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Characterisation of Hydrocarbon Pollutants in Soils from Selected Areas in Abraka, Delta State, Nigeria

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ABSTRACT: The concentration, distribution and sources of petroleum hydrocarbons in soils from selected areas in Abraka, Delta State, were evaluated. Soil samples were collected from areas suspected to be contaminated with petroleum hydrocarbons, which were also in proximity to human population. These areas included busy junctions, generator maintenance workshops, suya joint, drainage and fuel stations. Samples were extracted using n-hexane/dichloromethane mixture and quantified using gas chromatograph-flame ionization detector. The concentrations of n-alkanes ranged from <0.01 – 10,912 µg kg^{-1}, while molecular indices showed that the n-alkanes in the soils originated from different anthropogenic sources. For polycyclic aromatic hydrocarbons (PAHs), the $\sum$17 PAHs in soils ranged from 32 to 162 µg kg^{-1}. The decreasing order of PAHs followed the order: suya joint > generator maintenance workshops > drainage > fuel station > busy junction, while the occurrence pattern with respect to ring size was of the order: 3-rings > 4-rings > 2-Rings > 5-rings > 6-rings. The lower molecular weight (2-3 rings) and non-carcinogenic PAHs were predominant in the studied soils. The isomeric ratios and principal component analysis indicated that PAHs in these soils originated from high temperature combustion of biomass and fossil fuels, as well as traffic emissions.

Keywords: Polycyclic aromatic hydrocarbons, n-alkanes, Isomeric ratios, Principal component analysis

Introduction

Hydrocarbons include a class of organic chemical compounds that are composed of carbon and hydrogen as the elements only. They are naturally occurring, and are the principal constituents of petroleum and natural gas (Carey, 2021). Petroleum and natural gas are extensively used worldwide as fuel (Ahmed and Fakhruddin, 2018). Petroleum hydrocarbons consist mainly of saturates, aromatic hydrocarbons, resins and asphaltenes (i.e. *SARA* analysis) (Wang *et al*., 2006). The saturates (*n*-alkanes or aliphatic hydrocarbons) include paraffins – straight and branch chain alkanes; naphthalene – cycloalkanes; and unresolved complex mixtures (UCM); and are the major constituents of several refined petroleum products, such as diesel fuel, gasoline, kerosene, etc. (Adeniji *et al*., 2017). The aromatics are cyclic, planar compounds that resemble benzene in electronic configuration and chemical behavior, and they include polycyclic aromatic hydrocarbons (PAHs) and benzene, toluene, ethylbenzene and xylene (BTEX) (Wang *et al*., 2006).

The use of petroleum hydrocarbons and their fractions is on the increase in our society due to increasing urbanization, industrialization and population growth, and the occurrence of these compounds is increasingly altering the quality of that environment. Certain fractions of petroleum hydrocarbons display high toxicities to soil biota once they are present in the environment, and they have been associated with inducing severe health issues in humans (Ball and Truskewcz, 2013). Light fractions of petroleum hydrocarbon (e.g. diesel and gasoline) are used mainly in automobiles, and they have different n-alkanes and PAHs composition that distinguish one from another (Wang and Fingas, 2005).

The n-alkanes are mostly derived from anthropogenic (urbanisation, industrialisation, shipping and oil operations) and biogenic (terrestrial plants, algae, bacteria, etc.) sources (Sakari *et al*., 2008). PAHs can be

introduced into the environment from natural disasters, e.g. volcanic eruption, combustion of biomass (Ivwurie *et al.*, 2016). The anthropogenic sources of PAHs contribute significant concentrations to the environment, and they include - incomplete combustion of fossil fuels in power generation, internal combustion engines, refuse incineration (i.e. pyrogenic), and from petroleum spills, atmospheric depositions, offshore activities, natural oil seeps and transport of petroleum (i.e. petrogenic), etc. (Inengite *et al.*, 2010; Ilechukwu *et al.*, 2016). The fate of these released contaminants to the environment is important because they are mutagenic, toxic and carcinogenic (Adedosu *et al.*, 2012). Characteristics such as low water solubility, adsorption to particulate matter and lipophilicity make hydrocarbons a potential toxic group of environmental contaminants (Macias-Zamora *et al.*, 2002). Soil contamination in particular, can pose significant risk to human health and the environment via migration from soil to crops and groundwater, as well as transformation of several petroleum products into more lethal substances (Zhang *et al.*, 2015). Considering the proximity of many of these emission sources to human population, there is a high tendency for these contaminants to get to man, either through inhalation, ingestion or dermal contact.

The *n*-alkanes and PAHs levels are commonly used for characterizing organic matter in several environmental matrices, which can be used to identify, differentiate and determine their risk to human health and the environment (Yang *et al.*, 2011). Since n-alkanes are non-polar and are inherently stable to photodegradation, they can be employed in distinguishing between biogenic and petrogenic hydrocarbons (Gao and Chen, 2008; Ilechukwu *et al.*, 2016), identification of hydrocarbon pollution and their sources (Iwegbue *et al.*, 2016), as well as in the evaluation of the product of degradation of spilled hydrocarbon compounds in soil (Adedosu *et al.*, 2012). Therefore, the characterisation of petroleum hydrocarbons in contaminated soils is necessary tool for the assessment of environmental impacts and possible remediation (Stout *et al.*, 2007). Also, the identification of the impact of industrialization, urbanization and other anthropogenic activities on the environment requires background information and pre-development concentration of contaminants in environmental media (Wiklund *et al.*, 2012).

