Assessment of Polycyclic Aromatic Hydrocarbons Levels in Soil around Automobile Repair Workshops within Eket Metropolis, Akwa Ibom State, Nigeria

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Abstract **-The paper is aimed at investigating the levels of PAHs in the soil collected at various depths (0-10cm, 10-20cm and 20-30cm) from vicinity of automobile repair workshops within Eket metropolis, Nigeria. The soils were prepared using standard procedure in the laboratory and analysed for 16 US EPA priority PAHs using Gas Chromatography-Mass Spectrometer (GC-MS). The concentration of total PAHs in the contaminated soil ranged from 0.83 to 12.98mg/kg and did not follow regular pattern with depth. These levels according to European Commission is said to be moderately to heavily contaminated. The soils were relatively enriched with Low Molecular Weight PAHs. The soil in these sampling sites had low carcinogenic burden, hence moderate adverse health effect. Diagnostic ratio used in determining PAHs source reveals that they PAHs originated from mixed sources (Phytogenic, Petrogenic and Pyrogenic sources). It can be concluded that automobile repair activities contributed to the soil contamination with PAHs, hence it should be properly sited.**

Keywords **-PAHs, automobile, contamination, soil, underground water**

I. INTRODUCTION

In Nigeria, as in many other countries, petroleum hydrocarbon contamination is widespread. Pollution arising from the disposal of used engine oil is one of the environmental problems in Nigeria and is more widespread than crude oil pollution [1]. The indiscriminate disposal of these spent engine oils in the environment requires urgent attention. Contamination could be from mishandling, deliberate disposal, spilling and leakage of petroleum products such as gasoline, lubricating oils, diesel fuel, heating oils, used and spent engine oil.

Akwa Ibom State being one of the most populated states in Nigeria has resulted in an increase in number of vehicles that are used for commercial and private purposes. Since vehicles are prone to break downs, portions of land, sometimes reaching 5 hectares or more are used by groups for small scale auto mechanic workshop where they repair yards and offer services to the public. It is presumed that there are environment threats associated with this practice. According to reference [2], the hazard of environmental pollution through disposing used automobile oil on the ground in many mechanic villages in developing countries such as Nigeria is of great concern to public health and ecology. These unguided practices have worsened the rate at which used engine oils spread and contaminate the soils and water around the town. Studies in automobile repairs workshop sites have been carried out by many researchers [3]. Most of them focused on studying the implication of heavy metal contamination in soil by automobile repair activities without considering the effect of other petroleum hydrocarbon pollutants such as the persistent and ubiquitous polycyclic aromatic hydrocarbons (PAHs) present in the used of oil. These used oils and solvents form part of the most hazardous wastes commonly generated in auto-repair shops around cities in Nigeria [3], [4]. Polycyclic aromatic hydrocarbons (PAHs) are widely distributed in the environment, and some are carcinogenic to human being even at very low concentrations [5], [6], [7]. PAHs are derived from natural or petrogenic sources (including geogenic, forest fires and volcanic activities) and anthropogenic or pyrogenic sources (including oil leakages, oil spills and combustion of fossil fuels) [8]. PAHs are among the list of US EPA priority pollutants. US EPA has listed 16 PAHs as priority pollutants in wastewater and 24 PAHs in soil, sediments, hazardous solid waste and ground water [9], [10], [11], [12]. According to reference [13], PAHs sources are classified into three groups namely: (1) Biogenic (Vascular Plants) diagenetically derived PAHs (2) Petroleum related PAHs and (3) Combustion / pyrogenic related PAHs.

Reported cases of PAHs contamination in soil, sediment and water (surface and groundwater), have been documented by [13], [14], [15], [16], [17], [18], [19]. The present study is designed to investigate the pollution status of soil around Automobile workshops in Eket Local Government Area in Akwa Ibom State. Hence, the aim of this study is to investigate the levels of PAHs in the soil at various depths within the vicinity of automobile repair workshops. This will contribute to the existing data and provide basis for planning of future monitoring of PAHs in the area of study.

