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DISTRIBUTION, RISKS AND SOURCE APPORTIONMENT OF POLYCYCLIC AROMATIC HYDROCARBONS IN SOIL AROUND CHARCOAL PRODUCTION SITES IN SAPELE, DELTA STATE, NIGERIA

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ABSTRACT

The study investigated the concentrations, risks and sources of the USEPA sixteen priority polycyclic aromatic hydrocarbons (16-PAHs) in soils around charcoal production sites in Sapele, Delta State, Nigeria. A stain-less steel auger was used in collection of a total of 21 surface soil samples, the PAHs concentration were determined by a gas chromatograph equipped with mass spectrometry (GC-MS). The concentration of the soil PAHs varied from 338 to 5082 µg kg^{-1} for all the sites. The distribution pattern of PAHs in the soil were in the order of 3 Rings> 4 Rings> 5 Rings> 6 Rings and 2 Rings PAHs. The benzo(a)pyrene toxic equivalency (BaP_{TEQ}) and mutagenic equivalency (BaP_{MEQ}) values of PAHs in these soils ranged from 43.6 to 580 µg kg^{-1} and 45.8 to 541 µg kg^{-1} respectively. The ecological risk assessed using risk quotient suggested that there is low ecological risk to organisms in soil. The hazard index values indicated that there is the presence of non-carcinogenic effects on exposure to PAHs for children in 42 % of the soil samples. The total cancer risk values resulting from a child's and an adult's exposure of PAHs exceeded the target value of 1×10^{-6} suggesting that exposure to PAHs in these soils carries a significant risk of cancer to humans. The isomeric ratio indicated that the major sources of PAHs in these soils is high temperature combustion processes.

Keywords: PAHs, Exposure risks, Sources, Soil, Charcoal production sites

INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are a group of organic compounds that are produce during the incomplete combustion of organic materials like fossil fuel and biomass (Sekar *et al*., 2024; Emoyan *et al*., 2015b). There are made up of at least two fused aromatic rings, consisting solely of hydrogen and carbon atoms. These compounds can be divided into low molecular weight (LMW) PAHs, which feature two to three fused rings, and high molecular weight (HMW) PAHs, characterized by four or more rings. The number and arrangement of atoms within the molecule greatly influence the physicochemical properties, environmental behavior, and human health effects associated with PAH contamination. PAHs are persistent organic pollutants having a high toxicity profile that can cause mutagenicity, cancer and problems of the endocrine and immune systems (Xu *et al*., 2024). Additionally, irritability, vomiting, diarrhea, nausea and convulsion can be cause from acute exposure to PAHs. Longer exposure to PAHs could also harm the kidney, liver and induce cataracts (Sombiri *et al*., 2024). The United State Environmental Protection Agency US EPA, has classified PAHs as priority pollutants in their environmental catalog (CCME 2008). The 16 of the most prevalent and harmful PAHs listed by US EPA as priority pollutants in the environment (Iwegbue *et al*., 2019) include Naphthalene (Nap), Acenaphthylene (Acy), Acenaphythene (Acc) Fluorene (Flu), Anthracene (Ant), Phenanthrene (Phe), Fluoranthene (Flt), Pyrene (Pyr), Benzo (a)anthracene (BaA), Chrysene (chr), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)Pyrene (BaP), Indeno (1,2,3-cd) perylene ($I_{123\text{-cd}}$ P), Dibenzo(a,h) anthracene (DahA) and Benzo(ghi)perylene (Bghi P).

Soil is an important environmental sink that can provide valuable insights into past and present sources of contamination and pollution (Wang *et al*., 2015a). Due to their hydrophobic and persistent characteristics, PAHs exhibit a strong affinity for soil organic matter, allowing them to be effectively absorbed and remain in the soil for extended periods (He *et al*., 2019; Wang *et al*., 2015a). The food chain may get contaminated as a result of PAHs accumulation in soil, which may pose a potential human health risk (Emoyan *et al*., 2022; Okoye *et al*., 2021). Numerous studies on PAHs in soil have been conducted and the results obtained indicate that soil contamination with PAHs is regarded as a measure of the extent of environmental pollution caused by human activity. Additionally, information on regional pollution sources, the long ranges transport of PAHs, the rate of pollutant retention and their ultimate destination can be provided.

Sapele is an area that has various commercial, industrial production and processing facilities that introduce PAHs into the environment without adherence to national environmental guidelines. Due to their potency as carcinogens and mutagen, their release to the environment has led several studies on their adverse effect on environment and human health. Similarly, studies have been reported on PAHs concentration in coal production sites. However, no studies has been reported on the distribution, sources and risks of PAHs in soil around charcoal production site in Sapele, Delta State to the best of my knowledge. Therefore, this study was carried out to investigate the concentration, composition, sources, ecological risk and potential human risk of PAHs in soil around charcoal production site in Sapele.

Thus, it can be considered as an attempt to reduce hazardous pollutants deposition and occupational exposure, protect human health and associated risks from PAHs exposure. The findings from this study provides insights on the immediate environmental burden of the 16 PAHs priority pollutants. These information are required for designing a surveillance programs, managing environmental quality and creating pollution control techniques. The region of the study is dominated by industries, commercial and processing facilities as well as subsistence farming. However, the study is limited to investigating all the 16 priority PAHs, their pollution level, risks and sources in soils just around charcoal production sites in Sapele.

MATERIALS AND METHODS

Study area

Sapele city is a situated in the Niger Delta Region of Southern Nigeria along the Ethiope River in Western Delta State. The main town is located 68km south of Benin City and is connected to Warri and Benin by the A2 Federal Highway. It has geographical coordinates range of $5^{O}54^{I}$ to $5^{O}9^{I}$N and $5^{O}40^{I}$ to $5^{O}66^{I}$ E (Emoyan *et al*., 2015b). The climatic conditions of the area are of the Niger Delta region that is, high temperature and high humidity.

