



Physicochemical and Polycyclic Aromatic Hydrocarbons (PAHs) Analysis in Soil and Sediment from Vicinity of Ikot Akpaden, Akwa Ibom State, Nigeria

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

The study was undertaken to determine the levels of 16 priority PAHs in soil and sediments from some vicinities of Ikot Akpaden, Mkpat Enin. The soils were prepared using standard procedure in the laboratory and analyzed for 16 US EPA priority PAHs using Gas Chromatography-Mass Spectrophotometer (GC-MS). The soil samples were obtained from two sampling sites at Ikot Akpaden (Site A and C). Site C showed minimal PAHs concentration while site A recorded PAHs levels ranging from 0.01 to 4.25 mg/kg. According to European commission, the PAHs concentrations in soil samples of this study are moderate, but deleterious over time. The soils were

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negatively affected more with low molecular weight PAHs than High Molecular Weight PAHs. This study revealed that the sampling sites had low carcinogenic burden, hence would exhibit moderate adverse health effects to plants and animals. It was concluded that automobile repair activities in site A contributed to the soil contamination with PAHs; hence it should be properly sited.

Keywords: Polycyclic; aromatics; physicochemical; hydrocarbons; carcinogenic.

1. INTRODUCTION

“Polycyclic aromatic hydrocarbons (PAHs) can be widely found in the environment mainly due to long term anthropogenic sources of pollution. The inherent properties of PAHs such as heterocyclic aromatic ring structures, hydrophobicity and thermo stability have made them recalcitrant and highly persistent in the environment. PAHs pollutants have been determined to be highly toxic, mutagenic, carcinogenic, teratogenic, and immunotoxicogenic to various life forms. Rapid industrialization and urbanization have resulted in numerous anthropogenic activities, which have led to the random discharge of various pollutants into the environment” [1,2]. According to the United Nations Environmental Programme, the pollution of environment by PAHs is a serious environmental issue especially by automobiles.

“The PAH pollutants are ubiquitous and found equally in aquatic and terrestrial ecosystems, as well as in the atmosphere” [3]. “The rate of deposition of PAHs was found to accelerate in the soil/sediments due to their higher hydrophobicity and low aqueous solubility. They are strongly absorbed onto soil particles, and therefore, the soil ecosystem becomes an ultimate sink for PAHs” [4,5]. “Soil PAH pollution can be classified into three categories, namely; Unpolluted ($\sum\text{PAH} < 200 \text{ ng.g}^{-1}$), weakly polluted ($\sum\text{PAH} 200 < 600 \text{ ng.g}^{-1}$), and Heavy polluted ($\sum\text{PAH} > 1,000 \text{ ng.g}^{-1}$)” [6]. PAH

“Pollution, either directly or indirectly, is strongly affecting the health and wellbeing of humans,

along with other organisms across the planet” [7-9]. “Sediments and soils are the main sinks for PAHs in the environment and could contain about 90% of these compounds with longer half-life than the atmosphere or in plants” [10]. “This is because they are absorbed strongly to the organic fractions of sediments and soils” [11]. The aim of this study is to determine the physicochemical parameters and the levels of PAHs in soils and sediments within the vicinity of Ikot Akpaden, Akwa Ibom State, Nigeria.

2. MATERIALS AND METHODS

2.1 Sample Location

The study area was Ikot Akpaden automobile repair workshop located at Ikot Akpaden junction and Akwa Ibom State University, Ikot Akpaden campus.

2.2 Sampling

Three samples were collected at different sites to make a composite sample within the vicinity of an automobile repair workshop as site A and the school premises as Site C (control) in Ikot Akpaden at the depth of 0-15 cm. The two sites are indicated in Table 1. The soil samples were collected in January, 2022 between the hours of 2-4pm using stainless hand held auger and were wrapped with a cleaned, labeled aluminum foil. Samples were transported to the laboratory and air dried at room temperature for 7 days according to standard analytical procedure described by Ekanem et al. [12].

