic Hydrocarbons, Petrol Filling Stations, Soil Pollution, Diagnostic Ratio, benzo[a]pyrene Equivalent, Kogi State

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants comprising two or more fused benzenoid rings, and are among the United States Environmental Protection Agency (USEPA) priority pollutants owing to their toxicity, persistence, carcinogenic and mutagenic properties (Lorenzi *et al*., 2010; Kadili et al., 2021). PAHs are released into the environment from natural or petrogenic sources, such as geogenic seepage, forest fires and volcanic events, and from anthropogenic or pyrogenic sources, including oil leakages, fuel spillage and the incomplete combustion of fossil fuels (Nganje *et al*., 2014). Pyrogenic sources are typically associated with higher-molecular-weight PAHs, while petrogenic sources are more commonly linked to lower-molecular-weight congeners (Neff *et al*., 2003).

The proliferation of petrol filling stations is one of the most visible anthropogenic sources of soil contamination with PAHs in Nigeria, arising from leakage of underground storage tanks, spillage during fuel unloading and dispensing, and the absence of adequate oil/water separators and drainage control (Renata *et al*., 2012). In Kogi State, North-Central Nigeria, the central location of the State along major inter-state transit routes, coupled with an epileptic power supply that increases dependence on petrol-powered generators, has encouraged the indiscriminate siting of petrol filling stations, often without due consideration for environmental protection guidelines.

Benzo[a]pyrene (BaP), one of the most extensively studied PAHs, is a proven human carcinogen (WHO, 2000) and is frequently used as an index compound for assessing the carcinogenic potential of complex PAH mixtures through the benzo[a]pyrene toxic equivalency concentration (BaPeq) approach (Halek *et al*., 2008; Bortey-Sam et al., 2014). Molecular diagnostic ratios of individual PAH congeners are also widely applied to distinguish between petrogenic and pyrogenic sources of PAHs in environmental matrices (Yunker *et al*., 1996, 2002).

Globally, PAH contamination in soil, water, air, and sediment is a continuing public health concern. Studies have continued to link environmental PAH exposure to elevated cancer and respiratory disease risk across both developed and developing regions (Teixeira *et al*., 2024). In a recent global systematic review and meta-analysis of 79 studies across ecological media, Al-Assi *et al*. (2026) reported that, relative to other regions of the world, Nigeria, Iran, China and Egypt consistently record among the highest pooled PAH concentrations, particularly in industrially and vehicularly impacted soils.

Across Nigeria, recent studies continue to confirm petroleum-handling and combustion-related activities as an important source of soil PAH contamination. A recent systematic review of PAH pervasiveness and bioaccumulation in the Niger Delta region recommends a coordinated environmental health monitoring strategy across Nigeria's oil-producing communities to ensure residents' safety (Udom *et al*., 2023). Similarly, Akinsete and Olatimehin (2024) reported elevated

levels of priority PAHs and heavy metals with attendant health risks in urban roadside soils around heavy-traffic areas of Ibadan, Southwestern Nigeria. Reported concentrations and associated cancer risks continue to vary widely depending on site history, land use, and proximity to active spillage or combustion sources (Adesina *et al*., 2024; Odali et al., 2024). PAH contamination in Nigeria is not limited to the soil; a recent study detected all 16 USEPA priority PAHs in dust collected from banknotes in commercial banks in Benin City, with diagnostic ratio analysis indicating that most of these PAHs originated from pyrogenic sources, primarily vehicle and diesel emissions (Amayo *et al*., 2026). These data collectively point out the need for routine monitoring and contamination assessment of Nigerian soils, particularly around oil-handling facilities.

The present paper therefore focuses on the levels, ring-wise distribution, source apportionment, and preliminary carcinogenic risk of PAHs in soils from Kogi Central: Ajaokuta and Okene and Kogi West: Obajana and Lokoja, with the aim of providing baseline PAH contamination data for these two senatorial districts, for which no previously published data exist. Moreover, data for the Kogi East zone, comprising Ankpa, Anyigba, and Idah, have been reported elsewhere (Kadili *et al*., 2021).

MATERIALS AND METHODS

Study Area

Kogi State is located in the North-Central geopolitical zone of Nigeria (Latitude 7°45'00" N, Longitude 6°45'00" E), covering a total land area of 29,833 km². The State is divided into three senatorial districts, Kogi East, Kogi Central and Kogi West, corresponding to the Igala, Ebira and Okun ethnic areas respectively. This study covers Kogi Central (designated Zone 1), represented by Ajaokuta and Okene, and Kogi West (designated Zone 2), represented by Obajana and Lokoja, the State capital. The State hosts several industrial ventures, including the Ajaokuta Iron and Steel Complex and Obajana cement works, as well as numerous automobile mechanic workshops and petrol filling stations, which constitute anthropogenic sources of environmental pollution in the area. Petrol vending is one of the most lucrative businesses in the State owing to its central location along inter-state transit routes and the erratic public power supply, which sustains a high demand for petrol-powered generators.

Sampling

Only filling stations that had been in operation for ten years or more were sampled, since underground storage tanks and pipes become susceptible to leakage after ten to fifteen years of installation (USEPA, 1987). Three filling stations were randomly selected from each of Ajaokuta and Okene (Zone 1) and from each of Obajana and Lokoja (Zone 2), giving twelve filling station sampling points in total. At each filling station, an average of 110 g of composite topsoil (0-30 cm depth) was collected using a hand soil auger, from 6-10 auger borings taken at five different points within the vicinity of the station and homogenized (Nganje *et al.,* 2007; Cao *et al.,* 2019; Kadili *et al.,* 2021). A control (pristine) sample, free from petrol station, agricultural, mining, or industrial influence, was also collected from each town using the same procedure to serve as a background reference. Geographical coordinates of all sampling points were obtained using a Global Positioning System (GPS), as shown in Table 1 and Figure 1. Samples were wrapped in aluminum foil, placed in labelled plastic bags and transported to the laboratory for pretreatment and analysis.

