



Polycyclic Aromatic Hydrocarbons in Soils of Open Dumpsites in Warri Metropolis: Concentration and Human Health Risks Assessment

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Abstract

The presence of Polycyclic Aromatic Hydrocarbons (PAHs) in the environment has been implicated for various health conditions. It is therefore imperative to monitor their levels of concentrations in the soil, so as to avoid their accumulations in animals and human bodies through the food chain. In this work, levels of PAHs in soils of dumpsites in Warri metropolis were determined with Gas Chromatography- Mass Spectrometry (GC-MS). The risks to human health (both carcinogenic and non-carcinogenic) were then quantified for the general groups of receptors using the determined PAHs concentrations. Incidental ingestions and dermal contacts were considered as the major exposure pathways and were used in calculating the health risks. Total PAHs concentrations ($\Sigma 16$ PAHs) in the various dumpsites ranged from 518.2 - 18016.1 μ g/Kg. The non-cancer risk denoted by the total hazard index (HI) ranged from 0.23 – 7.13, while the range for total cancer risks (TCR) was from 5.9×10^{-5} – 8.07×10^{-4} . Incidental ingestion as exposure pathway contributed more (54.13%) to the mean non-cancer risks (HI) whereas; the mean total carcinogenic risks (TCR) had more contributions (74.21%) from dermal contacts.

Keywords: PAHs pollution, petrogenic, incidental ingestion, health risk, dumpsites, dermal absorption.

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1. Introduction

Pollution of Polycyclic Aromatic Hydrocarbons (PAHs) comes as results of three principal processes viz., pyrogenic, petrogenic, and biogenic. Pyrogenic sources result from incomplete combustion and pyrolysis of organic substances (Patel *et al.*, 2020; Emre *et al.*, 2024). Petrogenic PAHs are produced from crude oil maturation, crude oil and crude oil products, as well as fossils fuels such as coal and coal products (Balmer *et al.*, 2019). Biogenic PAHs are synthesized by biological species such as micro-organisms, phytoplankton, algae, and plants and by the transformation of natural organic precursors by diagenic processes (Mojiri *et al.*, 2019; Chokor, 2022). Though this latter process (biogenic) contributes to PAHs presence in the environment, large amount of PAHs in a contaminated environment has its root from anthropogenic activities (Chokor, 2021). PAHs have been implicated for its toxicity, carcinogenicity, mutagenicity, teratogenicity, immunotoxicity to several organisms (Abdel-Shafy and Mansour, 2016., Varjani *et al.*, 2017., Oliveira *et al.*, 2019., Patel *et al.*, 2020). Their inherent characteristics such as aromaticity, hydrophobicity, and thermostability have placed them in the rank of persistence organic pollutants. They thus persist in various environmental media where they exhibit broad range of biological toxicity (Sun *et al.*, 2021; Chokor and Achugwo, 2022; Caumo *et al.*, 2022). On the basis of their much abundance or concentrations and persistence in the environmental media, ease of exposure and toxicity to life forms, the United State Environmental Protection Agency (USEPA, 2014) has listed sixteen Polycyclic Aromatic Hydrocarbons (PAHs) as priority pollutants viz., naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Acp), fluorene (Flr), phenantrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), chrysene (Chr), benzo[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcP), dibenzo[a,h]anthracene (DhA), and benzo[g,h,i]perylene (BgP).

Warri is a heart to diverse industrial and commercial activities; it is characterized by numerous companies, factories, artisan workshops, shops and markets as well as schools whose activities generate large quantities of domestic, urban, and industrial solids wastes (Issa *et al.*, 2021). Most of these wastes ultimately end up in the various open dump sites across the city because of poor waste management policy operational in the State. These wastes dumps are occasionally bulldozed into clumps and set on fire as way of maintaining the sanitary of the environment. Some of these wastes contain polycyclic aromatic hydrocarbons (PAHs) which are released by degradations and / or leaching processes to contaminate the surrounding soils and waters bodies. Besides, the occasional burning of the wastes adds to the burden of PAHs in these environments because the burning is usually performed under suboptimum conditions. These wastes contain organic foods materials, papers, PVC plastics, wood, rubbers, toys, bathing shoes, computers and electronics parts, bicycles handles, sports items, tires,

automobile parts, containers used for storing pesticides and petroleum products, and other household, agricultural, and industrial products (Hoffer *et al.*, 2020). Many of these items listed above contain PAHs which on account of their indiscriminate disposal into open dump add to the burden PAHs in the soil environment. It is because these dumpsites could represent PAHs rich spots with potentials to impacts quality of nearby underground waters through particulate matter dispersal, and also on the account of the indiscriminate use of nearby plots to open dumpsites for the cultivation of crops and forages, that it was thought pertinent to examine the concentrations of PAHs and the associated risks in soils of open dumpsites in Warri metropolis.

2. Materials and methods

2.1. Study area and sample's locations

Warri is located at about longitude 5.45°E and latitude 5.31°N of the equator. It occupies the southern part of Delta State, Nigeria. It is one of the high density population cities in Nigeria. Going by the 2006 census figure (303,417) (NPC, 2006), and the population growth rate of 2.5% given by United Nations Department of Economic and Social Affairs Population Division (UNDESAPD, 2015); Warri is estimated to have a current population of about 473,227 occupying its 256 square kilometre. With its fast growing population, it has expanded to form a large metropolis with its neighbouring towns. Samples were collected from six different dumpsites in the metropolis, their coordinates were properly recorded viz: Merogun - MG (N05°30'36.8" E05°45'37.9"), Aladja - AJ (N05°29'13.6" E05°45'25.1"), Esisi – ES (N05°31'32.1" E05°44'57.1"), Okpaka - OK (N05°31'36.4" E05°49'23.1"), Osubi - OS (N05°35'35.8" E05°49'39.8"), and Dumorugbo – DM (N05°33'51.5" E05°46' 3.93").

