pp. 132-142 https://dx.doi.org/10.4314/johasam.v7i1.15

Evaluation of the Topsoil Quality for Polycyclic Aromatic Hydrocarbons Near Automobile Repair Facilities in Eleme, Rivers State, Nigeria

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Abstract

The activities of automobile repair workshops may have a negative impact on the immediate environment due to the kind of waste that is constantly generated and disposed of around these areas. With a view to ascertaining their possible impact on the surrounding soils, top soil samples were therefore collected from selected automobile repair shops in Eleme. The processed composite soil samples were analysed for their polycyclic aromatic hydrocarbon (PAH) content following standard analytical procedures. Results from the impacted sites as well as the control site revealed that PAHs were detected at these stations at varying concentrations in all of the topsoil sampled, following the order: Station 3 > Station 1 > Station 2. There was a considerable difference between the concentration of PAHs in the soil from the automobile repair shops and the control site. The total concentration (mg/kg) of the 16 US EPA PAHs in the soil samples ranged from 34.729 to 35.647, with a mean value of 35.305±1.561, which was markedly higher than the 2.116±0.185 concentration found in the control sample. Source identification and diagnostic ratios of polycyclic aromatic hydrocarbons in the soils revealed that the increased ratio of pyrogenic or combustion-based PAHs found in soil samples from different automobile repair stations is an indication that anthropogenic sources, especially combustion and spills of petroleum products, were the main sources of PAH component input. Therefore, the control of oil spills and automobile use of spent oils should be checked by providing central storage tanks that could be recycled for other purposes.

Keywords: automobile, Eleme, evaluation, mechanic village, polycyclic aromatic hydrocarbon, topsoil

INTRODUCTION

The establishment of automobile repair shops is a common practice in Eleme Local Government Area in particular and in Nigeria at large. Large portions of land are allocated for automobile activities and are designated as mechanic workshops or mechanic villages where automobile repair services are offered to the public (Timothy et al., 2022). The wastes generated comprise gaseous, liquid, and solid wastes. Toxic chemicals such as chlorinated compounds, solvents, glycols, polycyclic aromatic hydrocarbons (PAHs), etc. are produced (Timothy et al., 2023). Generally, PAHs are organic pollutants that are toxic, tenacious, and widely disseminated in the environment. Natural sources that release these organic pollutants into the environment include volcanoes and forest fires, but anthropogenic sources are the most common and are responsible for the majority of air pollution. Anthropogenic sources commonly include the burning of fossil fuels, which includes power plants, emissions from cars and other transportation, the burning of wood, the incineration of household and commercial waste, and a wide range of other activities (Eneji et al., 2017).

Although they are biodegradable, their sequestration and persistent nature make the process of biodegradability and their accessibility to chemical attack difficult. Additionally, because of their hydrophobic character, which results in very low water solubility and a high octanol-water partition coefficient, PAHs are strongly adsorbed on organic matter in soil and are less prone to biological and chemical deterioration. Different types of PAHs are formed based on combustion temperature, where high temperatures form simple PAHs and low temperatures create more complex PAHs (Eneji et al., 2017). Many compounds of PAHs enter water bodies, sediment, soil, and biological materials through the atmosphere. In the environment, polycyclic aromatic hydrocarbons (PAHs) are ubiquitous and can be found in sediments, soils, and waterways in both solution and adsorbed forms. Additionally, burning fossil fuels, burning other organic materials, or the processes involved in oil exploration and production all cause PAHs to enter the environment (Ribeiro et al., 2014). PAHs are widely spread in the environment, and some of them can cause cancer in people even at extremely low levels. Even though PAHs are present everywhere, they are more prevalent in locations like oil spill sites, gas works, coal gasification sites, and auto mechanic workshop sites. Several PAHs are known to have teratogenic, mutagenic, and carcinogenic properties, and their presence in soils raises concerns (Yu, 2002).

The Environmental Protection Agency (EPA) has designated sixteen (16) of the hundreds known PAHs as high-priority pollutants, including naphthalene (NAP), acenaphthene (ACE), acenaphthylene (ACY), fluorene (FLU), phenanthrene (PHEN), anthracene (ANTH), fluoranthene (FLTH), pyrene (PYR), benzo[a] anthracene (B[a]A), chrysene (CHRY), benzo[b] fluoranthene (B[b]F), benzo[k] fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), benzo[g,h,i] perylene (B[ghi]P), indeno [1,2,3-c,d]pyrene (IND), and dibenz[a,h]anthracene (D[ah]A). These 16 PAHs are of environmental concern because of their potential toxicity to humans and other organisms and because of their prevalence and persistence in the environment. Several PAHs are probable or known carcinogens (International Agency for Research on Cancer, 2006). Some of the properties of these priority hydrocarbon pollutants are listed below in Table 1. Automobile repair activities directly increase the levels of hydrocarbons in the soil environment, particularly polycyclic aromatic hydrocarbons, which are a major component of petroleum hydrocarbons (Joseph et al., 2017). Presumably, the activities of the auto mechanics in Eleme may have a negative impact on the immediate environment due to the kind of waste that is constantly generated and disposed of around these areas. Wastes generated and disposed of in the environment by automobile repair workshops are of great concern, given that these wastes are released into the environment without consideration for potential toxicological effects. Based on this assumption, the study evaluated the topsoil quality for polycyclic aromatic hydrocarbons near automobile repair facilities in Eleme, Rivers State, Nigeria, in order to determine any alteration of the concentration of PAHs as well as their potential danger.

