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Distribution Pattern and Potential Ecological Risks of PAHs in Soils in the Vicinities of Open Dumpsite in Yenagoa, Bayelsa, Nigeria

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Abstract
The concentrations, distributions, and associated risks of polycyclic aromatic hydrocarbons (PAHs) in soils of dumpsite and its vicinities were investigated. Composite samples were taken from the dumpsite and distances (15, 30, 60, 90, 120m) away from the foot of the dumpsite; as well as from a control site (2000m away). The determinations of PAHs were done with gas chromatography couple to mass spectrometer (GC-MS) after extractions with dichloromethane (DCM) and a silica gel clean-up. Total PAHs (Σ16PAHs) concentrations in the dumpsite soil and that of the control were 930.05, and 31.15 µg/kg respectively. Values of 238.57, 118.39, 75.56, 58.24, and 47.61µg/kg were obtained for the distances of 15, 30, 60, 90, and 120m away from the foot of the dumpsite respectively. Ecological risk assessment, implicated the dumpsite's soil to be of moderate pollution, while at distances of about 15m away from the dump, the effects seem negligible. The human toxicities assessment reveals that the concentrations of PAHs in soils of the dumpsites and its vicinities were still within safe limit. However, due to possible accumulations of PAHs in soils, it is recommended that appropriate measures be taken to regulate the management of wastes in the city of Yenagoa.

Keywords: Negligible concentration, toxic equivalence, risks assessment, pollution, health.

INTRODUCTION
Open dumpsites are common features in most Nigerian cities. Wastes from the cities, which include: domestic, urban, industrial, and agricultural wastes are often dumped on these sites. These dumpsites which are poorly managed could constitute source of pollution to neighbouring soil, air and water. Some researchers have implicated the dumpsites as rich spots for heavy metals and polycyclic aromatic hydrocarbons with its attendant impacts on the immediate environment (Ataikiru and Okieimen, 2019, Ekpete, *et al*., 2019 Chokor, 2024a). The degradation and or leaching of these wastes often lead to accumulations of pollutants in the nearby soils, emissions of obnoxious gases to surrounding air, and contaminations of nearby underground and surface waters. The accumulations of pollutants in soils impaired its ecological functions and results to the destabilization of the ecosystem (Chokor, 2019). Plants and animals in the neighbourhood of these contaminated soils may bio-accumulate

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some of these pollutants through the food chain with resultant effects on public health. Thus the necessity to monitor the ecological state of soils especially in relation to dangerous chemical pollutants such polycyclic aromatic hydrocarbons (PAHs).

PAHs are set of persistent toxic organic compounds having two or more fused benzene rings. They are important intermediates in the productions of various substances such as: plastics, plasticizers, dye, pigments, and pesticides, and are ubiquitous in the environment. PAHs toxicity, carcinogenicity, mutagenicity, teratogenicity, immunotoxicity to several organisms have been well documented (Abdel-Shafy and Mansour, 2016., Varjani *et al*., 2017., Oliveira *et al*., 2019., Patel *et al*., 2020). Due to public health concern, sixteen Polycyclic Aromatic Hydrocarbons (PAHs) have been listed as priority pollutants by the United State Environmental Protection Agency (USEPA, 2014) 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). Their occurrence in the environment might be due to natural or anthropogenic origin. Natural origin is mainly sourced from the synthesis by certain plants and bacteria; and those resulting from transformation of natural organic precursors by diagenetic processes (Mojiri *et al*., 2019). The emissions due to volcanic eruptions, natural forest fire, and moorland fire by lightning flashes constitute less significant sources of natural inputs (Patel *et al*., 2020). Though PAHs occurs naturally in the soils, large amount of it in a contaminated soil are largely due to anthropogenic inputs (Chokor, 2022; 2024b). Oil spills, offshore drilling, vehicular exhausts emissions, industrial pyrolysis, and runoff from industrial and urban areas constitute anthropogenic sources of PAHs (Roy *et al*., 2021). Coal and coal products, crude oil, and refined petroleum products contain PAHs. Incomplete combustion of organic materials (including foodstuffs and household products), fossil fuels, woods, and grasses similarly produces PAHs (Readman *et al*., 2002; Maioli *et al*., 2011).

