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Quantification, sources, and associated risks of 16-priority polycyclic aromatic hydrocarbons from selected land-use impacted soils

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Abstract. This study determined the spatial compositional occurrence, sources, and the associated risks of sixteen priority PAHs in soil depths from the selected land-use environments. Samples were collected from nine generator land-use sites in the top (0-15 cm) and sub (15-30 cm) soil depths. Sample extraction was by ultrasonication with dichloromethane/*n*-hexane and clean-up in silica gel/alumina packed column. The level of PAHs was determined using a gas chromatography-mass spectrometer (GC-MS). The concentrations of PAHs isomers and the Σ16 PAHs ranged from ND to 16876 $\mu g \cdot kg^{-1}$, and from 346 to 44052 $\mu g \cdot kg^{-1}$ respectively. The Σ16PAHs occurrence showed concentration load in the order of subsoil > topsoil. The ΣPAHs concentrations exceeded the DPR-EGAPSIN target and intervention value in 91% and 11% of the samples respectively. The total cancer risk ranged from low to moderate risk-based levels. The PAHs sources were attributed to low and high petroleum combustion emissions and stationary sources around the diesel combustion electricity generator in the land-use sites. This study revealed that the land-use activities associated with diesel combustion have contributed a significant amount of Σ16PAHs to the pollution load in the land-use sites with potential for ecological and human exposure risks.

Keywords: PAHs, soil pollution, exposure risks, anthropogenic, electricity, generator, diesel combustion, Niger Delta.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are environmental priority pollutants with two or more fused benzenoid rings in different orientations. The low molecular weight PAHs (LPAHs) and high molecular weight PAHs (HPAHs) originate from petrogenic, and pyrogenic sources respectively, while the LPAHs consist of 2-3 and the HPAHs contain 4-6 rings [1, 2]. The United States Environmental Protection Agency listed naphthalen (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), anthracene (Ant), phenanthrene (Phe), fluoranthene (Flt), pyrene (Pyr), and benzo(a)anthracene (BaA). Others are chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno (1,2,3-cd) perylene (I123-cdP), dibenzo(a,h)anthracene (DahA) and benzo(ghi)perylene (BghiP) as the 16 priority PAHs. Due to PAHs ecotoxicological, carcinogenic, long-range transport, and trans-boundary distribution behavior, PAHs are grouped as priority organic pollutants. Hence, the environmental occurrence of PAHs has attracted global attention [3, 4].

Soil is a repository of organic contaminants, and through diffuse and direct routes, human and natural sources have introduced several priority pollutants such as PAHs onto the soil [5-7]. The anthropogenic origin of PAHs includes the pyrolysis of fossil fuels, and incomplete burning of biomass, organic substances, industrial processes, and non-combustion derived petrogenic crude oil. These anthropogenic sources are mainly through non-traffic and traffic emissions, petroleum production and refining, solid waste and biomass burning, industrial processes, petroleum products spill and leakages, volcanic eruptions, and forest fires. Other man-made sources are emissions from ships, aircraft, railways, automobiles, off-road vehicle engines, and machines. The natural origin of PAHs is mainly through volcanic eruption and forest fire [8-10]. Through surface runoff, atmospheric transport and deposition, oil leakages, and wastewater discharge, PAHs are introduced into soil and water environments, and subsequent exposure through the food chain [11]. The introduction of PAHs onto soil matrix may alter soil characteristics and ecosystem functions, ground and surface water pollution, and food contamination [12]. Upon exposure through ingestion, inhalation, or dermal means, PAHs polluted soil above target and intervention values may affect human and ecological health [13].

In most developing countries such as Nigeria, Haiti, Lebanon, Yemen, Malawi, regular public electricity power supply is unavailable [14]. Hence, gasoline or diesel combustion generators are usually used as an alternative source of electricity for use in schools, telecom masts, residential estates, café, hotels, banks, fuel stations, eateries, and churches. The generators are of different brands and capacity, and usage duration. These land-use sites are associated with institutional, recreational, and residential environments. This depicts the potential for multi-array human exposures to PAHs contaminated dust, food or soil particles. Depending on

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the type, capacity, usage, and life span of the generator, the engine starting mode, the quality of lubricant oil and diesel or gasoline, are characterized by waste crank-case oil, diesel spills, and re-deposition of emitted particles from stationary exhausts that may contain various priority pollutants [15].

The combustion of petroleum hydrocarbons produces different priority organic and inorganic pollutants [16, 17]. The exposures to PAHs concentrations through inhalation, ingestion, and dermal exposures in environmental matrices, human bio-monitoring, and epidemiological studies have been documented [18-20]. However, there is a lack of reported data depicting the spatial occurrence of PAHs in soil depths from gasoline and diesel combustion electricity generator in schools, telecom masts, residential estates, café, hotels, banks, fuel stations, eateries, and churches.

Thus, the assessment of PAHs from these land-use impacted soils may provide empirical information that is useful for the evaluation of the anthropogenic impact of gasoline or diesel combustion electricity generators on the PAHs pollution load, characterize the sources and human and ecological health risks in the immediate environment. Therefore, this study determined the background occurrence, origin, human and ecological health risks of 16 priority PAHs in soil depths from the selected land-use sites.