Table 1: Physical and Chemical Properties of Polycyclic Aromatic Hydrocarbons

PAH	Chemical formula	Number of rings	Molecular weight ($gmol^{-1}$)	Pure solid Aqueous Solubility(µg/L)	Vapour pressure (Pa)
Naphthalene	$C_{10}H_8$	2	128.18	31690	10.4
Acenaphthene	$C_{12}H_{10}$	3	154.21	3420	2.9E-1
Acenaphthylene	$C_{12}H_{10}$	3	152.20	3930	8.9E-1
Fluorene	$C_{13}H_{10}$	3	166.22	1690	8.0E-2
Phenanthrene	$C_{14}H_{10}$	3	178.24	1000	1.6E-2
Anthracene	$C_{14}H_{10}$	3	178.24	45	8.0E-4
Fluoranthene	$C_{16}H_{10}$	4	202.26	206	1.2E-3
Pyrene	$C_{16}H_{10}$	4	202.26	130	6.0E-4
Benzo[a]anthracene	$C_{18}H_{12}$	4	228.30	5.7	2.8E-5
Chrysene*	$C_{18}H_{12}$	4	228.30	1.8	8.4E-5[a]
Benzo[b]fluoranthene*	$C_{20}H_{12}$	5	252.32	14	6.7E-5[a]
Benzo[k]fluoranthene*	$C_{20}H_{12}$	5	252.32	4.3	1.3E-8[a]
Benzo[a]pyrene*	$C_{20}H_{12}$	5	252.32	3.8	7.3E-7
Dibenz[a,h]anthracene*	$C_{22}H_{14}$	5	278.36	0.5	1.3E-8[a]
Benzo[g,h,i]perylene*	$C_{22}H_{12}$	6	276.34	0.26	1.4E-8
Indeno[1,2,3-c,d]pyrene*	$C_{22}H_{12}$	6	276.34	0.53	1.3E-8[a]

*PAHs classified by the U.S. EPA as possible human carcinogens,[a]at 20°C, others at 25°C(Rogers *et al*., 2002)

MATERIALS AND METHODS

Description of the Study Area

The study area is the Eleme local government area of Rivers State, located in the Niger Delta of Nigeria. Eleme Local Government Area is one of the 23 local governments in Rivers State in south-south Nigeria. And it is part of the Port Harcourt metropolitan area. Eleme Local Government Area is located at 4°47’15" (between 4°60’ and 4°35') north of the Equator and 7°8'37" (between 7° and 7°15’) east of the meridian. It covers an area of 138 square kilometres (km^2), and at the 2006 Census, it had a population of 190,884 (Obenade et al., 2020). The Eleme people are Eleme's main indigenous ethnic group, with ten main towns that include Agbonchia, Alesa, Aleto, Akpajo, Alode, Ebubu, Ekporo, Eteo, Ogale, and Onne. Eleme is bounded by six local government areas: on the north, Obio/Akpor and Oyigbo Local Government Areas; on the east, Tai Local Government Area; on the south, Ogu/Bolo and Okrika Local Government Areas; and on the west, Okrika and Port Harcourt City Local Government Areas (Wokocha et al., 2017).

Sample Locations

Three (3) different automobile repair shops located within three communities in the Eleme Local Government Area, which include Aleto (Station 1), Alesa (Station 2), and Onne (Station 3), were identified and selected as impacted sites, and a pristine farmland located not less than 100 km from each of the impacted sites was identified and chosen as a control site where there was no existing industry and/or no history of previously established industry in the locality.

Sample Collection

Three topsoil samples were collected six times from each impacted site as well as a control site from the three (3) different automobile repair shops identified using a hand auger. At each location, surface soil samples were randomly collected from the same depth of 0–20 cm to form composite samples (as prescribed by Marcus et al., 2017). Thus, a total of twenty-four (24) soil samples were collected and analysed six times within the period of eleven months (November 2021 to September 2022). In each month, three (3) top composite soil samples from the chosen automobile repair workshop were collected, stored in sample bags, and labelled as Station 1, Station 2, and Station 3, representing surface soil samples around automobile repair shops in selected communities in the Eleme local government areas. Control soil samples were also collected six times, just as those from the impacted sites, stored in polythene bags and coded as "control samples" (CS), and taken to the laboratory for laboratory preparation and analysis.