Yenagoa is a local government area, as well as the capital city of Bayelsa State, South-Southern Nigeria. It is located at within latitudes 4°49′N and 5°23′N, and also within longitudes 6°10′E and 6°33′E; with a population of over 352,285 occupying its 706km^2 according to the 2006 census figure (NPC, 2006). It is fairly industrialized town with vast commercial activities. These activities in addition to domestic and agricultural activities generate a lot of wastes that eventually find their ways into near-by dumpsites in the city. These wastes contain organic foods materials, wood, papers, PVC plastics, rubbers toys, bathing shoes, computers hardware, and electronics, bicycles handles, sports items, tires, automobile parts, containers that have been used for storing pesticides and petroleum products, as well as other household, agricultural, and industrial products (Chokor, 2024a). Most of the above listed items contain PAHs which on account of their indiscriminate disposal into open dump add to the burden PAHs in the soil environment. The heap of wastes in these dumpsites form unsightly seen in most parts of the cities; and are occasionally reduced by setting it on fire and bulldozing the accumulated ashes and non-combustibles into clumps. This process again, adds to the burden of PAHs as their combustion normally takes place under suboptimum conditions (Chokor, 2024a).

Although, some works have been done on the concentrations of PAHs in dumpsites (Olufunmilayo, 2015; Adeyi and Oyeleke, 2017; Ekpete, *et al*., 2019 Chokor, 2024a), there is paucity of information regarding their distributions in such vicinities. In this work, the distribution profiles of PAHs in soils of an open dumpsite along Tombia-Amassoma Road,

Yenagoa and its vicinities was determined with view to determine the potential ecological risks and toxicities to human health.

Materials and Methods

Study area

The study was conducted on soils from the vicinity of a dumpsite along Tombia-Amassoma Road, Yenagoa, Balyesa, South-Southern Nigeria (N04°58′27.57″ E06°19′30.56″).

Sampling and sample preparation

Composite sample were taken from the open dump with stainless steel auger. Five (5) soil sub-samples were taken from the core of the dumpsite (about 3 - 7m radially from the epicentre of the dumpsite) and bulked together to make the composite sample which was representative of the dumpsite. Spatial test samples were similarly taken at several increasing distances (15 – 120m) away from the foot of the dumpsite. A control (background) sample was also taken about 2 kilometres from the dumpsite. Samples were placed in pre-cleaned wide-mouth amber bottles and kept in ice chest at temperature below 4^{o}C for onward transportation to the laboratory for analysis.

PAHs extractions

Soil samples were air-dried in the dark for a period of about three (3) days. The samples were homogenized and sieved through a mesh (500µm). The aliquots of these samples (10g) were mixed with sufficient quantities of anhydrous sodium sulphate (Na_2SO_4) (about 5g) to eliminate moisture, and spiked with surrogate standard (10µg/mL of ρ-terphenyl and 2-fluorobiphenyl), wrapped in filter papers, position in thimbles and loaded into the main chamber of the soxhlet extractors. Extractions were performed 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, 2024a).

Sample clean-up and separations

Extracts cleaned-up were out on a column chromatograph (10mm i.d. X 30cm) pre-packed with activated silica gel (10g), lined at the top with anhydrous Na_2SO_4 (2cm thick) and glass wool at the bottom. The samples were first eluted with 20mL n-hexane to remove the aliphatic fractions followed by 20mL of dichloromethane (DCM) to obtain the aromatic fractions (Chokor and Ediagbonya, 2024; Chokor, 2024b). Concentrations of the aromatic fractions to about 2mL were done with rotary evaporator at 30^{o}C; after which 1.5mL of it were transferred into vials and stored at 4^{o}C awaiting gas chromatography-mass spectrometry (GC-MS) injections. Blanks samples were processed in similar manner for the purpose of quality assurance (Chokor and Ogonegbu, 2023).