2.2. Sampling and sample preparation

Composite samples were taken from the open dumps with stainless steel auger. Five (5) surface soil samples (0-15cm depth) were taken at distances of about 5 to 8m radially from the epicentre of each dumpsite after the remover of the covering wastes. These were bulked together to make the composite samples which were representatives for each dumpsite. Samples were placed in pre-cleaned wide-mouth amber bottles and kept in ice chest at temperature below 4°C for onward transportation to the laboratory for analysis.

2.3. PAHs extractions

Soil samples were air-dried in the dark for a period of about three (3) days; homogenized and sieved through a mesh (500µm). Aliquots of these samples (10g) were mixed with sufficient quantities of anhydrous sodium sulphate (Na₂SO₄) (about 5g) to remove moisture, and spiked with surrogate standard

(10 μ g/mL of *p*-terphenyl and 2-fluorobiphenyl). The mix were wrapped in filter papers, put in thimbles and loaded into the main chamber of the soxhlet extractors. Extractions were done with 200mL of dichloromethane (DCM) for 17hr. Extracts were dried by passing through packed columns of anhydrous sodium sulphate and reduced to about 2mL with rotary evaporators (Chokor and Achugwo, 2022).

2.4. Sample clean-up and separations

The extracts were cleaned by column chromatograph (10mm i.d. X 30cm) pre-packed with activated silica gel (10g), lined at the top with anhydrous Na₂SO₄ (2cm thick) and glass wool at the bottom. The aromatic were eluted with 20mL of dichloromethane solution; collected after aliphatic fractions elution (20mL *n*-hexane) (Chokor and Ediabonya, 2024). Concentrations of the aromatic fractions to about 2mL were done with rotary evaporator at 30°C; after which 1.5mL of it were transferred into vials and stored at 4°C awaiting gas chromatography-mass spectrometry (GC-MS) injections. Procedural blanks were performed for the purpose of quality assurance (Chokor and Ogonegbu, 2023).

2.5. Gas chromatography analysis

Polycyclic aromatic hydrocarbons (16PAHs) were determined by gas chromatography (Agilent 6890N) interfaced with a mass spectrometer as detector (Agilent 5975B Technologies, Santa Clara, USA). A DB-5 capillary column (30 m length $\times$ 0.25 μ m film thickness $\times$ 0.25 mm i.d.) was used for separation. Pure helium gas at a flow velocity of 1 mL/min was used as the carrier gas. Samples were injected into GC via a pulsed split-less mode with an injection volume of 1 μ L. The chromatograph had an initial column temperature of 70°C, which was maintained for 20 min, and was then increased at 25°C min⁻¹ to 150°C. The temperature was further raised to 200°C at 3°C min⁻¹, and finally to 300°C at 2°C min⁻¹. The mass spectrometer was operated in the electron ionization (EI) mode set at 70eV, and the temperature of the injection port, ion source, quadrupole and transfer line were 250, 230, 150 and 280 °C respectively.

2.6. Identification and quantification

PAHs were identified by comparison of EI-mass spectrum and specific ion fragment with those of mass spectral libraries as well as by comparing their chromatographic retentions time with those of standards. Quantifications were done using response factors related to the respective internal standards based on five-point calibration curves for the individual PAH. Deuterated PAH internal standard solutions (naphthalene-d₈, acenaphthene-10, phenanthrene-d₁₀, chrysene-d₁₂, and perylene-d₁₂) and surrogate standard solutions (2-fluorobiphenyl and 4-terphenyl-d₁₄) were also utilized in sample quantification

and quantifying procedural recovery. Recoveries were evaluated by the additions of PAHs standards mixture at three levels of 2, 6, & 10 μ g. The overall mean recovery percentage was estimated to be 93.17%. All data were corrected using this percent recovery.

2.7. Health risks assessment

The non-carcinogenic and carcinogenic risks of PAHs on human health were assessed with the assumption that the major path ways to humans are through incidental ingestion and dermal contacts of soils. The average daily doses (ADD) of PAHs through ingestions and dermal contacts were obtained from the generic equations (Eqs. 1 and 2) developed by the United State Environmental Agency (USEPA, 1991).

$$ADD_i = (Cs * IR * EF * ED * CF) / (Bw * AT_{nc}) \quad (1).$$

$$ADD_d = (Cs * SA * AF * DAF * EF * ED * CF) / (Bw * AT_{nc}) \quad (2).$$

Where: ADD_i and ADD_d are the average daily doses for ingestion and dermal contact ($\text{mg}_{\text{PAH}} \text{Kg}^{-1} \text{body weight}^{-1} \text{day}^{-1}$) respectively, Cs is the concentration of PAH in the soil ($\mu\text{g}_{\text{PAH}} \text{Kg}^{-1} \text{soil}$), IR is the ingestion rate (assumed to be 50mg day^{-1}), SA is the skin surface area (4700cm^2 available for contact), AF is the skin adherence factor ($0.3 \text{mg}_{\text{soil}} \text{cm}^{-2} \text{day}^{-1}$), DAF is the dermal absorption factor of 0.03 (connoting 3% of adhered soil to skin are adsorbed), EF is the exposure frequency (40day year^{-1}), ED is the exposure duration (10years), CF is the conversion factor ($10^{-3} \text{mg}_{\text{PAH}} \mu\text{g}_{\text{PAH}}^{-1} \times 10^{-3} \text{g}_{\text{soil}} \text{mg}_{\text{soil}}^{-1} = 10^{-6} \text{mg}_{\text{PAH}} \text{g}_{\text{soil}} \mu\text{g}_{\text{PAH}}^{-1} \text{mg}_{\text{soil}}^{-1}$), Bw is the body weight (53kg body weight), and AT_{nc} is the averaging time for non-carcinogenic risk (3650 days). The above parametric values were those recommended for general group of receptors (i.e., without divisions into sex or age intervals) by the Agency for Toxic Substances and Disease Registry (ATSDR, 2015). The non-cancer risks of each PAH were then evaluated using Eq. 3, 4, and 5.