Table 1. Coordinates of the sampling locations

Sampling sites	Location	Site code	Latitude (North)	Longitude (East)
A	Automobile Repair Workshop, Ikot Akpaden junction.	A ₁	04°37'26.1"	007°45'50.4"
		A ₂	04°37'26.7"	007°45'51.0"
		A ₃	04°37'26.7"	007°45'51.0"
C (Control)	The School premises (AKSU)	C ₁	04°37'19.7"	007°45'51.6"
		C ₂	04°37'20.0"	007°45'51.9"
		C ₃	04°37'20.0"	007°45'51.6"

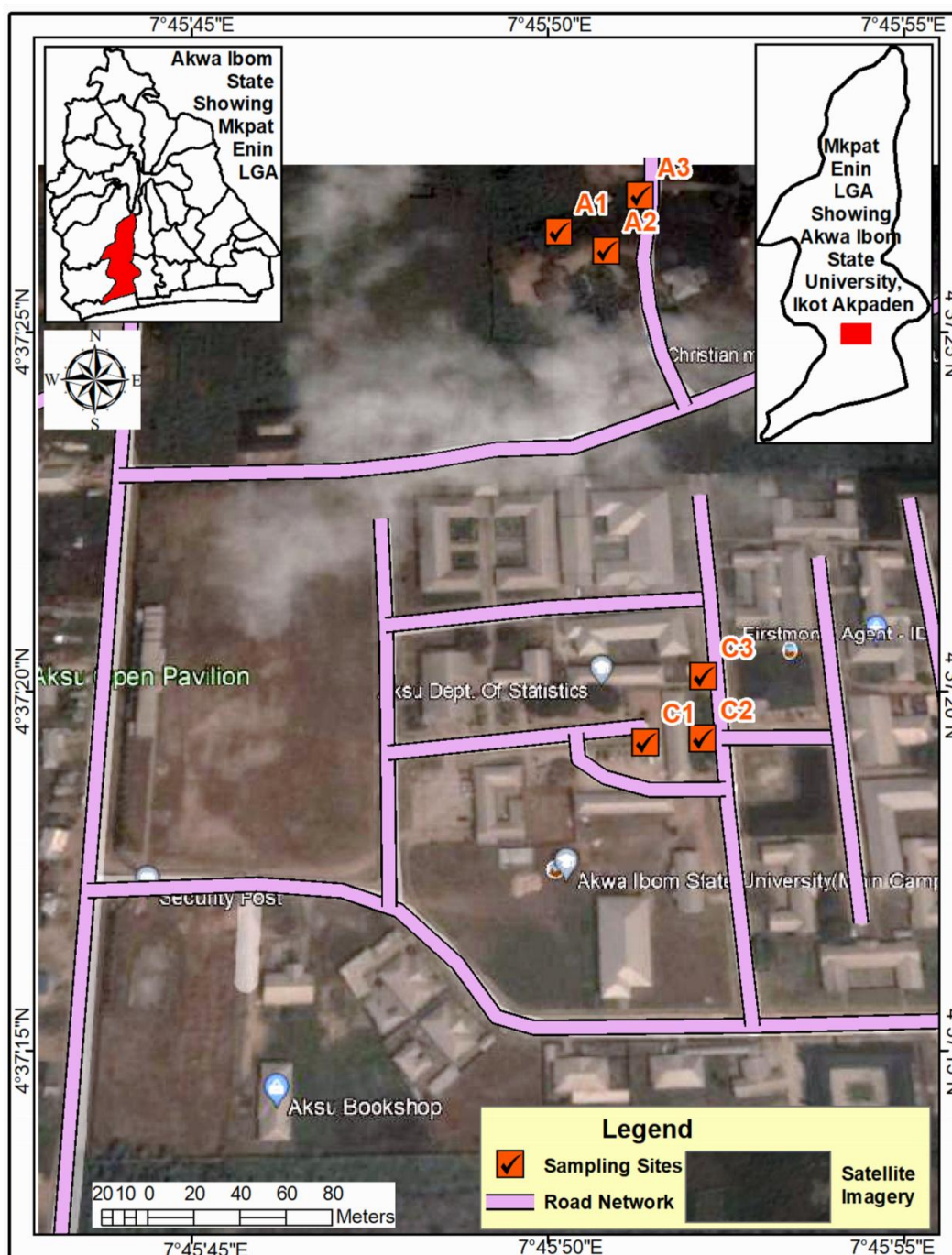


Fig. 1. location of sampling points of Ikot Akpaden Vicinity on the study map

2.3 Sample Preparation

10 g of each of the three samples from a particular site was weighed into a porcelain mortar (to obtain a homogenized sample) and was pulverized thoroughly with 10 g of anhydrous sodium sulphate (Na_2SO_4). The pulverized soil sample was poured into an extraction thimble ready for extraction [13].