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 ×0.25 µm film thickness × 0.25 mm i.d.) was used for the separations. Samples were injected into GC via a pulsed split-less mode with an injection volume of 1 µL. Pure helium gas at a flow velocity of 1 mL/min was used as the carrier gas. 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. The chromatographic column conditions were set

at initial temperature of 70°C held for 20 min, and then increased at 25°Cmin^{-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}.

Identification and quantification

Identifications of PAHs were done by comparing EI-mass spectrum and specific ion fragment with those mass spectral libraries; and also by comparing their chromatographic retentions time with those of standards. 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 used for sample quantification and quantifying procedural recovery ; and quantifications were done using response factors related to the respective internal standards based on five-point calibration curves for the individual PAH

Ecological risks assessment

Ecological risks of PAHs were examined using risk quotients (RQ) obtained from the negligible concentrations (NCs) and the maximum permissible concentrations (MPCs) of PAHs in soils; Equations 1 and 2

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

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

Where $C_{QV(NCs)}$ and $C_{QV(MPCs)}$ represent the quality values of the NCs and the MPCs in the soil respectively. The risk resulting from a combination of all 16 PAHs were appraised by calculating RQ∑PAHs(NCs) and RQ∑PAHs(MPCs) in which the values of RQ_{NCs} and RQ_{MPCs} of individual PAHs that are not less than one are added, as shown in equations 3 and 4.

$$\sum_{n}^{RQ} PAHs(NCs) = \sum_{i=1}^{16} RQi(NCs), \ \ where\ RQi(NCs) \geq 1 \quad (3)$$

$$\sum_{n}^{RQ} PAHs(MPCs) = \sum_{i=1}^{16} RQi(MPCs), \ \ where\ RQi(MPCs) \geq 1 \quad (4)$$

RQ_{NCs} < 1.0 implies that individual PAH compounds are of negligible concern; while, RQ_{MPCs} ≥ 1.0 indicates severe contamination by the individual compound that requires remediation. RQ_{NCs} ≥ 1.0 and RQ_{MPCs} < 1.0 connote moderate risk posed by a single PAH compound that might demand some control and remediation. Values of $\sum_n^{RQ} PAHs(NCs) \geq 800$ and $\sum_n^{RQ} PAHs(MPCs) = 0$ indicates moderate risk. Values of $\sum_n^{RQ} PAHs(NCs) < 800$ and $\sum_n^{RQ} PAHs(MPCs) \geq 1$ also indicate moderate risk. However, $\sum_n^{RQ} PAHs(NCs) \geq 800$ and $\sum_n^{RQ} PAHs(MPCs) \geq 1$ represent high risk due to ∑16PAHs in the ecosystem (Wang *et al.*, 2018).

Toxicity assessment of PAHs in soils

Toxic equivalent factors (TEFs) were applied in estimating the exposure risk posed by individual and total PAHs to human health. The toxicities of PAHs in soils were evaluated BaP toxic equivalent concentration (TEQ). The TEFs values for the 16PAHs were retrieved from USEPA (2003) and Nisbet and LaGoy (1992); and the total toxicity equivalence concentrations (∑TEQs) were calculated using equation 5.

$$\sum TEQs = \sum (Ci \ \ X \ \ TEFi) \quad (5)$$

Where C_i is the concentration of individual PAHs and TEF_i is the respective toxic equivalence factor.