$$HQ_i = ADD_i / RfD_i \quad (3).$$

$$HQ_d = ADD_d / RfD_d \quad (4).$$

$$HI = HQ_i + HQ_d \quad (5).$$

Where; HQ_i and HQ_d are the hazard quotients due to ingestion and dermal contact respectively, RfD_i and RfD_d represent the reference doses due to ingestion and dermal contact respectively. The reference doses were abstracted from EPA-IRIS database (USEPA, 2019).

The cancer risks for each PAH were calculated from equations 6, 7, and 8.

$$CRI = SFi \times CDI_i \quad (6)$$

$$CRd = SFi \times CDId \quad (7)$$

$$TCR = CRi + CRd \quad (8)$$

Where: CRi and CRd are the cancer risks due to ingestion and dermal contact respectively, and TCR is the total cancer risk. SFi and SFd are the cancer slope factors for ingestion and dermal contact respectively. The value of 7.3 and 25 mg⁻¹Kg day have been assigned as slope factors for incidental ingestion and dermal contact for benzo(a)pyrene (BaP) (USEPA, 1993; Knafla et al., 2006). The CDI_i and CDI_d represent the chronic daily intakes (mg_{PAH} Kg_{body weight}⁻¹ day⁻¹) for ingestion, and dermal contact respectively. They were obtained from Eqs 9 and 10 respectively.

$$CDI_i = \frac{(Cs * IR * EF * ED * CF)}{(Bw * ATc)} \quad (9).$$

$$CDId = \frac{(Cs * SA * AF * DAF * EF * ED * CF)}{(Bw * ATc)} \quad (10).$$

Where; Cs represent the B(a)P toxic equivalent concentration of PAH in soil, and ATc is the averaging time for carcinogenic risk (25550 days). The other terms have their usual meaning as presented above (Eqs. 1 and 2). The toxic equivalent concentrations (TEQ) for individual PAH are calculated by multiplying its concentration in soil by the toxic equivalent factor (TEF) (Eq 11). The TEF value for each PAH is shown in the TEF column of Table 3 (Nisbet and LaGoy, 1992)

$$\sum TEQ_{PAHs} = \sum (TEF_i \times C_{PAHi}) \quad (11)$$

3. Results and discussion

3.1. Concentrations, distributions, and compositions of PAHs in Dumpsites soils

Total polycyclic aromatic hydrocarbons ($\sum 16$ PAHs) concentrations in the various dumpsites (Table 1) ranged from 518.2 µg/Kg in OS to 18016.1 µg/Kg in ES dumpsite. The values in other dumpsites were: MG (6125.1 µg/Kg); AJ (5730.0 µg/Kg); OK (937.1 µg/Kg); and DM (11234.7 µg/Kg). The mean concentration for all dumpsites was 7093.5 ± 6639.1 µg/Kg. The large variation of PAHs concentrations in the various dumpsites as signalled by the huge standard deviation is implicative of the anthropogenic source of PAHs. Four levels of contaminations have been given by the European classification system (Zhengyu et al., 2013) viz: no pollution (< 200 µg/Kg), slight pollution (200 - 600 µg/Kg), moderate pollution (600 - 1000 µg/Kg), and serious pollution (> 1000 µg/Kg). The total PAHs concentrations of dumpsites' soils in this study can thus be judged as slightly polluted in OS and moderately polluted in OK, while the other dumpsites can be viewed as seriously polluted because their concentrations were much higher than 1000 µg/Kg. The range of values obtained in this study is comparable to those reported in some Nigerian soils: from E-waste dumpsites in Lagos and Ibadan (1756 - 2224 µg/Kg) (Adeyi and Oyeleke, 2017); dumpsites in Abeokuta (11000 - 41600 µg/Kg) (Olufumilayo et al., 2015); and around

automobile workshops in Eket metropolis (470 - 14850 $\mu\text{g/Kg}$) (Ekanem *et al.*, 2019). The range of values is also comparable to that reported for surface soils from the industrial areas of Banja Luka, Bosnia and Herzegovina (599 - 2848 $\mu\text{g/Kg}$) (Bjelić *et al.*, 2022). Individual PAH concentrations in the various sites ranged from not detectable (ND) to 2396.2 $\mu\text{g/Kg}$. Benzo[g,h,i]perylene (BgP) and Dibenzo[a,h]anthracene (DhA) were detected in moderately high quantity in Dumpsites ES and DM; but the other dumpsites did not show detectable amount of these two PAHs. The mean percent distributions of PAHs (Fig.1) show that the dominant PAHs were: BaA (13.3%), IcP (10.2%), BbF (9.1%), BkF (8.9%), Phe (8.1%), Ant (8.1%), and Chr (7.3%). These PAHs accounted for 65% of the total PAHs. The total concentrations of the seven carcinogenic PAHs viz: benzo(a)anthracene, indeno(1,2,3-cd)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, benzo(a)pyrene, and dibenzo(a,h)anthracene (listed in decreasing order of their mean concentrations in the soils) ranged from 318.0 – 9948.3 $\mu\text{g/Kg}$ with a mean of 3917.0 $\mu\text{g/Kg}$ representing 55.2 percent of the mean total PAHs.