Sample Preparation

The coning and quartering procedure was used to bulk down each composite sample in order to get a representative sample. To prevent microbial degradation, all samples were air-dried to a consistent weight. The air-dried samples were homogenised by grinding them in a clean porcelain mortar and pestle, sieved through a 2 mm plastic screen, and then stored in plastic cans with labels (Emoyan et al., 2020).

Sample Analysis

The polycyclic aromatic hydrocarbons in the soil samples were determined by extraction techniques using Soxhlet Extraction, and the extract was analysed with gas chromatography coupled with a mass spectrometer following a method prescribed earlier (Ekanem et al., 2019). Precisely 10g of the soil sample was carefully measured and mixed with 10g of anhydrous sodium sulphate, wrapped in filter paper, and placed in an extraction thimble of the Soxhlet extraction chamber. A 200-ml mixture of n-hexane and dichloromethane in a 3:1 ratio was poured into a 500-ml round-bottom flask containing a boiling chip (added to the solvent to make it boil more calmly). Following that, the extractor and condenser were appropriately connected to the flask. Using the reflux cycle at a rate of six cycles per hour, the sample was extracted for 24 hours.

At the completion of the extraction, the extract was allowed to cool. Using a glass column filled with activated neutral alumina, the soluble organic matter was separated into aliphatic and aromatic fractions. The column was well cleaned with redistilled n-hexane after 10g of alumina were put inside. The extract was applied to the alumina and allowed to elute, with the aliphatic fractions being removed using redistilled n-hexane, into a 25-ml container that had already been cleaned. With the use of a 50-ml 3:1 n-hexane/dichloromethane combination, the aromatic fraction was recovered. A rotary evaporator was used to condense the aromatic fraction to around 2.0 mL. Under the influence of a stream of nitrogen gas, this fraction was further concentrated to 1.0 mL and transferred into organic free sample vials that had already been cleaned and labelled. It was kept chilled at 4 °C until analysis by gas chromatography coupled with a mass spectrometer was done.

Source Determination and Diagnostic Ratio Assessment of PAHs

In order to distinguish between naturally occurring and anthropogenically produced PAHs in the environment, a diagnostic ratio has been used as a technique for identifying the sources of PAHs in an ecosystem. Numerous researchers have used the technique to identify the point origins of PAH pollution in the environment (Muze et al., 2020). The following source indicator ratios are used to determine the input sources of PAHs: Fluoranthene/Fluoranthene + Pyrene ratio (Flu/Flu + Py), Anthracene/Anthracene + Phenanthrene ratio (An/An + Ph), Benzo [a] anthracene/Benzo [a] anthracene + Chrysene ratio (BaA/BaA + Ch), and the LMW-PAHs to HMW-PAHs ratio. To determine where the hydrocarbon pollution originated, these diagnostic ratios are employed (Ilechukwu*et al*., 2016). When the computed ratio of low molecular weight PAHs (LMW) to high molecular weight PAHs (HMW) is greater than 1 (LMW/HMW >1), the origin may be from petrogenic input, whereas values less than 1 come from pyrogenic sources. Anthracene/anthracene + phenanthrene (An/An + Phe) ratio calculations show that anthracene has a petrogenic origin when the ratio is less than 0.1 and a pyrogenic origin when the ratio is greater than 0.1. In view of the higher molecular weight of PAHs, when the calculated ratio between Fluoranthene and Fluoranthene + Pyrene is greater than 0.5 (Flu/Flu+Py > 0.5), it is an indication that the origin is from pyrogenic sources, but if the ratio calculated is less than 0.4 (Flu/Flu+Py < 0.4), it suggests that it is of petrogenic origin.More source identification was performed by calculating the ratio of benzo [a] anthracene/benzo [a] anthracene + chrysene. When this ratio is less than 0.2 (BaA/BaA + Ch < 0.2), it is an indication of petrogenic input, but when the ratio is greater than 0.35 (BaA/BaA + Ch > 0.35), it reveals that it originated from pyrogenic input sources.

RESULTS AND DISCUSSIONS

Tables 2–5 show the results of PAHs in the topsoils of the studied locations of Aleto (Station 1), Alesa (Station 2), Onne (Station 3), and Eleme, as well as the control site. From the results, it is observed that in all the sample soils examined, PAHs were detected at these study stations at varying concentrations. The total concentration (mg/kg) at Station 1, Station 2, and Station 3 study locations were 35.540±1.607, 34.729±1.517, and 35.647±1.663, respectively, and ranged from 34.729 to 35.647. The order of total PAH contamination in Eleme's auto-mechanic workshops was Station 2 > Station 1 > Station 3, indicating the amount of activity in these areas.