RESULTS AND DISCUSSION

Concentrations and distributions of PAHs in the soils of dumpsite and its vicinities

The mean PAHs concentrations (µg/kg) in the dumpsite and various distances away are as shown in Table 1. The concentration of total PAHs (∑16PAHs) was as expected highest in the dumpsite core with mean of 930.67µg/kg. The value decreases with distance away from the foot of the dump. At distances of 15 and 30m away it was 238.57 and 118.39µg/kg respectively. The values were 75.56, 58.24, and 47.61µg/kg at distances of 60, 90, and 120m away from the foot of the dumpsite. The value for the control site was 31.15µg/kg which was relatively lower than that obtained at a distance of 120m away from the dumpsite. These decreasing values with distance away from the dumpsite; and the control value that was significantly lower than those at and close to the dumpsite is an indication that the dumpsite situated within the metropolis is a major anthropogenic source of PAHs in the soil environment. The fast decrease in value with distance may also connote that vertical migration down the soil is more predominant than lateral migration. This may spell danger of underground water contamination. A plot of concentrations with distance away from the base of the dumpsite is shown in Fig. 1. An extrapolation of these values shows that the concentration of the control (background level) value could only be obtained at a distance of about 148m away from the dump in this soil environment. Soil properties such as: pH, organic carbon, clay content has been implicated to affect the rate of retention and migration of contaminants in soils (Chokor, 2024b).

Table 1: Mean PAHs concentrations (µg/kg) in dumpsite and various distances away from it.

compound	No of Rings	Concentrations (µg/kg)						
		Core	15m	30m	60m	90m	120m	Control
Nap	2	ND	ND	ND	ND	ND	ND	ND
Acy	3	17.85	20.22	8.58	4.45	4.79	3.97	2.58
Acp	3	ND	ND	ND	ND	ND	ND	ND
Flr	3	190.37	26.96	13.73	8.89	7.18	3.97	3.22
Phe	3	107.08	33.72	10.3	2.22	4.79	3.97	2.58
Ant	3	73.37	13.48	5.15	2.22	2.39	1.98	1.29
Flt	4	113.03	13.48	6.87	4.44	7.18	1.98	2.58
Pyr	4	126.91	26.96	8.58	2.22	9.58	3.97	3.87
Chr	4	ND	ND	ND	ND	ND	ND	ND
BaA	4	ND	ND	ND	ND	ND	ND	ND
BbF	5	9.59	3.5	ND	ND	ND	ND	ND
BkF	5	3.52	1.92	ND	ND	ND	ND	ND
BaP	5	6.74	3.97	1.68	ND	0.78	ND	0.20
IcP	6	150.71	53.92	32.61	24.45	7.18	9.92	5.16
DhA	5	ND	ND	ND	ND	ND	ND	ND
BgP	6	130.88	40.44	30.89	26.67	14.37	17.85	9.67
∑16PAHs		930.05	238.57	118.39	75.56	58.24	47.61	31.15