2. Experimental

2.1. Description of the study area

The study sites are located in the Niger Delta, Nigeria, and lies within latitudes 5° – 8° E and 3° – 6° N, a subequatorial climate, long wet season, high humidity, an annual rainfall above 200 mm, and atmospheric temperature of 24 to 27 °C. The study area is characterized by the Oligocene-Pliestocene Benin Formation which consists of sands, gravels, clay lenses, and good aquifers regarded as the most prolific in Southern Nigeria [21, 22].

The geographical coordinates of the generator stand (GS) in the sample sites are GS1 - telecom masts (5° 47' 38" N, 6° 6' 49" E), GS2 - hotel (5° 4' 47" N, 6° 5' 39" E), GS3 – school (5° 46' 52" N, 6°7' 34" E), and GS4 - residential estate (5° 47' 38" N, 6° 6' 42" E), GS5 – café (5° 47' 93" N, 6° 7' 34" E). Others are GS6 - bank (5° 47' 35" N, 6° 6' 49" E), GS - church (5° 47' 45" N, 6° 6' 33" E), GS8 – eatery (5° 47' 11" N, 6° 6' 49" E), and GS9 – fuel station (5° 47' 92'' N, 6° 7' 34" E) (Figure 1). The land-use sites are predominantly located within institutional, recreational, and residential environments related to residential and commercial activities.

2.2. Sample collection

Using a stainless-steel auger of 2.5 cm diameter probe, a composite sample from a quadruplet sample was collected from each site on different days from February 2020 to March 2020. A total of 18 samples were collected at the top (0-15 cm) and the sub (15-30 cm) soil depths from an area of 100-200 cm^2 around each generator stand. Before analysis, twigs, and stones were removed, samples were air-dried and sieved over a < 2 mm stainless steel sieve and stored in a sealed polyethylene bag at 4 °C.

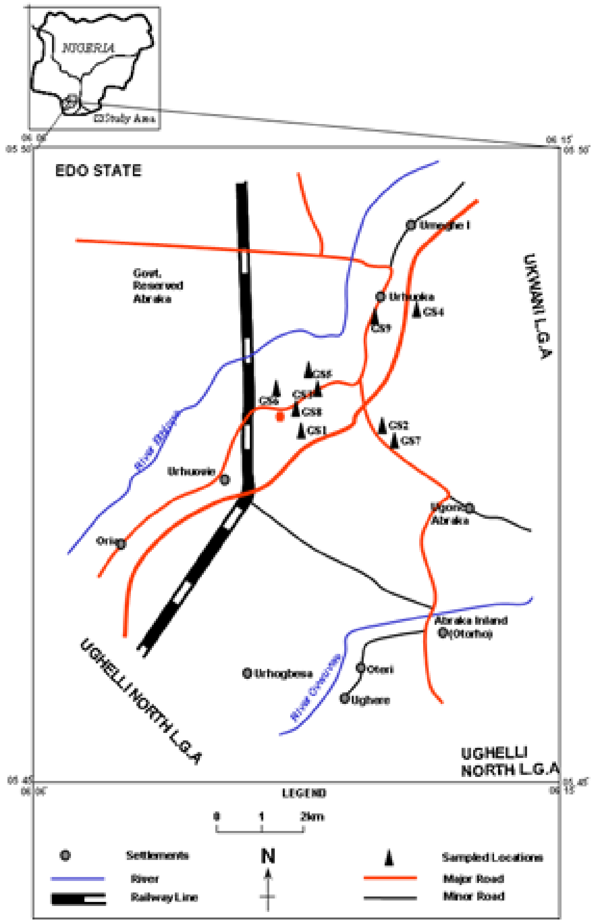

Figure 1. Map of Nigeria showing land-use sites (adapted from Emoyan *et al.* [21])

2.3. Extraction and analysis

The samples were extracted using the ultrasonic extraction method of USEPA-3550C [2, 19]. Thus, 10 g of the samples and Na_2SO_4 were mixed; the mixture was extracted with 50 mL ≥ 99.5% of *n*-hexane and dichloromethane in a ratio of 1:1 by volume, at 30 °C for 30 minutes. The extracts were filtered, and the process was repeated thrice with a fresh mixture of dichloromethane/*n*-hexane each time. Using a rotary evaporator, the extracts were evaporated to 1 mL and purified by solid-phase extractions with 2 g of Al_2O_3 (5% deactivated lower part). PAHs were eluted with 15 mL of dichloromethane and *n*-hexane (1:9) and 20 mL of dichloromethane and *n*-hexane (1:4). Using a nitrogen gas, the eluted fractions were mixed and evaporated to 0.5 mL. PAHs isomers were quantified using gas chromatograph (Agilent 6890, Agilent Aundate USA) equipped with mass selective detector spectrometer HP5 (cross-linked PHME siloxane) column with 0.25 mm x 30 m and 0.25 µm dimensions and film thickness respectively, was used to effect separation. The carrier gas was helium, in the split-less mode, the injection volume and injector temperatures were 2.0 µl and 250 °C respectively. At 4 °C/min, at 100 °C, the column temperature was raised to 310 °C as the final temperature. PAHs concentrations were monitored in selected ion monitoring (SIM) mode.