There was a marked difference between the concentration of PAHs in the soil from the automobile repair garages and the control site (Table 5). In contrast, these levels were highly above the value obtained from the control site of 2.116±0.185 mg/kg. This is an insinuation that the soils from the automobile repair shops have been contaminated and that the high concentrations of PAHs obtained from the soils of the impacted site are a result of the activities of the automobile repair shops in the area. Figure 1illustrates the comparison of the mean concentrations of polycyclic aromatic hydrocarbons in topsoils around selected automobile workshops in Eleme and the control site. The measured values from the studied locations were all higher than those of the control, except for the concentrations of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene, which were not detected in the sample soil obtained from the control site. Looking at the results generally, it was noted that the low molecular weight (LMW) PAHs had the highest concentrations, which suggests that LMW PAHs are easily lost into the atmosphere through volatilization and transported into the soil by water since their solubility in water is higher than that of the high molecular weight (HMW) PAHs (Eneji et al., 2017). This result differed from those observed by Alabi et al. (2019), who found higher concentrations of HMW PAHs (5 and 6-membered rings) in an investigation conducted in the soil of auto-mechanic workshops in Akure, Nigeria. Anegbe et al. (2016) also found the absence of LMW PAHs except fluorene and phenanthrene in all soil samples from the vicinity of mechanic workshops in Benin City, as well as Obini et al. (2013), who found very low concentrations of flourene and phenanthrene among the LMW PAHs and benzo[a]anthracene, benzo[k]fluoranthrene, and chrysene among the HMW PAHs in soil contaminated with spent motor engine oil in Abakaliki Auto-Mechanic Village, Nigeria.

Table 2: Mean levels of two-monthly determinations of PAHs in soil around automobile repair workshop at Aleto, Eleme (Station 1)

PAHs (mg/kg)	Months						Mean ± S.D
	November	January	March	May	July	September	
Na	5.216±0.081	3.716±0.052	4.624±0.061	4.726±0.042	4.218±0.041	4.116±0.097	4.436±0.482
Acy	4.644±0.012	2.644±0.114	4.735±0.023	2.439±0.014	1.550±0.002	3.544±0.061	3.259±1.165
Ace	4.827±0.067	3.927±0.091	4.916±0.053	3.467±0.051	2.810±0.021	3.811±0.074	3.960±0.736
Fl	4.710±0.012	2.710±0.031	5.420±0.011	2.817±0.071	1.610±0.031	2.610±0.023	3.313±1.316
Ph	3.961±0.031	1.761±0.043	4.709±0.032	2.762±0.034	3.751±0.007	3.761±0.078	3.451±0.945
An	5.579±0.065	4.680±0.071	5.419±0.066	4.611±0.091	3.379±0.040	3.380±0.031	4.508±0.872
Flu	2.984±0.016	2.884±0.100	2.764±0.023	3.184±0.060	5.784±0.005	2.784±0.010	3.397±1.077
Py	2.619±0.012	3.919±0.021	3.419±0.032	3.959±0.012	4.619±0.012	1.619±0.001	3.359±0.987
BaA	0.740±0.021	0.150±0.011	0.652±0.011	0.950±0.009	0.640±0.061	0.540±0.011	0.612±0.242
Ch	0.743±0.011	0.135±0.005	0.560±0.020	0.445±0.006	0.743±0.012	0.427±0.012	0.509±0.209
BbF	0.670±0.023	0.192±0.043	0.751±0.019	0.298±0.053	0.388±0.031	0.199±0.001	0.416±0.220
BkF	0.270±0.004	0.170±0.090	0.281±0.007	0.175±0.080	0.270±0.001	0.270±0.011	0.239±0.047
BaP	0.833±0.023	0.133±0.019	0.864±0.033	0.153±0.014	0.233±0.011	0.633±0.003	0.475±0.312
IP	0.754±0.031	0.156±0.029	0.762±0.025	0.556±0.026	0.754±0.210	0.354±0.002	0.556±0.232
DA	0.674±0.021	0.174±0.005	0.587±0.023	0.178±0.005	0.574±0.009	0.634±0.021	0.470±0.211
Bp	1.945±0.001	1.945±0.099	1.896±0.081	3.345±0.092	3.425±0.003	2.925±0.030	2.580±0.670
Total	**41.169±1.904**	**29.296±1.631**	**42.359±1.979**	**34.065±1.643**	**34.748±1.756**	**31.607±1.466**	**35.54±1.607**

Source: Field Survey (2022)

Table 3: Mean levels of two-monthly determinations of PAHs in soil around automobile repair workshop at Alesa, Eleme (Station 2)