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

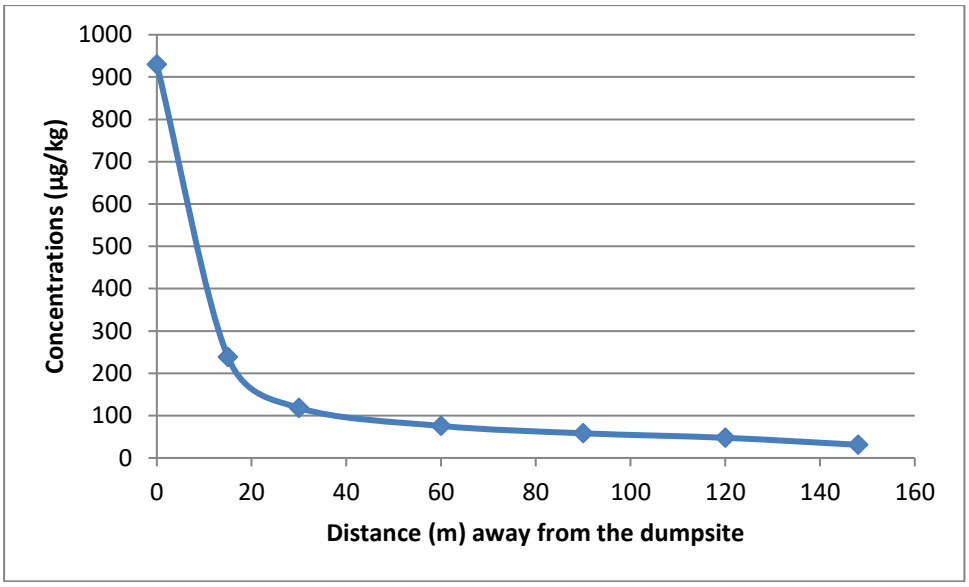

Fig. 1: Total concentrations (∑16PAHs) (µg/kg) of PAHs with distances away from the dumpsite

Soil contamination by PAHs is usually grouped into four levels: no pollution (<200µg/kg), slight pollution (200 - 600µg/kg), medium pollution (600 - 1000µg/kg), and serious pollution (>1000µg/kg) (Zhengyu *et al*., 2013). The concentrations of PAHs in the soil samples showed medium pollution at the core of the dumpsite, while slight pollution was observed at a distance of about 15m away from the dumpsite. Beyond this point, concentrations were below 200µg/kg indicating no pollutions. However, the evidence of PAHs contribution by the dumpsite was eminent as seen in the significance difference between these values and that of the control.

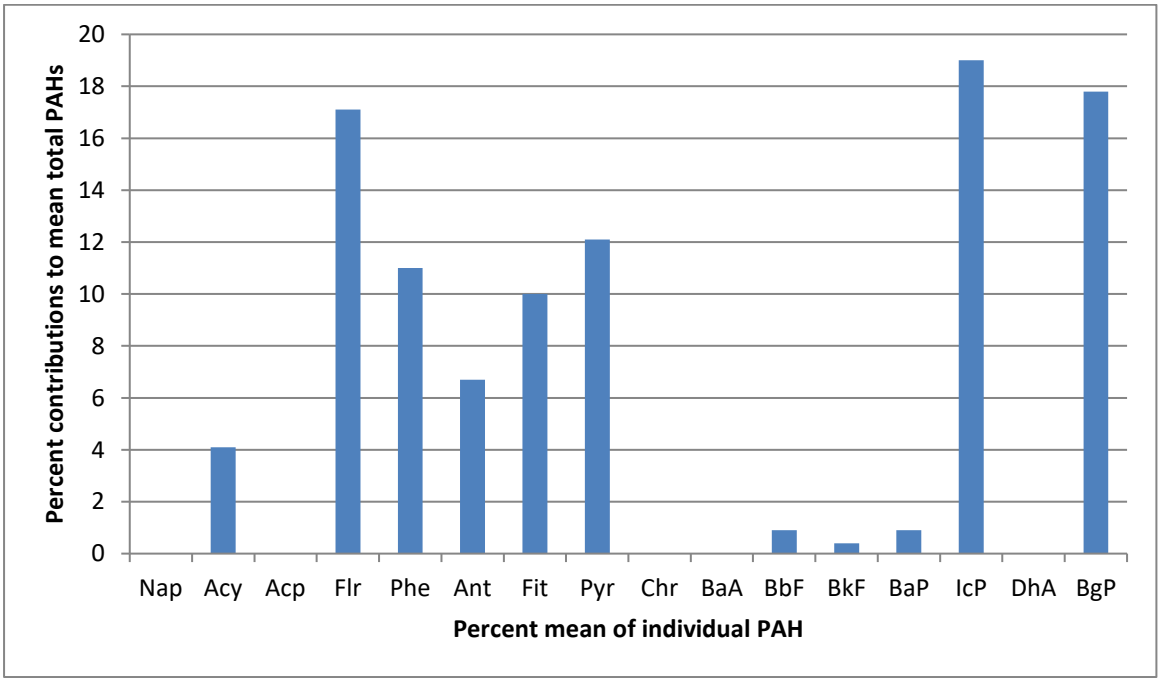

Fig. 2: Percentage proportions of individual PAH to the total mean PAHs (Σ16PAHs) concentration in the soils