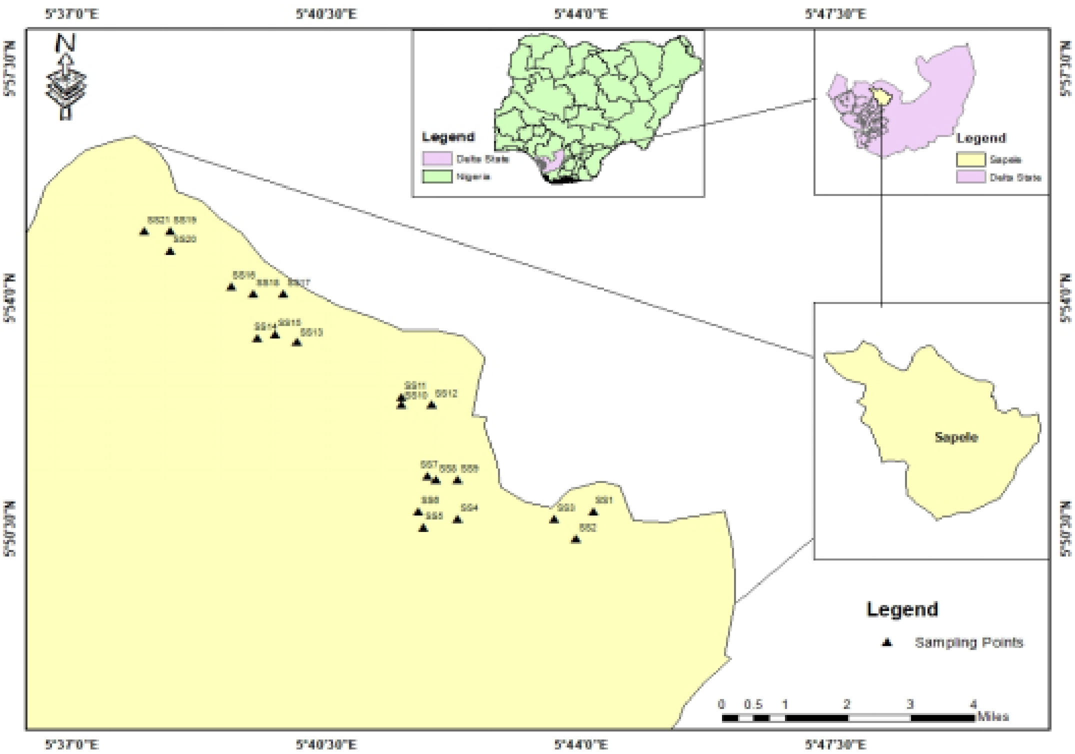

Figure 1: Map of Nigeria showing the location of the study area

Sample collection

A total of twenty- one surface soil samples were obtained from different site area. The soil samples were collected by a stainless-steel auger and were all transported to the laboratory immediately in an appropriately labeled and clean amber glass bottles in an ice- chest. After being allowed to air dry in the dark, the soil samples were sieved using 2mm mesh sieve and kept at -4°C until analysis.

Reagents

Reagents used includes Dichloromethane (DCM), n-hexane, anhydrous sodium sulphate (Merck, Germany), silica gel 60 – 200 mesh (lab tech chemicals), alumina (analytical grade) and a PAHs standard mixture containing the US EPA 16 priority PAHs (Supelco, Bella-fonte, PA, USA). These chemicals were acquired from several sales representative of the manufacturing companies' resident in Nigeria.

Extraction and quantification

Sample extraction and analysis were carried out following the US EPA-3550 C- ultrasonic extraction method as described in Akporhonor *et al.* (2021) and Iwegbue *et al*. (2020). Thus, 10g of soil samples was mixed with equal quantity of Na_2SO_4. The mixture was extracted using ultrasonication with 50ml of n-hexane / dichloromethane (DCM) [1:1v/v] at 30^{0}C for 30 minutes. The contents were filtered and the process was repeated three times by sonication of the residue with a fresh mixture of hexane/dichloromethane each time. Using a rotary evaporator, the extract will be reduced to 1ml and subsequently purified by solid phase extraction with silica gel and alumina by a chromatographic column. PAHs were finally eluted with 15ml n-hexane and Dichloromethane (1:1) mixture. The eluent was concentrated to about 0.5ml before PAHs analysis by means of nitrogen gas stream. The resulting extracts were analyzed using gas chromatography (Agilent 6890 Agilent Aundate USA) coupled with mass selective detector spectrometry (GC-MS), with each PAHs quantified separately. Separation was carried out on a HP5 column with 0.25µm film (thickness) and dimensions of 0.25mm by 30m. The initial temperature was increased from 100°C to 310°C as the final temperature at 4°C/min. The carrier gas was helium, the injection temperature and injection volumes were 250°C and 2.0µL respectively. The injection was performed at a split-less mode and data were acquired using the selective ion monitoring (SIM) mode. The PAHs determination was carried out by external calibration obtained with PAHs.

Quality assurance and quality control

Reagents and chemicals are of chromatographic grade. To ensure the accuracy and reliability of the results, methods blanks and spiked samples was included during the extraction and analysis process. The spike recovery method was employed to evaluate the efficiency of the PAHs extraction. A standard PAH mixture with known concentrations was added to the analysis samples, followed by reanalyzing these samples after following all analytical steps. The method blanks indicated that there were no detectable levels of PAH contamination.

Statistical analysis

All statistical analysis were done using the Microsoft Office Excel Software. The Isomer Pair Ratio was used to assess potential sources of polycyclic aromatic hydrocarbons (PAHs).

Ecological risks assessment

The PAHs ecological risk in soil around charcoal production site, Sapele was determined by means of the Risk Quotient (RQ) approach, adopted from Emoyan *et al* (2022; 2021) from Equation (1)

$$RQ_j = \frac{C_{PAHs}}{C_{QV}} \quad (1)$$

Where C_{PAHs} is the concentration value of PAHs and C_{QV} is the quality value of a given PAH compound. In calculating the RQs for each PAH compound the maximum permissible concentrations (MPCs) and negligible concentrations (NCs) were used as shown in Equation (2) and (3).

$$RQ_{(NCs)} = \frac{C_{PAHs}}{C_{QV(NCs)}} \quad (2)$$

$$RQ_{(MPCs)} = \frac{C_{PAHs}}{C_{QV(MPCs)}} \quad (3)$$

Where $C_{QV\ (NCs)}$ is the quality value of the negligible concentration and $C_{QV(MPCs)}$ is the quality value of the maximum permissible concentrations. The values of $C_{QV(NCs)}$ and $C_{QV(MPCs)}$ of the individual PAHs compounds are given in the Supporting Materials (Table S1). Equation (4) and (5) was used in calculating the total RQ, based on $RQ_{\sum PAHs(NCs)}$ and $RQ_{\sum PAHs(MPCs)}$ for the PAHs and just $RQ_{(NCs)}$ and $RQ_{(MPCs)}$ values ≥ 1 were used (Emoyan *et al*., 2022; 2021).

$$\sum RQ_{i(NCs)} = RQ_{\sum PAHs(NCs)} = \frac{C\sum_{PAHs}}{\sum C_{QV(NCs)}} \text{ (where } RQ_{i(NCs)} \geq 1\text{)} \quad (4)$$

$$\sum RQ_{i(MPCs)} = RQ_{\sum PAHs(MPCs)} = \frac{C\sum_{PAHs}}{\sum C_{QV(MPCs)}} \text{ (where } RQ_{i(MPCs)} \geq 1\text{)} \quad (5)$$

The significances of the RQ values is as follows: $RQ_{(MPCs)}$ values of < 1 signifies there's moderate risk and ≥1 implies high ecological risk, while $RQ_{(NCs)}$ values of 0 indicates risk-free and ≥ 1 signifies moderate ecological risk. When $RQ_{\sum PAH(NCS)} < 800$ and $RQ_{\sum PAHs(MPCS)} = 0$, it suggest low ecological risk; $RQ_{\sum PAH(NCS)} \leq 800$ and $RQ_{\sum PAHs(MPCS)} \geq 1$ signifies moderate ecological risk; $RQ_{\sum PAH(NCS)} \geq 800$ and $RQ_{\sum PAHs(MPCS)} \geq 1$ signifies high ecological risk (Emoyan *et al*., 2022; 2021).