Table 1: Sample Code, Coordinates and Site Description

Site/Control Code	Depth (cm)	Latitude	Longitude	Description of Site
AJAOKUTA				
F10	0-30	7.4402 N	6.6534 E	Vicinity of petrol station
F11	0-30	7.4339 N	6.6815 E	Vicinity of petrol station
F12	0-30	7.4322 N	6.6668 E	Vicinity of petrol station close to mechanic workshop
C4	0-30	7.4557 N	6.6357 E	Pristine site
OKENE				
F13	0-30	7.5623 N	6.2482 E	Vicinity of petrol station
F14	0-30	7.5499 N	6.2378 E	Vicinity of petrol station close to mechanic workshop
F15	0-30	7.5583 N	6.2424 E	Vicinity of petrol station
C5	0-30	7.5806 N	6.2437 E	Pristine site
OBAJANA				
F16	0-30	7.9213 N	6.4303 E	Vicinity of petrol station, close to a cassava farm
F17	0-30	7.9291 N	6.4047 E	Vicinity of petrol station
F18	0-30	7.9134 N	6.4412 E	Vicinity of petrol station close to residential area
C6	0-30	7.9199 N	6.4330 E	Pristine site
LOKOJA				
F19	0-30	7.8426	6.7466	Vicinity of petrol station, with motor park and open market
F20	0-30	7.7999	6.7421	Vicinity of petrol station close to shops and school
F21	0-30	7.7983	6.7240	Vicinity of petrol station close to motor park
C7	0-30	7.8025	6.7334	Pristine site

F = Filling Station Sample; C = Control Sample

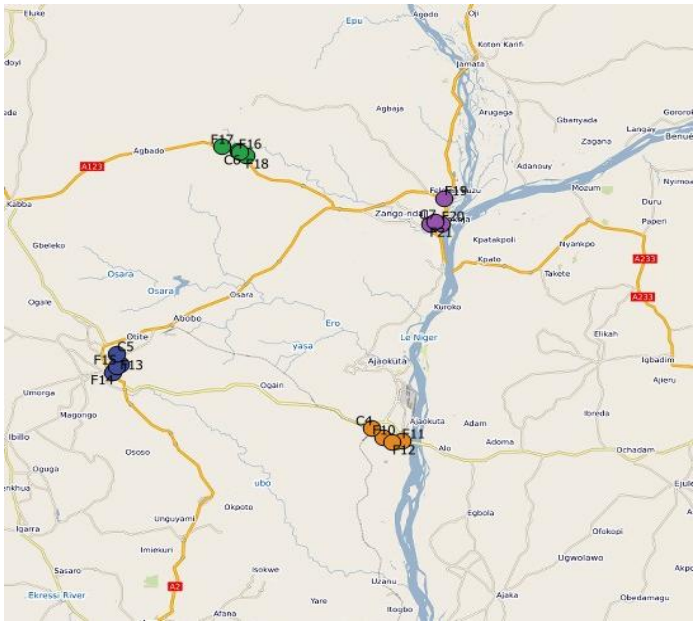

Figure 1: GPS Map of the Study Area Showing the Sampling Locations

Determination of Soil Physicochemical Parameters

Soil pH was determined as described by Anderson and Ingram (1989), as adopted by Ana et al. (2009). Fifty millilitres of distilled water was added to 20 g of soil sample in a glass beaker; the mixture was stirred for 10 min, left to stand for 30 min, stirred again for 2 min, and the pH of the supernatant was then measured using a digital pH meter after prior calibration. Total organic carbon (TOC) was determined by the Walkley-Black wet acid digestion method, as described by the Food and Agriculture Organization of the United Nations (FAO, 2020). One gram of soil was digested with 10 mL of 1N $K_2Cr_2O_7$ and 20 mL of concentrated H_2SO_4 on a hot plate at 135 °C, cooled, diluted to 200 mL with deionized water, and back-titrated with 0.4 N $FeSO_4$ using o-phenanthroline-ferrous complex (Ferroin) indicator, with the end-point taken as a color change from greenish to brown. Percentage organic carbon was calculated (based on a 77% recovery factor) as:

$$\%\ organic\ carbon = \frac{N(T-B) \times 0.003 \times 100}{W} \times C \quad (1)$$

where N is the normality of $K_2Cr_2O_7$, T and B are the volumes of $FeSO_4$ used in the sample and blank titrations, respectively; W is the mass of soil (g); and C is a correction factor (1.334). Percentage soil organic matter (SOM) was obtained as organic carbon × 1.729 (Ojo *et al.,* 2015).

Particle size distribution was determined by the hydrometer method (Bouyoucos, 1951; Day, 1965; Ugbune & Okuo, 2011; Anegbe *et al.,* 2016). Fifty-one grams of air-dried, 2 mm-sieved soil was dispersed in 50 mL of 5% sodium hexametaphosphate and 100 mL of distilled water, allowed to settle for 30 min, stirred for 15 min, and transferred to a 2 L glass cylinder made up to volume with distilled water. Hydrometer readings were taken 40 seconds (percentage silt) and 3 hours (percentage clay) after inverting and settling the suspension, with percentage sand obtained by difference.

Electrical conductivity (EC) was determined on the filtrate of the pH suspension using a conductivity meter, previously calibrated with standard potassium chloride solution (Olawoyin, 2012).

