

MAE-GC-MS Assessment of Polyaromatic Hydrocarbons in the Bitumen Belt of Ondo State, Southwestern Nigeria

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Abstract: Polyaromatic hydrocarbons (PAHs) are of particular concern because of their mutagenic and carcinogenic effect on diverse ecosystems. The regional PAHs concentration was determined in soil over the bitumen belt of Ondo state, Southwestern Nigeria using MAE-GC-MS technique. The spatial concentrations of PAHs in the study area did not show any appreciable variation in all the soil samples analysed most especially surface soil. The surface soil shows that PAHs are derived principally from pyrogenic origin typically bush burning while subsurface soil PAHs origins were both pyrogenic and petrogenic. Though, the distributions of PAHs in the study area were not of any public concern because their concentrations were lower than quoted contaminated averages, however, the petrogenic origin in some part of study area may arise from surface oozing of bitumen and thus a concern for crop production in the affected areas.

Keywords: Soil, Regional, Concentration, PAHs, Bitumen

1. Introduction

Polyaromatic hydrocarbons (PAHs) are organic compounds with two (e.g. naphthalene) or several (e.g. benzo (a) pyrene) fused rings [1, 2]. They are of particular concern because of their mutagenic and carcinogenic properties [3, 4]. In the first place, this raises issues about human health risks [4, 5], because they are converted into products that can interact with Deoxyribonucleic acid (DNA) causing untold health hazards (1). Environmental contamination is by complex of PAHs and not by single compound [6]. Processes that introduce PAHs into the environment take place almost everywhere in the ecological system [7]. Polycyclic aromatic hydrocarbons released into the atmosphere have a strong affinity for airborne organic particles and can be moved great distances by air currents. The molecules are eventually transported to earth as wet or dry particulate deposition [8].

Polyaromatic hydrocarbons are found in air, water, sediment and soil; and through these they enter into food web [5, 9]. They can be bioconcentrated or bioaccumulated by organisms that lack capacity for effective biotransformation

[10]. Mammals' especially human being occupies the highest level in the food chain; the observed toxicity, mutagenesis and carcinogenicity become an important health issue for consideration in respect of the concentration of PAHs in the environment especially soil. To determine soil concentration of PAHs is therefore an important source of information. Sample preparation and analytical techniques used in the determination of PAHs in soil are diverse [6, 7, 11-13] and the concentrations of PAHs observed in environmental media in Nigeria are varied [14-22].

The present study area is part of the Nigeria bitumen belt that extends from Lagos state through Ogun, Ondo and terminates in Edo State (Figure 1). Presently in Ondo State bitumen belt, there has not been any significant exploitation other than occasional outcrops and seepages of the bitumen oil in area where deposits were close to the surfaces. There is paucity of information on regional concentrations of PAHs in the belt; the presently available knowledge is site specific. There have been recent demarcations of the belts into blocs for investors for possible commencement of bitumen exploitation. This study therefore attempts to examine the regional concentration of PAHs in the surface and subsurface

soil samples in the whole bitumen belt with a view to report across the belt prior to bitumen exploitation. perhaps for the first time the regional concentrations of PAHs