2.4. Quality control/assurance

The quality assurance was conducted to determine the precision, accuracy, and reproducibility of the extraction, clean-up, and the PAHs analysis method. The Na_2SO_4, *n*-hexane ≥ 99.5%, and dichloromethane were purchased from Chengdu Kelong Chemical Reagent Company, Chengdu, China; Sigma-Aldrich, St. Louis, Missouri, USA, and chromatographic-grade purity was purchased from Water Company, Milford, MA, USA respectively. To avoid cross-contamination during sample collection and preparation, equipment and containers were cleaned with detergent and solvent rinsed. Deuterated PAHs (from Fisher Scientific, Hampton NY, USA) were added as internal standards to compensate for losses and contamination. Duplicate sample analyses and GC-MS equipment operations performance were checked. The recovery method was used to determine PAHs extraction efficiency. A known concentration of a standard PAHs mixture was added to selected sample aliquots that have been previously analyzed and reanalyzed. Recoveries for PAHs are in the range of 82.4 to 99.2%. The relative standard deviation for duplicate sample analyses was less than 7%. The values of r^2 in the calibration lines for Σ16-PAHs ranged from 0.9996 to 0.9998. The limits of quantification (LOQ) are the PAHs concentration that produced a signal-to-noise ratio of 10 and the Limits of detection (LOD) is the concentration of the PAHs that produced a signal-to-noise ratio of 3. The LOD and LOQ values of PAHs were 0.01 $\mu g \cdot kg^{-1}$ and 0.1 $\mu g \cdot kg^{-1}$ respectively.

2.5. Human health risk

The human health risk was assessed using the total cancer risk, hazard index, BaP toxic equivalent factor (BaP_{TEF}), and BaP mutagenic equivalent factor (BaP_{MEF}) models [15, 19, 23]. The definition and values of variables used in the non-cancer, cancer and ecological risks are presented in the supplementary materials (Tables S1 and S2).

2.5.1. Total cancer risk. The total cancer risk was evaluated as the summation of the carcinogenic risk of the accidental ingestion, inhalation and dermal exposure pathways. The total cancer risk was determined as the ratio of the chronic daily intake to oral slop of PAHs isomers as described by Emoyan *et al.* and Iwegbue *et al.* [2, 19].

The qualitative description of total cancer risk is given as follows: $\geq 10^{-1}$ = very high; $> 10^{-3}$ to 10^{-1} = high; $> 10^{-4}$ to 10^{-3} = moderate; 10^{-6} to 10^{-4} = low and $\leq 10^{-6}$ = very low. The cancer risk of 10^{-6} (the probability that one in a million population of equally exposed persons have the potential of developing cancer related or cancer ailment) is considered as the acceptable risk value [23-25].

2.5.2. Hazard index. The non-carcinogenic risk in terms of hazard index (HI) is the summation of the individual hazard quotients (HQs) of the accidental ingestion, inhalation and dermal contact route of exposure as described by Emoyan *et al.* and Iwegbue *et al.* [2, 19].

The significance of HI values is expressed as: HI > 1 and < 1, indicating adverse non-carcinogenic risk and no adverse non-carcinogenic risk respectively. The definition and values of other variables used are presented in the supplementary materials (Tables S1 and S2).

2.5.3. BaP carcinogenic equivalent (BaP_{TEQ}) and BaP mutagenic equivalent (BaP_{MEQ}). The BaP carcinogenic equivalent (BaP_{TEQ}) and the BaP mutagenic equivalent (BaP_{MEQ}) for the individual PAHs were evaluated as by Emoyan *et al.* and Iwegbue *et al.* [2, 19]. The BaP_{MEFs} of the seven carcinogenic PAHs that were used are presented in the supplementary material (Tables S1 and S2).

2.6. Ecological risk

The ecological risk of PAHs was assessed using the Risk Quotient (RQ) and Soil Quality Guidelines (SQGs) ecological risk criteria.

2.6.1. Risk quotient (RQ), the negligible concentrations (NCs) and maximum permissible concentrations (MPCs) for PAH compound were used in evaluating the RQs as by Emoyan *et al.* and Iwegbue *et al.* [2, 19].

The total risk quotient was evaluated based on $RQ_{\Sigma PAHs(NCs)}$ and $RQ_{\Sigma PAHs(MPCs)}$ for the PAHs, and only $RQ_{(NCs)}$ and $RQ_{(MPCs)}$ values ≥ 1 were applied as by Emoyan *et al.* and Iwegbue *et al.* [2, 19].

$RQ_{(MPCs)}$ and $RQ_{(NCs)}$ values of 0 and ≥ 1 depicts risk free and moderate ecological risk respectively. $RQ_{(MPCs)}$ values ≥ 1 and less than 1 depicts high and moderate ecological risk respectively. $RQ_{\sum PAH(NCS)}$ and RQ∑PAHs(MPCS) values < 800 and = 0, ≤ 800 and ≥ 1, ≥ 800 and ≥ 1 depicts low ecological risk, moderate ecological risk, and high ecological risk of the Σ16 PAHs [19].