Sample Preparation

Composite samples were screened to remove plant debris and stones, air-dried at room temperature, homogenized, and sieved through a 2 mm mesh. Samples designated for PAH analysis were stored in amber glass bottles and refrigerated at -4 °C prior to extraction (Mosaed *et al.,* 2015; Cao *et al.,* 2019).

Extraction and Clean-up of PAHs

PAHs were extracted following a modified USEPA method 8270 (Tong *et al.,* 2018; Emoyan *et al.,* 2020). Ten grams of milled soil, mixed with 1 g of pre-heated (650 °C) anhydrous sodium sulphate to absorb residual moisture, was extracted with 20 mL of acetone/dichloromethane (1:1, v/v) by vortex mixing for 20 min. A buffer-salt mixture of 0.5 g sodium acetate and 3 g anhydrous $MgSO_4$ was added to promote phase separation, and the mixture was centrifuged at 2500 rpm for 5 min. The supernatant was collected, and the residue was re-extracted twice. The combined extract was concentrated to 1 mL under a mild stream of nitrogen at 36 °C. Clean-up was carried out on a glass column (15 cm × 1 cm) packed with activated silica gel (60-200 mesh) topped with anhydrous sodium sulphate, pre-eluted with 30 mL dichloromethane. The extract was eluted with 3 × 10 mL portions of dichloromethane, and the eluate was evaporated to dryness under nitrogen prior to GC-MS analysis.

Quality Assurance/Quality Control

o-Terphenyl was used as a surrogate standard to monitor extraction efficiency; 5 µL of a 5.0 µg/L working standard was spiked into each 1 mL extract. Percentage recovery, calculated as the ratio of measured to spiked concentration expressed as a percentage, ranged from 94.0 to 101.6%. Control (pristine) samples were analyzed alongside filling station samples for comparison.

GC-MS Analysis

The 16 USEPA priority PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene) were quantified using a Hewlett Packard (HP) 6890 Gas Chromatograph-Mass Spectrometer fitted with dual injector and column, under the conditions summarized in Table 2.

Table 2: GC-MS Programming Conditions

Component	Condition
Injector Temperature	280 °C
Oven Temperature Program	130 °C hold 1 min, 5 °C/min to 300 °C, hold 9 min
Detector Temperature	320 °C
Carrier Gas	Helium
Make-up Gas	Argon/Methane
Column Flow Rate (RTX-XLB)	2.0 mL/min
Column Flow Rate (Rtx-CLPAH)	1.0 mL/min
Injection Volume	1 µL
Data System	HP Chem Station

Source Apportionment: Diagnostic Ratios

The relative proportions of low-molecular-weight (LMW, 2-3 rings) to high-molecular-weight (HMW, 4-6 rings) PAHs, and isomer-pair ratios (Ant/(Ant+Phe), BaA/(BaA+Chr), Flt/(Flt+Pyr), Pyr/Flt, InP/(InP+BP)), were computed from the mean PAH concentrations to distinguish petrogenic from pyrogenic sources, following the diagnostic thresholds of Yunker et al. (1996, 2002) as adopted by Emoyan et al. (2020). The diagnostic ratio approach is widely applied in large-scale PAH source apportionment studies, where isomer-pair ratios and ring-wise composition profiles are used together to isolate petrogenic from pyrogenic contributions through multiple urban soils (Wang *et al.*, 2022).

Benzo[a]pyrene Equivalent Concentration (BaPeq)

Because BaP is generally regarded as the largest contributor to the carcinogenic potential of environmental PAH mixtures (Halek *et al.,* 2008), the toxic equivalency factors (TEFs) of Tsai et al. (2004), as adopted by Bortey-Sam et al. (2014), were used to convert individual PAH concentrations to BaP-equivalent concentrations as follows:

$$BaPeq = \Sigma\,(C_i \times TEF_i) \quad (2)$$

where C_i is the concentration of an individual PAH and TEF_i is its corresponding toxic equivalency factor (Table 3).

Table 3: Toxic Equivalency Factors (TEF) Used for BaPeq Calculation (Tsai *et al.*, 2004)

PAH	Abbreviation	No. of Rings	TEF
Naphthalene	Nap	2	0.001
Acenaphthylene	Acy	3	0.001
Acenaphthene	Ace	3	0.001
Fluorene	Flu	3	0.001
Anthracene	Ant	3	0.010
Phenanthrene	Phe	3	0.001
Fluoranthene	Flt	4	0.001
Pyrene	Pyr	4	0.001
Benzo[a]anthracene*	BaA	4	0.10
Chrysene*	Chr	4	0.010
Benzo[b]fluoranthene*	BbF	5	0.10
Benzo[k]fluoranthene*	BkF	5	0.10
Benzo[a]pyrene*	BaP	5	1.0
Dibenzo[a,h]anthracene*	DBA	6	1.0
Indeno[1,2,3-cd]pyrene*	InP	6	0.10
Benzo[g,h,i]perylene	BP	6	0.010

*Carcinogenic PAH

Statistical Analysis

Descriptive statistics (minimum, maximum, mean and standard deviation) were computed from the individual PAH concentrations of the twelve filling-station samples in Zones 1 and 2. Comparisons between the two zones followed the approach used in Kadili, 2021, in which Analysis of Variance (ANOVA) at 95% confidence level and Student's t-test ($\alpha = 0.05$) were used to compare pollutant concentrations at sample locations with their respective control values.