Some studies have shown that the concentration of hydrocarbons in soil vary, depending on the source of hydrocarbon. Ivwurie *et al.* (2016) reported that soils from selected communities in Delta State had PAH input from liquid fossil fuel due to crude oil spill in the area and vehicular emissions. Emoyan *et al.* (2020a) reported that the levels of aliphatic hydrocarbons in soils from petroleum tank farms in the Niger Delta ranged from 14.3-889.7 mg kg^{-1}, which were within the UNEP guideline value of 10,000 mg kg^{-1}. Adedosu *et al.* (2012) determined the levels of n-alkanes and PAHs in soils from gas plants. The soils were classified as being moderately polluted, and the pollution level was attributed to the gas flaring activities that occurred in previous years in the area. Adedosu *et al.* (2013) also characterized aliphatic hydrocarbons and polycyclic aromatic hydrocarbon (PAHs) levels in soil from oil sand deposits in Ondo State, Nigeria. The PAHs level were reported to range from 10.04 - 36.07 mg kg^{-1}, which indicated that the soils were not polluted with PAHs. Iwegbue *et al.* (2016) determined the concentration of PAHs and assessed the health risk of the determined PAHs in urban soil in the Niger Delta. The concentration of 16-PAHs ranged from 188 - 684 µg kg^{-1}, while the concentration of carcinogenic PAHs ranged from 28.5-571 µg kg^{-1}. Emoyan *et al.* (2011) showed that petrogenic processes were the main sources of PAHs in soils in the vicinity of fuel stations in Abraka, Delta State. Emoyan *et al.* (2020) also observed significant seasonal variation in PAHs level in soils from selected vehicle parks in Southern Nigeria, and the principal source of PAHs in the soils was pyrogenic, mostly from emissions from vehicular traffic and combustion.

The aim of this study was to evaluate the concentration, distribution pattern and identification of the source of n-alkanes and PAHs in soils from selected areas in Abraka, Delta State, Nigeria.

Materials and methods

Study area: The study area, Abraka, is located between latitude 5°45^1 and 5°50^{1}N, and longitude 6° and 6°15^{1}E. According to UNDP (2006), the rainfall pattern is characteristic of the rainforest zone with mean annual rainfall of 3000 mm. Temperatures are high and fairly constant all through the year. Average monthly temperature for the warmest months (February to April) range from 28°C to 33°C while the average monthly temperature for the coolest months (June – September) range between 21°C and 23°C. A map of Delta State, indicating the study area, is shown in Figure 1.
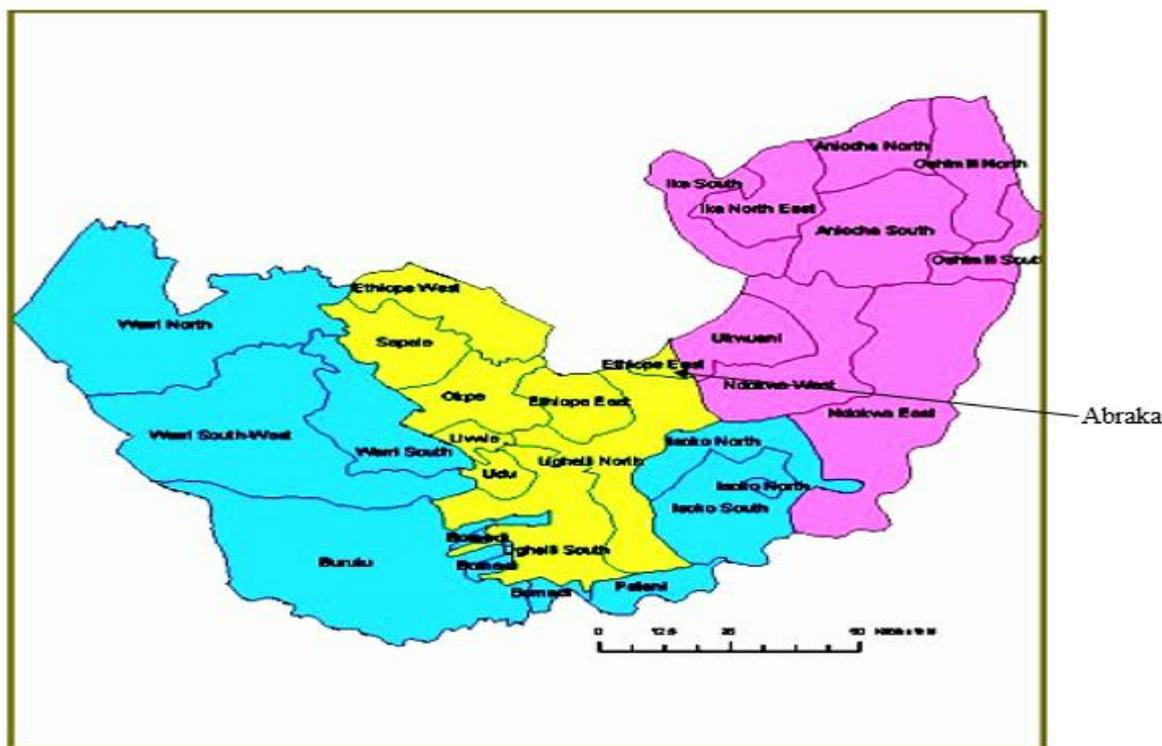
Figure 1: Map of Delta State, indicating the study area

Sample collection: Soil samples for this study were collected from areas suspected to be contaminated with petroleum products, and that were in close proximity to human population in Abraka, Delta State. These areas were investigated to evaluate the concentrations of n-alkanes and PAHs arising from the nature of activities in the locations. The areas selected for the study were; busy junctions, fuel stations, generator maintenance workshops, drainage, and suya joint (areas where beef is smoked over hot charcoal). A sample that served as control was collected from a virgin farmland that was not probably exposed to such contamination.

Composite top-soil samples (comprising 3 to 4 samples from each location and mixed) from the identified locations above were collected at a depth 0-10 cm using a stainless steel soil auger. The samples were transferred into aluminum foil, kept in cooler with ice packs and transported to the laboratory. In the laboratory, the samples were air-dried in the dark at room temperature, after which foreign objects such as leaves, sticks, rocks, etc. were removed. The samples were then ground (size reduced) with mortar and pestle, sieved using 2 mm mesh and kept in amber bottles prior to analyses.

Sample extraction: The extraction of n-alkanes and PAHs was done using the ultrasonication method (EPA Method 3550B) (US EPA, 1996). 10.0 g of soil sample was weighed individually into a 100 mL glass beaker and homogenized with 10.0 g of anhydrous Na_2SO_4 until a completely dry homogenate was obtained. 20 mL of dichloromethane (DCM) was added to the dry homogenate soil sample inside a 100 mL beaker. This was then shaken for 30 minutes in a mechanical shaker, transferred to a sonicator and sonicatation was carried out for 30 minutes at 70°C. After sonication, 5.0 g of anhydrous Na_2SO_4 was added to the samples again to remove any residual water molecules. This was allowed to stand for 15 minutes. The extract was then reduced to 2 mL (i.e. concentrated) in a rotary evaporator.