II. MATERIALS AND METHODS

Fifteen soil samples were collected within the vicinity of five (5) automobile repair workshops in Eket metropolis at depths of 0-10cm, 10-20cm and 20-30cm. The five automobile repair workshops includes (1) Automobile repair workshops at Edem Udo street (EU) (2) Automobile repair workshops at Etebi Idung Iwak street (EIW) (3) Automobile repair workshops at Nkubia street (NK) (4) Automobile repair workshops at Grace Bill road (GB) and (5) Automobile repair workshops at RCC road (RCC). The soil samples were collected using stainless hand held auger and were wrapped with a cleaned, labeled aluminum foil, then transported to the laboratory. In the laboratory, soil samples were air dried in a dust free environment at room temperature for 7days. The soil samples were pulverized with a porcelain mortar and pestle and sieved through a 2mm mesh sized sieve and stored in the refrigerator at 4°C prior to extraction and analysed. The US EPA 3540C (soxhlet extraction) reference method was employed in the extraction of PAHs in the soil samples. Briefly, 10g of the soil samples were blended thoroughly with 10g of anhydrous sodium sulphate and placed in an extraction thimble. 200ml of the extraction solvent mixture (Hexane: dichloromethane in the ratio of 300ml:100ml) was poured into a 500ml round bottom flask containing one boiling chip. The flask is then attached to the extractor and the sample extracted for 16-24hours at 4-6cycles/hours. The extract is allowed to cool after complete extraction [20].

The soluble organic matters were fractionated into aliphatic and aromatic fractions using a glass column packed with activated neutral alumina. 10g of the alumina was packed into the column and properly cleaned with redistilled hexane. The extract was poured onto the alumina and was allowed to elute using the redistilled hexane to remove the aliphatic fractions into pre cleaned 25ml container. The aromatic fraction was recovered by using the mixture of hexane and dichloromethane in ratio of 3:1. The aromatic fraction was concentrated to approximately 1.0ml using rotary evaporator. The obtained extract was stored in pre-cleaned and labeled organic free glass vials with screw caps. It was refrigerated at 4°C until analysis.

The soil extracts were analysed by Gas chromatography coupled to mass spectrometer (HP 6890) following US EPA 8270-C method for the 16 US EPA priority PAHs [Naphthalene (Nap), Acenapthalene(Ace), Acenapthylene (Acy), Phenanthrene (Phe), Anthracene (Ant), Fluorene (Flu), Fluoranthene (Fla), pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chr), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene(BaP), Indeno(1,2,3-cd)pyrene (IcdP), Dibenzo(a,h)anthracene (DbA) and Benzo(ghi)perylene (BghiP)]. The operational conditions used for GC analysis is stated in table I. Agilent chemstation software was used for data processing [21]. Quality control and accuracy were evaluated by sequence analysis for all parameters accompanied with GC measures (such as blanks, duplicates and standards) to check interferences and validation of analytical procedures used. **Table I: GC/MS Analysis condition**

Gas Chromatograph	**HP 6890 powered with HP Chemstation software**
Injection mode	Split
Split ratio	20:1
Carrier gas	Helium
Inlet temperature	270°C
Final temperature	320°C
Column type	HP 5
Column dimension	30m×0.25mm×0.25mm
Oven program	Initial temperature at 65°C for 3mins Ramp at 10.10mins
Detector	Mass spectrometer
Detector temperature	320°C
Carrier gas	Helium @ 30.0psi
Injector	Auto sampler (ALS)
Injection volume	1µL
Transfer line temperature	280°C
MS ACQUISITION PARAMETERS	
Acquisition mode	Selective Ion Mode (SIM)
Mass range	128 – 202amu (Group 1-12)
Dwell time	25Seconds
Resulting EM Vat	1694.1

III. RESULTS AND DISCUSSION

1. Concentrations of PAHs in soil

As seen in tables II and III, the sum of concentration of PAHs (Σ16 EPA PAHs) did not follow regular pattern with depth at all the sites. The Σ16 EPA PAHs in soil collected at EU, EIW, NK, GB and RCC varied between 2.48 - 4.85mg/kg, 0.92 - 3.83mg/kg, 0.83 – 1.42mg/kg, 1.62 - 12.98mg/kg and 1.62 - 4.11mg/kg respectively. This reflects that the soil at GB had the highest Σ16 EPA PAHs with depth of 10-20cm (12.98mg/kg) contributing to the bulk. This might be due to the physicochemical properties (porosity, pH and bulk density) of the soil at this study area. According to the European commission classification system of soil contamination, Σ16 EPA PAHs < 0.20mg/kg show no contamination, 0.20 - 0.60mg/kg correspond to weak contamination, 0.60 - 1.0mg/kg corresponds to moderate contamination and > 1.0mg/kg indicates heavy contamination [22]. Following this classification, it can be said that the soil in this study area is moderately to heavily contaminated. The spatial variation in the composition of PAHs with depths at the sampling sites observed could be attributed to the different transport mechanisms at the different sites.