RESULTS AND DISCUSSION

Physicochemical Properties of Soils

The pH of soils in Zone 1 ranged from 5.70 to 6.30, and in Zone 2 from 5.22 to 6.50, with a combined mean of 5.85 for the two zones, within the slightly acidic range typical of soils in the study area. Total organic carbon (TOC) ranged from 0.430 to 1.58% (mean 1.17%) and soil organic matter (SOM) from 0.750 to 2.75% (mean 2.04%) across the two zones. Electrical conductivity (EC) ranged from 16.0 to 26.0 µS/cm (mean 20.3 µS/cm). Particle size analysis showed the soils to be predominantly sandy, with mean sand, silt, and clay contents of 76.7%, 11.4%, and 12.0%, respectively (Tables 4 and 5).

Table 4: Physicochemical Parameters of Soil Samples from the Vicinity of Filling Stations in Zone 1 (Kogi Central)

Sample Code	pH	TOC (%)	SOM (%)	EC (µS/cm)	Sand (%)	Silt (%)	Clay (%)
Ajaokuta							
F10	5.80	0.520	0.910	23.0	68.5	13.0	18.5
F11	5.70	0.430	0.750	24.0	69.8	16.2	14.0
F12	6.00	1.20	2.09	26.0	77.8	9.00	13.2
C4	5.80	0.830	1.45	22.0	75.4	9.60	15.0
Okene							
F13	6.30	0.720	1.25	24.0	68.3	20.0	11.7
F14	5.90	1.23	2.14	19.0	75.5	14.0	10.5
F15	5.70	1.53	2.67	17.0	80.7	10.3	9.00
C5	6.20	0.630	1.09	25.0	82.7	8.80	8.50

Table 5: Physicochemical Parameters of Soil Samples from the Vicinity of Filling Stations in Zone 2 (Kogi West)

Sample Code	pH	TOC (%)	SOM (%)	EC (µS/cm)	Sand (%)	Silt (%)	Clay (%)
Obajana							
F16	5.60	1.31	2.28	21.0	68.9	12.4	18.7
F17	5.80	1.30	2.26	20.0	76.3	7.90	15.8
F18	6.00	1.41	2.46	19.0	75.3	10.2	14.5
C6	6.10	0.800	1.39	20.0	70.6	12.2	17.2
Lokoja							
F19	5.22	1.49	2.59	17.0	86.9	9.10	4.00
F20	5.70	1.58	2.75	16.0	84.8	10.2	5.00
F21	6.50	1.33	2.32	18.0	87.3	4.00	8.70
C7	5.90	0.710	1.24	21.0	83.1	6.90	10.0

Levels of PAHs in Zones 1 and 2

PAH concentrations (µg/kg) in soils from the vicinity of filling stations in Zones 1 and 2 are presented in Tables 6 and 7, respectively, while Figure 2 shows total PAH concentrations in soil samples in the study area. Of the sixteen USEPA priority PAHs, benzo[a]anthracene, chrysene, benzo[k]fluoranthene and benzo[g,h,i]perylene were not detected in any Zone 1 sample, while benzo[k]fluoranthene, benzo[a]pyrene and benzo[g,h,i]perylene were not detected in Zone 2 samples. Total PAH (Σ16PAHs) concentrations in Zone 1 ranged from 0.540 to 5.52 µg/kg (mean 2.55 µg/kg), and in Zone 2 from 2.14 to 5.90 µg/kg (mean 3.45 µg/kg). For the two zones combined (n = 12 filling-station samples), Σ16PAHs ranged from 0.540 to 5.90 µg/kg with a mean of 3.00 µg/kg. Benzo[a]pyrene was detected only at F15 (Zone 1; 0.100 µg/kg) among the filling-station samples and in the control sample C4 (0.240 µg/kg).

Table 6: Levels of PAHs (µg/kg) in Soils from the Vicinity of Filling Stations in Zone 1

		AJAOKUTA			OKENE				
PAH	**ABB**	**F10**	**F11**	**F12**	**C4**	**F13**	**F14**	**F15**	**C5**
Naphthalene	Nap	ND	ND	0.460	0.920	0.640	1.18	0.600	0.420
Acenaphthylene	Acy	0.120	0.100	ND	0.380	0.180	0.340	0.200	0.260
Acenaphthene	Ace	0.0800	0.0800	ND	ND	0.300	0.560	1.84	ND
Fluorene	Flu	ND	ND	ND	ND	ND	0.240	0.200	ND
Anthracene	Ant	0.420	0.360	0.780	ND	ND	0.580	0.180	ND
Phenanthrene	Phe	ND	ND	0.220	ND	0.260	ND	0.220	ND
Fluoranthene	Flt	ND	ND	1.78	0.280	0.260	0.440	1.62	0.180
Pyrene	Pyr	ND	ND	ND	ND	ND	ND	0.560	ND
Benz[a]anthracene*	BaA	ND	ND	ND	ND	ND	ND	ND	ND
Chrysene*	Chr	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[b]fluoranthene*	BbF	ND	ND	ND	ND	ND	ND	ND	0.200
Benzo[k]fluoranthene*	BkF	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[a]pyrene*	BaP	ND	ND	ND	0.240	ND	ND	0.100	ND
Dibenzo[a,h]anthracene*	DBA	ND	ND	ND	ND	ND	0.0800	ND	ND
Indeno[1,2,3-cd]pyrene*	InP	ND	ND	ND	ND	ND	0.300	ND	ND
Benzo[g,h,i]perylene	BP	ND	ND	ND	ND	ND	ND	ND	ND
Σ16PAHs	-	0.620	0.540	3.24	1.82	1.64	3.72	5.52	1.06
Σ7*PAHs	-	ND	ND	ND	0.240	ND	0.380	0.100	0.200

*Carcinogenic PAH; ND = Not Detected.