2.6.2. Soil quality guidelines (SQGs). The ecological effect range low (ERL), the biological effect range medium (ERM), the threshold effect level (TEL) and the probable effect level (PEL) are the SQGs used for the ecological risk assessment [26, 27]. The value of individual PAH less than ERL or TEL, between ERL and ERM or between TEL and PEL, and greater than ERM or PEL values depicts low, moderate, and high ecological risks respectively. The values of ERL, ERM, TEL and PEL used are presented in the supplementary materials (Tables S1 and S2).

2.7. Data treatment

The statistical package for the social sciences (SPSS) version 19 was used for all statistical data treatments. Descriptive statistics was used to establish the existence of significant variation in the Σ16-PAHs concentrations. PAHs isomer ratio was used to evaluate the principal sources of PAHs. In all the data treatment and computations of health risks, the value of zero was used where the concentration of a given PAH isomer was below the detection limit.

3. Results and discussion

3.1. Concentrations of Σ16PAHs

The occurrence of the 16 priority PAHs in the land-use sites is presented in Table 1. The concentration of PAH isomers and the Σ16 PAHs ranged from ND to 16876 $\mu g \cdot kg^{-1}$ and from 346 to 44052 $\mu g \cdot kg^{-1}$ respectively. The Σ16-PAHs occurrence show concentration load in the order of subsoil > topsoil (Table 1). The levels of PAHs varied significantly ($p < 0.05$) with irregular concentration trends with soil depth. For example, the top and subsoil depths had 46% and 54% of the Σ16-PAHs concentrations, respectively. Concerning soil depths, the Σ16-PAHs had the concentrations load in the top and subsoil depths in the order of GS2 > GS5 GS8 > GS9 > GS6 > GS7 > GS4 > GS1 > GS3, and GS2 > GS6 GS7 > GS9 > GS4 > GS8 > GS5 > GS1 > GS2 respectively. The Σ16-PAHs soil profile concentration trend could be ascribed to the soil physicochemical properties and PAHs behavior. Reported studies have shown that organic pollutant mobility is partly common with vertical rather than horizontal distribution [28]. Also, the nature and strength of the sources, biological and chemical reactions within the soil horizon, and the retention capacity, mechanical, biological disturbances within the soil profiles, and the characteristics of PAHs could be ascribed to observe PAHs. Environmental factors such as weathering, leaching, photolysis, volatilization, and hydrolysis could influence occurrence variation of the Σ16-PAHs in the soil depths. Also, this variation is adduced to the contamination period and removal mechanisms of PAHs from soil depths, and the influence of wet season in pollutant dilution [29-31].

The Department of Petroleum Resources-Environmental Guideline and Standards for the Petroleum Industry in Nigeria (DPR-EGASPIN) target and intervention thresholds are the existing standard regulatory levels for PAHs in soils/sediments in Nigeria. The intervention and target values for PAHs in the soil are set at 40000 $\mu g\cdot kg^{-1}$ and 1000 $\mu g\cdot kg^{-1}$ respectively [32]. The total PAHs in the land-use sites exceeded the DPR-EGAPSIN target value in 91% of the samples, and 11% of the samples had PAHs concentrations above the DPR-EGAPSIN intervention values (Table 1). The occurrence of the Σ16-PAHs falls in the heavily contaminated, highly polluted, and the very highly polluted classification of PAHs pollution in soil [33, 34].

3.2. Compositional and profiles of Σ16PAHs

The individual and ring-based percentage compositional patterns of the ∑16-PAHs are presented in Figures 2 and 3 respectively, and the supplementary materials (Table S3). Concerning soil depth and sample sites, the PAHs compositional patterns varied, and the individual percentage concentration load is in the order of topsoil < subsoil. Also, the percentage composition of the ring PAHs is in the order of 3 > 5 > 4 > 2 > 6, while the seven carcinogenic PAHs (7CPAHs) had percentage composition of 27%. The 3 and 5 ring PAHs are the dominant ring PAHs in the samples. The concentrations of 3-5 ring PAHs accounted for 89%, and the 2 and 6 ring PAHs accounted for 11% of the ∑16-PAHs in all sample sites. The low percentage of 2 and ring PAHs is adduced to PAHs weak association with organic matter hence, increased leaching and volatilization from soil surfaces [35]. The percentage concentrations of the 7CPAHs in the samples ranged from 17.7 at GS2 to 89.5% at GS1. The compositional pattern of the ∑16-PAHs is attributed to the presence of higher molecular petroleum fractions such as heavy oil and diesel [36]. The observed ∑16-PAHs may accumulate around the land-use environments, distribute to non-point sources, and persist in the soil compartments.

In this study, soils in the land-use sites are characterized as disturbed soil that may enhance high permeability level of observed ∑16-PAHs from topsoil to subsoil, pollute shallow ground and surface water resources, and bioaccumulate in living tissues upon exposures. This may pose ecological and human occupational hazards. Similarly, due to possible potential hazards, and the favorable environmental factors and soil physicochemical characteristics, the observed PAHs may restrict available options for land reuse due to potential exposure hazards [2, 35, 37].