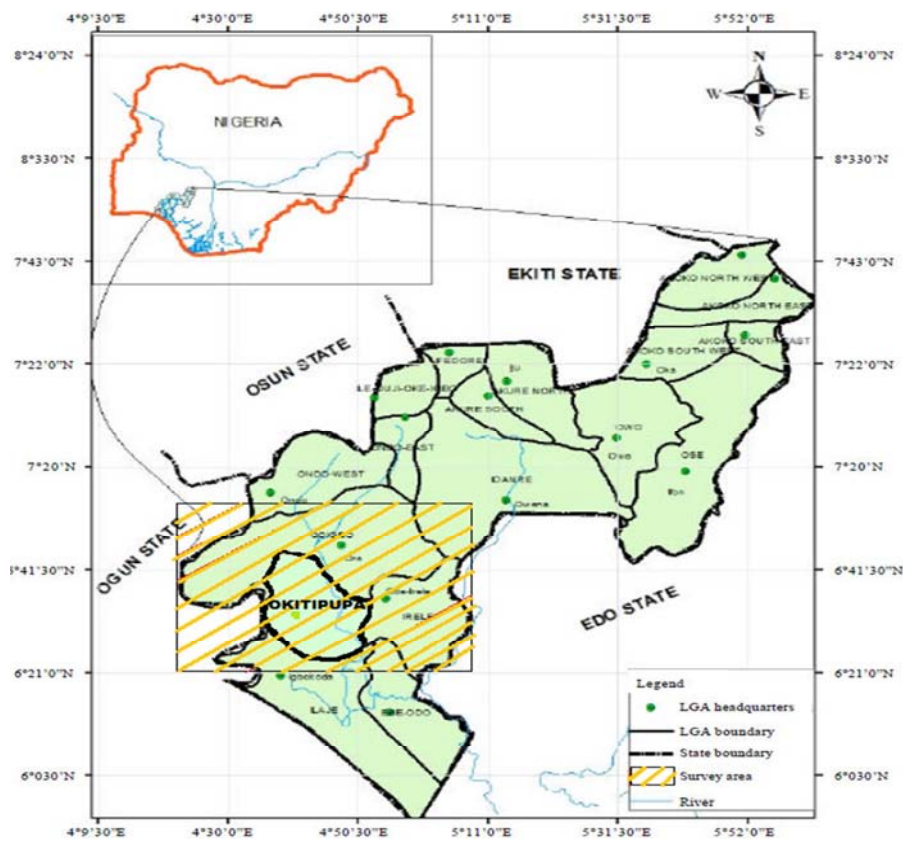


Figure 1. Map Showing the Study Area.

2. Experimental

2.1. Microwave-Assisted Extraction of PAHs

A CEM MARS Xpress Microwave Accelerated Reaction System (CEM Corporation, Matthews, NC, USA) was used. This system allowed up to 40 extraction vessels to be irradiated simultaneously. In this study, portions of 2.00 g soil was weighed into 55 ml perfluoroalkoxy (PFA) polymer extraction vessels equipped with Teflon-sealed lip-tight caps and polyetheretherketone (PEEK)-liners. Microwave power was 1600 W (100%). The extraction solvent was 25 ml n-hexane and acetone (4:1, v/v). The extraction was performed in temperature-controlled mode. The extraction temperature was 110°C and programmed as follows: ramp to 110°C for 10 min, holding at 110°C for 15 min. After the extraction completed, soil and solvent were separated by filtration into a pear-shaped flask [23].

2.2. Sample Concentration for PAHs

The extracts was transferred to 100-mL pear-shaped flasks and evaporated to nearly dryness under reduced pressure of 150 mbar at 35°C using a rotary evaporator (Buchi Switzerland Rotavapor R-210 fitted with thermostated heating bath B-491 and vacuum controller V-850). An

additional 10 ml n-hexane was added to the concentrated extracts and evaporated to a small volume (about 1 ml). Then the sample was transferred to 1.5 ml chromatographic vial for gas chromatography analysis [16].

2.3. Sample Analysis for PAHs

The PAHs were quantified by internal calibration performed with a GC/MS (Agilent GC6890/5973MSD). For PAHs analysis, a HP-5 MS column (Agilent, length 30 m, i.d. 0.25 mm, film thickness 0.25 mm) was employed with the following temperature program: 60–280°C at 6°C min⁻¹, isothermal holding at 280°C for 20 min using helium as the carrier gas. The instrument was operated with an initial flow of 1.2 mL min⁻¹, head pressure 0.03 Mpa, and injection mode as follows: splitless (1 mL), temperature of injector: 280°C. The MS was operated using the electron impact (EI) ionization mode at 70 eV, scanning from 50 to 550 mass units at 0.82 s scan⁻¹. All PAHs were determined by selective ion monitoring (SIM) [24].