Preparation of packed fractionating column: Glass columns were packed with chromatograph glass wool, and 10 g of 60-120 mm mesh silica gel pre-conditioned (baked) at 105 °C overnight was dissolved with DCM to form slurry, and the slurry was added into the column. 5 g of anhydrous sodium sulphate was added to the fractionating glass column to absorb water and this was condition with 10 mL of DCM prior to extraction.

Clean-up procedure for n-alkanes and quantification: The column was eluted with 10 mL of hexane, then, the eluate was concentrated to 1 mL in a round bottom flask using a rotary evaporator. The concentrate was transferred into a 2 mL Teflon screw-cap vial and labelled ready for GC-FID aliphatic analysis (prior to analysis, the round bottom flask was rinsed with acetone).

The n-alkanes concentration in the concentrated extracts was determined using a gas chromatograph with flame ionization detector (Agilent 6890, Palo, Alto, CA, USA). A 1.0 µL aliquot of the sample was injected into the GC via pulsed splitless mode. The carrier gas was hydrogen with a flow velocity of 1.0 mL min^{-1}. The temperature of the column was initially programmed at 50 °C for 5 min, thereafter, ramped to 300 °C at 5 °C

min^{-1} with 10 min held on time. The temperature of the sample injection port and detector was programmed at 280 °C and 300 °C respectively. Identification of *n*-alkanes was done by matching the retention times of the samples with those of n-alkanes authentic standards.

Clean-up procedure for PAHs and quantification: Into the same column containing 1 mL of extracted sample, the column was eluted with 10 mL of DCM (US EPA Method b100, US EPA, 1986). The eluate was collected in a solvent rinsed 100 mL conical flask. The eluate was transferred into a round bottom flask and concentrated to 1 mL using a rotary evaporator. The concentrate was pipetted into a clean 2 mL Teflon screw-cap vial and cap tightly and labelled ready for GC-MSD PAHs analysis

The sample was then injected into the GC-MSD for PAH analysis using the Agilent 6890-5973N Gas Chromatograph-Mass Selective Detector (GC-MSD). Agilent Technologies Inc MSD Chemstation G1701DA D.03.00.611 software was used in quantifying PAHs results in ppm (part per million)

Quality control/assurance and statistical analysis: In order the check the efficiency of the extraction process for target PAHs, the spike recoveries of the isotopically labeled and unlabeled PAHs in matrix spike samples were carried out. Analysis of method blanks was also carried out. The data were analyzed statistically with SPSS.

Source identification of n-alkanes

Ratio of low molecular weight to high molecular weight (LMW/HMW): The LMW/HMW alkanes ratio <1 depicts *n*-alkanes associated with higher plants, marine animals and sedimentary bacteria, while the ratio of LMW/HMW alkanes close to 1 relates to *n*-alkanes arising from petroleum and plankton sources, and LMW/HMW value >2 suggests contamination from fresh oil input (Gao and Chen, 2008).

Carbon Preference Index (CPI): This is defined as the ratio of odd-numbered *n*-alkane to even-numbered *n*-alkane. The CPI was calculated using the equation below on the entire carbon range (Aboul-Kassim and Simoneit, 1995):

$$CPI_{25-33} = 0.5 \times \left[\frac{C25+C27+C29+C31+C33}{C24+C26+C28+C30+C32} \right] + \left[\frac{C25+C27+C29+C31+C33}{C26+C28+C30+C32+C34} \right]$$

n-alkanes in biogenic materials, such as algae, generally show an odd predominance and thus CPI values higher than 1, while, petrochemical-derived n-alkanes exhibit a wide distribution range, with no predominance of odd over even n-alkanes, give values close to 1.

Natural n-alkane ratio (NAR): The NAR was evaluated using the ratio below:

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

NAR close to 1 designates input by higher terrestrial or marine plants (Aly Salem *et al*., 2014).

Terrigenous/aquatic n-alkane ratio (TAR): The ratio of terrigenous to aquatic *n*-alkanes was used to evaluate the contributions of terrigenous and aquatic sources of hydrocarbons. It was evaluated using the below ratio:

$$TAR = \frac{C27 + C29 + C31}{C15 + C17 + C19}$$

TAR > 1 represents terrestrial input, while TAR <1 represents aquatic input (El Nemr *et al*., 2016).

n-alkane/isoprenoid ratio: The ratios *n*-C_{17}/pristane and *n*-C_{18}/phytane, are usually employed to distinguish the presence of freshly derived and degraded petroleum hydrocarbons in sediments (Gao *et al*., 2007). A value <1 is for degraded petroleum and >1 for fresh input.

Average carbon chain length (ACL): This index is useful for the identifying environmental changes for a given ecosystem. An unchanging value of ACL shows that the changes occurring in an environment are minimal (El Nemr *et al*., 2013). It was evaluated using the ratio below:

$$ACL = \frac{25\ (C25) + 27\ (C27) + 29\ (C29) + 31\ (C31) + 33\ (C33)}{C25 + C27 + C29 + 31 + C33}$$

Source identification of Polycyclic Aromatic Hydrocarbons

Diagnostic isomeric ratios: The diagnostic ratios of some PAHs isomers have been employed in identifying their potential sources. The diagnostic ratios of PAHs isomers that will be used in this study and their interpretations in relation to the result of source evaluation of PAHs, are defined in the Table 1 below.

Table 1: Diagnostic ratios for PAHs

Isomeric ratio	Range	Sources
BaP/BghiP	0.3-0.44	Automobile Exhaust
	0.9-6.6	Coal combustion sources
Phen/Ant	< 10.0	Pyrolytic
	>10.0	Petrogenic
Flt/Pyr	<1.0	Petrogenic
	>1.0	Pyrolytic
LMW/HMW	< 1.0	Combustion of fossil fuels or wood
	> 1.0	Petrogenic sources
BaA/(BaA + Chry)	< 0.2	Petroleum
	0.2-0.35	Petroleum combustion
	> 0.35	Coal and biomass combustion
IndP/ (IndP + BghiP)	<0.2	Petroleum origin/input
	0.2-0.5	Petroleum Combustion
	>0.5	Coal, wood, grass combustion
Ant/(Ant + Phen)	< 0.10	Petroleum input
	> 0.10	Combustion process
Flt/(Flt + Pyr)	< 0.4	Petroleum origin
	0.4-0.5	Petroleum combustion
	> 0.5	Coal and biomass/diesel
Total Index	< 4.0	Low temperature combustion processes
	> 4.0	High temperature combustion processes

Source: (Lawal, 2017)

Results

Concentration and distribution of n-alkanes in soil: The total concentration of n-alkanes in soils from the different sources ranged from 24.0 µg kg^{-1} at busy junctions to 58,269 µg kg^{-1} at generator repair workshops (Figure 2). The concentrations and relative composition of n-alkanes in soils across the studied areas showed significant variations ($p<0.05$).