2.4 Physicochemical Analysis

The Physicochemical parameters determined in the samples are; temperature, pH, salinity, electrical conductivity and total dissolved solids (TDS). 10 g of each of the three sample points from site A and C were weighed and pulverized thoroughly to obtain an homogenized sample of A and C respectively and was transferred into a

beaker. 59 ml of deionized water was added and allowed for 30 minutes to equilibrate [1,14].

Conductivity meter with dual purposes was used to determine electrical conductivity later switch over for the determination of other parameters in the solution using standard analytical methods [1].

Table 2. GC- analysis

Gas chromatograph	HP6890 powered with HP Chem. station software
Injection mode	Split
Split ratio	20:1
Carrier gas	Helium
Inlet temperature	270°C
Final temperature	320°C
Column type	HP5
Column dimension	30mX0.25mmX0.25mm
Oven program	Initial tempt. at 65oC for 30mins, Ramp at 10.10mins
Detector	Mass Spectrometer
Detector temperature	320°C
Carrier gas	Helium @30.0pSi
Injector	Auto sampler (ALS)
Injection volume	1UI
Transfer line temperature	280°C
MS Acquisition Parameter	
Acquisition mode	Selective Ion Mode (SIM)
Mass range	128-202amu (Group 1-12)
Dwell time	25Seconds
Resulting	1694.1

2.5 Solvent Extraction

“10 g of the soil sample in triplicate was weighed and mixed with 10g of anhydrous sodium sulphate (Na₂SO₄), and then ground using porcelain mortar and pestle until homogeneous powder was obtained. The powdered samples were transferred into soxhlet thimble then placed in a round bottomed flask before connecting to soxhlet setup. The soxhlet extraction was done using 200 cm³ of acetone and dichloromethane (in the ratio of 1:1) at 65°C. The extract was allowed to cool after complete extraction” [15,16]

2.6 Sample Clean-up

“The concentrated extract was cleaned off the interfering compounds using Column Chromatography. The Chromatographic column (2 cm internal diameter and 10cm long) was

packed with 5 g activated Silica gel (60-120 merge size) followed by 2 g of anhydrous sodium sulphate. The column was preconditioned with 10 ml of n-hexane followed by 10 cm³ of dichloromethane. The extract was added into the column and was first eluted with 10 ml n-hexane to remove saturated hydrocarbons which was subsequently discarded. This was followed by the addition of 10 ml dichloromethane to elude the PAHs” [17].

3. RESULTS AND DISCUSSION

3.1 Physicochemical Parameters of Soil

The results of the physicochemical parameters determined in the study include; temperature, pH, electrical conductivity, salinity and total dissolved solids as given in Table 3.

3.1.1 Temperature

There were significant differences in the temperature of the two sites. The temperature of site A and site C (control) were 27.8°C and 28.2°C respectively. The temperature recorded in both sites correlate with Alkali et al. [18]. The temperatures of the two sites were slightly different from the FEPA standard.

3.1.2 Salinity

The salinity values of the soil samples were 0.10% and 0.00% respectively indicating low salinity status of the soil. High salinity decreases plant growth and water quality resulting in lower crop yields. It kills plants, leaving bare soil that is prone to erosion [14].

3.1.3 Electrical conductivity

The EC of the soil samples ranged from 18.91 to 31.3 (µS/cm). The conductivity of the soil samples showed a greater difference when compared to FEPA standard. In a similar study; Shivanna & Nagendrappa [19], found that the soil EC ranged from 0.26 d/sm to 0.485d/sm indicating low salinity status.

3.1.4 pH

Highest value of pH was recorded at Site A and lowest at Site C. The pH of the soil sample ranged from 7.3 to 7.4 and slightly alkaline. The pH values obtained in this study corresponds to those reported by Shivanna & Nagendrappa [19]. In a similar study in Nigeria, Osakwe & Okolie

[20] found that the soil pH had a mean value of 5.15 ± 0.48 . According to Sanchez [21] and Yerima & Van Ranst [22], "in soils where pH in water is higher than pH in KCl, the exchange complexes of such soils are dominated by negatively charged colloids and as consequences, cation exchange capacity prevails". "Soil pH plays a great role in the occurrence of some mangrove species such as *Nypa* palms" [23]. According to Akoto et al. [24] "the deviation from the natural background pH level of 7.0 is attributed to the presence of dissolved carbonates and bicarbonates, which are known to affect pH of most surface water". "The pH values were within

the WHO and USEPA recommended guideline for water courses standards of 6.5 to 8.5" [25,26].