Table 1. PAHs concentrations ($\mu g\cdot kg^{-1}$) in soils

	GS1		**GS2**		**GS3**		**GS4**		**GS5**		**GS6**		**GS7**		**GS8**		**GS9**	
	A	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**
Nap	32	8	4776	4	34	5134	33	2571	2405	1288	1219	3211	626	2891	1515	2089	1367	2650
Acy	138	2	4206	4	4	32	71	17	2139	11	1071	21	571	19	1355	15	1213	18
Ace	46	4	6472	44	2	7238	24	3621	3248	1833	1625	4535	825	4078	2036	2955	1831	3745
Flu	50	8	6394	30	100	2764	75	1386	3235	708	1667	1736	871	1561	2053	1135	1860	1435
Ant	404	34	4092	118	6	16876	205	8455	2149	4287	1077	10581	641	9518	1395	6902	1236	8742
Phen	1872	6	3156	6	28	88	950	6	2053	6	1041	6	995	6	1524	6	1282	6
Flt	1556	2	5342	6	72	348	814	175	3078	91	1575	219	1195	197	2136	144	1856	182
Pyr	56	4	1858	6	16	862	36	434	947	648	482	541	259	595	603	568	542	581
BaA	42	2	1584	12	22	800	813	7	1199	10	1006	8	1006	8	1102	9	1006	8
Chry	22	16	492	6	1078	1452	550	729	521	1091	800	910	675	1000	598	955	699	978
BbF	1850	16	4712	56	48	5268	3281	2662	3997	3965	3639	3314	3639	3639	3818	3476	3639	3558
BkF	10	296	760	6	ND	606	0	451	380	229	0	417	0	434	190	331	95	374
BaP	2	84	230	12	148	250	75	167	153	90	150	170	113	168	133	129	141	149
DahA	22	152	2	10	22	172	12	91	12	132	17	111	12	121	15	116	15	119
IndP	22	14	12	26	14	156	18	91	15	124	15	107	16	115	16	111	15	113
BghiP	180	ND	4	ND	54	64	92	0	48	0	73	32	70	16	61	8	72	20
Total	**6304**	**648**	**44092**	**346**	**1648**	**42110**	**7049**	**20863**	**25576**	**14508**	**15456**	**25920**	**11513**	**24368**	**18548**	**18950**	**16868**	**22678**
2Rings	32	8	4776	4	34	5134	33	2571	2405	1288	1219	3211	626	2891	1515	2089	1367	2650
3Rings	2510	54	24320	202	140	26998	1325	13485	12823	6844	6481	16880	3903	15182	8363	11013	7422	13946
4Rings	1676	24	9276	30	1188	3462	2213	1345	5745	1839	3862	1678	3134	1800	4439	1675	4102	1748
5Rings	1884	548	5704	84	218	6296	3368	3371	4541	4415	3806	4012	3763	4363	4155	4053	3890	4200
6Rings	202	14	16	26	68	220	110	91	63	124	88	139	86	131	76	119	87	133
7C	1970	580	7792	128	1332	8704	4749	4198	6276	5638	5626	5037	5460	5487	5870	5128	5609	5299