The distribution of n-alkanes in the soils was observed to vary with location and the nature of human activities within the selected areas. Pristane, phytane and several other n-alkanes were detected in the soil samples. The distribution of carbon numbers of n-alkanes across the five sites is represented in Figures 3 to 7. The distribution ranged from $C_{10} - C_{39}$, with peak concentration recorded for C_{34}. The carbon number distribution of n-alkanes was $C_{19} - C_{20}$, C_{26} and C_{35} for soils from the busy junction and those within the vicinity of some fuel stations, respectively. For generator maintenance workshops, the carbon number distribution was from $C_{11} - C_{13}$ and $C_{16} - C_{39}$. There was however no detected n-alkanes in the control sample.

Hopane biomarkers were detected in soils from the vicinity of generator maintenance workshops, and they were found to range from $C_{27} - C_{35}$, with a maximum concentration recorded for C_{34}. Also, the $C_{27} - C_{29}$ sterane biomarkers were detected only in soil samples from the vicinity generator maintenance workshops.
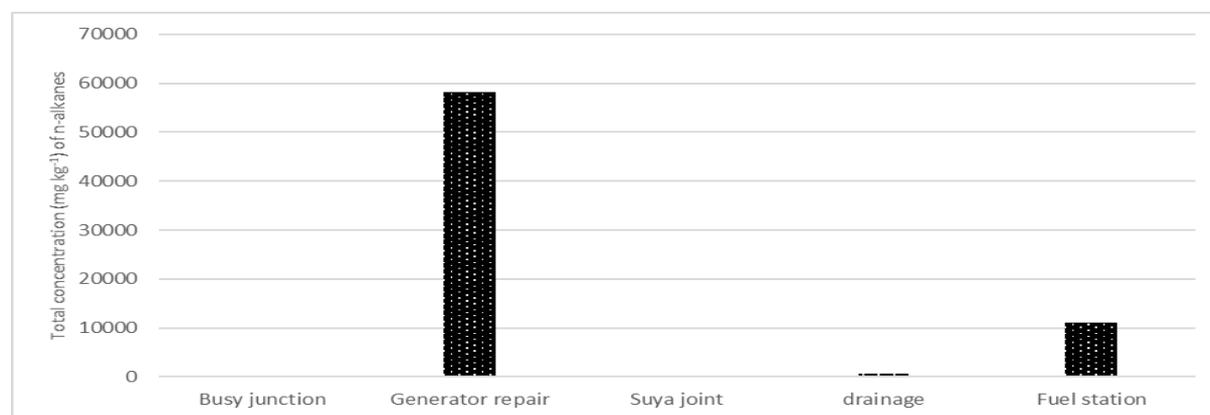
Fig. 2: Total concentration of n-alkanes in soils
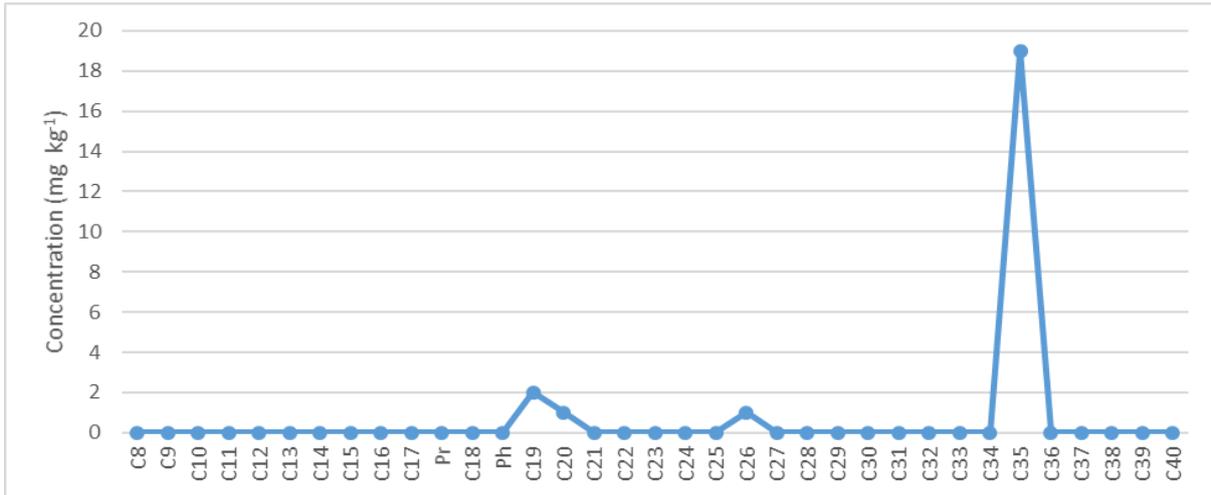
Fig. 3: Concentration and carbon number distribution of n-alkanes in soil from busy junction
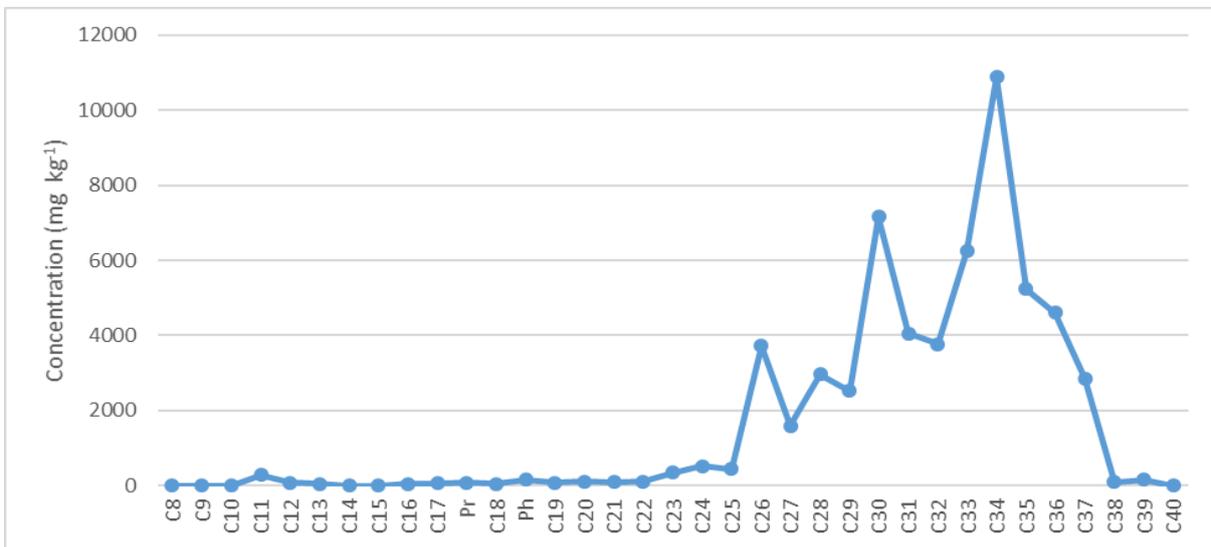
Fig. 4: Concentration and carbon number distribution of n-alkanes in soil from generator maintenance workshop
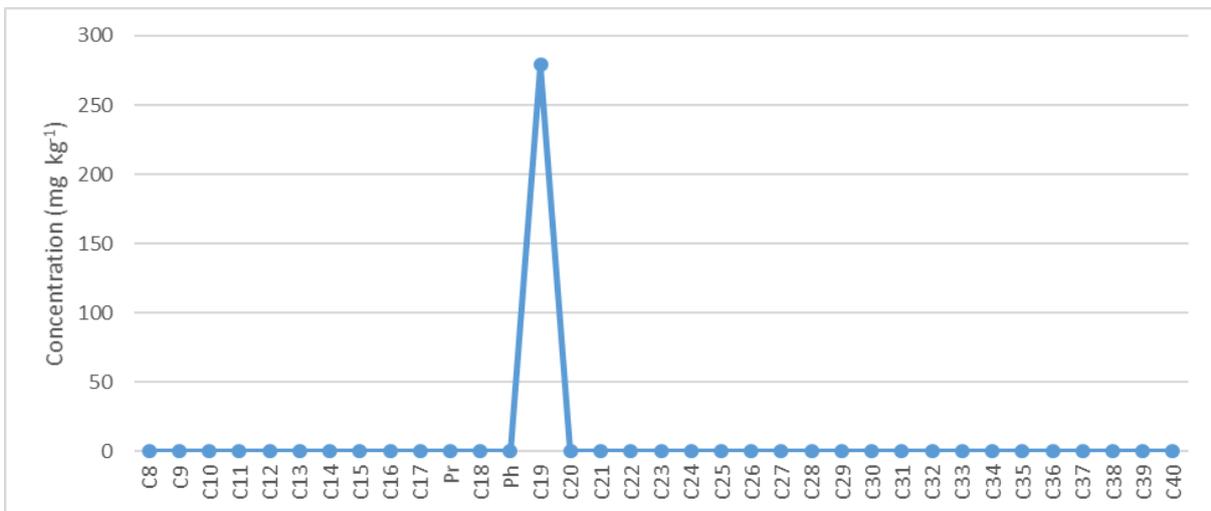
Fig. 5: Concentration and carbon number distribution of n-alkanes in soil from suya joint
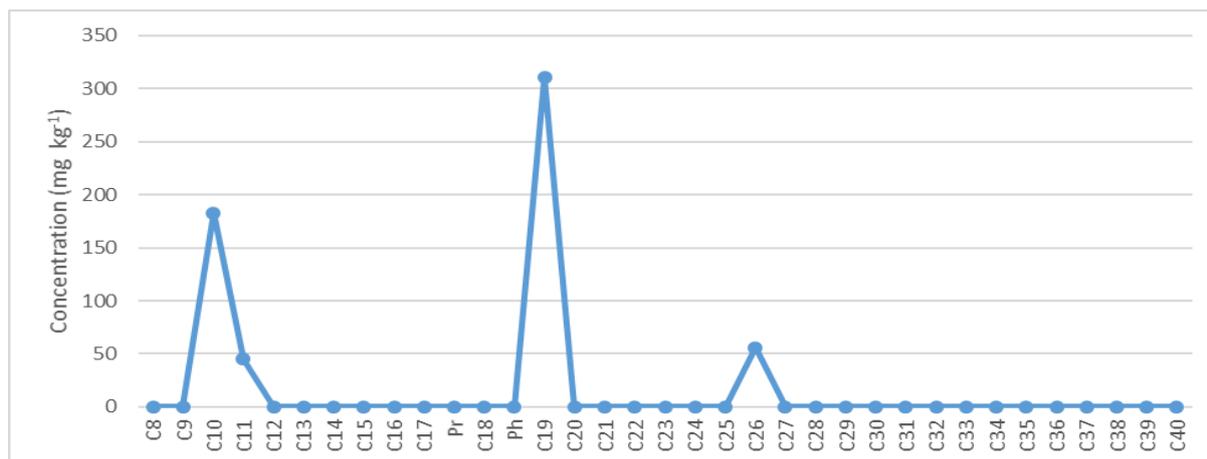
Fig. 6: Concentration and carbon number distribution of n-alkanes in soil from drainage
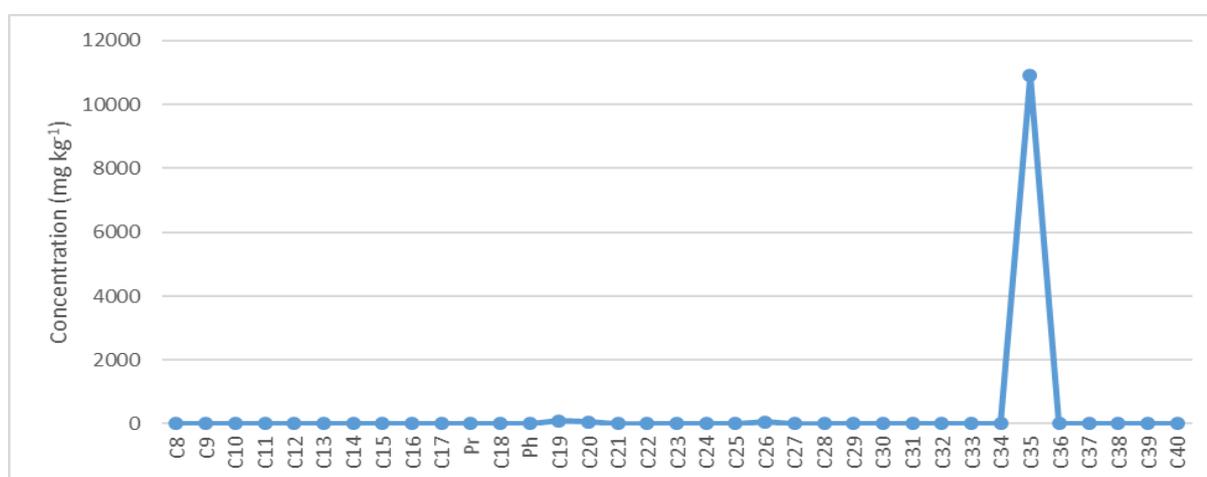
Fig. 7: Concentration and carbon number distribution of n-alkanes in soil from fuel station