Table 7: Levels of PAHs (µg/kg) in Soils from the Vicinity of Filling Stations in Zone 2

		OBAJANA			LOKOJA				
PAH	**ABB**	**F16**	**F17**	**F18**	**C6**	**F19**	**F20**	**F21**	**C7**
Naphthalene	Nap	0.620	0.620	0.120	0.420	0.860	2.44	0.860	0.120
Acenaphthylene	Acy	ND	ND	0.660	0.140	0.320	0.240	ND	0.640
Acenaphthene	Ace	0.100	0.100	0.240	0.220	0.520	0.560	0.840	0.480
Fluorene	Flu	ND	ND	0.480	0.320	0.220	0.240	0.340	0.220
Anthracene	Ant	0.360	0.360	0.220	ND	0.380	0.780	0.280	ND
Phenanthrene	Phe	0.180	0.180	ND	ND	0.220	ND	0.140	0.200
Fluoranthene	Flt	0.880	0.900	0.200	0.640	1.74	0.640	0.840	0.180
Pyrene	Pyr	ND	ND	0.180	0.360	0.260	ND	ND	ND
Benz[a]anthracene*	BaA	ND	ND	0.0800	ND	ND	0.300	ND	ND
Chrysene*	Chr	ND	ND	0.180	ND	ND	ND	ND	ND
Benzo[b]fluoranthene*	BbF	ND	ND	0.0600	ND	ND	ND	ND	ND
Benzo[k]fluoranthene*	BkF	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[a]pyrene*	BaP	ND	ND	ND	ND	ND	ND	ND	ND
Dibenzo[a,h]anthracene*	DBA	ND	ND	0.0800	ND	0.160	0.0800	ND	0.0800
Indeno[1,2,3-cd]pyrene*	InP	ND	ND	ND	ND	ND	0.620	ND	ND
Benzo[g,h,i]perylene	BP	ND	ND	ND	ND	ND	ND	ND	ND
Σ16PAHs	-	2.14	2.16	2.50	2.10	4.68	5.90	3.30	1.92
Σ7*PAHs	-	ND	ND	0.400	ND	0.160	1.00	ND	0.0800

*Carcinogenic PAH; ND = Not Detected

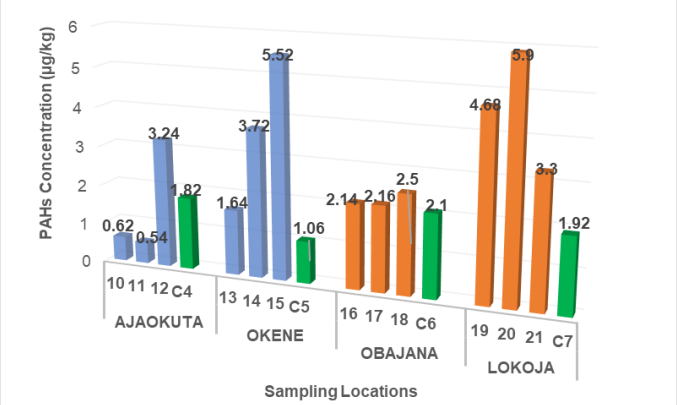

Figure 1: Total PAH Concentrations in Soil Samples in the Study Area

Descriptive Statistics and Ring-wise Distribution

Descriptive statistics of individual PAH concentrations for the combined Zone 1 and Zone 2 filling-station samples (n = 12) are presented in Table 8 and Figure 3. Naphthalene (mean 0.700 µg/kg) and fluoranthene (mean 0.775 µg/kg) were the most abundant individual PAHs. Low molecular weight (2-3 ring) PAHs accounted for 65.7% of total detected PAHs, four-ring PAHs accounted for 30.2%, while five- and six-ring PAHs contributed the least, at 4.12%. Furthermore, as shown in Figure 4, the ring-wise percent abundance of PAHs between the two zones was generally comparable. The low molecular weight (2-3 ring) PAHs dominate the profile in both Zone 1 (66.36%) and Zone 2 (65.18%). Similarly, there is nearly an even distribution of the four-ring PAHs in Zone 1 (30.5%) and Zone 2 (29.98%), while the high molecular weight (5-6 ring) PAHs made up the smallest fraction in both zones, with Zone 2 (4.84%) slightly higher than Zone 1 (3.14%). This near-identical distribution pattern across the two zones suggests a similar mix of PAH sources and formation routes operating at petrol filling stations in both Kogi Central and Kogi West.

This distribution is in line with the pattern earlier reported for the entire Kogi State study area, where 2-3 ring PAHs also dominated (67.4%), a trend attributed to the greater volatility, water solubility, and consequent mobility of low molecular weight PAHs relative to high molecular weight congeners (Kadili, 2021; Wilson & Jones, 1993; Andersson *et al.*, 2003).