PAHs (mg/kg)	Months						Mean ± S.D
	November	January	March	May	July	September	
Na	4.116±0.097	4.218±0.041	5.011±0.091	3.227±0.051	3.625±0.040	3.926±0.041	4.021±0.551
Acy	3.544±0.061	1.550±0.002	4.401±0.073	1.652±0.012	2.631±0.032	2.021±0.032	2.633±1.038
Ace	3.811±0.074	2.810±0.021	3.830±0.044	2.910±0.010	2.890±0.023	3.930±0.022	3.363±0.496
Fl	2.610±0.023	1.610±0.031	4.311±0.013	1.914±0.035	2.625±0.060	2.819±0.073	2.648±0.858
Ph	3.761±0.078	3.751±0.007	3.462±0.056	3.753±0.009	3.663±0.018	4.633±0.030	3.837±0.371
An	3.380±0.031	3.379±0.040	4.320±0.040	3.475±0.041	3.484±0.025	3.537±0.082	3.596±0.329
Flu	2.784 ±0.010	5.784±0.005	2.658±0.020	5.384±0.015	2.652±0.011	4.412±0.011	3.946±1.313
Py	1.619±0.001	4.619±0.012	3.217±0.011	4.720±0.022	5.679±0.020	5.541±0.029	4.233±1.417
BaA	0.540±0.011	0.640±0.061	0.572±0.009	0.640±0.050	0.442±0.031	0.394±0.081	0.538±0.093
Ch	0.427±0.012	0.743±0.012	0.468±0.019	0.875±0.012	1.463±0.017	1.107±0.001	0.847±0.360
BbF	0.199±0.001	0.388±0.031	0.256±0.011	0.368±0.021	0.488±0.030	0.383±0.031	0.347±0.094
BkF	0.270±0.011	0.270±0.001	0.228±0.010	0.200±0.001	0.271±0.052	0.219±0.001	0.243±0.029
BaP	0.633±0.003	0.233±0.011	0.647±0.030	0.283±0.013	0.524±0.027	0.254±0.021	0.429±0.177
IP	0.354±0.002	0.754±0.210	0.607±0.009	0.784±0.010	0.763±0.032	0.821±0.012	0.681±0.161
DA	0.634±0.021	0.574±0.009	0.599±0.031	0.970±0.009	0.534±0.019	0.586 ±0.006	0.650±0.146
Bp	0.925±0.030	3.425±0.003	0.927±0.036	1.465±0.003	4.714±0.022	4.845±0.042	2.717±1.683
Total	**29.607±1.465**	**34.748±1.756**	**35.514±1.761**	**32.62±1.607**	**36.448±1.642**	**39.428±1.871**	**34.729±1.517**

Source: Field Survey (2022)

Table 4: Mean levels of two-monthly determinations of PAHs in soil around automobile repair workshop at Onne, Eleme (Station 3)

PAHs (mg/kg)	Months						
	November	January	March	May	July	September	Mean ± S.D
Na	3.616±0.031	3.621±0.031	3.625±0.040	3.926±0.041	3.716±0.052	4.218±0.041	3.787±0.221
Acy	2.544±0.012	2.220±0.012	2.631±0.032	2.021±0.032	2.644±0.114	1.550±0.002	2.268±0.393
Ace	2.811±0.032	3.812±0.032	2.890±0.023	3.930±0.022	3.927±0.091	2.810±0.021	3.363±0.528
Fl	1.610±0.023	2.911±0.023	2.625±0.060	2.819±0.073	2.710±0.031	1.610±0.031	2.381±0.552
Ph	3.761±0.010	4.731±0.010	3.663±0.018	4.633±0.030	1.761±0.043	3.751±0.007	3.717±0.975
An	3.380±0.022	3.584±0.022	3.484±0.025	3.537±0.082	4.680±0.071	3.379±0.040	3.674±0.456
Flu	2.784±0.001	4.312±0.001	2.652±0.011	4.412±0.011	2.884±0.100	5.784±0.005	3.805±1.137
Py	5.619±0.030	5.340±0.030	5.679±0.020	5.541±0.029	3.919±0.021	4.619±0.012	5.120±0.643
BaA	0.140±0.001	0.314±0.001	0.442±0.031	0.394±0.081	0.150±0.011	0.640±0.061	0.347±0.173
Ch	1.426±0.011	1.257±0.011	1.463±0.017	1.107±0.001	0.135±0.005	0.743±0.012	1.022±0.463
BbF	0.388±0.031	0.361±0.041	0.488±0.030	0.383±0.031	0.192±0.043	0.388±0.031	0.367±0.083
BkF	0.270±0.001	0.269±0.001	0.271±0.052	0.219±0.001	0.170±0.090	0.270±0.001	0.245±0.038
BaP	0.233±0.021	0.154±0.021	0.524±0.027	0.254±0.021	0.133±0.019	0.233±0.011	0.255±0.128
IP	0.754±0.012	0.801±0.012	0.763±0.032	0.821±0.012	0.156±0.029	0.754±0.210	0.675±0.233
DA	0.574±0.009	0.486±0.006	0.534±0.019	0.586±0.006	0.174±0.005	0.574±0.009	0.488±0.144
Bp	4.925±0.032	4.943±0.032	4.714±0.022	4.845±0.042	1.945±0.099	3.425±0.003	4.133±1.112
Total	**34.835±1.706**	**39.116±1.854**	**36.448±1.642**	**39.428±1.871**	**29.296±1.631**	**34.748±1.756**	**35.647±1.663**