Assessment of health risk

The risks associated with human exposure with PAHs in soil are evaluated using the BaP toxicity equivalency factors. The cancer risk and mutagenic risk of PAHs in soil were identified by the use of carcinogenic equivalency factors (TEFs) and mutagenic equivalency factors (MEFs) proposed by (Nisbet and LaGoy 1992) and (Durant *et al*.,1996) respectively as described in equations (6) and (7).

$$BaP_{TEQ} = \sum C_i \times BaP_{TEF} \quad (6)$$

$$BaP_{MEQ} = \sum C_i \times BaP_{MEF} \quad (7)$$

Where BaP_{TEF} is the carcinogenic potency and BaP_{MEF} is the mutagenic potency of the PAHs relative to that of BaP and C_i represents the concentrations of the individual PAHs compound. The BaP_{TEF} and BaP_{MEF} values for the seven individual carcinogenic PAHs are shown in the Supporting Materials (Table S4).

Evaluation of non-carcinogenicity and carcinogenicity

The USEPA model equations USEPA (2009; 1989) were adopted in order to assess the health risks associated with human exposure to PAHs through the three exposure pathways (ingestion, inhalation and dermal contact). The hazard index (HI), which represents the non-carcinogenic risk were gotten from the calculation of the total hazard quotients resulting from the major exposure pathways as shown in Equation (8)-(12). The hazard index values significance is stated as; HI > 1 signifies adverse non-carcinogenic risk while, HI < 1 signifies there is no adverse non-carcinogenic risk.

$$\text{Hazard Index (HI)} = \sum HQ = HQ_{ing} + HQ_{inh} + HQ_{dermal} \quad (8)$$

$$HQ = \frac{CDInc}{RfD} \quad (9)$$

$$CDI_{ing\text{-}nc} = \frac{C \times IngR \times EF \times ED \times CF}{BW \times ATnc} \quad (10)$$

$$CDI_{inh\text{-}nc} = \frac{C \times InhR \times EF \times ET \times ED}{PEF \times 24 \times ATnc} \quad (11)$$

$$CDI_{derm\text{-}nc} = \frac{C \times SA \times AF \times ABSd \times EF \times ED \times CF}{BW \times ATnc} \quad (12)$$

For carcinogenic risks, the Incremental Lifetime Cancer Risk (ILCR) was evaluated

$$ILCR = ILCR_{ing} + ILCR_{inh} + ILCR_{dermal} \quad (13)$$

$$ILCR_{ing} = \frac{C \times IngR \times EF \times ED \times CF \times SFO}{BW \times ATca} \quad (14)$$

$$ILCR_{inh} = \frac{C \times InhR \times EF \times ED \times IUR}{PEF \times ATca} \quad (15)$$

$$ILCR_{dermal} = \frac{C \times SA \times AF \times ABSd \times EF \times ED \times CF \times SFO \times GIABS}{BW \times ATca} \quad (16)$$

Where IUR means inhalation unit risk (mg m^{-3}); Accordingly, CDI_{ing}, CDI_{inh}, CDI_{dermal} stands for the chronic daily intakes of PAHs through the three exposure pathways ; $ILCR_{ing}$, $ILCR_{inh}$ and $ILCR_{dermal}$ are assigned to the cancer risks relating to the ingestion, inhalation and dermal contact with PAHs respectively. C represent the concentration of PAHs, AF (mg cm^{-2}) represent skin to soil adherence factor, ABS_d represent dermal absorption factor, ATnc and ATca are the respective average time for non-carcinogenic and carcinogenic effects; EF stands for exposure frequency, ET represent exposure time (h d^{-1}), ED represent exposure duration; PEF represent soil to air particulate emission factor (m^3 kg^{-1}), IngR stands for ingestion rate (mg d^{-1}) and InhR represent inhalation rate (m^3d^{-1}); SA represent surface area of the skin (cm^2 $event^{-1}$), SFO represent oral slope factor (mg kg^{-1} d^{-1}), BW stands for average human body weight (kg), GIABS represent gastrointestinal absorption and CF represent conversion factor (10^{-6}). The specified toxicological values for PAHs and related variables used in the risk assessment are presented in Supporting Materials (Tables S4 and S5).

RESULTS AND DISCUSSION

Concentration of PAHs in the sites

In this study, the concentration of PAH compounds at 21 sampling sites are shown in Table 1. The concentration of ∑16-PAHs in 21 soil samples ranged from 338 to 5082 µgkg^{-1}, and its soil profile varied significantly. The results likely arise from human activities and environmental factors such as leaching, weathering, photolysis, volatilization, and hydrolysis, which significantly influence the occurrence and distribution of PAHs in soil profiles. The high values obtained in the study might also be as a result of charcoal pollution. Charcoal ash and gases produced by the combustion of charcoal are released into the atmosphere and can also contaminate soil. Charcoal ash is known to contain toxic residues, such as PAHs (Rouhani *et al*., 2024; Zhang *et al.,* 2019). Maliszewska- Kordybach 1996, classification method can be used to assess the level of PAHs contamination in soil. The criteria are defined as follows: not contaminated (<200µgkg^{-1}), slightly contaminated (200-600µgkg^{-1}), contaminated (600-1000µgkg^{-1}) and highly contaminated (>1000µgkg^{-1}). For the samples collected, 90.4% are highly contaminated, 4.8% are contaminated and 4.8% are slightly contaminated with PAHs. Table 2 shows a comparison of the concentration of the PAHs obtained in this study, along with the levels reported for soils in the literature. The concentration of ∑16-PAHs in the sampling sites were comparable with PAHs concentration reported for soils of coal resource city, Huainan, China (Zhang *et al*., 2020) and with the reported range for urban soils in the literature (Ehigbor *et al*., 2020). Although the ∑16 PAHs concentration already stated in soils in the Niger Delta, Nigeria (Emoyan *et al.,* 2022 ; Iwegbue *et al*., 2016 ; Ugwu and Ukoha 2016) were much lower. From this study, it was observed that the levels of PAHs in most soil samples were greater than the PAHs target value of 1000µgkg^{-1} proposed by the Dutch Government.