The Low Molecular Weight PAHs (LMW PAHs) were generally present in lower concentrations in all the sampling sites except Napthalene at GB study site. Anthracene and phenanthrene among all LMW PAHs were detected in all the samples. The High Molecular Weight PAHs

(HMW PAHs) were well distributed in almost all the samples analysed. This is due to their persistence in the environment and more PAHs could have accumulated within years. Pyrene had the highest total concentration in all the samples. Fluoranthene had the lowest concentration among all the HMW PAHs in all the samples analysed.

2. PAHs distribution pattern in the study area.

Figure I shows the composition pattern of PAHs detected in the soil samples by the number of rings. 2-ring PAHs was predominated in GB study area although it was not well distributed. Generally 3-ring PAHs had the highest concentration, next to the 2-ring PAHs. The 6-ring PAHs had the lowest concentration. The transport of 5- and 6-ring PAHs to the subsurface are probably with dissolved organic matter or colloids. As seen in table III, at some specific locations such as GB (12.98mg/kg) and EU (4.85mg/kg), PAHs levels were high. This shows that the major source of PAHs contamination is mostly point source. The occurrence of LMW PAHs is due to the dry deposition of particles from the atmosphere that contains adsorbed PAHs such as naphthalene and phenanthrene. The probable source of these compounds is organic matter combustion due to low temperature [23]. This pattern of concentration has been seen by other researchers such as [24], [25], [26].

TABLE II: Mean Concentration of Studied PAHs in mg/kg of Soil Samples from Automobile Repair Vicinity

SITES	DEPTHS (cm)	PAHs COMPOUNDS (mg/kg)																	
		Nap	Acy	Ace	Flu	Ant	Phe	Fla	Pyr	Chr	BaA	BbF	BkF	BaP	IcdP	DbA	BghiP	Mean	S.D.
EU	0 – 10	0.28	-	-	-	0.37	0.41	-	1.10	0.26	0.24	0.68	0.30	0.29	0.48	-	0.44	0.44	0.25
	10 – 20	-	0.11	-	-	0.62	0.78	-	0.23	0.09	0.07	0.41	-	0.12	0.26	-	0.17	0.29	0.24
	20 – 30	-	0.24	-	-	-	1.03	-	0.15	-	0.13	0.72	-	0.09	-	-	0.12	0.35	0.37
EIW	0 – 10	-	-	-	0.31	0.18	0.52	-	0.45	0.12	-	-	0.02	0.17	-	-	0.22	0.25	0.17
	10 – 20	-	-	0.31	0.28	0.45	0.87	-	0.20	0.38	-	0.19	-	0.28	0.35	0.13	0.39	0.35	0.20
	20 – 30	-	-	-	0.19	0.06	-	-	0.34	0.11	-	-	0.08	0.09	-	0.05	-	0.13	0.10
NK	0 – 10	-	-	0.11	-	0.09	0.10	0.01	0.07	-	-	-	-	0.19	0.05	-	0.21	0.10	0.07
	10 – 20	-	-	-	-	0.28	0.24	-	0.42	0.36	-	-	-	-	0.12	-	-	0.28	0.12
	20 – 30	-	0.52	0.03	-	-	0.19	-	0.05	-	-	0.14	-	0.07	0.01	-	0.13	0.14	0.16
GB	0 – 10	0.01	-	-	0.18	0.38	0.36	0.01	-	-	0.13	0.22	-	0.18	0.03	-	0.12	0.16	0.13
	10 – 20	11.22	0.13	-	-	0.07	0.12		-	0.42	0.28	0.37	-	0.20	0.08	0.09	-	1.30	3.49
	20 – 30	2.51	0.31	-	-	0.07	-		-	0.49	-	0.19		0.11	0.07	-	0.16	0.49	0.83
RCC	0 – 10	-	0.91	0.53	-	0.87	0.33		0.09	0.27	0.31	-	-	0.43	0.18	-	0.19	0.41	0.28
	10 – 20	-	-	0.41	-	0.51	-		-	0.10	0.24	-	-	0.25	0.11	-	-	0.27	0.16
	20 – 30	-	0.73	0.42	-	0.26	0.09		0.01	0.06	-	-	-	-	0.12	-	0.18	0.23	0.24