Table 8: Descriptive Statistics of PAH Concentrations in Zones 1 and 2 (n = 12)

PAH	Abb.	Rings	Min (µg/kg)	Max (µg/kg)	Mean (µg/kg)	SD	Abundance (%)
Naphthalene	Nap	2	ND	2.44	0.700	0.654	
Acenaphthylene	Acy	3	ND	0.660	0.180	0.195	
Acenaphthene	Ace	3	ND	1.84	0.435	0.513	
Fluorene	Flu	3	ND	0.480	0.143	0.166	
Anthracene	Ant	3	ND	0.780	0.392	0.230	
Phenanthrene	Phe	3	ND	0.260	0.118	0.108	
Σ 2-3 Ring PAHs	-	-	-	-	1.968	-	65.7
Fluoranthene	Flt	4	ND	1.78	0.775	0.648	
Pyrene	Pyr	4	ND	0.560	0.0833	0.173	
Benz[a]anthracene*	BaA	4	ND	0.300	0.0317	0.0876	
Chrysene*	Chr	4	ND	0.180	0.0150	0.0520	
Σ 4 Ring PAHs	-	-	-	-	0.905	-	30.2
Benzo[b]fluoranthene*	BbF	5	ND	0.0600	0.00500	0.0173	
Benzo[k]fluoranthene*	BkF	5	ND	ND	ND	ND	
Benzo[a]pyrene*	BaP	5	ND	0.100	0.00830	0.0289	
Dibenzo[a,h]anthracene*	DBA	6	ND	0.160	0.0333	0.0535	
Indeno[1,2,3-cd]pyrene*	InP	6	ND	0.620	0.0767	0.192	
Benzo[g,h,i]perylene	BP	6	ND	ND	ND	ND	
Σ 5-6 Ring PAHs	-	-	-	-	0.124	-	4.12
Σ16PAHs	-	-	0.540	5.90	3.00	1.75	100

*Carcinogenic PAH; ND = Not Detected; Min/Max/Mean/SD Computed from the 12 Filling-Station Samples (F10-F21); Abundance Calculated on Total Detected PAH Mass

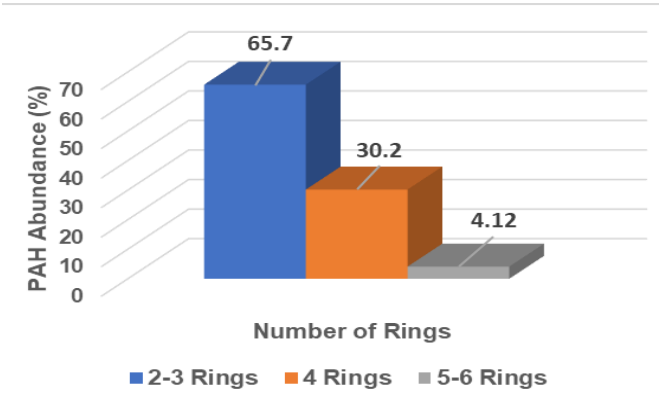

Figure 3: Ring-wise Percent Abundance of PAHs in the Study Area

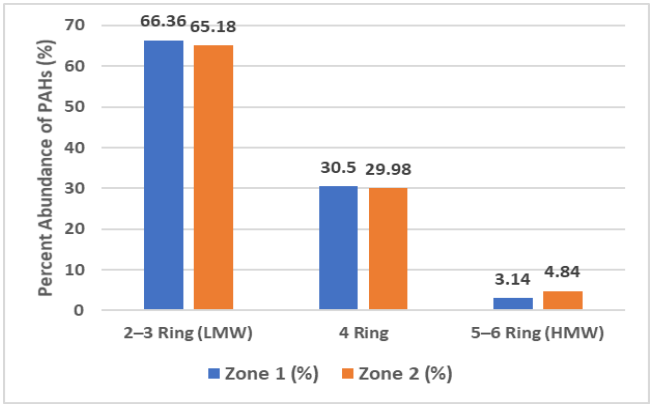

Figure 4: Ring-wise Percent Abundance of PAHs in Zones 1 and 2

Soil Pollution Status

Comparison of the mean concentrations of individual PAHs in Zones 1 and 2 against the Dutch maximum permissible concentrations (MPC) for PAHs in soil (Verbruggen, 2012) showed that all sixteen priority PAHs, including the seven carcinogenic congeners, were well below their respective MPC values (Table 9), indicating that soils in the vicinity of petrol filling stations in Zones 1 and 2 were practically unpolluted with respect to PAHs during the period of investigation. This finding is consistent with the earlier observation for Kogi East study area (Kadili *et al.*, 2021), and with the Dutch Intervention limit of 40,000 µg/kg for total PAHs in soil for residential land use (VROM, 2000), which was also not exceeded.

Table 9: Soil Status of Zones 1 and 2 with Respect to Individual PAH Maximum Permissible Concentrations

PAH	Abb.	Mean (µg/kg)	MPC (µg/kg)	Soil Status
Naphthalene	Nap	0.700	690	Unpolluted
Acenaphthylene	Acy	0.180	170	Unpolluted
Acenaphthene	Ace	0.435	680	Unpolluted
Fluorene	Flu	0.143	1,600	Unpolluted
Anthracene	Ant	0.392	340	Unpolluted
Phenanthrene	Phe	0.118	3,600	Unpolluted
Fluoranthene	Flt	0.775	4,800	Unpolluted
Pyrene	Pyr	0.0833	1,800	Unpolluted
Benz[a]anthracene*	BaA	0.0317	190	Unpolluted
Chrysene*	Chr	0.0150	1,600	Unpolluted
Benzo[b]fluoranthene*	BbF	0.00500	790	Unpolluted
Benzo[k]fluoranthene*	BkF	ND	790	Unpolluted
Benzo[a]pyrene*	BaP	0.00830	160	Unpolluted
Dibenzo[a,h]anthracene*	DBA	0.0333	180	Unpolluted
Indeno[1,2,3-cd]pyrene*	InP	0.0767	380	Unpolluted
Benzo[g,h,i]perylene	BP	ND	490	Unpolluted
Σ16PAHs	-	3.00	-	-

MPC = Dutch Maximum Permissible Concentration (Verbruggen, 2012); *Carcinogenic PAH; ND = Not Detected