3. Results and Discussion

3.1. Regional Concentration Patterns of PAHs

All PAHs were identified and determined in all soil samples (Tables 1-2); the spatial concentration of PAHs in

the study area did not show any appreciable variation as most data obtained were almost constant for all the PAHs in all the soil samples analysed. This is especially true for surface soil samples (Figures 2-3). The relative individual dominance of PAHs in surface soil were in the order dibenzo (a, h) perylene > benzo (b) fluoranthene = benzo (g, h, i) perylene (Figure 2) while the subsurface samples show two different patterns namely dibenzo (a, h) anthracene > benzo (b) fluoranthene = chrysene > benzo (g, h, i) perylene = indeno (1, 2, 3, cd) pyrene; and then acenaphthene > fluorine > phenanthrene (Figure 3). The surface soil samples shows that 2-3, 4- and 5-rings PAHs are equally dominant in all the sample analysed (Figure 2) while in the subsurface soil samples, two patterns were observed. The first pattern follow a similar trend with surface samples with 2-3, 4- and 5- rings PAHs showing equal dominancy while in the second pattern 2-3 rings PAHs are the dominant PAHs having 60% contribution to total concentration of PAHs (Figure 3). The total PAHs (Σ PAHt) values of the surface soil samples ranged from 1.99 mg/kg to 2.06 mg/kg with a mean value of 2.02 mg/kg (Table 1); while that of the subsurface soil samples ranged from 1.52 mg/kg to 1.56 mg/kg with a mean value of 1.53 mg/kg (Table 2). The concentration of total PAHs in all samples analysed are less than 250 ng/g (which represent contamination) (25), hence the area under study are free from PAHs contamination. Olajire et al (2007) [17] had earlier reported values of Σ PAHt in soil samples taken from the vicinity of Agbabu bitumen field to be in the range 101.6 to 180.6 (ng/g DW). For surface soil samples the organic carbon normalized PAHs (PAHs/OC) concentration ranged from 0.8896 to 1.2679 with an average of 1.0446. The majority of samples have values above one (Table 1); while for subsurface samples it ranges from 1.278 to 3.676 with mean value of 1.0816 (Table 2); all values are above one. The total concentration of potentially carcinogenic PAHs which includes benzo (a) anthracene, benzo (b) fluoranthene, benzo (a) pyrene, indeno (1, 2, 3, cd) pyrene and dibenzo (a, h) anthracene varied from 0.81 to 0.83 with an average value of 0.82 for surface samples (Table 1) while this is constant all through the analysed samples for subsurface samples at a value of 0.82 (Table 2). All these quoted values did not indicate contamination of PAHs in the study area.

3.2. Diagnostics Sources of PAHs

A number of parent and alkyl PAHs have been used to interpret PAHs sources in the environment [26]. In order to characterize PAHs with respect to sources, a number of diagnostics ratio are conventionally in use [1, 15, 21, 22, 26-35]. Flt/Pyr and Phen/Anth [29]; ratio of Flt/Flt+Pyr [30]; Anth/Anth+Phen; BaA/BaA+Chry; InP/InP+BgP [1]; total index:

$\text{Anth}/(\text{Anth}+\text{Phen})/0.1 + \text{Flt}/(\text{Flt}+\text{Pyr})/0.4 + \text{BaA}/(\text{BaA}+\text{Chr})/0.2 + \text{InP}/(\text{InP}+\text{BgP})/0.2$ [1]. The sources of PAHs in this study were investigated using the following diagnostics parameters. A Flt/Flt+Pyr ratio of <0.4 indicates PAHs suggests typical petroleum contamination e.g. crude oil, diesel etc, while Flt/Flt+Pyr > 0.5 indicates PAHs from combustion of grass, wood and coal and $0.4 < \text{Flt}/\text{Flt}+\text{Pyr} < 0.5$ from liquid fossil