A = Topsoil; B = Subsoil

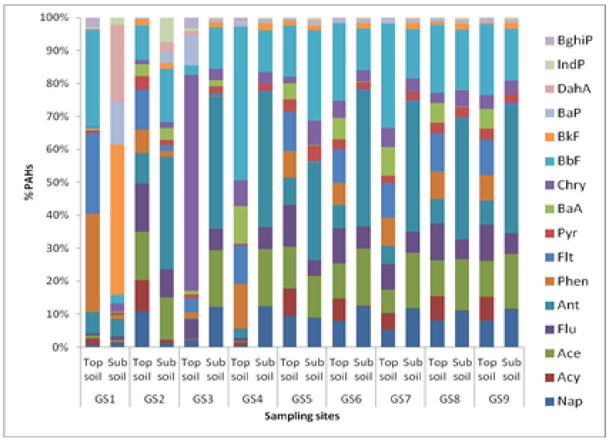

Figure 2. Individual PAHs compositional (%) pattern in soils

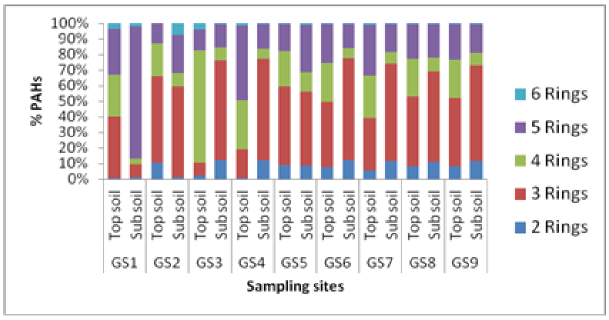

Figure 3. Ring based compositional (%) pattern of PAHs in soils

3.3. Comparison of Σ16PAHs with ΣPAHs from other studies

The concentration of the Σ16-PAHs in this study was compared with the concentration of PAHs from other studies for different land use. For example, Nganje *et al.* [38] studied ∑16-PAHs, the concentration ranged from 16.06 to 25,547.75 µg·kg^{-1} with a mean concentration of 2,906.36 µg·kg^{-1} in soils around fuel-oil spillage from a tank farm distribution facility, Esuk Utan, Calabar municipality, Nigeria. Nganje *et al.* [39] reported ∑16PAHs, the concentration ranged from 6130 to 173720 µg·kg^{-1} in petroleum handling facilities in Calabar, Nigeria. Sojinu *et al.* [40] reported Σ28-PAHs, the concentration ranged from 0.024 to 0.12 µg·kg^{-1} (average: 0.08 µg·kg^{-1}) in soils from host communities of oil exploration sites in the Niger Delta Nigeria. Emoyan *et al.* [41] reported ∑16-PAHs, the concentration ranged from 0.82 to 62.98 µg·kg^{-1} in soils around fuel stations in the Niger Delta Nigeria. Cai *et al.* [42] investigated the pollutant levels and the retention characteristics of PAHs in soils and sediment from the bank–water-level-fluctuating zone (WLFZ)–water systems in Hanfeng Lake, Three Gorges, and China. The concentrations of the Σ16-PAHs in their study ranged from 21.8 to 1324 µg·kg^{-1} dry wt. Liu *et al.* [43] investigated the pollution status of PAHs in soils in the northwest Qinling Mountains: concentrations, probable sources, and potential risks of hydrocarbons. The levels of PAHs in their study ranged from 0.0462 to 101 µg·kg^{-1} dry wt. Ekanem *et al.* [44] reported ∑16-PAHs, the concentration ranged from 830 to 12980 µg·kg^{-1} for soils from automobile repair workshops within Eket metropolis, Akwa Ibom State, Nigeria.

The Σ16-PAHs occurrences in the land-use sites were relatively higher than the concentrations of ∑PAHs concentrations of other reported studies. This can be attributed to multiple, direct, and diffuse contribution to the Σ16-PAH load [45-47].

3.4. Ecological risk of PAHs

3.4.1. RQ$_{ΣPAHs(NCs)}$ and RQ$_{ΣPAHs(MPCs)}$. The RQΣPAHs(NCs) and RQΣPAHs(MPCs) levels are presented in the supplementary materials (Tables S4 and S5). The RQΣPAHs(NCs) and RQΣPAHs(MPCs) levels ranged from 135 to 25042. The results showed that 83% and 89% of the samples had RQΣPAHs(NCs) and RQΣPAHs(MPCs) levels above 800 and > 1 respectively, suggesting high ecological risk from soil or dust exposure from soil or dust in the land-use sites. Ace, Flu, Pyr, DahA, and BghiP are the PAHs isomers that contributed significant value to the ecological risk levels.

3.4.2. Comparison of Σ16PAHs with SQG. The ecological risk assessment of the Σ16-PAHs was based on a comparison of PAHs concentrations with SQGs for PAHs as presented in the supplementary materials (Table S6). The values depict that 0.0 to 22% and 0.0 to 22% of the soil samples showed PAH isomer levels less than their TEL and ERL values respectively. Also, 0.0% and 0.0 to 5 of the samples showed concentrations of PAH isomer between TEL-PEL and ERL-ERM respectively. However, 78 to 100% and 78 to 100% of the samples showed PAH isomer concentrations greater than their PEL and ERM, respectively. This depicts a low ecological risk on biota on exposure to PAHs.

3.5. Human health risk of PAHs

3.5.1. BaPTEQ and BaPMEQ. The BaPTEQ and BaPMEQ occurrence ranged from 31.5 to 1052 µg·kg^{-1} and 38.7 to 1822 µg·kg^{-1} respectively, supplementary materials (Table S7). The 7CPAHs have a significant impact on BaPTEQ and BaPMEQ levels. The BaPTEQ and BaPMEQ concentrations were lower than those reported for soil with different anthropogenic activities. For example, BaPTEQ and BaPMEQ levels ranged from 84170 ×10^{3} to 1186170 × 10^{3}, and 8724 × 10^{3} to 1237830 × 10^{3} µg·kg^{-1} respectively [48]. However, BaPTEQ and BaPMEQ concentrations were higher than the reported levels in dust from urban catchments [49], and 61% of the samples had BaPTEQ concentrations higher than 600 µg·kg^{-1} Canadian soil quality guideline maximum permissible value for BaPTEQ [20].