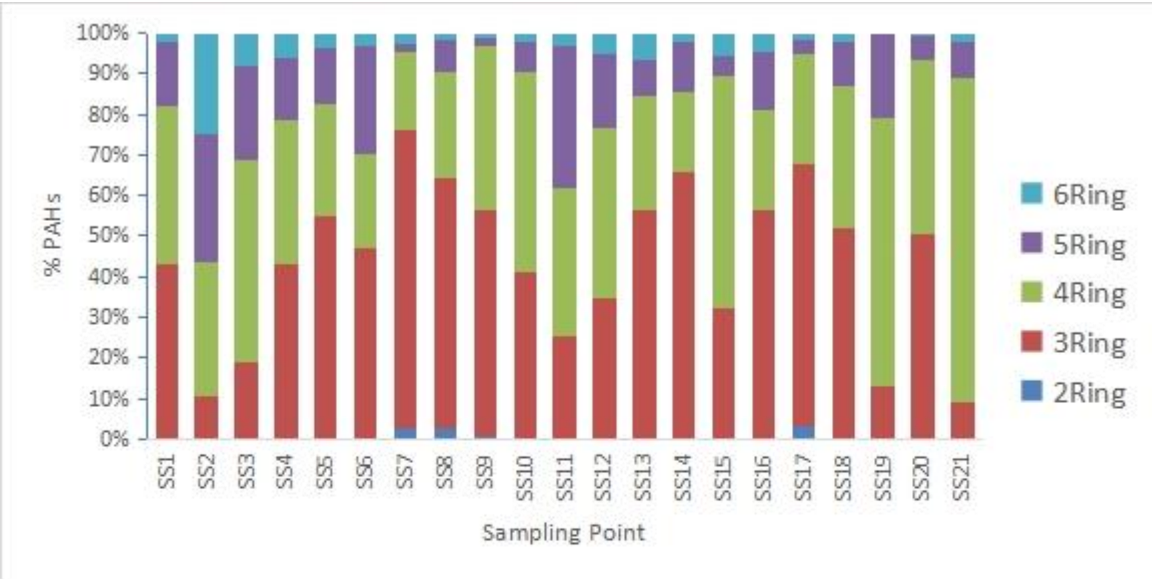

Figure 2: PAH profile in soil around charcoal production sites in Sapele

Compositional Pattern

The composition pattern of polycyclic aromatic hydrocarbons in the soils is shown in Figure 2. The occurrence pattern follows this order: 3-ring > 4-ring > 5-ring > 6-ring > 2-ring. Notably, the 3-ring and 4-ring PAHs are the most dominant compounds in the soil, emphasizing their significance. Naphthalene, the only 2-ring PAH varied from not detected to 136µgkg^{-1} and constituted 0.0 to 3.3% of the ∑16-PAHs. The concentration of 3-ring PAHs (Acy+Ace+Flu+Ant+Phe) range from 36 to 2668µgkg^{-1} and accounted for 9.0 to 73.6% of the ∑16-PAHs . The concentration of 3- ring PAHs is in the order of Phe>Ace > Flu >Acy> Ant. The concentration of 4- ring PAHs (Flt+ Pyr+ BaA + Chr) ranged from 112 to 1874µgkg^{-1} and constituted 19.2 to 79.8% of the ∑16-PAHs. The concentration of 4- ring PAHs are in the order of Flt >Pyr>Chr>BaA. The concentration of 5- ring PAHs (BbF + BkF + BaP+ DahA) range from 34 to 1762µgkg^{-1} and constituted 1.9 to 34.7% of the ∑16-PAHs. The concentration of 5- ring PAHs are in the order of BbF>BkF>BaP>DahA. The occurrence of 6- ring PAHs (IndP + BghiP) range from not detected to 182µgkg^{-1} and accounted for 0.0 to 8.1% of the ∑16-PAHs. The concentration of ∑6 ring PAHs are in the order of IndP > BghiP. In this study 4 to 6 ring PAHs accounted for 52.4% of PAHs in the soil samples, while PAHs with 2 to 3 ring accounted for 47.6% of ∑16-PAHs. Naphthalene, a 2-ring PAH compound, was below the detection limit at most sampling sites. This is likely attributable to its weak binding with organic matter, which results in greater losses via volatilization (Tesi *et al*., 2016). The dominance of the HMW PAHs could also be as a result of their volatile nature and octanol- water partition coefficient (Kow). Generally, Low molecular weight (LMW) PAHs are mainly from petrogenic sources and high molecular weight (HMW) PAHs are mainly contributed by pyrogenic sources (Zhang *et al*., 2020). The HMW PAHs (52.4%) content was greater than the LMW PAHs (47.6%) content, indicating that majority of PAH formation likely originate from the pyrogenic processes, like charcoal combustion.

Ecological risk assessment of PAHs in soil

The ecological risk assessment of PAHs in soil was assessed using $RQ_{\sum PAHs(NCs)}$ and $RQ_{\sum PAHs(MPCs)}$. The $RQ_{\sum PAHs(NCs)}$ and $RQ_{\sum PAHs(MPCs)}$ values in this study are shown in Table 3a and 3b. The $RQ_{\sum PAHs(NCs)}$ for the ∑16 PAHs values varies from 101 to 886 and $RQ_{\sum PAHs(MPCs)}$ for the ∑16 PAHs varies from 0.0 to 5.30. Most of the soil samples analyzed had $RQ_{\sum PAHs(NCs)}$ values which was less than 800 suggesting the ecological risk of PAHs in these soils is low. The $RQ_{\sum PAHs(MPCs)}$ values investigated shows 66.7% were greater than 1 and 33.3% less than 1 which suggests a moderate ecological risk of the ∑16 PAHs. (Emoyan *et al.,* 2022; 2021).

Table 1: PAHs concentrations (µg/kg) in soil from the charcoal production sites

	SS1	SS2	SS3	SS4	SS5	SS6	SS7	SS8	SS9	SS10	SS11	SS12	SS13	SS14	SS15	SS16	SS17	SS18	SS19	SS20	SS21
Nap	ND	ND	ND	ND	ND	ND	88	86	14	0	0	0	0	0	0	4	136	0	0	0	0
Acy	170	0	22	380	468	232	506	398	170	104	294	178	78	174	58	366	148	320	0	0	0
Ace	398	0	28	160	216	246	340	262	246	232	324	362	154	392	78	204	1904	232	0	0	26
Flu	262	18	36	100	176	228	620	416	218	0	142	88	540	832	232	532	238	472	0	420	42
Ant	290	18	32	120	280	88	416	230	16	146	298	166	332	176	54	292	104	206	74	570	32
Phen	394	0	34	276	196	284	662	572	358	194	220	200	442	334	174	448	274	242	58	1010	32
Flt	544	32	266	292	158	112	224	440	230	436	346	510	342	88	858	176	566	672	116	486	422
Pyr	440	14	24	158	174	192	378	156	192	0	358	140	180	170	64	184	382	118	460	668	468
BaA	190	18	32	50	48	146	14	164	186	114	190	112	110	242	70	178	58	84	90	220	132
Chry	210	48	86	344	284	90	48	44	120	266	980	450	138	78	70	266	114	124	0	342	152
BbF	0	0	32	160	98	262	10	66	4	0	786	170	122	72	16	180	42	90	116	84	50
BkF	0	0	12	76	126	260	6	108	8	0	746	198	54	206	16	170	40	86	44	92	48
BaP	528	0	18	94	76	74	8	68	18	106	188	120	72	82	56	64	50	114	50	52	38
IndP	72	84	66	76	46	44	86	44	24	36	98	88	134	28	46	60	32	28	0	26	30
DahA	26	106	124	36	34	18	44	6	4	16	42	38	0	0	0	52	24	24	0	0	0
BghiP	0	0	0	76	42	24	6	0	0	0	70	58	48	32	60	98	32	32	0	0	0
∑16 PAHs	3524	338	812	2398	2422	2300	3456	3060	1808	1650	5082	2878	2746	2906	1852	3274	4144	2844	1008	3970	1472
2Ring	0	0	0	0	0	0	88	86	14	0	0	0	0	0	0	4	136	0	0	0	0
3Ring	1514	36	152	1036	1336	1078	2544	1878	1008	676	1278	994	1546	1908	596	1842	2668	1472	132	2000	132
4Ring	1384	112	408	844	664	540	664	804	728	816	1874	1212	770	578	1062	804	1120	998	666	1716	1174
5Ring	554	106	186	366	334	614	68	248	34	122	1762	526	248	360	88	466	156	314	210	228	136
6Ring	72	84	66	152	88	68	92	44	24	36	168	146	182	60	106	158	64	60	0	26	30
LMW-PAHs	1514	36	152	1036	1336	1078	2632	1964	1022	676	1278	994	1546	1908	596	1846	2804	1472	132	2000	132
HMW-PAHs	2010	302	660	1362	1086	1222	824	1096	786	974	3804	1884	1200	998	1256	1428	1340	1372	876	1970	1340