fuel combustion such as vehicular exhaust emission [30]. The Flt/Flt+Pyr ratio in this study is a constant value of 0.5 (Table 1) for surface samples and between 0.48 and 0.54 for subsurface samples (Table 2). It implies that the PAHs are of pyrolytic/combustion origin (i.e. during bush burning activities) for the majority of both surface and subsurface samples with exception of sample 18 for subsurface sample which could results from combustion of liquid fossil fuel during vehicular or boat activities. The ratio BaA/BaA+Chry and InP/InP+BgP of <0.2 indicates petroleum inputs while values >0.35 and >0.5 respectively indicates pyrolytic source [22, 26, 31] and in-between indicates mixed sources [32]. The values obtained for the first ratio in this study for both surface and surface samples (0.485) indicated that the sources of PAHs are from pyrolytic source (>0.35) while that of the second ratio for both surface and subsurface samples (0.467) indicated a liquid fossil fuel origin. It is equally generally accepted that Flt/Pyr < 1 and Flt/Pyr > 1 are respectively petrogenic and pyrogenic sources. This ratio for the analysed samples show that the source of PAHs is pyrolytic as the values are either 1 or >1 except for subsurface sample 18 which is slightly less (0.923). The ratio Naph/Phen is used to assume the presence of fresh and unweathered petroleum if it is greater than unity [15, 33]. For the majority of sites this ratio for surface soil samples indicated petrolytic origin as the majority of values are greater than unity; while for subsurface samples, there are two patterns, samples 1 to 12 are generally either slightly less or greater than unity (0.86-1.54) indicating petrogenic origin and samples 13 to 19 are generally lower than unity (0.31-0.39) indicating pyrogenic. Olajire et al (2005) [15] has expressed fear that ambiguity and difficulty usually occur in interpretation of results using more than two criteria and they concluded that the reliability of results of these ratios should be checked by the amount of particular PAHs compounds. They therefore said that the predominance of 2-3 rings PAHs indicates a petrogenic sources and the predominance of 4-6 rings PAHs is related to pyrolytic. This can be expressed in terms of ratio of 2-3 rings/4-6 rings PAHs and that values >1 is petrogenic while <1 is pyrolytic. It was equally expressed as ratio of low molecular weight { Σ (phenanthrene, anthracene, fluoranthene and pyrene)} and high molecular weight { Σ (benzo(a)anthracene, chrysene, benzo(a)pyrene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3,cd)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene)} based on a combustion matrix of PAH compounds with a cutoff point of 1 between petrogenic (>1) and pyrogenic (<1) by Soclo, et al, (2000) [34]. Based on this study, the values obtained for surface samples were all <1 indicating pyrolytic origin while subsurface samples shows pyrolytic PAHs origin for samples 1 to 12 (<1) and petrogenic sources for samples 13 to 19 (>1). Orecchio, (2010) [35] and Zhang, et al (2011) [1] have equally expressed a similar fear to Olajire et al (2005) [15] that as the source of PAHs in a matrix could be different and occasional, they proposed a total index as sum of all ratio normalised for limit (low temperature-high temperature source) to

characterized the source of PAHs. They considered PAHs originating by high temperature processes (combustion) when the total index was >4 while lower values indicated low temperature source (petroleum products). The total index for

the investigated surface soil samples is >4 (6.00) indicating high temperature source while for subsurface soil samples is slightly <4 (3.78-3.92) indicating probably low temperature source (petrogenic).