Source: Field Survey (2022)

Table 5: Mean levels of PAHs in soil across the three selected automobile repair workshops in Eleme

PAHs (mg/kg)	Stations 1	2	3	Range	**Mean ± S.D**	Control
Na	4.436±0.482	4.021±0.551	3.787±0.221	3.787 – 4.436	4.081±0.268	ND
Acy	3.259±1.165	2.633±1.038	2.268±0.393	2.268 – 3.259	2.720±0.409	ND
Ace	3.960±0.736	3.363±0.496	3.363±0.528	3.363 – 3.960	3.562±0.281	ND
Fl	3.313±1.316	2.648±0.858	2.381±0.552	2.381 – 3.313	2.781±0.392	ND
Ph	3.451±0.945	3.837±0.371	3.717±0.975	3.451 – 3.837	3.669±0.161	ND
An	4.508±0.872	3.596±0.329	3.674±0.456	3.596 – 4.508	3.926±0.413	ND
Flu	3.397±1.077	3.946±1.313	3.805±1.137	3.397 – 3.946	3.716±0.233	ND
Py	3.359±0.987	4.233±1.417	5.120±0.643	3.359 – 5.120	4.237±0.719	ND
BaA	0.612±0.242	0.538±0.093	0.347±0.173	0.347 – 0.612	0.499±0.112	0.162±0.019
Ch	0.509±0.209	0.847±0.360	1.022±0.463	0.509 – 1.022	0.793±0.213	0.155±0.011
BbF	0.416±0.220	0.347±0.094	0.367±0.083	0.347 – 0.416	0.377±0.029	0.577±0.050
BkF	0.239±0.047	0.243±0.029	0.245±0.038	0.239 – 0.245	0.242±0.002	0.123±0.011
BaP	0.475±0.312	0.429±0.177	0.255±0.128	0.255 – 0.475	0.386±0.095	0.163±0.020
IP	0.556±0.232	0.681±0.161	0.675±0.233	0.556 – 0.681	0.637±0.058	0.192±0.021
DA	0.470±0.211	0.650±0.146	0.488±0.144	0.470 – 0.650	0.536±0.081	0.163±0.010
Bp	2.580±0.670	2.717±1.683	4.133±1.112	3.787 – 4.436	3.143±0.702	0.581±0.011
Total	**35.540±1.607**	**34.729±1.517**	**35.647±1.663**	**34.729 – 35.647**	**35.305±1.561**	**2.116±0.185**

Source: Field Survey (2022)