Table 2: A comparison of PAHs concentrations in charcoal soil with those of other soil worldwide

Location	Soil types	Number of PAHs	Concentration range	References
Sapele, Nigeria	Charcoal soil	16	338 – 5082	This study
Huainan, China	Coal soil	16	109.94 – 1105.30	Zhang *et al*.,2020
Lagos, Nigeria	Urban	16	111 – 15,577	Ehigbor *et al*., 2020
Warri, Nigeria	Urban	16	188 – 684	Iwegbue *et al*., 2016
Tianjin, China	Industrial	16	58.2 – 9160	Shi *et al*., 2020
Kogi, Nigeria	Agricultural/Commercial	16	1.58 – 7.58	Kadili *et al*., 2021
Niger Delta, Nigeria	Agricultural/Commercial	16	4.49 – 447.86	Emoyan *et al*., 2022
Lanzhou, China	Urban	22	115 – 12,100	Jiang *et al.,* 2016
River Niger, Nigeria	Floodplain	16	811.8 – 10,651.4	Tesi *et al*., 2016
Kutahya, Turkey	Rural/Urban/Industrial	16	36.47 – 1435.4	Dumanoglu *et al*., 2017
Nasarawa, Nigeria	Charcoal soil	18	12,680 – 16,930	Zakari *et al.,* 2024
Huanghuai, China	Agricultural	16	15.7 – 1247.6	Yang *et al*., 2012
Okobo, Nigeria	Coal soil	16	100 – 400	Ugwu and Ukoha 2016
Delta State, Nigeria	Charcoal soil	16	3,762 – 59,580	Isioma and Iniaghe 2023
Oyo State, Nigeria	Charcoal soil	28	200.11 – 1847.44	Omodara *et al*., 2019

Table 3a: ∑RQ(NC) of PAHs in soil from the charcoal production sites

	Nap	Acy	Ace	Flu	Ant	Phen	Flt	Pyr	BaA	Chry	BbF	BkF	BaP	IndP	DahA	BghiP	$\sum RQ_{(NC)}$
SS1	0	100	59	16	85	11	11	24	100	13	0	0	330	19	14	0	783
SS2	0	0	0	1	5	0	1	1	9	3	0	0	0	22	59	0	101
SS3	0	13	4	2	9	1	6	1	17	5	4	2	11	17	69	0	162
SS4	0	224	24	6	35	8	6	9	26	22	20	10	59	20	20	16	503
SS5	0	275	32	11	82	5	3	10	25	18	12	16	48	12	19	9	577
SS6	0	136	36	14	26	8	2	11	77	6	33	33	46	12	10	5	455
SS7	13	298	50	39	122	18	5	21	7	3	1	1	5	23	24	1	631
SS8	12	234	39	26	68	16	9	9	86	3	8	14	43	12	3	0	581
SS9	2	100	36	14	5	10	5	11	98	8	1	1	11	6	2	0	309
SS10	0	61	34	0	43	5	9	0	60	17	0	0	66	9	9	0	314
SS11	0	173	48	9	88	6	7	20	100	61	99	94	118	26	23	14	886
SS12	0	105	53	6	49	6	11	8	59	28	22	25	75	23	21	12	501
SS13	0	46	23	34	98	12	7	10	58	9	15	7	45	35	0	10	408
SS14	0	102	58	52	52	9	2	9	127	5	9	26	51	7	0	7	517
SS15	0	34	11	15	16	5	18	4	37	4	2	2	35	12	0	12	207
SS16	1	215	30	33	86	12	4	10	94	17	23	22	40	16	29	20	651
SS17	20	87	280	15	31	8	12	21	31	7	5	5	31	8	13	7	580
SS18	0	188	34	30	61	7	14	7	44	8	11	11	71	7	13	7	512
SS19	0	0	0	0	22	2	2	26	47	0	15	6	31	0	0	0	150
SS20	0	0	0	26	168	28	10	37	116	21	11	12	33	7	0	0	468
SS21	0	0	4	3	9	1	9	26	69	10	6	6	24	8	0	0	175

Table 3b: ∑RQ(MPC) of PAHs in soil from the charcoal production sites

	Nap	Acy	Ace	Flu	Ant	Phen	Flt	Pyr	BaA	Chry	BbF	BkF	BaP	IndP	DahA	BghiP	$\sum RQ_{(MPC)}$
SS1	0.00	1.00	0.59	0.16	0.85	0.11	0.11	0.24	1.00	0.13	0.00	0.00	3.30	0.19	0.14	0.00	5.30
SS2	0.00	0.00	0.00	0.01	0.05	0.00	0.01	0.01	0.09	0.03	0.00	0.00	0.00	0.22	0.59	0.00	<1
SS3	0.00	0.13	0.04	0.02	0.09	0.01	0.06	0.01	0.17	0.05	0.04	0.02	0.11	0.17	0.69	0.00	<1
SS4	0.00	2.24	0.24	0.06	0.35	0.08	0.06	0.09	0.26	0.22	0.20	0.10	0.59	0.20	0.20	0.16	2.24
SS5	0.00	2.75	0.32	0.11	0.82	0.05	0.03	0.10	0.25	0.18	0.12	0.16	0.48	0.12	0.19	0.09	2.75
SS6	0.00	1.36	0.36	0.14	0.26	0.08	0.02	0.11	0.77	0.06	0.33	0.33	0.46	0.12	0.10	0.05	1.36
SS7	0.13	2.98	0.50	0.39	1.22	0.18	0.05	0.21	0.07	0.03	0.01	0.01	0.05	0.23	0.24	0.01	4.20
SS8	0.12	2.34	0.39	0.26	0.68	0.16	0.09	0.09	0.86	0.03	0.08	0.14	0.43	0.12	0.03	0.00	2.34
SS9	0.02	1.00	0.36	0.14	0.05	0.10	0.05	0.11	0.98	0.08	0.01	0.01	0.11	0.06	0.02	0.00	1.00
SS10	0.00	0.61	0.34	0.00	0.43	0.05	0.09	0.00	0.60	0.17	0.00	0.00	0.66	0.09	0.09	0.00	<1
SS11	0.00	1.73	0.48	0.09	0.88	0.06	0.07	0.20	1.00	0.61	0.99	0.94	1.18	0.26	0.23	0.14	3.90
SS12	0.00	1.05	0.53	0.06	0.49	0.06	0.11	0.08	0.59	0.28	0.22	0.25	0.75	0.23	0.21	0.12	1.05
SS13	0.00	0.46	0.23	0.34	0.98	0.12	0.07	0.10	0.58	0.09	0.15	0.07	0.45	0.35	0.00	0.10	<1
SS14	0.00	1.02	0.58	0.52	0.52	0.09	0.02	0.09	1.27	0.05	0.09	0.26	0.51	0.07	0.00	0.07	2.30
SS15	0.00	0.34	0.11	0.15	0.16	0.05	0.18	0.04	0.37	0.04	0.02	0.02	0.35	0.12	0.00	0.12	<1
SS16	0.01	2.15	0.30	0.33	0.86	0.12	0.04	0.10	0.94	0.17	0.23	0.22	0.40	0.16	0.29	0.20	2.15
SS17	0.20	0.87	2.80	0.15	0.31	0.08	0.12	0.21	0.31	0.07	0.05	0.05	0.31	0.08	0.13	0.07	2.80
SS18	0.00	1.88	0.34	0.30	0.61	0.07	0.14	0.07	0.44	0.08	0.11	0.11	0.71	0.07	0.13	0.07	1.88
SS19	0.00	0.00	0.00	0.00	0.22	0.02	0.02	0.26	0.47	0.00	0.15	0.06	0.31	0.00	0.00	0.00	<1
SS20	0.00	0.00	0.00	0.26	1.68	0.28	0.10	0.37	1.16	0.21	0.11	0.12	0.33	0.07	0.00	0.00	2.83
SS21	0.00	0.00	0.04	0.03	0.09	0.01	0.09	0.26	0.69	0.10	0.06	0.06	0.24	0.08	0.00	0.00	<1