Table 1: Concentrations ($\mu\text{g/Kg}$) of PAHs in the Dumpsites' soils

Compound	No of Rings	Concentrations ($\mu\text{g/Kg}$)					
		MG	AJ	ES	OK	OS	DM
Nap	2	37.0	28.3	637.5	30.4	30.5	742.4
Acy	3	16.3	4.3	499.7	17.2	16.5	626.4
Acp	3	62.6	64.1	719.5	5.9	6.0	841.7
Flr	3	160.9	394.9	1151.4	3.1	9.6	1000.3
Phe	3	198.1	331.4	1464.1	35.5	48.3	1381.4
Ant	3	327.6	1030.6	1460.1	16.7	28.3	586.1
Fit	4	169.5	321.9	610.9	89.9	32.3	218.8
Pyr	4	392.9	493.3	1237.0	75.1	28.8	695.3
Chr	4	575.5	673.7	1319.5	46.8	12.2	489.5
BaA	4	960.1	270.3	2396.2	121.2	4.2	1908.7
BbF	5	1307.9	585.2	1647.4	92.6	46.4	212.2
BkF	5	668.5	124.2	1605.9	109.9	33.9	1251.4
BaP	5	572.0	254.6	877.6	85.7	140.7	142.6
IcP	6	676.2	1153.2	1845.1	207.1	80.6	396.6
DhA	5	ND	ND	256.6	ND	ND	349.6
BgP	6	ND	ND	287.5	ND	ND	391.6
$\Sigma 16\text{PAHs}$		6125.1	5730.0	18016.1	937.1	518.2	11234.7

*MG: Merogun; AJ: Aladja; ES: Esisi; OK: Okpaka; OS: Osubi; DM: Dumorugbo; Nap: naphthalene; Acy: acenaphthylene; Acp: acenaphthene; Flr: fluorene; Phe: phenantrene; Ant: anthracene; Flt: fluoranthene; Pyr: pyrene; Chr: chrysene; BaA: benzo[a]anthracene; BbF: benzo[b]fluoranthene; BkF: benzo[k]fluoranthene; BaP: benzo[a]pyrene; IcP: indeno[1,2,3-cd]pyrene; DhA: dibenzo[a,h]anthracene; and BgP: benzo[g,h,i]perylene

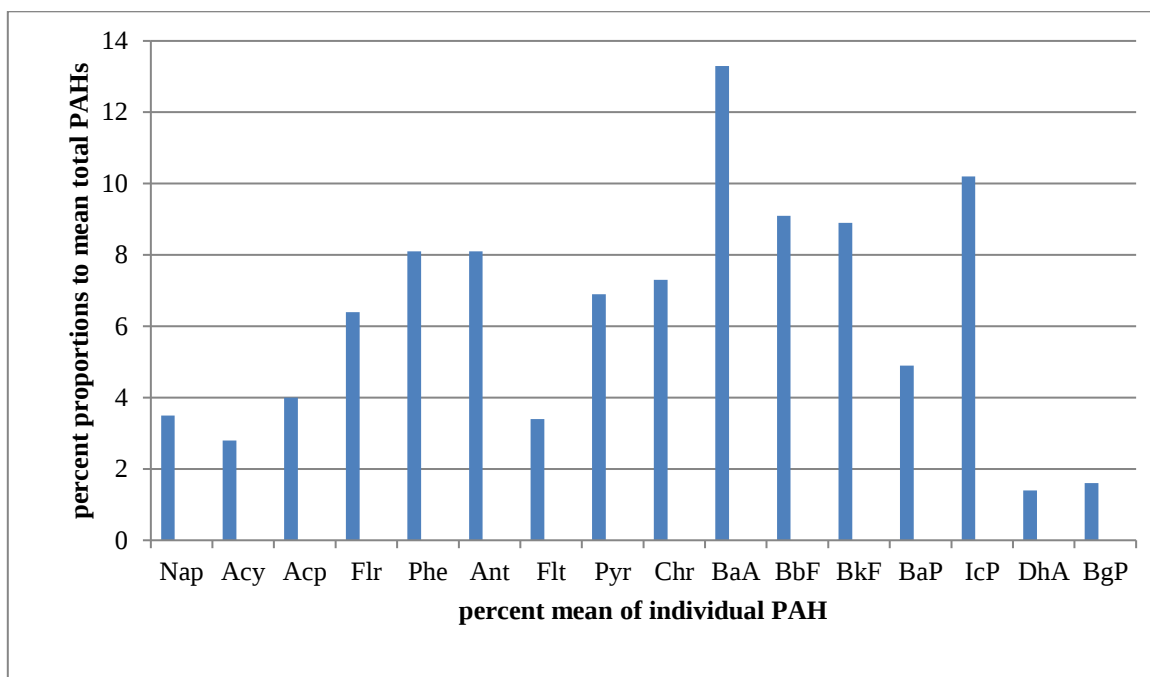


Fig.1: The mean percent proportions of individual PAHs to the mean total PAHs ($\Sigma 16\text{PAHs}$) concentration in the dumpsites

Fig. 2 shows the proportions of the ring forms of PAHs in dumpsites' soils. The two-to-three rings PAHs make up 11.61 – 46.09% of the total PAHs in the dumpsites' soils; while four ring PAHs constituted 14.93 – 35.54% of the total PAHs. The percent compositions of five-to-six rings PAHs relative to the total PAHs ranged from 24.43 – 58.21%.