Source identification of n-alkanes in soils: The indices used for source identification of n-alkanes in this study are shown in Table 2. The major hydrocarbon (MH) in soils from two of the studied sites (busy junctions and fuel stations) was nC_{35}; nC_{19} was the major hydrocarbon in soils from the drainage and suya joints, while nC_{34} was the major hydrocarbon in soils from generator maintenance workshops.

The CPI values of soils in the studied sites ranged from 0.0 and 0.7. Apart from soils in the vicinity of generator maintenance workshops, all CPI values were 0.0. A CPI value of 0.7 at generator repair shops thus indicated input from recycled organic matter and petroleum products such as lubricating oil.

The ratio of LMW/HMW alkanes in these soils was observed to range from 0.00 to 0.2, which suggest the soils were contaminated with *n*-alkanes associated with higher plants, marine animals and sedimentary bacteria

Table 2: Molecular indices of n-alkanes in soils

Index	Busy Junction	Generator Maintenance Workshops	Suya Joint	Drainage	Fuel Station
MH	C35	C34	C19	C19	C35
LMW/HMW	0.2	0.1	0.0	0.0	0.0
CPI	0.0	0.7	0.0	0.0	0.0
$n\text{-}C_{29}/n\text{-}C_{17}$	0.0	43.3	0.0	0.0	0.0
TAR	1.0	44.4	1.0	1.0	0.0
NAR	0.1	0.0	1.0	0.7	-0.1
ACL	0.0	30.9	0.0	0.0	0.0

Concentration of PAHs in soils: The total concentration ranged from 32 – 162 µg kg^{-1}, with a mean value of 103.6 µg kg^{-1}. The decreasing order of PAHs on location basis followed the order: suya joint > generator maintenance workshops > drainage > fuel station > busy junction. Benzo[a]pyrene, which is regarded as the most carcinogenic PAH congener, was detected only in soil samples from the vicinity of generator maintenance workshops, with a concentration of 6 µg kg^{-1}. Analysis of Variance (ANOVA) result indicated that the concentrations of PAHs in these soils varied significantly (p-value < 0.05; Fcal > Fcrit) with respect to locations.
Profile and distribution of PAHs in soil: The concentrations of detected 2-ring PAHs (i.e. Nap) ranged from 6 µg kg^{-1} ug/kg at busy junctions to 52 µg kg^{-1} at generator maintenance workshops. 3-ring PAHs (Acy + Ace + Flu + Phe + Ant + Car) was highest in suya joint (162 µg kg^{-1}) and least in busy junctions (8 µg kg^{-1}). For 4-ring PAHs (Flt and Pyr), their concentrations were more in generator maintenance workshops, followed by busy junctions, but absent in the other three locations. Similarly, the concentration 5-6 ring PAHs were highest in generator maintenance workshops, followed by busy junctions, and absent in the remaining three locations.

Table 3: Concentration of PAHs concentrations in soil samples

	Concentration (µg kg^{-1})				
	Busy Junction	**Generator Maintenance Workshop**	**Suya Joint**	**Drainage**	**Fuel Station**
Nap	6.0	52.0	ND	ND	ND
Acy	ND	ND	ND	ND	ND
Ace	ND	6.0	ND	ND	ND
Flu	ND	8.0	ND	ND	ND
Phen	ND	26.0	2.0	ND	ND
Ant	ND	22.0	2.0	ND	ND
Car	8.0	8.0	158	128.0	36.0
Flt	6.0	8.0	ND	ND	ND
Pyr	8.0	1ND	ND	ND	ND
BaA	ND	ND	ND	ND	ND
Chry	ND	ND	ND	ND	ND
BbF	ND	8.0	ND	ND	ND
BkF	ND	6.0	ND	ND	ND
BaP	ND	6.0	ND	ND	ND
DahA	ND	ND	ND	ND	ND
IndP	ND	ND	ND	ND	ND
BghiP	4.0	ND	ND	ND	ND
Total	**32.0**	**16.0**	**162**	**128.0**	**36.0**
2-Rings	6.0	52.0	ND	ND	ND
3-Rings	8.0	ND	162	128	36.0
4-Rings	14.0	18.0	ND	ND	ND
5-Rings	ND	20.0	ND	ND	ND
6-Rings	4.0	ND	ND	ND	ND
LMW	6.0	114	4.0	ND	ND
HMW	18.0	38	ND	ND	ND
Carcinogenic	ND	20	ND	ND	ND
Non-carcinogenic	32.0	140	162.0	128.0	36.0

ND = not detected; LMW = lower molecular weight; HMW = higher molecular weight

Source identification of PAHs: The isomeric ratios of PAHs in soil are shown in Table 4. The Ant/(Ant +Phe) ratio for the studied soils ranged from 0.0 – 0.5. This ratio was > 0.1 in soil samples in the vicinity of generator maintenance workshops and suya joints. The ratio of Flt/(Flt + Pyr) in soil samples also ranged from 0.0 – 0.4. Only soils from two locations (busy junctions and generator maintenance workshops) had non zero values. The values obtained (0.4 in both locations) indicated that the origin of PAHs in these environments is petroleum combustion since combustion processes occur in vehicular engines on the highway (i.e. busy junctions), and in gasoline generator maintenance workshops.
The LMW PAH/HMW PAH ratios ranged from 0.0 – 3.2. Only busy junctions and generator maintenance workshops had non-zero values. The values obtained were 0.8 (for busy junctions) and 3.2 (for generator maintenance workshops). The source of PAHs from busy junctions is pyrogenic (i.e. from partial combustion of gasoline/diesel in the internal combustion engines of automobiles), while the source of PAHs in soils within the vicinity of generator maintenance workshops is petrogenic (i.e. from crude oil or its refined products, mainly lubricating/spent engine oil).