Table 4: BaP_{TEQ} and BaP_{MEQ} concentrations (µg/kg) of PAHs in soil from the charcoal production sites

	BaA	Chry	BbF	BkF	BaP	IndP	DahA	BaPTEQ	BaA	Chry	BbF	BkF	BaP	IndP	DahA	BaPMEQ
SS1	19.0	0.2	0.0	0.0	528.0	7.2	26.0	580	15.6	17.2	0.0	0.0	43.3	5.9	2.1	84
SS2	1.8	0.0	0.0	0.0	0.0	8.4	106.0	116	1.5	0.8	0.0	0.0	0.0	26.0	30.7	59
SS3	3.2	0.1	3.2	0.1	18.0	6.6	124.0	155	2.6	1.5	8.0	1.3	18.0	20.5	36.0	88
SS4	5.0	0.3	16.0	0.8	94.0	7.6	36.0	160	4.1	5.8	40.0	8.4	94.0	23.6	10.4	186
SS5	4.8	0.3	9.8	1.3	76.0	4.6	34.0	131	3.9	4.8	24.5	13.9	76.0	14.3	9.9	147
SS6	14.6	0.1	26.2	2.6	74.0	4.4	18.0	140	12.0	1.5	65.5	28.6	74.0	13.6	5.2	200
SS7	1.4	0.0	1.0	0.1	8.0	8.6	44.0	63	1.1	0.8	2.5	0.7	8.0	26.7	12.8	53
SS8	16.4	0.0	6.6	1.1	68.0	4.4	6.0	103	13.4	0.7	16.5	11.9	68.0	13.6	1.7	126
SS9	18.6	0.1	0.4	0.1	18.0	2.4	4.0	44	15.3	2.0	1.0	0.9	18.0	7.4	1.2	46
SS10	11.4	0.3	0.0	0.0	106	3.6	16.0	137	9.3	4.5	0.0	0.0	106	11.2	4.6	136
SS11	19.0	1.0	78.6	7.5	188	9.8	42.0	346	15.6	16.7	197	82.1	188	30.4	12.2	541
SS12	11.2	0.5	17.0	2.0	120	8.8	38.0	197	9.2	7.7	42.5	21.8	120	27.3	11.0	239
SS13	11.0	0.1	12.2	0.5	72.0	13.4	0.0	109	9.0	2.3	30.5	5.9	72.0	41.5	0.0	161
SS14	24.2	0.1	7.2	2.1	82.0	2.8	0.0	118	19.8	1.3	18.0	22.7	82.0	8.7	0.0	153
SS15	7.0	0.1	1.6	0.2	56.0	4.6	0.0	69	5.7	1.2	4.0	1.8	56.0	14.3	0.0	83
SS16	17.8	0.3	18.0	1.7	64.0	6.0	52.0	160	14.6	4.5	45.0	18.7	64.0	18.6	15.1	180
SS17	5.8	0.1	4.2	0.4	50.0	3.2	24.0	88	4.8	1.9	10.5	4.4	50.0	9.9	7.0	88
SS18	8.4	0.1	9.0	0.9	114.0	2.8	24.0	159	6.9	2.1	22.5	9.5	114	8.7	7.0	171
SS19	9.0	0.0	11.6	0.4	50.0	0.0	0.0	71	7.4	0.0	29.0	4.8	50.0	0.0	0.0	91
SS20	22.0	0.3	8.4	0.9	52.0	2.6	0.0	86	18.0	5.8	21.0	10.1	52.0	8.1	0.0	115
SS21	13.2	0.2	5.0	0.5	38.0	3.0	0.0	60	10.8	2.6	12.5	5.3	38.0	9.3	0.0	78

Table 5: Hazard index of PAHs in soil from charcoal production site

	CHILD				ADULT			
	HQING	**HQINH**	**HQDERM**	**HI**	**HQING**	**HQINH**	**HQDERM**	**HI**
SS1	5.78E-01	5.78E-01	5.78E-01	1.73	7.22E-02	5.31E-04	3.75E-02	1.10E-01
SS2	1.73E-02	6.38E-06	2.52E-02	4.25E-02	2.17E-03	1.59E-05	1.12E-03	3.31E-03
SS3	1.24E-01	4.56E-05	8.29E-02	2.07E-01	1.55E-02	1.14E-04	8.04E-03	2.37E-02
SS4	3.70E-01	1.36E-04	2.39E-01	6.09E-01	4.62E-02	3.40E-04	2.40E-02	7.05E-02
SS5	3.55E-01	1.31E-04	3.14E-01	6.69E-01	4.44E-02	3.27E-04	2.30E-02	6.78E-02
SS6	3.44E-01	1.26E-04	3.64E-01	7.07E-01	4.29E-02	3.16E-04	2.23E-02	6.55E-02
SS7	8.22E-01	7.64E-04	9.49E-01	1.77	1.03E-01	1.91E-03	5.33E-02	1.58E-01
SS8	7.29E-01	7.20E-04	7.01E-01	1.43	9.12E-02	1.80E-03	4.73E-02	1.40E-01
SS9	4.02E-01	2.21E-04	3.75E-01	7.77E-01	5.03E-02	5.53E-04	2.61E-02	7.69E-02
SS10	3.00E-01	1.10E-04	1.09E-01	4.09E-01	3.75E-02	2.76E-04	1.94E-02	5.72E-02
SS11	4.09E-01	1.51E-04	2.98E-01	7.07E-01	5.12E-02	3.76E-04	2.65E-02	7.81E-02
SS12	4.04E-01	1.49E-04	2.39E-01	6.44E-01	5.06E-02	3.72E-04	2.62E-02	7.72E-02
SS13	5.42E-01	1.99E-04	7.63E-01	1.30	6.77E-02	4.98E-04	3.51E-02	1.03E-01
SS14	5.72E-01	2.10E-04	1.08E+00	1.65	7.15E-02	5.26E-04	3.71E-02	1.09E-01
SS15	4.57E-01	1.68E-04	4.09E-01	8.66E-01	5.71E-02	4.20E-04	2.96E-02	8.71E-02
SS16	5.62E-01	2.27E-04	7.61E-01	1.32	7.02E-02	5.69E-04	3.64E-02	1.07E-01
SS17	9.19E-01	1.05E-03	5.84E-01	1.50	1.15E-01	2.63E-03	5.96E-02	1.77E-01
SS18	6.00E-01	2.21E-04	7.13E-01	1.31	7.50E-02	5.52E-04	3.89E-02	1.14E-01
SS19	8.46E-02	3.11E-05	3.08E-02	1.15E-01	1.06E-02	7.77E-05	5.48E-03	1.61E-02
SS20	7.73E-01	2.84E-04	7.21E-01	1.49	9.66E-02	7.10E-04	5.01E-02	1.47E-01
SS21	1.89E-01	6.94E-05	1.13E-01	3.02E-01	2.36E-02	1.74E-04	1.22E-02	3.60E-02