3.1.4.1 Total Dissolved Solids (TDS)

There was a notable significant difference between the values of TDS in both sites with site A recording 945mg/L and site C 15.71 mg/L. Similar study carried out by Alkali et al. [18] showed higher values (542.47 to 1538.50 mg/L) than what is reported in this work. Ftsum et al. [27] in Elala River, Ethiopia showed TDS values ranging between 700 to 1328 mg/L which were equally higher.

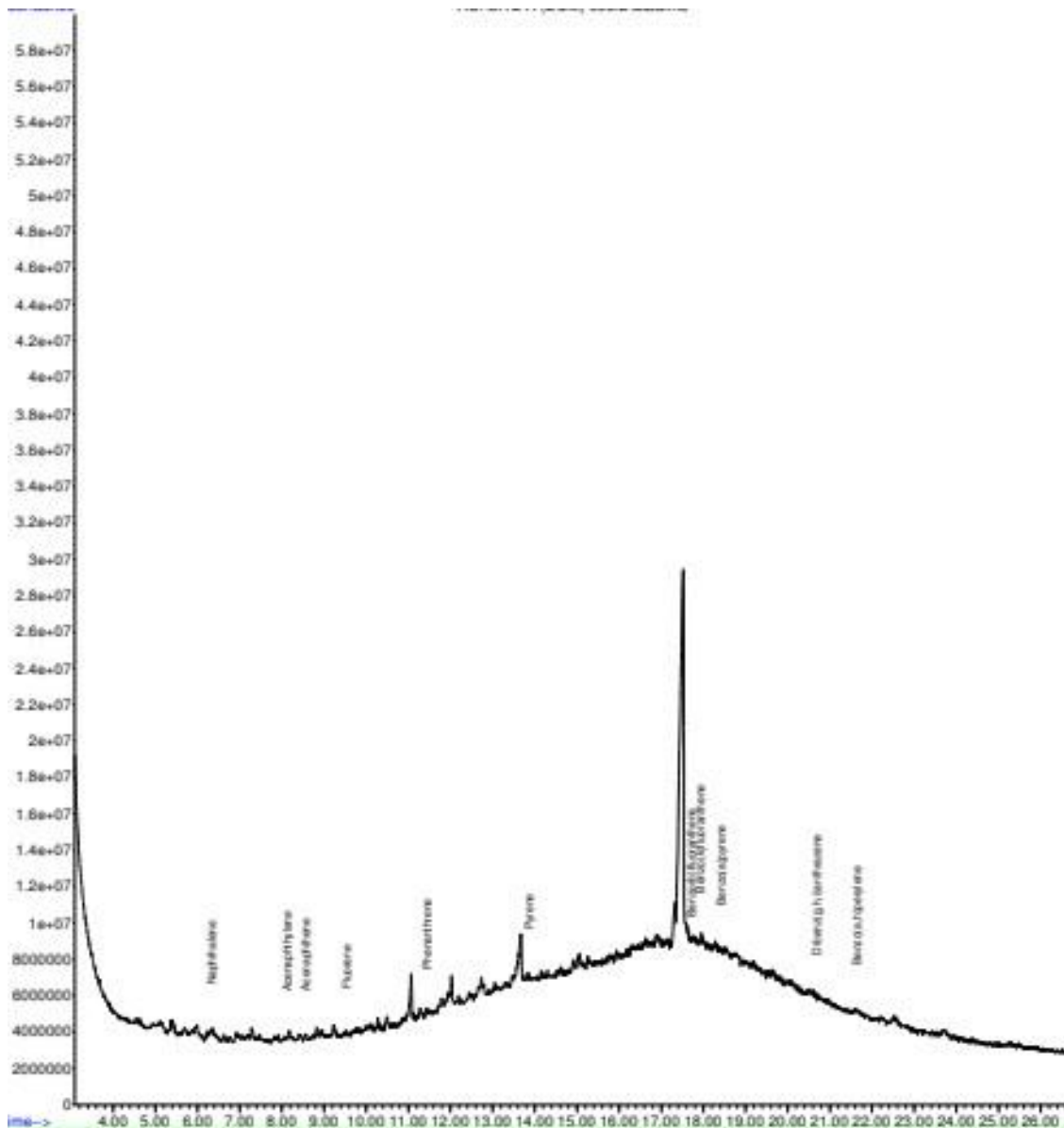


Fig. 2. PAHs in site A

3.1.4.2 Concentrations of PAHs in Soil

The concentrations of the 16 priority PAH components (mg/kg) in the soil samples collected from Ikot Akpaden automobile repair workshop are presented in Table 4. The GC-MS fingerprints confirming the presence of these analyte in the samples are shown in Figs. 2-3.

The 16 priority PAHs recommended by WHO and USEPA were found present at site A except for anthracene, fluoranthene, benzo (a) anthracene, chrysene and indeno (1,2,3-cd)

perylene which were either non-existent or below detection limit. The average PAHs level varied from a minimum of 0.01 mg/kg to a maximum of 4.25 mg/kg (Table 4).

Spatially, the highest PAHs concentrations were recorded at site A (4.53 mg/kg). Site A is an automobile workshop with a high incidence of careless discharge of automobile effluents, like used engine oil and petroleum products; this may have led to the introduction of PAHs and other petroleum hydrocarbons into the soil.

Table 3. Values of physicochemical parameters of soil in site A and site C (control)

Site	Temperature (°C)	Salinity (%)	EC (µS/cm)	TDS (mg/L)	pH
A	27.8	0.00	18.91	945.0	7.4
C (control)	28.2	0.10	31.3	15.71	7.3
FEPA standard	40.0	—	4.00	2000	7.0