Table 4: Isomeric ratios of PAHs in soil

	Busy Junction	Generator Maintenance Workshop	Suya Joint	Drainage	Fuel Station
BaA/(BaA+Chry)	0.0	0.0	0.0	0.0	0.0
IndP/(IndP+BghiP)	0.0	0.0	0.0	0.0	0.0
Ant/(Ant+Phen)	0.0	0.5	0.5	0.0	0.0
Flt/(Flt+Pyr)	0.4	0.4	0.0	0.0	0.0
LMW/HMW	0.8	3.2	0.0	0.0	0.0
COMB PAHs/TPAHs	0.6	0.2	0.0	0.0	0.0
BaP/BghiP	0.0	0.0	0.0	0.0	0.0
Total Index	0.0	0.0	0.0	0.0	0.0

Correlation analysis of PAHs: The result of the interrelationship between PAHs in soil samples are shown in Table 5. When two parameters correlate, it indicates that they are from a common source. As shown in the Table, significant positive correlation ($r^2 > 0.5$) were observed between PAHs compounds at 0.01 and 0.05 level of significance indicating common sources.

Principal Component Analysis (PCA): The PCA result is shown in Table 6 and Figure 7. Two components were identified and accounted for 97.195 % of the variability in the data set. Component 1 accounted for 72.218 % of the total variance and was characterised by high positive loading (> 0.7) of Nap, Ace, Flu, Phen, Ant, BbF, BkF and BaP. Nap, Ace, Flu, Phen, Ant and BbF are markers for wood combustion (Kavouras *et al.* 2001); BkF is a marker for traffic emission (Yang *et al.* 2011) while BaP is a marker for coal combustion (Dong and Lee 2009). Thus Component 1 indicated that the PAHs were from pyrogenic processes such as wood and coal combustion as well as traffic emission. Component 2 accounted for 24.977 % of the total variance and has high positive loading of Flt, Pyr and BghiP with high negative loading for Car. Flt and Pyr are indicators for coal combustion (Dong and Lee 2009) while BghiP is an indicator for traffic emission (Yang *et al.* 2011). Thus component 2 suggested that PAHs are from coal combustion and traffic emissions as high negative loading of Car indicates it is from a different source.

Table 5: Pearson correlation coefficient of PAHs in soil samples

	Nap	Ace	Flu	Phen	Ant	Car	Flt	Pyr	BbF	BkF	BaP	BghiP
Nap	1.00											
Acy	0.00											
Ace	0.99*	1.00										
Flu	0.99*	1.00*	1.00									
Phen	0.99*	1.00*	1.00*	1.00								
Ant	0.99*	1.00*	1.00*	1.00*	1.00							
Car	-0.54	-0.47	-0.47	-0.42	-0.41	1.00						
Flt	0.82*	0.75*	0.75*	0.73*	0.72*	-0.76	1.00					
Pyr	0.79*	0.72*	0.72*	0.70*	0.70*	-0.76	1.00*	1.00				
BbF	0.99*	1.00*	1.00*	1.00*	1.00*	-0.47	0.75*	0.72*	1.00			
BkF	0.99*	1.00*	1.00*	1.00*	1.00*	-0.47	0.75*	0.72*	1.00*	1.00		
BaP	0.99*	1.00*	1.00*	1.00*	1.00*	-0.47	0.75*	0.72*	1.00*	1.00*	1.00	
BghiP	-0.14	-0.25	-0.25	-0.27	-0.28	-0.47	0.46**	0.49**	-0.25	-0.25	-0.25	1.00

*Pearson correlation significant at 0.01 level of significance
**Pearson correlation significant at 0.01 level of significance

Table 6: PCA of PAHs in the soils

	Component	
	1	2
Nap	**.954**	.298
Ace	**.982**	.189
Flu	**.982**	.189
Phen	**.986**	.154
Ant	**.987**	.148
Car	-.324	**-.801**
Flt	.609	**.782**
Pyr	.577	**.805**
BbF	**.982**	.189
BkF	**.982**	.189
BaP	**.982**	.189
BghiP	-.424	**.884**
Variance %	72.218	24.977
Cumm Var %	72.218	97.195
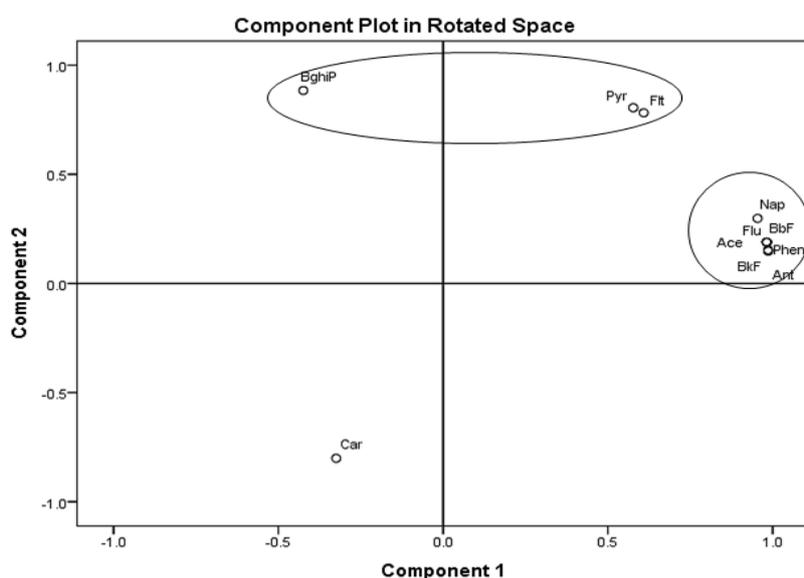
Fig. 7: PCA plot of PAHs in the soils

Discussion

The study area, Abraka, is an urbanized town, owing to the presence of the Delta State University. Over the last few years, there has been an increase in the number of inhabitants, as well as an increase in the number of vehicles. Similarly, there has also been an upsurge in the number of individuals engaged in skilled labour, such as automobile and generator maintenance specialists, increased number of fuel stations, etc.