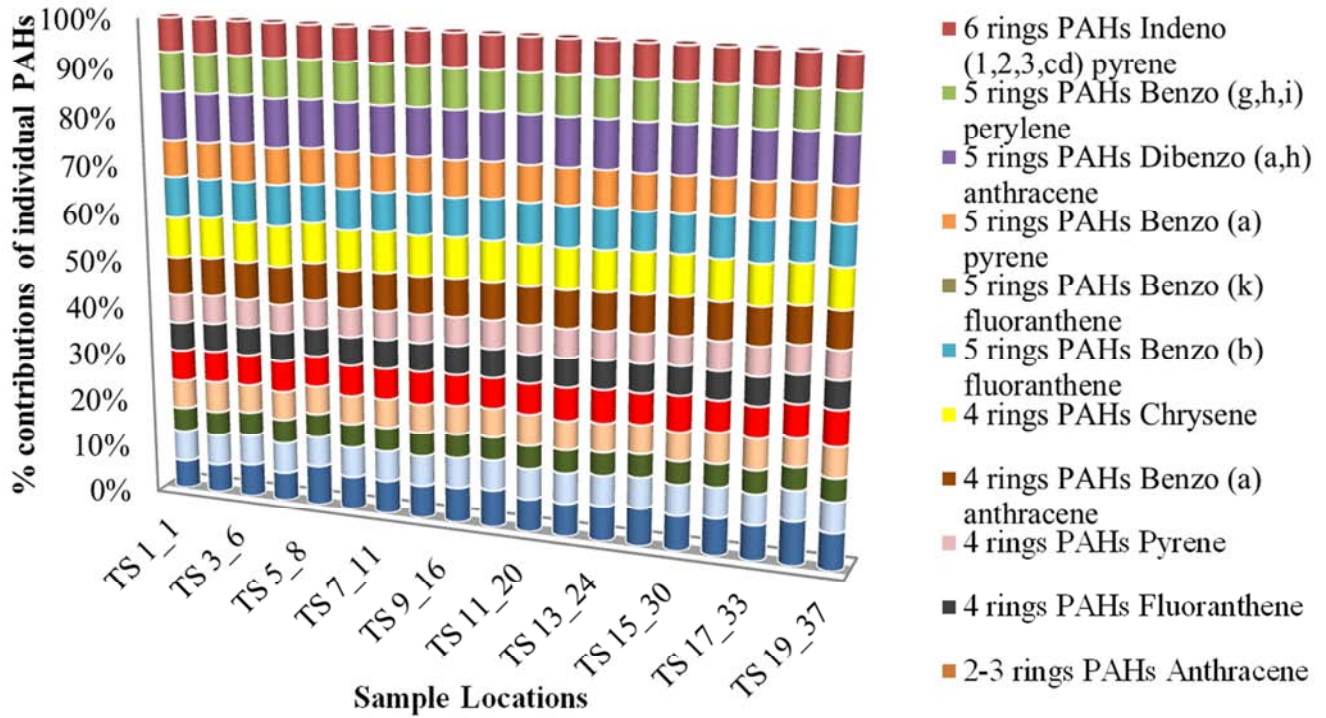


Figure 2. Characteristic Distribution Patterns of various PAHs in Surface Soil Samples.