Table 6: Total cancer risk of PAHs in soil from charcoal production site

	CHILD				ADULT			
	ILCRing	**ILCRinh**	**ILCRderm**	**TCR**	**ILCRing**	**ILCRinh**	**ILCRderm**	**TCR**
SS1	5.42E-02	3.01E-09	1.97E-02	7.39E-02	3.69E-03	4.11E-09	1.92E-03	5.61E-03
SS2	1.08E-02	6.03E-10	3.95E-03	1.48E-02	7.40E-04	8.23E-10	3.84E-04	1.12E-03
SS3	1.45E-02	8.12E-10	5.27E-03	1.98E-02	9.88E-04	1.11E-09	5.12E-04	1.50E-03
SS4	1.49E-02	8.77E-10	5.43E-03	2.03E-02	1.02E-03	1.20E-09	5.27E-04	1.54E-03
SS5	1.22E-02	7.48E-10	4.44E-03	1.66E-02	8.32E-04	1.02E-09	4.32E-04	1.26E-03
SS6	1.31E-02	8.48E-10	4.75E-03	1.78E-02	8.90E-04	1.16E-09	4.62E-04	1.35E-03
SS7	6.03E-03	3.45E-10	2.19E-03	8.22E-03	4.11E-04	4.71E-10	2.13E-04	6.24E-04
SS8	9.70E-03	5.96E-10	3.53E-03	1.32E-02	6.61E-04	8.13E-10	3.43E-04	1.00E-03
SS9	4.09E-03	2.37E-10	1.49E-03	5.58E-03	2.79E-04	3.23E-10	1.45E-04	4.24E-04
SS10	1.28E-02	7.22E-10	4.66E-03	1.75E-02	8.74E-04	9.85E-10	4.53E-04	1.33E-03
SS11	3.23E-02	2.18E-09	1.17E-02	4.40E-02	2.20E-03	2.97E-09	1.14E-03	3.34E-03
SS12	1.84E-02	1.13E-09	6.71E-03	2.51E-02	1.26E-03	1.55E-09	6.52E-04	1.91E-03
SS13	1.02E-02	5.97E-10	3.71E-03	1.39E-02	6.95E-04	8.14E-10	3.61E-04	1.06E-03
SS14	1.10E-02	7.11E-10	4.02E-03	1.51E-02	7.53E-04	9.70E-10	3.91E-04	1.14E-03
SS15	6.48E-03	3.70E-10	2.36E-03	8.84E-03	4.42E-04	5.04E-10	2.29E-04	6.71E-04
SS16	1.49E-02	9.18E-10	5.43E-03	2.03E-02	1.02E-03	1.25E-09	5.28E-04	1.54E-03
SS17	8.40E-03	4.99E-10	3.06E-03	1.15E-02	5.72E-04	6.81E-10	2.97E-04	8.69E-04
SS18	1.49E-02	8.69E-10	5.41E-03	2.03E-02	1.01E-03	1.18E-09	5.25E-04	1.54E-03
SS19	6.63E-03	3.88E-10	2.41E-03	9.04E-03	4.52E-04	5.29E-10	2.34E-04	6.87E-04
SS20	8.05E-03	5.05E-10	2.93E-03	1.10E-02	5.49E-04	6.88E-10	2.85E-04	8.34E-04
SS21	5.58E-03	3.39E-10	2.03E-03	7.62E-03	3.81E-04	4.62E-10	1.97E-04	5.78E-04

Health risk Assessment from PAHs

Bap Equivalency Factors

Table 4, above shows the calculated BaP_{TEQ} and BaP_{MEQ} concentrations for seven carcinogenic PAHs. The BaP_{TEQ} value and BaP_{MEQ} value at all sites ranged between 44 to 580µgkg^{-1} and 46 to 541µgkg^{-1} respectively. The levels of BaP, DahP and IndP in the soil had a substantial impact on the values of BaP_{TEQ} and BaP_{MEQ}. The values of BaP_{TEQ} and BaP_{MEQ} obtained in these soils had greater values than those previously recorded in Nigeria. The values reported 5.43 to 197 µgkg^{-1} and 9.66 to 195µgkg^{-1} for BaP_{TEQ} and BaP_{MEQ} respectively (Iwegbue *et al*., 2016) and also 0.11 to 168µgkg^{-1}and 0.08 to 146µgkg^{-1} respectively (Emoyan *et al*., 2022). However, compared to the values previously recorded in the Niger Delta, the BaP_{TEQ} and BaP_{MEQ} level found in this study were lower. The BaP_{TEQ} and BaP_{MEQ} reported varied from 84.17 to 1186.17µgkg^{-1} and 87.24 to 123.83µgkg^{-1} respectively (Olawoyin *et al*., 2012) and reported values of N.D to 4090µgkg^{-1} and N.D to 4150µgkg^{-1} respectively (Tesi *et al*., 2016). The soil samples investigated shows the BaP_{TEQ} level exceeded the Dutch target value of 33µgkg^{-1} for BaP_{TEQ}.

Estimation of non-carcinogenic potencies

The results of non-carcinogenic risk of PAHs associated with the exposure of infants and adults were evaluated using the hazard indexes as shown in Table 5. The hazard quotient (HQ) values obtained in this study followed the order HQ_{ing} >HQ_{derm} > HQ_{inh}. for human exposure to PAHs. With the exception of the child's exposure to PAHs, the HQ values for the individual exposure pathways were below one. The hazard index values obtained indicated there is a presence of non-carcinogenic health effects for children exposed to PAHs in soils and absence of non-carcinogenic health effects for adults who are exposed to PAHs in these soils. Children's exposure had higher HI values than adult's exposure, and this is as a result of child's lower body weight and shorter exposure duration.

Estimation of carcinogenic potencies

The ILCR values via soil ingestion, inhalation, and dermal contact for child's and adult's exposure around charcoal production sites in Sapele are presented in Table 6. The incremental life cancer risk (ILCR) obtained for children exposed to carcinogenic PAHs varied from 4.09×10^{-3} to 5.42×10^{-2}, 2.37×10^{-10} to 3.01×10^{-9}, 1.49×10^{-3} to 1.97×10^{-2} for the respective exposure pathways. However, the ILCR values for adult's exposure through the exposure pathways varied from 2.79×10^{-4} to 3.69×10^{-3}, 3.23×10^{-10} to 4.11×10^{-9}, 1.45×10^{-4} to 1.92×10^{-3} respectively. The estimated cancer risk for PAHs via inhalation was lower when compared to the ingestion and dermal contact exposure pathways. However, the TCR values in all sites are in range 5.58×10^{-3} to 7.39×10^{-2} for children and 4.24×10^{-4} to 5.61×10^{-3} for adults. The target values of 10^{-6} was exceeded by the ILCR values obtained from adults and child's exposure to PAHs through ingestion and dermal contact pathways. This implies that PAHs in these soils through ingestion and dermal contact pathways have a significance carcinogenic risks for human exposure. Estimated ILCR values from inhaling soil particles varied from 10^{-10} to 10^{-9} which is regarded as insignificant and does not pose any health risk to people of different ages.