Source Apportionment: Diagnostic Ratios

Molecular diagnostic ratios computed from the mean PAH concentrations in Zones 1 and 2 are presented in Table 10. The LMW/HMW ratio (1.91, > 1.0) suggested a petrogenic contribution, consistent with fuel spillage at the filling stations. However, the isomer-pair ratios, Ant/(Ant+Phe) = 0.768 (> 0.1), Flt/(Flt+Pyr) = 0.903 (> 0.4) and BaA/(BaA+Chr) = 0.679 (> 0.2), all exceeded the thresholds associated with petroleum sources, pointing instead to a predominantly pyrolytic (combustion-derived) origin, consistent with automotive emissions, biomass and fuel combustion within and around the filling stations. The InP/(InP+BP) ratio of 1.0 (driven by the absence of detectable benzo[g,h,i]perylene in both zones) is also indicative of a combustion source (Yunker *et al.,* 2002). Therefore, the diagnostic ratios suggest that PAHs in Zones 1 and 2 originated from a mixed but predominantly pyrogenic source, with a smaller petrogenic contribution from fuel spillage and leakage, in agreement with the source pattern earlier reported by Kadili (2021) for the entire Kogi State study area (60% pyrolytic, 40% petrogenic).

Table 10: Diagnostic Ratios of PAHs in Zones 1 and 2 (Based on Mean Concentrations)

PAH Ratio	Value (Zones 1+2)	Threshold	Inferred Source
LMW/HMW	1.91	> 1.0 = Petrogenic	Petrogenic
Phe/Ant	0.302	-	-
Ant/(Ant+Phe)	0.768	< 0.1 Petrogenic; > 0.1 Pyrolytic	Pyrolytic
Chr/BaA	0.474	< 0.4 = Petrogenic	Pyrolytic
BaA/(BaA+Chr)	0.679	< 0.2 Petrogenic; > 0.2 Pyrolytic	Pyrolytic
Flt/(Flt+Pyr)	0.903	< 0.4 Petrogenic; > 0.4 Pyrolytic	Pyrolytic
Pyr/Flt	0.108	> 1.0 = Petrogenic	Petrogenic
InP/(InP+BP)	1.00	< 0.2 Petrogenic; > 0.2 Pyrolytic	Pyrolytic

Diagnostic Thresholds Adopted from Yunker et al. (1996, 2002) and Emoyan et al. (2020)

Benzo[a]pyrene Equivalent Concentration (BaPeq)

The BaPeq of total detected PAHs (Σ16BaPeq) in Zones 1 and 2 ranged from 0.00164 to 0.184 µg/kg, with a mean of 0.0595 µg/kg (Table 11). The mean BaPeq contributed by the seven carcinogenic PAHs alone (Σ7BaPeq) was 0.0532 µg/kg, representing about 89% of Σ16BaPeq, confirming that the carcinogenic congeners, particularly BaA, DBA, InP and BaP, dominate the toxic equivalency burden despite their low absolute concentrations. The highest BaPeq (0.184 µg/kg) was recorded at F20 (Lokoja, Zone 2), showing its relatively high indeno[1,2,3-cd]pyrene content. The mean Σ16BaPeq value obtained (0.0595 µg/kg) is several orders of magnitude below the 600 µg/kg Canadian Soil Environmental Quality guideline value for Σ16BaPeq (Yu *et al.,* 2020), and also below levels reported for more heavily polluted sites, such as 1,245 µg/kg (Cao *et al.,* 2019), 157.6 µg/kg (Bortey-Sam *et al.,* 2014) and 6,655.1 µg/kg (Yu *et al.,* 2020). This suggests low carcinogenic potential associated with PAH-contaminated soils near petrol filling stations in Zones 1 and 2 during this investigation.

Table 11: Benzo[a]pyrene Equivalent Concentrations (BaPeq, µg/kg) for all Samples

Sample	Σ16BaPeq	Σ7*BaPeq
F10	0.00440	ND
F11	0.00378	ND
F12	0.0103	ND
F13	0.00164	ND

Sample	Σ16BaPeq	Σ7*BaPeq
F14	0.119	0.110
F15	0.107	0.100
F16	0.00538	ND
F17	0.00540	ND
F18	0.0999	0.0958
F19	0.168	0.160
F20	0.184	0.172
F21	0.00582	ND
Mean	0.0595	0.0532

*Σ7 Refers to the Seven Carcinogenic PAHs (BaA, Chr, BbF, BkF, BaP, DBA, InP); ND = Not Detected

Because the mean and range of BaPeq values obtained for Zones 1 and 2 fall within the same order of magnitude previously reported for the whole Kogi State study area (mean 0.140 µg/kg, range 0.230 - 1.94 µg/kg), for which Incremental Lifetime Cancer Risk (ILCR) values computed using the standard USEPA exposure model (USEPA, 1996; Yang *et al.,* 2014) were found to lie between 10^{-11} and 10^{-10} for children and adults across the ingestion, dermal and inhalation pathways, well below the USEPA acceptable risk range of 10^{-6} to 10^{-4} (USEPA, 1993), the carcinogenic health risk associated with PAH-contaminated soils in Zones 1 and 2 can reasonably be inferred to be likewise negligible.

Statistical Analysis

Results show no significant difference in the total PAH levels in the four sampled towns ($F(3,8) = 3.02$, $p = 0.094$). Although mean values were numerically higher in Okene and Lokoja, concentrations at filling stations were, however, significantly higher than at pristine control sites ($t = -2.30$, $p = 0.038$).