3.5.2. Cancer and non-cancer risk

The rationale behind the risk assessment is exposure; hence the human health risk evaluation was reported for the topsoil. Cancer and non-cancer risks of infants and adults exposure to PAHs in the topsoil are presented in the supplementary materials (Tables S8 and S9), and Figures 4 and 5. The carcinogenic risk levels of the soils from these land-use sites through ingestion, inhalation, and dermal contacts for infants and adults ranged from 1.68 ×10^{-2} to 8.13 ×10^{-2}, 1.48 ×10^{-9} to 7.32 ×10^{-9} and 7.32 ×10^{-3} to 2.96 ×10^{-2}, and 1.15 ×10^{-4} to 5.60 ×10^{-3}, 1.64×10^{-9} to 8.07 ×10^{-9} and 5.99 ×10^{-4} to 2.92×10^{-3} respectively. The inhalation cancer risk was lower than the ingestion and dermal exposure routes risk. However, the total cancer risk ranged from 2.28 × 10^{-2} to 8.78 × 10^{-2} and 175 × 10^{-3} to 8.51 × 10^{-3} for infants and adults respectively. The cancer risk for infants via ingestion and dermal contacts was higher than for adults, depicting potential adverse health effects upon infant's exposure to PAHs polluted soil. PAHs carcinogen sensitivity in infants is higher than adults; hence more susceptible to pollutants exposure in soil because of the infant's smaller body weight and higher frequency of physical contact with soil at playtime hours [15, 48]. The inhalation cancer risk for infants was lower than for adults; this is ascribed to the longer exposure time for adults. The potential risk for infants and adults scenarios were greater than the standard acceptable risk value (> 10^{-4}), depicting a potential for human carcinogenic risk. However, the total cancer risk levels fall in the low and moderate-risk boundaries based on the standard risk classifications [24].

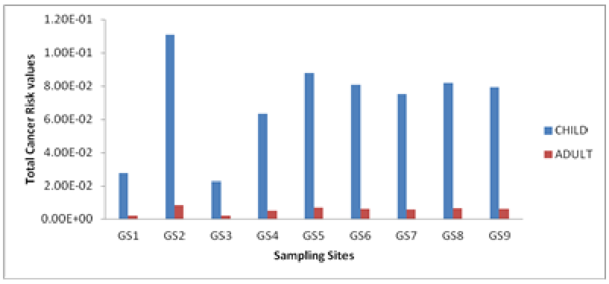

Figure 4. Total cancer risk value for infants and adults of PAHs in soils

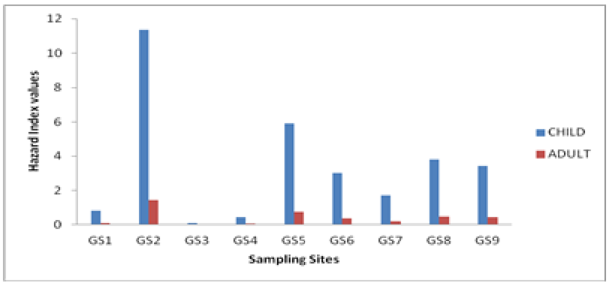

Figure 5. Hazard index value for infants and adults of PAHs in soils

The HQ is in the order of HQING > HQDERM > HQINH. The HQ and HI levels for infants and adults were less than 1, suggesting no-adverse non-carcinogenic health effects for human exposure to the soil in the land-use sites. The HI values for the infant's exposures were higher than that of the adult's exposure; this is attributed to the higher exposure duration of infants and the smaller body weight.

3.6. Source identification of PAHs

3.6.1. PAHs ratios. The anthropogenic and natural sources of PAHs have been distinguished using PAH isomer ratio [50, 51]. The Ant/(Ant + Phe), Flt/(Flt + Pyr), BaA (Chr + BaA), I123-cdP/(I123-cdP+BghiP), BaP/BghiP, LMW/HMW and ΣCOMB/ΣPAHs were the PAHs diagnostic source ratios used in this study (Table 2). The ratio of BaA/(BaA+Chr) ranged from 0.01 to 0.76, these ratios were > 0.35 in 56% of the samples suggesting combustion biomass, wood, and grass as origin of PAHs. The I123-cdP/(I123-cdP+BghiP) ratio ranged from 0.11 to 1.00, and 56% of the samples were > 0.5, suggesting petroleum input as sources of PAHs. The ratio of Ant/(Ant+Phe) ranged from 0.18 to 1.00. The Ant/(Ant+Phe) ratios were > 0.1 in all the samples, suggesting low and high-temperature combustion processes as sources of PAHs. The Flt/(Flt+Pyr) ratio ranged from 0.12 to 0.97 indicating biomass, petroleum, and wood combustion, as the origin of PAHs. The ΣLMW/ΣHMW ratio ranged from 0.11 to 3.45, the ratios depict that 33% of the samples are from the combustion of wood or fossil fuels. The CPAHs/TPAHs ratios ranged from 0.22 to 0.88 suggesting combustion processes as the origin of PAHs. The BaP/BghiP ratios ranged from 0.01 to 57.50. The BaP/BghiP ratios suggest that PAHs origins are from wood combustion in 66% of the samples. The total index values ranged from 4.34 to 16.10, and were greater than 4 in all samples; suggesting high-temperature combustion processes as sources of PAH in soils in the land-use sites.