Table III: PAH Concentrations in Associated Soil by Number of Rings and Related PAH Parameters

SAMPLES	DEPTHS (cm)	ΣLMW PAHs	ΣHMW PAHs	Σ16EPA PAHs	ΣPAHcarc	2-ring	3-ring	4-ring	5-ring	6-ring
EU	0 – 10	1.06	3.79	4.85	2.69	0.28	0.78	1.60	1.27	0.92
	10 – 20	1.51	1.35	2.86	1.12	-	1.51	0.39	0.53	0.43
	20 – 30	1.27	1.21	2.48	1.06	-	1.27	0.28	0.81	0.12
EIW	0 – 10	1.01	0.98	1.99	0.53	-	1.01	0.57	0.19	0.22
	10 – 20	1.91	1.92	3.83	1.72	-	1.91	0.58	0.60	0.74
	20 – 30	0.25	0.67	0.92	0.33	-	0.25	0.45	0.22	-
NK	0 – 10	0.30	0.53	0.83	0.45	-	0.30	0.08	0.19	0.26
	10 – 20	0.52	0.90	1.42	0.48	-	0.52	0.78	-	0.12
	20 – 30	0.74	0.40	1.14	0.35	-	0.74	0.05	0.21	0.14
GB	0 – 10	0.93	0.69	1.62	0.68	0.01	0.92	0.14	0.40	0.15
	10 – 20	11.54	1.44	12.98	1.44	11.22	0.32	0.70	0.66	0.08
	20 – 30	2.89	1.02	3.91	1.02	2.51	0.38	0.49	0.30	0.23
RCC	0 – 10	2.64	1.47	4.11	1.38	-	2.64	0.67	0.43	0.37
	10 – 20	0.92	0.70	1.62	0.70	-	0.92	0.34	0.25	0.11
	20 – 30	1.50	0.37	1.87	0.36	-	1.50	0.07	-	0.30

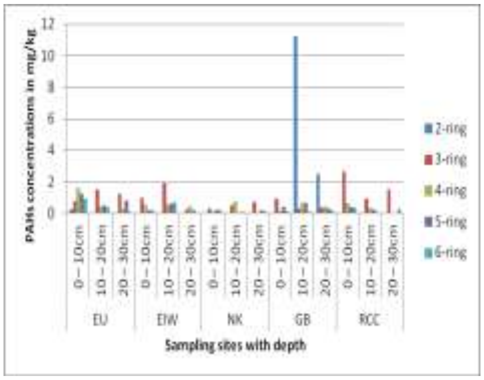

Figure 1: Analysis of the Results Based on Number of Rings for Soil

The concentration of benzo(a)pyrene at the various depths and sites were less than 1mg/kg and below the range of 1.08-1.32mg/kg for UK Generic Assessment Criteria (GAC) [27]. Value of benzo(a)pyrene above this ranges are considered to be a potential risk in the environment for human health. Thus, the values obtained in the present study revealed that the environment is considered safe in terms of benzo(a)pyrene concentrations.

3. Sources of PAHs

It is important to identify the origin and potential sources of PAHs in the environment to assess the environmental risk. Diagnostic ratios of PAHs can be used to derive the sources of pollution [28], [29], [30], [31], [32].

Table IV shows the diagnostic ratios of the PAHs obtained in this study and their possible sources. The ratio of LMW PAHs (2-3 ring) to HMW PAHs (4-6 ring) was employed to differentiate between sources. LMW/HMW >1 signifies a probable petrogenic origin for PAHs while <1 are generally considered to indicate a predominance of pyrogenic sources [33]. On the average, there was predominance of LMW PAHs over HMW PAHs in soil from the vicinity of GB and RCC. The ratio LMW/HMW in these soil samples (GB and RCC) were greater than 1 (>1) at all depths, hence, petrogenic source. EU, EIW and NK had an average ratios of 0.82, 0.80 and 1.00 respectively, hence, pyrogenic source. This ratio was not used to ascertain the source of PAHs because the LMW PAHs were not well distributed among the study areas.