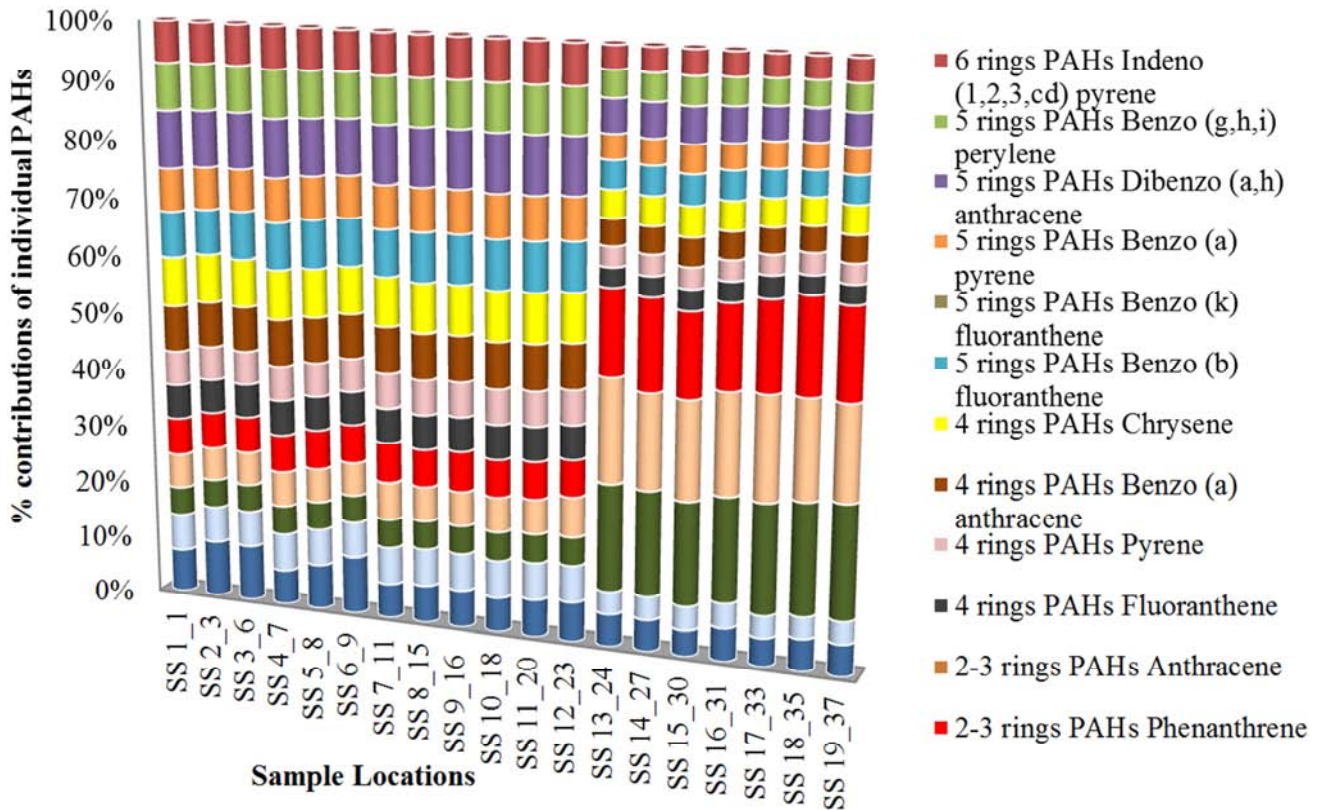


Figure 3. Characteristic Distribution Patterns of Various PAHs in Subsurface Soil Samples.

Table 1. Environmental Index of Polyaromatic Hydrocarbons (PAHs) in the Surface Soil Samples.

	TS 1_1	TS 2_3	TS 3_6	TS 4_7	TS 5_8	TS 6_9	TS 7_11	TS 8_15	TS 9_16	TS 10_18
ΣPAHs (2-3 rings)	0.60	0.61	0.62	0.60	0.65	0.62	0.62	0.63	0.63	0.64
ΣPAHs (4 rings)	0.57	0.57	0.57	0.57	0.57	0.57	0.57	0.57	0.57	0.57
ΣPAHs (5 rings)	0.51	0.51	0.52	0.51	0.51	0.51	0.51	0.51	0.51	0.51
ΣPAHs (6 rings)	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14
ΣPAHs (4-6 rings)	1.39	1.38	1.40	1.39	1.38	1.39	1.38	1.39	1.38	1.39
ΣPAHt	1.99	1.99	2.02	1.99	2.03	2.01	2.00	2.02	2.01	2.03
ΣCPAHs	0.82	0.81	0.83	0.82	0.81	0.82	0.81	0.82	0.81	0.82
%Organic carbon	2.11	2.00	1.88	1.88	2.75	1.59	1.87	1.74	2.56	2.04
ΣPAHt/OC	0.95	1.00	1.07	1.06	0.74	1.27	1.07	1.16	0.78	1.00
Fla/Fla+Pyr	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
BaA/BaA+Chrys	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48
LMW/HMW	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.33	0.32	0.32
Naph/Phen	0.92	0.92	1.08	0.92	1.31	1.08	1.08	1.00	1.15	1.23
Fla/Pyr	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
IndcdP/IndcdP+BghiP	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47
Total Index	6.01	6.01	6.01	6.01	6.01	6.01	6.01	6.01	6.01	6.01
Ratio of ΣPAHs (2-3 rings)/ΣPAHs (4-6 rings)	0.43	0.44	0.44	0.43	0.47	0.45	0.45	0.45	0.46	0.46

Table 1. Continued.