Compositions of PAHs in soils of dumpsite and its vicinities

The mean percent contributions to total PAHs (∑16PAHs) in the soils of dumpsite and its vicinities are as shown in Fig 2. Some PAHs including: Nap, Acp, Chr, BaP, and DhA were

below detection limits in the soils, others such as: BbF, BkF, and BaP were detected only at the dumpsite's soil or few meters (15 – 60m) away. At greater distances away, their concentrations in the soils either become negligible or fall below detection limits. Among the five-to-six rings PAHs, IcP and BgP were the predominant PAHs, having mean compositions of 19.0 and 17.8% relative to the total PAHs in the soils respectively. Pyr and Flt constituting 12.1 and 10.0% of the total PAHs respectively were the most dominant four-rings PAHs in the soils. Flr (17.1% of ∑16PAHs) was the most predominant three-rings PAHs in the soils. This was followed by: Phe (11.0%), Ant ((6.7%), and Acy (4.1%).

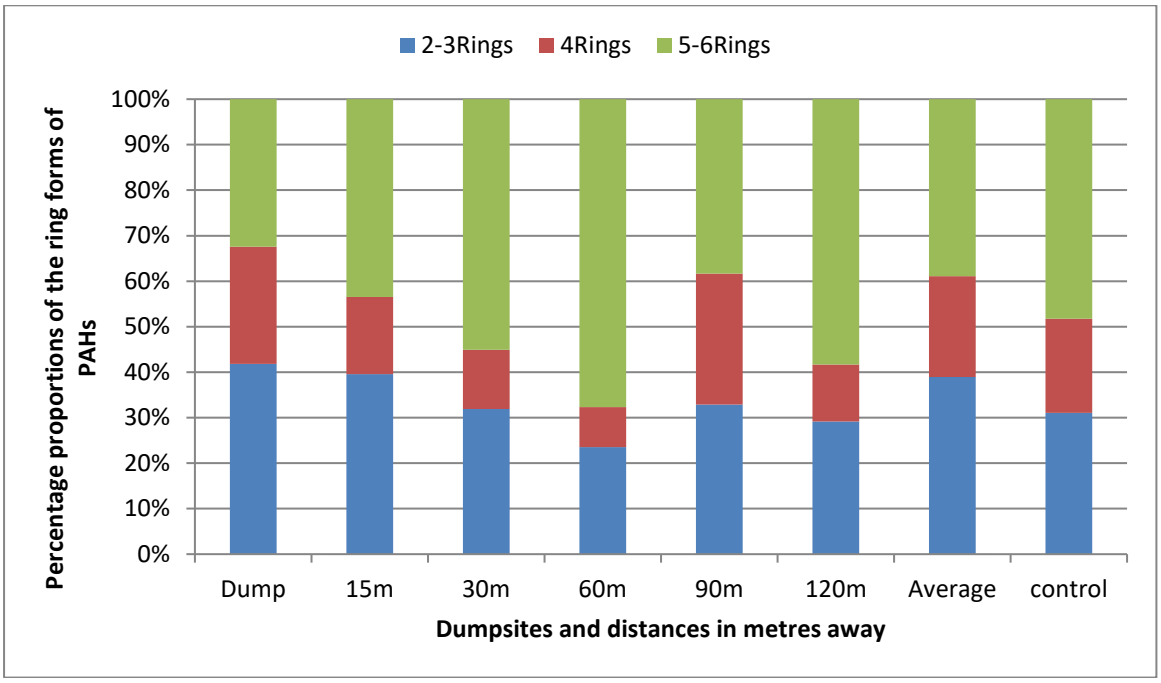

Fig. 3: PAHs composition in soils showing percentage proportions of 2 - 3 rings, 4 rings, and 5 - 6 rings PAHs.