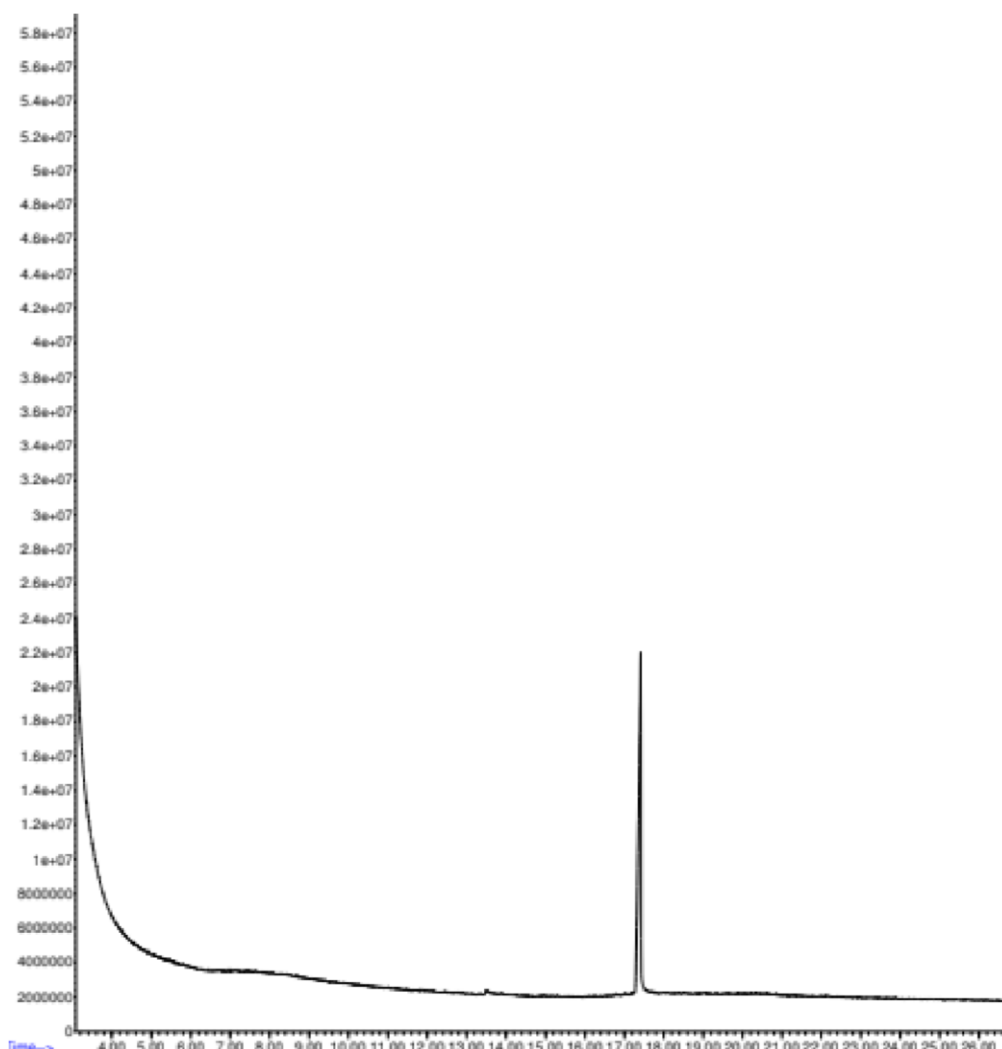


Fig. 3. PAHs in site C

Table 4. Concentration of 16 priorities PAH components assayed in the soil samples

PAH Component (mg/kg)	Site A	Site C
Naphthalene	4.25	nd
Acenaphthylene	0.03	nd
Acenaphthene	0.01	nd
Fluorene	0.05	nd
Phenanthrene	0.07	nd
Anthracene	nd	nd
Anthracene	nd	nd
Fluoranthene	nd	nd
Pyrene	0.03	nd
Benzo(a)anthracene	nd	nd
Chrysene	nd	nd
Benzo(k)fluoranthrene	0.02	nd
Benzo(b)fluoranthrene	0.01	nd
Benzo(a)pyrene	0.02	nd
Indeno(1,2,3-cd)perylene	nd	nd
Dibenzo(a,h)anthracene	0.02	nd
Benzo(g,h,i)perylene	0.02	nd

Comparism of the total concentration of PAHs in site A was higher than in site C.

This may be attributed to the minimal industrial activities in the site C, which is situated in the Ikot Akpaden campus of Akwa Ibom State University. However, the level of PAHs in site A are in variance with values in several reviewed literature. It was reported [28] that the values of PAHs in soil in industrial, residential and agricultural areas of central South Africa ranged from 44 ng/g to 39000ng/g. This range of values is lower than the result of the present study.

However, higher values of PAHs (584.44 µg/g) in soil were recorded in Sapele municipality, Nigeria [29]; Balogun-Birro dumpsite, Nigeria [30] indicated a PAH concentration of 5.6491 mg/kg. Generally, the PAHs in soil of site A are higher than WHO standard of 4 mg/kg. According to the European commission classification system of soil contamination, £16 priority PAHs < 0.20 mg/kg show no contamination, 0.20-0.60 mg/kg corresponds to weak contamination, 0.60 - 1.0 mg/kg corresponds to moderate contamination and >1.0 mg/kg indicates heavy contamination. Following this classification, it can be said that the soil in this study area is moderately contaminated. The lower molecular weight PAHs (LMW PAHs) were generally present in lower Concentration in all the two sites except Naphthalene at site A.