	TS 11_20	TS 12_23	TS 13_24	TS 14_27	TS 15_30	TS 16_31	TS 17_33	TS 18_35	TS 19_37
ΣPAHs (2-3 rings)	0.63	0.63	0.64	0.64	0.65	0.65	0.64	0.68	0.67
ΣPAHs (4 rings)	0.57	0.57	0.57	0.57	0.57	0.57	0.57	0.57	0.57
ΣPAHs (5 rings)	0.51	0.51	0.51	0.51	0.51	0.51	0.51	0.51	0.51
ΣPAHs (6 rings)	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14
ΣPAHs (4-6 rings)	1.39	1.39	1.39	1.38	1.38	1.39	1.39	1.39	1.39
ΣPAHt	2.02	2.02	2.03	2.02	2.03	2.04	2.03	2.07	2.06
ΣCPAHs	0.82	0.82	0.82	0.81	0.81	0.82	0.82	0.82	0.82
%Organic carbon	2.27	1.79	2.1235	1.9382	1.6294	1.8441	1.6176	1.8794	1.9912
ΣPAHt/OC	0.89	1.13	0.956	1.0422	1.2458	1.1062	1.2549	1.1014	1.0346
Fla/Fla+Pyr	0.50	0.50	0.5	0.5	0.5	0.5	0.5	0.5	0.5
BaA/BaA+Chrys	0.48	0.48	0.4848	0.4848	0.4848	0.4848	0.4848	0.4848	0.4848
LMW/HMW	0.32	0.33	0.3304	0.3246	0.3421	0.3217	0.3217	0.3304	0.3391
Naph/Phen	1.08	1.00	1.0714	1.2308	1	1.2308	1.1538	1.3571	1.0667
Fla/Pyr	1.00	1.00	1	1	1	1	1	1	1
IndcdP/IndcdP+BghiP	0.47	0.47	0.4667	0.4667	0.4667	0.4667	0.4667	0.4667	0.4667
Total Index	6.01	6.01	6.0076	6.0076	6.0076	6.0076	6.0076	6.0076	6.0076
Ratio of ΣPAHs (2-3 rings)/ΣPAHs (4-6 rings)	0.45	0.45	0.4604	0.4638	0.471	0.4676	0.4604	0.4892	0.482

Table 2. Environmental Index of Polyaromatic Hydrocarbons (PAHs) in the Subsurface Soil Samples.