The proportions of two-to-three rings PAHs (Fig. 3) in the soils of dumpsite and its vicinities ranged from ranged from 23.53 – 41.79% of the total PAHs; while, that of four-rings PAHs was from 8.81 – 28.78%. The five-to-six rings PAHs constituted 32.41 – 58.33% of the total PAHs. The mean percent proportions relative to the total PAHs for two-three rings, four-rings, and five-to-six rings PAHs were: 38.93, 22.15, and 38.93% respectively; while, that of the control were: 31.04, 20.71, and 48.25 percent respectively. It is usual to classify PAHs as low molecular weight (LMW) and high molecular weight (HMW). The two and three rings PAHs are considered as LMW while, those with four or more are regarded as HMW. The higher proportions of HMW PAHs in soils tend to suggest that the source of PAHs in the soils is majorly pyrogenic. Pyrogenic contaminations are usually characterized by predominance of high molecular weight (HMW) PAHs (four to six rings PAHs) while low molecular weight (LMW) PAHs (two and three rings PAHs) are dominant with petrogenic inputs (Yunker *et al*., 2012; Tobiszewski, 2019).

Table 2: Statistical descriptions of $RQ_{(NCs)}$ of PAHs in soils of dumpsite and distances away

		$RQ_{(NCs)}$						
Cpds	NCs	core	15m	30m	60m	90m	120m	control
Nap	1.4	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acy	1.2	14.88	16.85	7.15	3.71	3.99	3.31	2.15
Acp	1.2	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Flr	1.2	158.64	22.47	11.44	7.41	5.98	3.31	2.68
Phe	5.1	21.00	6.61	2.02	0.44	0.94	0.78	0.51
Ant	1.2	61.14	11.23	4.29	1.85	1.99	1.65	1.08
Flt	26	4.35	0.52	0.26	0.17	0.28	0.08	0.10
Pyr	1.2	105.76	22.47	7.15	1.85	7.98	3.31	3.23
Chr	107	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BaA	2.5	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BbF	2.5	3.84	1.40	0.00	0.00	0.00	0.00	0.00
BkF	24	0.15	0.08	0.00	0.00	0.00	0.00	0.00
BaP	2.6	2.59	1.53	0.65	0.00	0.30	0.00	0.08
IcP	59	2.55	0.91	0.55	0.41	0.12	0.17	0.09
DhA	2.6	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BgP	75	1.75	0.54	0.41	0.36	0.19	0.24	0.13
RQ∑PAHs		376.49	82.56	32.05	14.82	19.95	11.58	9.13

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

Ecological risks of PAHs in the soils of dumpsite and its vicinities

The risk quotients obtained from negligible concentrations (RQ_{NCs}) for the individual PAH are shown in Table 2. Some PAHs have RQ_{NCs} values that were higher than one (1) in the dumpsite and distances away. Acenaphthylene (Acy), fluorene (Flr), phenantrene (Phe), anthracene (Ant), and pyrene (Pyr) were particularly higher than one (1) in most sampled sites indicating that these individual PAHs may not be of negligible concern. The sum of RQ_{NCs} that were higher than one (1); that is $RQ\sum PAHs_{NCs}$ for the sites were: 376.49, 82.56, 32.05, 14.82, 19.95, and 11.58 at the dumpsite, and 15, 30, 60, 90, and 120meter away from the foot of the dump respectively. The $RQ\sum PAHs_{NCs}$ control value was 9.13. These values were however less than 800. The risk quotients obtained from maximum permissible concentrations of PAHs (RQ_{MPCs}) (Table 3) shows that the PAHs have values that were less than one (1) in almost all the sampled sites (the dumpsites and distances away) except in the dumpsite where flourene (Flr) and pyrene (Pyr) had values that were little higher than one (1). Thus, the only $RQ\sum PAHs_{MPCs}$ with value higher than one was also at the dumpsite. This implies that flourene (Flr) and pyrene (Pyr) individually might exhibit severe pollutions at the dumpsite, while other PAHs individually will not show sign of severe contamination. The inference from the above is that PAHs such as: Acy, Flr, Phe, Ant, and Pyr will exhibit moderate pollution in the dumpsites and distances away from it since their RQ_{NCs} were greater than one (1), but their RQ_{MPCs} were less than one. Also, the combine effects of total PAHs (∑16PAHs) will result to moderate pollution in soil at the dumpsite since $\sum_n^{RQ} PAHs(NCs) < 800$ and $\sum_n^{RQ} PAHs(MPCs) \geq 1.0$. However, $\sum_n^{RQ} PAHs(MPCs)$ been less than one (1) at distances away from the dumpsite, implies that the combine effects of PAHs might be negligible at distances away.