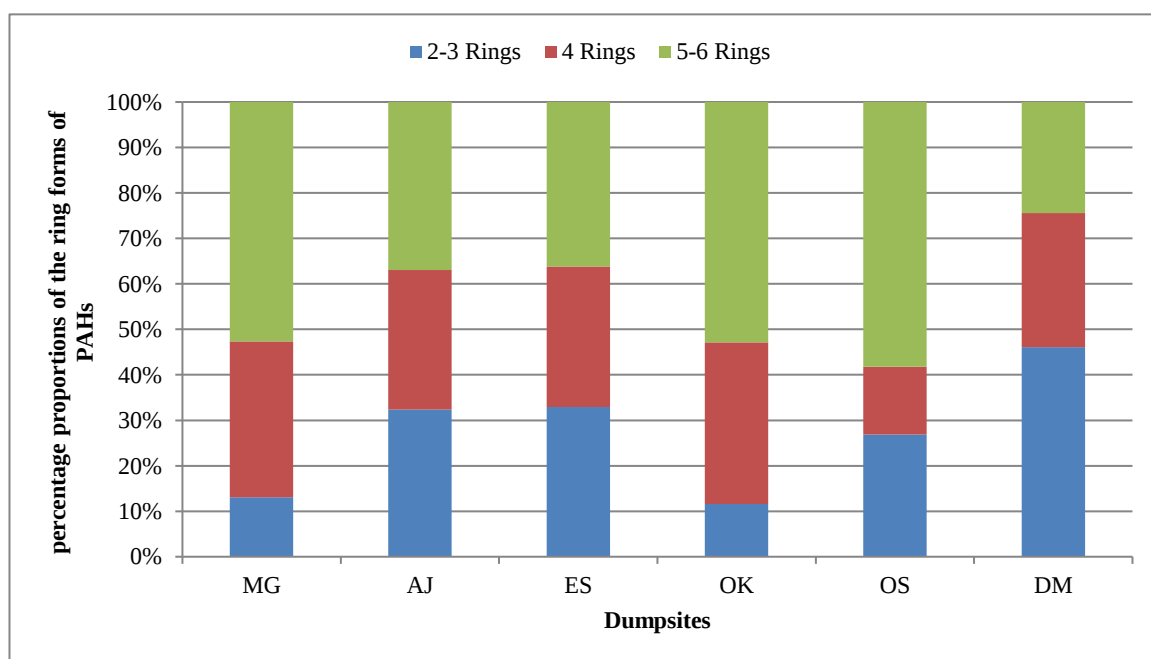


Fig. 2: PAHs proportions in soils showing percentage proportion of 2 – 3 rings, 4 rings, and 5-6 rings PAHs at each dumpsite

The mean percentage compositions of two-to-three rings, four ring, and five-to-six rings PAHs were: 27.16, 29.30, and 43.55% respectively. Two-to-three rings' PAHs are usually classified as low-molecular weight PAHs (LWM), while those with four or more rings are considered as high molecular weight (HMW). The large proportions of the HMW relative to the LMW PAHs are implicative that the sources of PAHs in these dumpsites were largely pyrogenic.

3.2. Health risks assessment

Table 2: Calculated values for hazard index (HI) and total cancer risks (TCR) in the various dumpsites

Parameter	MG	AJ	ES	OK	OS	DM	Ave
$\sum_{16}HQ_i$	1.673	1.149	3.864	0.236	0.124	2.082	1.521
$\sum_{16}HQ_d$	1.415	0.972	3.269	0.200	0.105	1.761	1.287
HI	3.09	2.12	7.13	0.44	0.23	3.84	2.81
$\sum_{16}CR_i$	1.01×10^{-4}	5.2×10^{-5}	2.07×10^{-4}	1.5×10^{-5}	1.7×10^{-5}	9.6×10^{-5}	8.2×10^{-5}
$\sum_{16}CR_d$	2.95×10^{-4}	1.52×10^{-4}	6.0×10^{-4}	4.4×10^{-5}	4.9×10^{-5}	2.78×10^{-4}	2.36×10^{-4}
TCR	3.96×10^{-4}	2.04×10^{-4}	8.07×10^{-4}	5.9×10^{-5}	6.6×10^{-5}	3.74×10^{-4}	3.18×10^{-4}

The calculated hazard quotients (from both incidental ingestions and dermal contacts) for individual PAH were all less than one (<1) (see Tables S1 and S2 for additional information). This indicate that individual PAH alone will not cause any non-cancer health effects on the public. However, the sum of the sixteen PAHs hazard quotients for both ingestion and dermal contact shown in Table 2, reveal that dumpsites at MG, AJ, ES, and DM had incidental ingestion summed hazard quotients ($\sum_{16}HQ_i$) that are larger than one. These same sites (MG, ES, & DM) except AJ also had dermal contact summed hazard quotients that were higher than unity. The summed hazard quotients for incidental ingestions at all sites were higher than those due to dermal contacts. The overall sum for both dermal contact and incidental ingestion hazard quotients; that is the hazard index (HI) for sixteen PAHs ($\sum_{16}HQ_i + \sum_{16}HQ_d$) was highest in Esisi (ES) (7.13). The lowest value (0.23) was at Osubi (OS). The values in other dumpsites were: MJ (3.09), AJ (2.12), OK (0.44), and DM (3.84). The average value for all the dumpsites was 2.81. The obtained values which were greater than one in most sites except OK and OS implied that these PAHs collectively, are capable of causing substantial non-carcinogenic harms to the public in these environments.

The toxic equivalent quotients (TEQs) calculated for the individual, the sum of seven carcinogenic ($\sum_7TEQs$), and the total for the sixteen PAHs ($\sum_{16}TEQs$) for various dumpsites is presented in Table 3.