The cancer risk values for children through ingestion and skin contact are higher than those of adults, due to their frequent physical interaction with soil during playtime, hand to mouth behavior, and lower body weight (Tesi *et al*., 2016). The USEPA considered cancer risk values of 10^{-6} as non-significant and acceptable, and values greater than 10^{-4} as significant and unacceptable, while the New York State Department of Health (NYSDH) categorizes cancer risk values as follows: a value of $\leq10^{-6}$ is considered very low; value from 10^{-6} to 10^{-4} as low; value from 10^{-4} to $<10^{-3}$ as moderate; value from 10^{-3} to 10^{-1} as high and value of $\geq10^{-1}$ as very high (Man *et al*., 2013). The TCR values for both adults and child's exceeded the permissible range of 10^{-6} to 10^{-4} indicating a high risk of cancer and requires remedial measures to lower the risk.

Source Estimates from PAHs Diagnostic Ratios

PAH isomeric ratios such as Ant/(Ant + Phe), Flt/(Flt +Pyr), BaA/(BaA + Chry), IndP/(IndP + BghiP) , CPAHs/ TPAHs, BaP/ BghiP, LMW/HMW and the total index have been adopted for the purposes of source identification (Tesi et al., 2021; Emoyan et al., 2022). The PAHs isomeric ratio in this soil are shown in Table 7. Ant/(Ant +Phe) ratio <0.10 indicates petroleum input while values >0.10 is characteristics of combustion processes, Flt/(Flt + Pyr) <0.4 signifies petroleum combustion and >0.5 implies coal and biomass combustion. BaA/(BaA + Chry) ratio <0.2 signifies petroleum origin, 0.2 to 0.35 implies petroleum combustion and >0.35 indicates coal and biomass combustion, IndP/(IndP + BghiP) ratio <0.2 indicates petroleum inputs, between 0.2 and 0.5 is characterized as petroleum combustion and >0.5 as coal, wood and grass combustion. BaP/BghiP ratio ranged between 0.3 to 0.44 thus indicating automobile exhaust sources and 0.9 to 6.6 suggests coal combustion sources. LMW/HMW ratio of <1.0 suggest combustion of fossil fuels or wood and ratio of >1.0 indicates petrogenic sources. CPAHs/TPAHs ratio of <1.0 signifies combustion processes and >1.0 indicates petrogenic sources.

The ratio of BaA/ (BaA + Chry) ranged from 0.13 to 1.00, the values calculated were >0.35 in 57% of all sites. This signify that the PAHs are from combustion of coal and biomass sources. The IndP/(IndP + BghiP) ratio ranged from 0.38 to 1.00, having 67% of all sites >0.5 implying that PAHs are mostly from coal, wood and grass combustion. The Ant/(Ant + Phe) ratio ranged from 0.24 to 1.00, exceeding 0.1 at all sites, indicating combustion processes. The Flt/(Flt + Pyr) ratio varied from 0.20 to 1.00, revealing that 19%, 24%, and 57% of soil samples were linked to petroleum origin, petroleum combustion, and coal and biomass combustion, respectively. The LMW/HMW ratio ranged from 0.10 to 3.19, with 52% of samples below 1.0 and 48% above 1.0. These findings suggest that the soil samples originate from the combustion of fuels or wood and indicate petrogenic sources. The ratios of CPAHs/ TPAHs varied from 0.65 to 3.56 thus, suggesting that coal combustion are the major sources of PAHs in these soils. The total index values ranged from 6.29 to 15.10. All sites had a total index value > 0.4 which indicates that the major cause of PAHs concentration in soil around the charcoal production sites are high temperature combustion processes.

Table 7: Isomeric ratios of PAHs

	BaP/ BghiP	LMW/ HMW	CPAHs/ TPAHs	BaA/ (BaA+Chry)	IndP/ (IndP+BghiP)	Ant/ (Ant+Phen)	Flt/ (Flt+Pyr)	Total Index (TI)
SS1	0.00	0.75	0.51	0.48	1.00	0.42	0.55	10.00
SS2	0.00	0.12	0.53	0.27	1.00	1.00	0.70	15.10
SS3	0.00	0.23	0.58	0.27	1.00	0.48	0.92	10.50
SS4	1.24	0.76	0.47	0.13	0.50	0.30	0.65	6.29
SS5	1.81	1.23	0.37	0.14	0.52	0.59	0.48	8.84
SS6	3.08	0.88	0.35	0.62	0.65	0.24	0.37	7.67
SS7	1.33	3.19	0.22	0.23	0.93	0.39	0.37	7.79
SS8	0.00	1.79	0.28	0.79	1.00	0.29	0.74	10.66
SS9	0.00	1.30	0.33	0.61	1.00	0.04	0.55	6.83
SS10	0.00	0.69	0.51	0.30	1.00	0.43	1.00	10.29
SS11	2.69	0.34	0.55	0.16	0.58	0.58	0.49	8.96
SS12	2.07	0.53	0.54	0.20	0.60	0.45	0.78	8.70

SS13	1.50	1.29	0.35	0.44	0.74	0.43	0.66	9.62
SS14	2.56	1.91	0.24	0.76	0.47	0.35	0.34	9.02
SS15	0.93	0.47	0.63	0.50	0.43	0.24	0.93	8.06
SS16	0.65	1.29	0.31	0.40	0.38	0.39	0.49	7.93
SS17	1.56	2.09	0.29	0.34	0.50	0.28	0.60	6.93
SS18	3.56	1.07	0.41	0.40	0.47	0.46	0.85	9.68
SS19	0.00	0.15	0.66	1.00	0.00	0.56	0.20	11.11
SS20	0.00	1.02	0.42	0.39	1.00	0.36	0.42	8.62
SS21	0.00	0.10	0.79	0.46	1.00	0.50	0.47	10.51

CONCLUSION

This study assessed the levels of polycyclic aromatic hydrocarbons (PAHs) in surface soils from charcoal production sites in Sapele, Delta State. The concentration of PAHs in the soil at various locations in the charcoal production area of Sapele exceeds the Dutch target value. The compositional analysis of the PAHs showed a predominance of three-ring PAHs. The hazard index values indicate a significant non-carcinogenic risk associated with children's exposure to PAHs. Furthermore, the incremental lifetime cancer risk (ILCR) values, based on different exposure routes, were found to follow this order: ingestion > dermal contact > inhalation. The study revealed that cancer risk values exceeded permissible target limits, indicating both acute and chronic human cancer risks. This study shows that the total cancer risk value for children was found to be higher than that for adults. The ecological risk value obtained from this study indicated a low ecological risk to organisms in soil of these areas around charcoal production sites. The use of diagnostic ratios for source identification and apportionment strongly suggested the contamination have input of charcoal and are from both petrogenic and pyrogenic sources. This work highlights the carcinogenic risk of PAHs in soil near charcoal production sites, emphasizing the need for immediate actions to reduce human exposure to these harmful substances. However, appropriate measures such as strict adherence to set guidelines and regular monitoring of these pollutants are necessary in ensuring further mitigation of these pollutants in the environment.

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