In this study, the concentrations and relative composition of n-alkanes in soils across the studied areas showed significant variations ($p<0.05$), which could be due to variances in sources input, circulation, sedimentation and degradation patterns (Frena *et al*., 2017). The observed total concentration of n-alkanes were within the UNEP recommended limit of 10,000 µg kg^{-1} in soils from busy junction, drainage and suya joint. However, samples from fuel station had concentrations of n-alkanes that slightly exceeded the UNEP limit, while the concentrations of these hydrocarbons in soil samples from generator maintenance workshops greatly exceeded the UNEP limit. This shows that soil samples from the vicinity of generator maintenance workshops are heavily contaminated with n-alkanes, while fuel stations are moderately contaminated with n-alkanes.

Hopane and sterane biomarkers were detected only in soils from the vicinity of generator maintenance workshops. Although, hopanes are not recognized as environmental pollutants, their persistent natures make it

possible for them to be used as geochemical biomarkers in oil pollution (Boehm *et al.,* 2001). Hopanes are reportedly present in higher boiling petroleum products such as lubricating oils and asphalt (Simoneit, 1985). This could be the reason for their presence in lubricating oils, and the presence of these biomarkers suggests wide-scale contamination from oil and grease (Rushdi *et al*., 2013). These biomarkers were however not detected in soils in the vicinity of busy junctions, fuel stations and suya joints. This observation suggests that hopane and sterane are not present in lower boiling petroleum products such as gasoline and diesel fuel (Rushdi *et al*., 2013). For samples from fuel stations, the distribution of n-alkanes indicates that only C_{19} and C_{35} were detected. The generally poor distribution of n-alkanes in this location could be attributed to the fact that, many fuel stations have concrete floors around their reservoir tanks, and as such, samples are usually collected just outside the station; this is in contrast to the report of Emoyan *et al.* (2020a) where an even distribution of n-alkanes, ranging from $C_8 - C_{40}$ was detected in soils from petroleum tank farms in Delta State.

The ACL value of soils ranged from 0.0 – 30.9 with 4 of the locations having ACL values of 0.0, which suggests minimal disturbance arising from any intense anthropogenic activities in these 4 sites. However, the presence of n-alkanes of different carbon lengths in generator maintenance workshops showed that their sources in this site were many (Fagbote and Olanipekun, 2013).

The natural n-alkanes ratio (NAR) indicates that the NAR value close to zero is associated with crude oil contamination and its derivatives, while values close to 1 indicates hydrocarbon input from higher terrestrial or marine plants (Mille *et al.,* 2007; Aly Salem *et al*. 2014; Iwegbue *et al*., 2016). The NAR values of -0.1 and 0.0 were obtained for soils from fuel stations and generator repairs, respectively, which indicated input from petroleum hydrocarbon compounds.

With respect to PAHs, soils can be classified as non-contaminated when the total PAHs concentrations are below 0.2 mg kg^{-1}; weakly contaminated if the values is in the range of 0.2 – 0.6 mg kg^{-1}; contaminated when the values are between 0.6 and 1 mg kg^{-1}; and, heavily contaminated when the total PAHs concentrations are greater than 1 mg kg^{-1} (Maliszewska-Kordybach, 1996; DPR, 2002). Based on this classification, the investigated soils in this study can be regarded as relatively non-polluted with PAHs, since all the determined PAHs concentrations were within the 1 mg kg^{-1} target value set by DPR (2002). Low concentration of PAHs in soils from busy junctions were observed, compared to the reports of Emoyan *et al.* (2020b) for PAHs in soils from car parks. The measured concentrations are also low when compared with results from soils from the gas flaring sites, pipeline explosion sites and flow stations (Adedosu *et al*., 2012), and much lower than reports for soils from commercial areas and crude oil spilled sites (Onyema *et al*., 2015). The total PAHs concentration in soil from fuel stations is relatively low compared to Nganje *et al*. (2007) for soils from petroleum handling facilities in Calabar.

The carcinogenicity, mutagenicity and toxicity of PAHs is a function of their molecular structures, wherein low molecular weight PAHs (<3 rings) often display acute toxicities and low carcinogenicities; while, high molecular weight PAHs (>3 rings) show low toxicities and very high carcinogenicities and mutagenicity (Ivwurie *et al*., 2016). All soils except those from generator maintenance workshops were typically non-carcinogenic, since the carcinogenic congeners were not detected in them. In this study, the results obtained indicates that the soils contained higher loads of non-carcinogenic PAHs than carcinogenic PAHs. This observation could be attributed to the idea that the non-carcinogenic PAHs are majorly the low molecular weight PAHs and predominanted in these soils compared to the higher molecular weight PAHs, which are majorly carcinogenic PAHs. This suggests that humans exposed to these PAHs in these soils are not at high risk of cancer.

Conclusion

The major findings of this study are summarized a follows:
  i. The total n-alkanes concentration in soil samples were within the UNEP guideline value of 1 mg kg^{-1} except in soils from fuel station and generator maintenance workshops.
 ii. The presence of n-alkanes in soils from both fuel station and generator maintenance workshops were from petroleum hydrocarbon compounds, based on the molecular indices used in this study;
iii. The low molecular weight (2-3 rings) PAHs and non-carcinogenic PAHs were the predominant PAHs in the soils studied;
 iv. The concentrations of the total PAHs in the soils studied were all within the DPR target value of 1 mg kg^{-1} and are therefore, regarded as being relatively uncontaminated with PAHs;
  v. 6-ringed PAHs were not detected in any of the soil samples;
 vi. The isomeric ratios and PCA used for source apportionment showed that n-alkanes in the studied soils originated from high-temperature combustion of biomass and fossil fuels such as wood and coal as well as traffic emissions.

In conclusion, soils from generator maintenance workshops and fuel stations were shown to be heavily impacted with n-alkanes than soils from other environments that were investigated. However, the soils were relatively uncontaminated with PAHs. Also, the low molecular weight and non-carcinogenic PAHs were the predominant PAHs in these soils, while the calculated isomeric ratios for PAHs in these soils traced their origin to high-temperature combustion of biomass and fossil fuels such as wood and coal as well as traffic emissions.

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