Discussion

PAH Concentrations in Zones 1 and 2

The mean Σ16PAHs concentration was higher in Zone 2 (3.45 µg/kg) than in Zone 1 (2.55 µg/kg). Within Zone 2, Lokoja recorded higher total PAH levels than Obajana, which may be attributable to the higher vehicular traffic density, congestion, and combustion activity associated with Lokoja as the State capital, where filling stations are frequently sited along major roads and close to motor parks and markets. Previous studies have similarly reported elevated PAH concentrations in urban and roadside soils compared with less congested areas (Wild & Jones, 1995; Mosaed *et al.,* 2015).

The PAH concentrations recorded in Zones 1 and 2 were generally lower than those reported for petrol station and mechanic workshop soils elsewhere in Nigeria and beyond, for example, 4.28-29.77 mg/kg reported by Nganje et al. (2014) for Calabar Metropolis and 8,682.927 µg/kg reported by Anegbe et al. (2016) for mechanic workshop soils in Benin City. Similarly, more recent studies in Nigeria report elevated levels of PAHs at petroleum-impacted sites; for instance, mean ΣPAH concentrations of 5.58-6.4 µg/g were recorded around automobile repair workshops in Ado-Ekiti (Adesina *et al.,* 2024), while soils around gas-flaring points in the Niger Delta showed ΣPAH concentrations several orders of magnitude higher than those recorded in the present study. This is traceable to the much longer history of hydrocarbon combustion at those sites (Odali *et al.,* 2024). The comparatively low PAH levels recorded in the present study suggest that soils in the area have not yet experienced contamination of a similar magnitude, probably attributable to a shorter or less intense history of major fuel spillage in the study locations relative to the sites of these studies, as well as differences in soil physicochemical characteristics, transport mechanisms and other ecological conditions determining PAH accumulation and degradation.

Benzo[a]pyrene concentrations at all sampled sites in Zones 1 and 2 were below 1 µg/kg, and hence far below the UK generic assessment criteria range of 1.08-1.32 mg/kg for residential land use (Cheng & Nathanail, 2009), supporting the conclusion that the sampled soils were not contaminated with respect to this priority carcinogen.

Ring-wise Distribution and Soil Characteristics

The dominance of low molecular weight (2-3 ring) PAHs in Zones 1 and 2 mirrors patterns commonly reported for soils close to fresh fuel sources, since LMW PAHs, being more volatile and water-soluble, are readily transported and deposited relative to high molecular weight congeners, which tend to be more persistent once formed by high-temperature combustion processes (Means *et al.,* 1980; Wilson & Jones, 1993). The predominantly sandy texture of soils in the two zones (mean sand content 76.7%), with correspondingly lower clay content, implies a comparatively lower adsorptive capacity for PAHs, favoring greater mobility and reduced accumulation relative to finer-textured soils (Xu *et al.,* 2014).

Source Apportionment

The diagnostic ratios computed for Zones 1 and 2 indicate a predominantly pyrolytic origin for the detected PAHs, consistent with combustion of fuel, wood, and biomass associated with vehicular movement, generator use and open burning around filling stations, with a smaller petrogenic input reflected in the LMW/HMW and Pyr/Flt ratios, likely arising from direct fuel spillage and leakage at the stations. This mixed-source pattern parallels the interpretation for the wider Kogi State study area, and is consistent with reports that PAHs with two to four rings are more volatile and mobile, and can therefore originate from petrogenic sources even where the bulk of detected PAHs reflect pyrogenic input (Itodo *et al.,* 2019). A similar diagnostic-ratio-based source-identification approach applied to banknote dust in Benin City likewise attributed detected PAHs predominantly to diesel and vehicular emissions, alongside wood/coal combustion (Amayo *et al.,* 2026). This finding reinforces that combustion-derived PAHs remain the dominant source signature across diverse contaminated matrices in Nigerian urban and peri-urban settings.

Human Health Risk Implication

The consistently low BaPeq values obtained across all sampled sites in Zones 1 and 2, well below international soil quality guideline values, together with the inferred negligible ILCR levels, suggest that direct ingestion, dermal contact and inhalation exposure to PAH-contaminated soil dust in the vicinity of petrol filling stations in Kogi Central and Kogi West did not, at the time of this study, constitute an appreciable carcinogenic health risk to residents of the two

districts. However, this differs from findings from more heavily petroleum-impacted Nigerian sites, where total ILCR values for both adults and children have been reported to exceed the WHO/USEPA acceptable risk threshold of 10^{-6} by several orders of magnitude (Adesina *et al.*, 2024). The results show comparatively lower carcinogenic burden associated with PAH contamination in filling station soils in the study area. Nonetheless, because PAHs are persistent, bioaccumulative, and toxic even at low concentrations, persistent monitoring is needed, particularly given the ongoing proliferation of filling stations in the study area.

CONCLUSION

Soils in the vicinity of petrol filling stations in Zone 1 (Ajaokuta and Okene) and Zone 2 (Obajana and Lokoja), representing Kogi Central and West Senatorial districts of Kogi State, Nigeria, contained all sixteen USEPA priority PAHs except benzo[k]fluoranthene, with total PAH concentrations ranging from 0.540 to 5.90 µg/kg (mean 3.00 µg/kg), below the Dutch maximum permissible concentrations for individual and total PAHs. Low molecular weight (2-3 ring) PAHs dominated the PAH profile (65.7%), and diagnostic ratio analysis indicated that the detected PAHs were derived mainly from pyrolytic sources, with a smaller petrogenic contribution. The mean benzo[a]pyrene equivalent concentration (0.0595 µg/kg) was far below international soil quality guideline values, denoting a low carcinogenic potential from PAH exposure in the study area. These results provide baseline PAH contamination data for Kogi Central and Kogi West Senatorial Districts, complement previously reported data for Kogi East, and support continued environmental monitoring around petrol filling stations in Kogi State.

Conflict of Interest Statement

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

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