Other diagnostic ratios of PAHs used to trace the pollution sources include Phen/Ant, Ant/(Ant +Phen) and IcdP/ (IcdP + BghiP). Values of Phen/Ant >10, Ant/(Ant +Phen) <0.1 and IcdP / (IcdP + BghiP) <0.2 indicates a petrogenic origin of pollution. In the study site Phen/Ant and Ant/(Ant +Phen) for the soils at all depths except depth 20-30cm at EU, EIW, NK and GB were <10 and <0.1 respectively. This indicated a pyrogenic source of PAHs. The ratio IcdP / (IcdP + BghiP) in almost all the studied samples were within the range 0.07 to 0.67. This indicates mixed sources (phytogenic, pyrogenic and petrogenic sources). Some of the studied samples such as EU(20-30cm), EIW (0-10cm and 20-30cm), NK (10-20cm), GB (20-30cm) and RCC (20-30cm) the sources were not determined (nd) because of the zero value of the nominator and/or denominator. Generally, the source of PAHs in the soil samples can be attributed to pyrogenic and petrogenic sources.

Table IV: PAHs Diagnostic Ratios for Soil Samples

Site	Depth	Phen/ Ant	Ant/ (Ant+ Phen)	IcdP/ (IcdP + BghiP)	LMW/ HMW
EU	0-10cm	1.11	0.47	0.52	0.28
	10-20cm	1.26	0.44	0.60	1.12
	20-30cm	nd	nd	nd	1.05
EIW	0-10cm	2.89	0.26	nd	1.03
	10-20cm	1.93	0.34	0.47	0.99
	20-30cm	nd	nd	nd	0.37
NK	0-10cm	1.11	0.47	0.19	0.57
	10-20cm	0.86	0.54	Nd	0.58
	20-30cm	nd	nd	0.07	1.85
GB	0-10cm	0.95	0.51	0.20	1.35
	10-20cm	1.71	0.37	nd	8.01
	20-30cm	nd	nd	0.30	2.83
RCC	0-10cm	0.38	0.73	0.49	1.80
	10-20cm	nd	nd	0.67	1.31
	20-30cm	0.35	0.74	nd	4.05
Petrogenic origin		>10	<0.1	<0.2	>1.0
Pyrogenic origin		<10	>0.1	0.2-0.5	<1.0
Phytogenic origin		-	-	>0.5	-

Ant; Anthracene, **Phe;** Phenanthrene, **IcdP;** Indeno(1,2,3-cd)Pyrene, **BghiP;** Benzo(ghi)Perylene, **nd**: cannot be determined because of the zero value of the nominator and/or denominator.

4. Estimation of Carcinogenic Potency of the Soil

The health risk of these PAHs to human was accessed by estimating its carcinogenic potency. International Agency for Research on Cancer (IARC) and the United States Environmental Protection Agency (US EPA) reported Benzo(a)anthracene(BaA), Chrysene(Chr), Benzo(b)fluoranthene(BbF), Benzo(k) fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno(1,2,3-cd)pyrene (IcdP), Dibenzo(a,h)anthracene (DbA) and Benzo(ghi)perylene (BghiP) as possible human carcinogens. These possible carcinogens were detected in the samples. The carcinogenic potency of PAHs was estimated by calculating the concentrations of individual carcinogenic PAHs in terms of benzo(a)pyrene equivalent (BaPeq) which is represented as follows in equation (1) below.

$$\text{Total BaPeq} = \Sigma_i (C_i * TEF_i) \qquad (1)$$

Where C_i and TEF_i is the concentration and the corresponding toxic of individual PAHs and is the corresponding TEF value of one for benzo(a)pyrene. The TEQ of individual PAHs was calculated based on the toxic equivalency factor (TEF) values proposed by [34]. Benzo(a)pyrene was detected in almost all the samples with the highest concentration detected at RCC (0.43mg/kg) sampling site at depth of 0-10cm. Benzo(a)pyrene was not detected in NK (10-20cm) and RCC (20-30cm). The lowest concentration of Benzo(a)pyrene was detected in NK (20-30cm).