3.6.2. Principal component analysis (PCA). The PCA has been employed for the identification of pollutant sources [52, 53]. The PCA results for the topsoil show two-component factors accounting for 92.766% of the variability, supplementary materials (Table S10). Factor 1 explained 67.142% with a characteristic high loading of Nap, Acy, Ace Flu, Ant, Phe, Flt, Pyr, BaA, and BkF. Factor 2 explains 25.625% with a characteristic moderate loading of Chr and BaP. Nap, Flt, and Pyr BaA Chr and BaP are a marker for wood combustion emission-products of diesel/gasoline and natural gas combustion [51, 54, 55]. In the PCA results for the subsoil, two-component factors were identified and accounted for 89.887% of the variability. Factor 1 explains 56.496% of the total variance with a high loading of Nap, Acy, Ace Flu, Ant, Flt, Pyr, Chr, BbF BkF BaP, DahA, and I123-cdP, and factor 2 accounts for moderate loading of Phe and BaA. The PAHs in factors 1 and 2 in the subsoil are indicators of wood and gasoline combustion of low-temperature pyrogenic processes, emission from traffic sources, and by-products of natural gas and diesel combustion [51, 55, 56]. Thus, the PCA results depict that PAHs in the land-use soils are emission from wood, gasoline, and diesel combustion, traffic, and non-traffic, combustion of low-temperature pyrogenic processes.

Table 2. Diagnostic ratios of PAHs in soils

Sites	Depth	BaA/(BaA+Chr)	IndP/(IndP+BghiP)	Ant/(Ant+Phe)	Flt/(Flt+Pyr)	LMW/HMW	COMB PAHs/TPAHs	BaP/BghiP	Total index
GS1	Top soil	0.66	0.11	0.18	0.97	0.68	0.59	0.01	7.69
	Sub soil	0.11	1.00	0.85	0.33	0.11	0.67	0.00	11.89
GS2	Top soil	0.76	0.75	0.56	0.74	1.94	0.34	57.50	12.82
	Sub soil	0.67	1.00	0.95	0.50	1.47	0.38	0.00	16.10
GS3	Top soil	0.02	0.21	0.18	0.82	0.12	0.88	2.74	4.32
	Sub soil	0.36	0.71	0.99	0.29	3.22	0.23	3.91	13.86
GS4	Top soil	0.60	0.16	0.18	0.96	0.24	0.81	0.82	7.48

Sites	Depth	BaA/(BaA+Chr)	IndP/(IndP+BghiP)	Ant/(Ant+Phe)	Flt/(Flt+Pyr)	LMW/HMW	COMB PAHs/TPAHs	BaP/BghiP	Total index
	Sub soil	0.01	1.00	1.00	0.29	3.34	0.23	0.00	12.76
GS5	Top soil	0.70	0.24	0.51	0.76	1.47	0.40	3.18	10.99
	Sub soil	0.01	1.00	1.00	0.12	1.28	0.43	0.00	12.34
GS6	Top soil	0.56	0.17	0.51	0.77	0.99	0.50	2.06	10.12
	Sub soil	0.01	0.77	1.00	0.29	3.45	0.22	5.30	12.30
GS7	Top soil	0.60	0.19	0.39	0.82	0.65	0.61	1.61	9.34
	Sub soil	0.01	0.88	1.00	0.25	2.87	0.25	10.52	12.41
GS8	Top soil	0.65	0.21	0.48	0.78	1.14	0.47	2.19	10.38
	Sub soil	0.01	0.93	1.00	0.20	2.24	0.30	16.12	12.41
GS9	Top soil	0.59	0.17	0.49	0.77	1.09	0.48	1.98	10.14
	Sub soil	0.01	0.85	1.00	0.24	2.73	0.26	7.47	12.33

3.7. Implications for environmental and human health

The Σ16-PAHs occurrence in this study showed human and ecological health risk relationships with other reported studies. The continual usage of gasoline or diesel combustion electricity generator and persistent human exposures to the Σ16-PAHs in these land-use soils may increase the potential for cancer and non-cancer risks to inhabitants and workers. However, this is dependent on the exposure routes, concentrations, and exposure duration [57-59]. Through diffuse and direct migration, infiltration, the observed PAHs concentrations could pollute the surrounding terrestrial, and ground, and surface water ecosystems in the wet season [45]. However, this scenario may be determined by water chemistry, and the water-rock interaction of the study area [60, 61]. The distribution and sources of Σ16PAHs may promote human and ecological health risks through the exposure routes of ingestion, inhalation, and dermal contacts to soil and dust particles in these land-use sites.

4. Conclusions

This study revealed that the Σ16-PAHs exhibited concentration load in the order of subsoil > topsoil. The Σ16-PAHs had the concentration load in the top and subsoil is in the order of GS2 > GS5 GS8 > GS9 > GS6 > GS7 > GS4 > GS1 > GS3 and GS2 > GS6 GS7 > GS9 > GS4 > GS8 > GS5 > GS1 > GS2 respectively. This study has also shown that the Σ16-PAHs exceeded the DPR-EGAPSIN target and intervention value in 91% and 11% of the samples respectively, and the occurrence of the Σ16-PAHs falls within the boundaries of heavily contaminated, highly polluted, and the very highly polluted categories of the standard pollution classification of PAHs in soils. Our results established that the total cancer risk levels fall in the low to moderate risk-based levels on the qualitative risk classification. The PAHs sources were attributed to fuel storage and evaporative losses from fuel service stations**,** gasoline and diesel combustion generators**,** traffic and non-traffic emissions**,** and stationary sources**.** This study has revealed that the use of gasoline and diesel generator contributed a significant amount to the Σ16-PAHs pollution load in the land-use sites with potential for ecological and human occupational exposure risks.

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Conflicts of interest

The authors declare none.

Author contributions

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