“Higher molecular weight PAHs (HMW PAHs) were well distributed in site A. Naphthalene had

the highest total concentration in all the samples. Fluoranthene had the lowest concentration among all the HMW PAHs in site A. The less volatile, high molecular PAHs tend to bind more tightly to soils posing a remediation challenge” [31]. This observation is contrary to the results obtained by Adedosu et al. [32]; who found that higher molecular weight PAHs were more dominant in the soil sample investigated.

The International Agency for Research on Cancer (IARC) and 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.

PAHs in soil are taken up by plants in the vicinity, which are eventually consumed by humans. It has been stated that PAHs in human leads to several health problems, with the most serious effect being its carcinogenicity [12] Therefore, it is importance to constantly monitor the levels of PAHs in soil and sediment to safeguard human health.

4. CONCLUSION

The overall trend in the levels of physicochemical parameters show the pH, conductivity, temperature, TDS were within those recommended by FEPA. From the study, the levels of PAHs varied between the two sampling sites under investigation. Out of the 16 priority PAHs analyzed, it is worth noting that anthracene, fluoranthene, benzo(a)anthracene, chrysene and indeno[1,2,3cd]perylene were not detected in both sampling sites. The levels of PAHs were significantly higher in site A compared to those at site C. Fig. 3 reveals that the sample site A (automobile repair workshop) had the highest carcinogenic burden and hence it is said to have a risk of long term adverse health effect.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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