	SS 1_1	SS 2_3	SS 3_6	SS 4_7	SS 5_8	SS 6_9	SS 7_11	SS 8_15	SS 9_16	SS 10_18
ΣPAHs (2-3 rings)	0.63	0.68	0.68	0.6	0.65	0.7	0.62	0.61	0.62	0.6
ΣPAHs (4 rings)	0.57	0.57	0.57	0.57	0.57	0.57	0.57	0.57	0.57	0.57
ΣPAHs (5 rings)	0.67	0.67	0.68	0.67	0.68	0.68	0.67	0.68	0.68	0.68
ΣPAHs (6 rings)	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14
ΣPAHs (4-6 rings)	1.38	1.38	1.39	1.38	1.39	1.39	1.38	1.39	1.39	1.39
ΣPAHt	1.52	1.52	1.53	1.52	1.53	1.53	1.52	1.53	1.53	1.53
ΣCPAHs	0.81	0.81	0.82	0.81	0.82	0.82	0.81	0.82	0.82	0.82
%Organic carbon	0.70	0.96	0.88	0.77	1.03	0.88	1.11	0.90	0.91	0.43
ΣPAHt/OC	2.16	1.58	1.75	1.97	1.48	1.77	1.37	1.70	1.68	3.68
Fla/Fla+Pyr	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
BaA/BaA+Chrys	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.49
LMW/HMW	0.32	0.32	0.32	0.32	0.33	0.33	0.33	0.32	0.33	0.32
Naph/Phen	1.15	1.54	1.54	0.92	1.14	1.5	0.86	1	0.93	0.92
Fla/Pyr	1	1	1	1	1	1	1	1	1	1
IndcdP/IndcdP+BghiP	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47
Total Index	3.83	3.83	3.83	3.83	3.83	3.83	3.83	3.83	3.83	3.83
Ratio of ΣPAHs (2-3 rings)/ΣPAHs (4-6 rings)	0.46	0.49	0.49	0.43	0.47	0.50	0.45	0.44	0.45	0.43

Table 2. Continued.

	SS 11_20	SS 12_23	SS 13_24	SS 14_27	SS 15_30	SS 16_31	SS 17_33	SS 18_35	SS 19_37
ΣPAHs (2-3 rings)	0.61	0.64	2.17	2.08	1.95	2.1	2.25	2.33	2.21
ΣPAHs (4 rings)	0.57	0.57	0.57	0.57	0.57	0.57	0.59	0.58	0.57
ΣPAHs (5 rings)	0.68	0.68	0.68	0.68	0.69	0.68	0.69	0.68	0.68
ΣPAHs (6 rings)	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14
ΣPAHs (4-6 rings)	1.39	1.39	1.39	1.39	1.4	1.39	1.42	1.4	1.39
ΣPAHt	1.53	1.53	1.53	1.53	1.54	1.53	1.56	1.54	1.53
ΣCPAHs	0.82	0.82	0.82	0.82	0.83	0.82	0.83	0.82	0.82
%Organic carbon	0.99	0.87	0.91	0.79	1.20	0.91	1.05	0.71	0.97
ΣPAHt/OC	1.55	1.75	1.69	1.94	1.28	1.67	1.49	2.16	1.58
Fla/Fla+Pyr	0.5	0.5	0.5	0.5	0.5	0.5	0.54	0.48	0.5
BaA/BaA+Chrys	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48
LMW/HMW	0.37	0.32	0.67	0.69	0.63	0.65	0.72	0.76	0.70
Naph/Phen	1	1.08	0.38	0.35	0.31	0.39	0.32	0.34	0.35
Fla/Pyr	1	1	1	1	1	1	1.17	0.92	1
IndcdP/IndcdP+BghiP	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47	0.47
Total Index	3.83	3.83	3.83	3.83	3.83	3.83	3.92	3.78	3.83
Ratio of ΣPAHs (2-3 rings)/ΣPAHs (4-6 rings)	0.44	0.46	1.56	1.50	1.39	1.51	1.58	1.66	1.59

4. Conclusion

The regional concentration of PAHs in the study area did not show appreciable variation as most data obtained were almost constant for all the PAHs in all the soil samples analysed; this is especially true for surface soil samples. The distributions of PAHs in the study area are not of any public concern because their concentrations were lower than quoted contaminated averages. The diagnostics source apportionment indicates that the surface soil PAHs are derived principally from pyrogenic sources which atypically bush burning that was predominant in the study area; this was in contrast to the conclusion drawn by Olajire et al (2007) of both pyrogenic and petrogenic origin. The subsurface soil could either be pyrogenic for samples 1 to 12 or petrogenic for samples 13 to 19. This demarcation is significant when considering the sample location within the study area; samples 1 to 12 were slightly outside the bitumen belt while samples 13 to 19 were clearly located on the belt. This may be a contaminated source from near-surface bitumen deposits and a probable concern for crop production in the area.

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