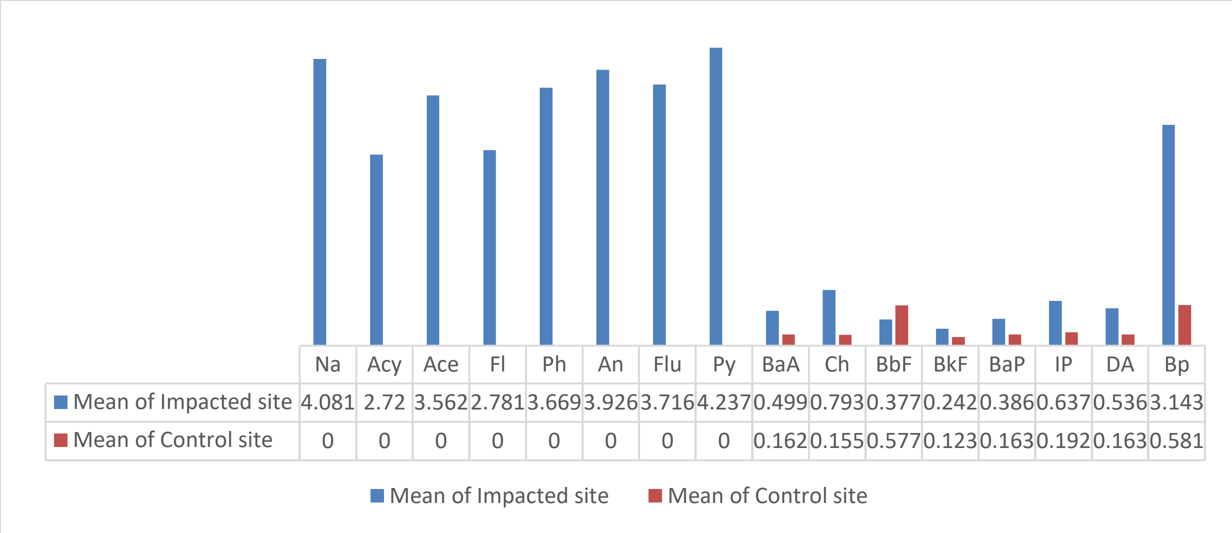

Figure 1: Mean concentrations of polycyclic aromatic hydrocarbon of topsoil around selected automobile workshops in Eleme in comparison with the control within the sampled period

The concentration of total PAHs in this study was similarly in the same range of 245±21 to 23400±25 µg/kg as noted in soils at automobile workshops by Ipeaiyeda and Ogungbemi (2020), but lower than the range of 214.83±14.875 to 404.16 ± 69.940 mg/kg as reported in the soil environment around Selected Auto-Technicians' Workshop in ObioAkpor, Rivers State, Nigeria (Daniel et al., 2020). On the other hand, the concentrations observed in the present study were higher than the concentration ranges of 0.14 and 0.21 mg/kg as obtained in soil from an auto-mechanic workshop in Akure City, Nigeria, by Alabi et al. (2019); 1.998 and 8.682 mg/kg gotten from soil at the vicinity of mechanic workshops in Benin City by Anegbe et al. *(2016)*; < 0.02 to 1.80 mg/kg as found in the soil of auto-mechanic workshops at Alaoji, Aba and Elekahia, Port Harcourt, Niger Delta, Nigeria, by Muze et al. (2020); 0.0184 ± 0.02 to 0.1385 ± 0.2 mg/kg as assayed in soil contaminated with spent motor engine oil in Abakaliki Auto-Mechanic Village by Obini et al. (2013); 0.83 to 12.98mg/kg as examined in soil around automobile repair workshops within Eket Metropolis, Akwa Ibom State, Nigeria by Ekanem et al. (2019); 66.4 - 5321.9 µg/kg as observed in soils from selected vehicle-parks in southern Nigeria by Emoyan et al. (2020); 325–1122.8 µg/kg as noted in soil around auto-mechanic workshops in major towns in Benue State, Nigeria by Eneji et al (2017); 3.246 - 6.890 mg/kg as observed in soil from auto-mechanic workshops along Ikokwu Mechanic Village, Port Harcourt, Nigeria (Akomah & Osayande, 2018).

Based on how long the mechanics' workshops have been operating, the presence of PAHs may be attributable to the ongoing dumping of spent engine oil. The study thus demonstrates that organic soil content contributes to the sequestration of PAHs in the soil-water system. According to Ipeaiyeda and Ogungbemi (2020), most auto lubricants that leak on soil contain polycyclic aromatic hydrocarbons (PAHs), which have been identified as probable human carcinogens and are major contaminants associated with used engine oil and are typically deposited on soil surfaces. Due to the leaking of vehicle lubricants and the careless abandonment of tyres and spare parts, auto repair shops have been identified as a possible source for the enrichment of soils with heavy metals and polycyclic aromatic hydrocarbons. These pollutants are carried into the storm sewer system by rain and leached into the groundwater. Used engine oil spreads fast and eventually seeps into bodies of water (Anegbe et al., 2016). Regular use of petroleum-based products, including gasoline, frequently leads to the substantial and unavoidable spilling of the majority of these products into the environment. The top soils of the examined car shops included PAHs, primarily as a result of the auto mechanics' improper treatment and disposal of used oil. For both plants and animals, as well as people who interact with the environment either directly or indirectly, this may have a number of detrimental health effects (Daniel et al., 2020).

According to Alabi et al. (2019), residents of an auto-mechanic village may be predisposed to a greater risk of cancer due to long-term exposure to PAHs through contaminated soils, rivers, and groundwater because auto-mechanic activities are constant. Since there is no dose at which PAH's carcinogenic effects do not occur, the values of PAH found in this study should be considered seriously and should not be taken for granted.