Table 3: The Toxic Equivalent Quotients (TEQs) for PAHs in the various dumpsites

PAHs	TEF	TEQs ($\mu\text{g/Kgdw}$)							
		MG	AJ	ES	OK	OS	DM	mean	%mean contribution
Nap	0.001	0.04	0.03	0.64	0.03	0.03	0.74	0.25	0.03
Acy	0.001	0.02	0.00	0.50	0.02	0.02	0.63	0.20	0.03
Acp	0.001	0.06	0.06	0.72	0.01	0.01	0.84	0.28	0.04
Flr	0.001	0.16	0.39	1.15	0.00	0.01	1.00	0.45	0.06
Phe	0.001	0.20	0.33	1.46	0.04	0.05	1.38	0.58	0.08
Ant	0.01	3.28	10.31	14.60	0.17	0.28	5.86	5.75	0.76
Fit	0.001	0.17	0.32	0.61	0.09	0.03	0.22	0.24	0.03
Pyr	0.001	0.39	0.49	1.24	0.08	0.03	0.70	0.49	0.06
Chr	0.01	5.76	6.74	13.20	0.47	0.12	4.90	5.20	0.69
BaA	0.1	96.01	27.03	239.62	12.12	0.42	190.87	94.35	12.48
BbF	0.1	130.79	58.52	164.74	9.26	4.64	21.22	64.86	8.58
BkF	0.1	66.85	12.42	160.59	10.99	3.39	125.14	63.23	8.36
BaP	1	572.00	254.60	877.60	85.70	140.70	142.60	345.53	45.69
IcP	0.1	67.62	115.32	184.51	20.71	8.06	39.66	72.65	9.61
DhA	1	ND	ND	256.60	ND	ND	349.60	101.03	13.36
BgP	0.01	ND	ND	2.88	ND	ND	3.92	1.13	0.15
$\sum 7\text{TEQs}$		939.03	474.63	1896.86	139.25	157.33	873.99	746.85	98.76
$\sum 16\text{TEQs}$		943.34	486.57	1920.65	139.67	157.79	889.27	756.21	100

Nap: naphthalene; Acy: acenaphthylene; Acp: acenaphthene; Flr: fluorine; Phe: phenanthrene; Ant: anthracene; Flt: fluoranthene; Pyr: pyrene; Chr: chrysene; BaA: benzo[a]anthracene; BbF: benzo[b]fluoranthene; BkF: benzo[k]fluoranthene; BaP: benzo[a]pyrene; IcP: indeno[1,2,3-cd]pyrene; DhA: dibenzo[a,h]anthracene; and BgP: benzo[g,h,i]perylene.

The values for individual PAH ranged from ND – 239.62 $\mu\text{g/Kg}$. The $\sum 16\text{TEQs}$ value was lowest in OK (139.67 $\mu\text{g/Kg}$) and highest in ES (1920.65 $\mu\text{g/Kg}$). The values ($\mu\text{g/Kg}$) in other dumpsites were: MG (943.34), AJ (486.57), OS (157.79), and DM (889.27). The average value for the dumpsites was 756.21 $\mu\text{g/Kg}$. Except for the dumpsite at Esihi (ES), the values for the others were lower than the standard TEQ value of 1000 $\mu\text{g/Kg}$ established by the World Health Organization (Qu et al., 2020). Three (3) out of the six (6) dumpsites also had values that were lower than the 600 $\mu\text{g/Kg}$ TEQs standard of the Canadian Soil Quality Guidelines (CCME, 2010). The major contributor to PAHs toxicity as indicated by mean TEQs values for all dumpsites was benzo(a)pyrene (BaP) contributing 45.69% of the total TEQs. Other contributors include: DhA (13.36%), BaA (12.48%), IcP (9.61%), BbF (8.58%), and BkF (8.36%). The TEQs values for the seven carcinogenic PAHs ($\sum 7\text{TEQs}$) in this study ranged from 157.33 – 1896.86 $\mu\text{g/Kg}$ (mean: 746.85 $\mu\text{g/Kg}$). These values are comparable to: 24 - 2937 $\mu\text{g/Kg}$ (mean: 733 $\mu\text{g/Kg}$) reported in summer for soil in Urban Park, Northwest China (Ailijiang et al., 2022), the 8.92 – 827.16 $\mu\text{g/Kg}$ (mean: 189.91 $\mu\text{g/Kg}$) in sediments of the Aba River (Chokor and Achugwo, 2022), and the 299.0 – 839.8 and 368.2 – 974.6 $\mu\text{g/Kg}$ for dry and wet seasons soils around automobile repairs workshops in Eket metropolis (Ekanem et al., 2019). They were however much higher than the reported

values of: 23.270 – 368.63 $\mu\text{g/Kg}$ (mean: 151.223 $\mu\text{g/Kg}$) in soils of industrial areas of Bosnia and Herzegovina (Bjelić *et al.*, 2022), 11.90 – 277.19 $\mu\text{g/Kg}$ in surface soils of petroleum contaminated areas of Loess Plateau, China (Wang *et al.*, 2018), and the 0.30 - 656 $\mu\text{g/Kg}$ (mean: 96 $\mu\text{g/Kg}$) in winter for soil in Urban Park (Ailijiang *et al.*, 2022). This implied that PAHs in the dumpsites showed comparatively high toxicity. The order of toxicity based on the TEQs values was: ES > MG > DM > AJ > OS > OK.