The extent of carcinogenic burden of the different sampling sites was determined by comparing the % of ΣPAHcarc in Σ16 EPA PAHs for all the study areas. Table III and figure II reveals that Edem Udo automobile repair workshop (EU) had the highest carcinogenic burden with a percentage of 55% (0-10cm), 39% (10-20cm) and 43% (20-30cm) and hence it is said to have a risk of long term adverse health effect. Grace bill automobile repair workshop had the lowest carcinogenic burden with a percentage of 42% (0-10cm), 11% (10-20cm) and 26% (20-30cm) in the dry season. Thus moderate adverse health effect. The extent of carcinogenic burden of the different sampling sites was determined by comparing the % of ΣPAHcarc in Σ16 EPA PAHs for all the study areas.

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Also to access the risk of long term adverse health effect , total BaPeq value was calculated using equation (1) and presented in table V. The calculated total BaPeq values in this study at different sampling sites varied from 0.2990mg/kg to 0.8398mg/kg.

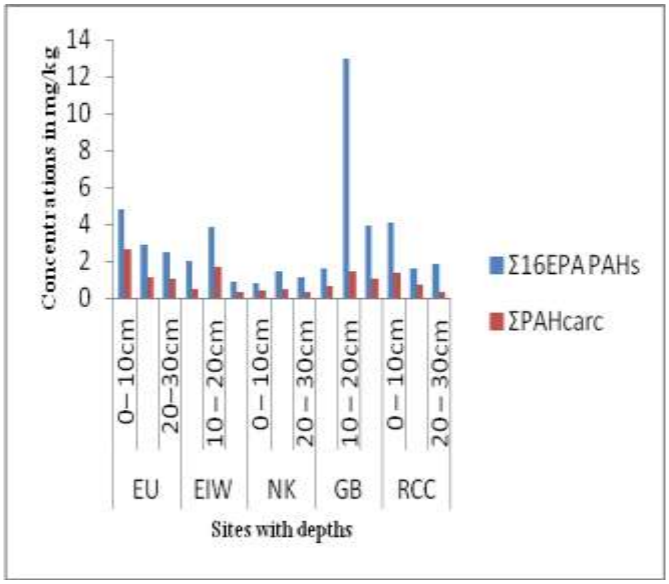

Figure 2: Concentrations of carcinogenic PAHs at each of the sampling points

Table V: Carcinogenic Potency of PAHs in soil

Carcinogenic PAHs	**TEF**	**BaPeq**				
		EU	**EIW**	**NK**	**GB**	**RCC**
Chrysene	0.01	0.0035	0.0061	0.0036	0.0091	0.0043
Benzo(a)anthracene	0.1	0.0440	0.0000	0.0000	0.0410	0.0550
Benzo(b)fluoranthene	0.1	0.1810	0.0190	0.0140	0.0780	0.0000
Benzo(k)fluoranthene	0.1	0.0300	0.0100	0.0000	0.0000	0.0000
Benzo(a)pyrene	1	0.5000	0.5400	0.2600	0.4900	0.6800
Indeno(1,2,3-cd)pyrene	0.1	0.0740	0.0350	0.0180	0.0180	0.0410
dibenzo(a,h)anthracene	1	0.0000	0.1800	0.0000	0.0900	0.0000
Benzo(ghi)perylene	0.01	0.0073	0.0061	0.0034	0.0028	0.0037
TOTAL		**0.8398**	**0.7962**	**0.2990**	**0.7289**	**0.7840**

IV. CONCLUSION

The sum of concentration of PAHs did not follow regular pattern at all the sampling sites with depth. According to European Commission classification system of soil contamination, the PAH concentration reported in this study is said to be moderately to heavily contaminated. the distribution pattern of PAHs detected in this soil samples by number of rings shows that 2-ring PAHs predominated in GB study area although it was not well distributed. 6-ring PAHs had the lowest concentration while 3-ring PAHs had the highest concentration next to 2-ring PAHs. The extent of carcinogenic burden of the different study area as determined by comparing the % of ΣPAHcarc in Σ16 EPA PAH and calculating the total BaPeq reveals a moderate adverse health effect but their potential harmful effects should not be overlooked as PAHs constitute environmental human health risk. Diagnostic ratio used for source determination revealed that the PAHs in this study are majorly from both petrogenic and pyrogenic origins. The results in this research provides additional contribution to the background value for future pollution monitoring in the soils around the study area. It can be concluded that automobile repair activities had contributed to the soil contamination with PAHs, hence proper Environmental Impact Assessment should be conducted before an automobile repair workshop be sited.

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