Source Identification and Diagnostic Ratios of PAHs in the Soils

Table 6: Diagnostic Ratios of PAHs in soil Sample from Eleme

Stations	∑LMW PAHs	∑HMW PAHs	LMW/HMW	An/(An+Ph)	Flu/(Flu+Py)	BaA/(BaA+Ch)
1	22.927	12.613	1.817727741	0.566402814	0.502812315	0.545941124
2	20.098	14.631	1.37365867	0.483788511	0.482455068	0.388447653
3	19.190	16.457	1.16606915	0.497091057	0.426330532	0.253469686
Petrogenic			> 1	< 0.1	< 0.4	< 0.2
Pyrogenic			< 1	> 0.1	> 0.5	> 0.35

LMW (Low Molecular Weight), HMW (High Molecular Weight), An (anthracene), Ph (phenanthrene), Flu (fluoranthene), Pyr (pyrene), BaA (benzo [a] anthracene), Ch (chrysene)

The sum of LMW PAHs was 22.927; HMW was 12.613; and the ratio LMW/HMW was 1.817727741. The An/(An+Ph) ratio was 0.566402814, the Flu/(Flu+Py) ratio was 0.502812315, and the BaA/(BaA+Ch) ratio was 0.545941124. The sum of LMW and HMW at Station 2 was 20.098 and 14.631, respectively. LMW/HMW was 1.37365867, An/(An+Ph) was 0.483788511, Flu/(Flu+Py) was 0.482455068, and BaA/(BaA+Ch) was 0.388447653. At Station 3, the summation values of LMW and HMW were 19.190 and 16.457, respectively, and the LMW/HMW ratio was 1.16606915. The An/(An+Ph) ratio was 0.497091057, the Flu/(Flu+Py) ratio was 0.426330532, and the BaA/(BaA+Ch) ratio was 0.253469686.

The sources and nature of polycyclic aromatic hydrocarbons have a resultant effect on their pattern of distribution or spread in an environment and are very effective in the evaluation of their overall detrimental effects on the environment. The pattern of occurrence relative to the polycyclic aromatic hydrocarbon ratio is an excellent tool for predicting, identifying, and diagnosing its source and origin in any given environment, as well as separating the various input sources. The pattern and nature of spreading in the levels of polycyclic aromatic hydrocarbons in the different soil samples in this investigation are impacted by the source implications and spreading of PAHs, and these effects are superimposed by the results recorded for the source diagnosis and identification. As a result, the source diagnosis was calculated primarily using the ratios or proportions among the distinct PAHs, and it was then interpreted in light of the range that each ratio falls into.

The increased ratio of pyrogenic or combustion-based PAHs found in the soil samples from different car garage stations indicated that anthropogenic sources, especially combustion and spills of petroleum products, were the main sources of PAH component input. Approximately 20 million gallons of used engine oil are produced annually by mechanic shops in Nigeria, according to Alabi et al. (2019), who also lamented the lack of industry-standard practices for managing spent oil in these facilities.

According to Muze et al. (2020), the results of the diagnostic ratio of phenanthrene to anthracene point to a pyrogenic origin. He observed that all of the An/Phe+An values were below one, suggesting that the PAHs are of petrogenic origin. In the six sample locations that were examined, the values of the Fla/Pyr ratio were all less than one, with the exception of one sample, indicating that the PAHs in these samples were of petrogenic origin, whereas those in the other samples were of pyrogenic origin. The values observed for Fla/Pyr+Fla in all but one of the sample sites were less than 0.5, indicating that the PAHs in that sample were due to emissions from petroleum products, whereas those in the other samples were due to diesel emissions. This may be a result of the auto mechanics' actions in the locations under investigation. These PAHs are present in the research area as a result of the burning of carbonaceous materials, as shown by the ratios of 0.24 and 0.30 for Ba/Ba+Chy in two study locations. Additional samples produced results greater than 0.35, showing the presence of PAHs from both combustion and vehicle emissions. PAHs are most likely produced during the combustion of biomass and petroleum products, according to the values of the Ind/Ind+B(ghi)p ratio. He came to the conclusion that the results of the diagnostic ratio analysis indicate that the petroleum products from the vehicles repaired in the mechanic villages are the primary cause of the PAHs.

Similar to this, Ekanem et al. (2019) reported that the diagnostic ratio used for source determination revealed that the PAHs in the study were primarily from both petrogenic and pyrogenic origins. They assessed PAHs levels in soil around auto repair workshops within Eket Metropolis, Akwa Ibom State, Nigeria and came to the conclusion that soil contamination with PAHs was a result of automotive maintenance activity.

CONCLUSION

The results of polycyclic aromatic hydrocarbons in the soils of the studied locations of Eleme and part of Khana, as well as the control site, revealed that PAHs were detected at these stations at varying concentrations in all of the sample soils examined. There was a marked difference between the concentration of PAHs in the soil from the automobile repair garages and the control site. Looking at the results generally, it was noted that the low molecular weight (LMW) PAHs had the highest concentrations, which suggests that LMW PAHs were easily lost into the atmosphere through volatilization and transported into the soil by water since their solubility in water is higher than that of the high molecular weight PAHs. According to source identification and diagnostic ratios of polycyclic aromatic hydrocarbons in the soils, combustion and spills of petroleum products were the main sources of PAH component input.

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