The cancer risks due to ingestions for individual PAH ranged from ND – 9.462×10^{-5} with majority of the values been much less than the 10^{-6} upper limit of the United State Environmental Protection Agency (USEPA, 2001) (Table S3). The total cancer risks due to ingestions (CRI) at each dumpsite in order of magnitude were: ES (2.07×10^{-3}), MG (1.017×10^{-4}), DM (9.59×10^{-5}), AJ (5.246×10^{-5}), OS (1.70×10^{-5}), and OK (1.51×10^{-5}). The average value for the dumpsites was 8.15×10^{-5} (Table 2). These values were 15 – 2070 times higher than the upper limit established by USEPA and connote that the risk of getting cancer due to ingestions is 15 – 2070 in a million rather than one (1) in a million established standard (USEPA, 2001). Similarly, the cancer risks resulting from dermal contacts of individual PAH were for the most part, less than 10^{-6} (Table S4), signifying that individual PAH alone will not cause any carcinogenic harm. However, Table 2 shows that the combinations of risks due to dermal contacts for the sixteen PAHs ($\sum 16\text{CR}_d$) for all dumpsites were greater than the 10^{-6} standard with the lowest been 4.36×10^{-5} obtained in OK (Okpaka). This implied that collectively, there is a chance of 43 – 599 in a million of the general public having cancer due to dermal contact with the soils from these dumpsites as compared to one (1) in a million USEPA recommended standard. The total cancer risk (TCR) which is the summation of cancer risks due to ingestions and dermal contacts are displayed in a row of Table 2. The order of the dumpsites soil's probability to cause cancer to the general public was: ES (8.07×10^{-4}) > MG (3.96×10^{-4}) > DM (3.74×10^{-4}) > AJ (2.04×10^{-4}) > OS (6.6×10^{-5}) > OK (5.9×10^{-5}). The USEPA viewed one in a million ($\text{TCR} = 10^{-6}$) lifetime cancer risk acceptable; while an instance of lifetime cancer risk of one in ten thousand or greater ($\text{TCR} = 10^{-4}$) is considered as serious (USEPA, 2001). The TCRs calculated in this study were 58 – 807 times greater than the standard 10^{-6} established by the USEPA. These indicate their abilities to cause adverse effects on human health and the requirement of risk management actions.

Conclusion

The study reveals that dumpsites soils in Warri metropolis contain significant amount of PAHs that could impact the health of the public. Majority of the dumpsites had total PAHs ($\sum 16\text{PAHs}$) concentrations values that were larger than $1000 \mu\text{g/Kg}$ connoting serious pollutions of PAHs in the soils. Except for the dumpsites at Okpaka (OK) and Osubi (OS), the others had hazard index (HI) values that were larger

than one implying that these sites hold the abilities to cause non-cancer risks to human. Also, the total cancer risks (TCR) values calculated were all greater than 10^{-6} , signifying an increased chance - greater than the usual acceptable one in a million probabilities - to carcinogenic health effects. This calls for the need to improve waste management system and curb unregulated disposal of urban and/or industrial and domestic wastes.

Conflict of Interest

The author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary Information

Table S1. Calculated Hazard quotients (HQ) and Hazard indices (HI) due to incidental ingestions

PAHs	RfD	MG	AJ	ES	OK	OS	DM	Ave.
Nap	0.02	0.0002	0.0001	0.0033	0.0002	0.0002	0.0038	0.0013
Acy	0.02	0.0001	0.0000	0.0026	0.0001	0.0001	0.0032	0.0010
Acp	0.06	0.0001	0.0001	0.0012	0.0000	0.0000	0.0015	0.0005
Flr	0.04	0.0004	0.0010	0.0030	0.0000	0.0000	0.0026	0.0012
Phe	0.000307	0.0667	0.1116	0.4931	0.0120	0.0163	0.4652	0.1941
Ant	0.04	0.0008	0.0027	0.0038	0.0000	0.0001	0.0015	0.0015
Fit	0.04	0.0004	0.0008	0.0016	0.0002	0.0001	0.0006	0.0006
Pyr	0.03	0.0014	0.0017	0.0043	0.0003	0.0001	0.0024	0.0017
Chr	0.000307	0.1938	0.2269	0.4444	0.0158	0.0041	0.1648	0.1750
BaA	0.000307	0.3233	0.0910	0.8069	0.0408	0.0014	0.6428	0.3177
BbF	0.000307	0.4405	0.1971	0.5548	0.0312	0.0156	0.0715	0.2184
BkF	0.000307	0.2251	0.0418	0.5408	0.0370	0.0114	0.4214	0.2129
BaP	0.000307	0.1926	0.0857	0.2955	0.0289	0.0474	0.0480	0.1164
IcP	0.000307	0.2277	0.3884	0.6214	0.0697	0.0271	0.1336	0.2446
DhA	0.000307	0.0000	0.0000	0.0864	0.0000	0.0000	0.1177	0.0340
BgP	0.04	0.0000	0.0000	0.0007	0.0000	0.0000	0.0010	0.0003
$\sum 16HI_i$		1.6732	1.1490	3.8637	0.2361	0.1239	2.0816	1.5213

Table S2. Calculated Hazard quotients (HQ) and Hazard indices (HI) due to dermal contacts

PAHs	RfD	MG	AJ	ES	OK	OS	DM	Ave.
Nap	0.02	0.00016	0.00012	0.00279	0.00013	0.00013	0.00325	0.00110
Acy	0.02	0.00007	0.00002	0.00219	0.00008	0.00007	0.00274	0.00086
Acp	0.06	0.00009	0.00009	0.00105	0.00001	0.00001	0.00123	0.00041
Flr	0.04	0.00035	0.00086	0.00252	0.00001	0.00002	0.00219	0.00099
Phe	0.000307	0.05644	0.09442	0.41712	0.01011	0.01376	0.39356	0.16424
Ant	0.04	0.00072	0.00225	0.00319	0.00004	0.00006	0.00128	0.00126
Fit	0.04	0.00037	0.00070	0.00134	0.00020	0.00007	0.00048	0.00053
Pyr	0.03	0.00115	0.00144	0.00361	0.00022	0.00008	0.00203	0.00142
Chr	0.000307	0.16396	0.19194	0.37593	0.01333	0.00348	0.13946	0.14802
BaA	0.000307	0.27353	0.07701	0.68268	0.03453	0.00120	0.54379	0.26879
BbF	0.000307	0.37262	0.16672	0.46935	0.02638	0.01322	0.06046	0.18479
BkF	0.000307	0.19046	0.03538	0.45752	0.03131	0.00966	0.35652	0.18014
BaP	0.000307	0.16296	0.07254	0.25003	0.02442	0.04009	0.04063	0.09844
IcP	0.000307	0.19265	0.32855	0.52567	0.05900	0.02296	0.11299	0.20697
DhA	0.000307	0.00000	0.00000	0.07311	0.00000	0.00000	0.09960	0.02878
BgP	0.04	0.00000	0.00000	0.00063	0.00000	0.00000	0.00086	0.00025
$\sum 16HI_d$		1.41553	0.97205	3.26870	0.19976	0.10481	1.76105	1.28699

Table S3. Calculated Cancer risks (CR_i) due to incidental ingestions

PAHs	MG	AJ	ES	OK	OS	DM	Ave.
Nap	3.99E-09	3.05E-09	6.87E-08	3.28E-09	3.29E-09	8.00E-08	2.71E-08
Acy	1.76E-09	4.64E-10	5.39E-08	1.85E-09	1.78E-09	6.75E-08	2.12E-08
Acp	6.75E-09	6.91E-09	7.76E-08	6.36E-10	6.47E-10	9.07E-08	3.05E-08
Flr	1.73E-08	4.26E-08	1.24E-07	3.34E-10	1.04E-09	1.08E-07	4.89E-08
Phe	2.14E-08	3.57E-08	1.58E-07	3.83E-09	5.21E-09	1.49E-07	6.22E-08
Ant	3.53E-07	1.11E-06	1.57E-06	1.80E-08	3.05E-08	6.32E-07	6.20E-07
Fit	1.83E-08	3.47E-08	6.59E-08	9.69E-09	3.48E-09	2.36E-08	2.59E-08
Pyr	4.24E-08	5.32E-08	1.33E-07	8.10E-09	3.11E-09	7.50E-08	5.25E-08
Chr	6.20E-07	7.26E-07	1.42E-06	5.05E-08	1.32E-08	5.28E-07	5.60E-07
BaA	1.04E-05	2.91E-06	2.58E-05	1.31E-06	4.53E-08	2.06E-05	1.02E-05
BbF	1.41E-05	6.31E-06	1.78E-05	9.98E-07	5.00E-07	2.29E-06	6.99E-06
BkF	7.21E-06	1.34E-06	1.73E-05	1.18E-06	3.65E-07	1.35E-05	6.82E-06
BaP	6.17E-05	2.75E-05	9.46E-05	9.24E-06	1.52E-05	1.54E-05	3.73E-05
IcP	7.29E-06	1.24E-05	1.99E-05	2.23E-06	8.69E-07	4.28E-06	7.83E-06
DhA	0.00E+00	0.00E+00	2.77E-05	0.00E+00	0.00E+00	3.77E-05	1.09E-05
BgP	0.00E+00	0.00E+00	3.10E-07	0.00E+00	0.00E+00	4.22E-07	1.22E-07
$\sum 16CR_i$	1.02E-04	5.25E-05	2.07E-04	1.51E-05	1.70E-05	9.59E-05	8.15E-05

Table S4. Calculated Cancer risks (CR_d) due to dermal contacts

PAHs	MG	AJ	ES	OK	OS	DM	Ave.
Nap	1.16E-08	8.84E-09	1.99E-07	9.50E-09	9.53E-09	2.32E-07	7.84E-08
Acy	5.09E-09	1.34E-09	1.56E-07	5.37E-09	5.15E-09	1.96E-07	6.15E-08
Acp	1.96E-08	2.00E-08	2.25E-07	1.84E-09	1.87E-09	2.63E-07	8.85E-08
Flr	5.03E-08	1.23E-07	3.60E-07	9.68E-10	3.00E-09	3.12E-07	1.42E-07
Phe	6.19E-08	1.04E-07	4.57E-07	1.11E-08	1.51E-08	4.32E-07	1.80E-07
Ant	1.02E-06	3.22E-06	4.56E-06	5.22E-08	8.84E-08	1.83E-06	1.80E-06
Fit	5.29E-08	1.01E-07	1.91E-07	2.81E-08	1.01E-08	6.83E-08	7.51E-08
Pyr	1.23E-07	1.54E-07	3.86E-07	2.35E-08	9.00E-09	2.17E-07	1.52E-07
Chr	1.80E-06	2.10E-06	4.12E-06	1.46E-07	3.81E-08	1.53E-06	1.62E-06
BaA	3.00E-05	8.44E-06	7.49E-05	3.79E-06	1.31E-07	5.96E-05	2.95E-05
BbF	4.09E-05	1.83E-05	5.15E-05	2.89E-06	1.45E-06	6.63E-06	2.03E-05
BkF	2.09E-05	3.88E-06	5.02E-05	3.43E-06	1.06E-06	3.91E-05	1.98E-05
BaP	1.79E-04	7.95E-05	2.74E-04	2.68E-05	4.40E-05	4.45E-05	1.08E-04
IcP	2.11E-05	3.60E-05	5.76E-05	6.47E-06	2.52E-06	1.24E-05	2.27E-05
DhA	0.00E+00	0.00E+00	8.02E-05	0.00E+00	0.00E+00	1.09E-04	3.16E-05
BgP	0.00E+00	0.00E+00	8.98E-07	0.00E+00	0.00E+00	1.22E-06	3.54E-07
$\sum 16CR_d$	2.95E-04	1.52E-04	6.00E-04	4.36E-05	4.93E-05	2.78E-04	2.36E-04