Table 3: Statistical descriptions of $RQ_{(MPCs)}$ of PAHs in soils of dumpsite and distances away

		$RQ_{(MPCs)}$						
Cpds	MPCs	core	15m	30m	60m	90m	120m	control
Nap	140	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acy	120	0.15	0.17	0.07	0.04	0.04	0.03	0.02
Acp	120	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Flr	120	1.59	0.22	0.11	0.07	0.06	0.03	0.03
Phe	510	0.21	0.07	0.02	0.00	0.01	0.01	0.01
Ant	120	0.61	0.11	0.04	0.02	0.02	0.02	0.01
Flt	260	0.43	0.05	0.03	0.02	0.03	0.01	0.01
Pyr	120	1.06	0.22	0.07	0.02	0.08	0.03	0.03
Chr	10700	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BaA	250	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BbF	250	0.04	0.01	0.00	0.00	0.00	0.00	0.00
BkF	2400	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BaP	260	0.03	0.02	0.01	0.00	0.00	0.00	0.00
IcP	5900	0.03	0.01	0.01	0.00	0.00	0.00	0.00
DhA	260	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BgP	7500	0.02	0.01	0.00	0.00	0.00	0.00	0.00
RQ∑PAHs		2.64	0.00	0.00	0.00	0.00	0.00	0.00

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

The potential toxic effects of PAHs in soils of dumpsite and its vicinities

The toxic equivalent quotient (TEQ) for the sixteen PAHs are as presented in Table 4. The total TEQs (∑TEQs) values for the dumpsite was 25.72 µg/kg dw. The value decreases to 10.56 and 5.35 µg/kg at distance of 15 and 30m away from the dumpsite respectively. At distances of 60, 90, and 120m, the values were: 2.76, 1.70, and 1.21µg/kg. The value for the control was 0.84 µg/kg dw. The major contributors to toxicities as reflected in TEQs values in the soils samples were: IcP (mean: 61.40; range: 0 – 88.71), BaP (mean: 23.80; range: 0 – 45.91), and BgP (mean: 11.51; range: 0 – 14.37). The total TEQs (∑16TEQs) (25.72 µg/kg) obtained for the dumpsite in this study, was well below the safe limit of 600 µg/kg TEQs established by the Canadian soil quality guidelines for the protection of the environment and human health (CCME, 2010). The value was however, higher than those from rural soils samples of Dongjiang River Basin, China (8.36 µg/kg) (Zheng *et al*., 2014); and the soils of Yellow River Delta (11.92 µg/kg) (Yuan *et al*., 2014). The values were also comparable those of the soils of Liache Estuary (30.0 µg/kg) (Li *et al*., 2014), and Xinzhon (34 µg/kg) (Zhoa *et al*., 2014). The value however, were much lower than the mean value (756.21µg/kg) obtained for dumpsites soils in Warri, Nigeria (Chokor, 2024a), and soils of Xi'an (421.05 µg/kg) (Wang *et al*., 2018).

Table 4: TEQs values for the sixteen priority PAHs in the dumpsite and distances away (m)

		TEQs						
PAHs	TEFs	core	15m	30m	60m	90m	120m	control
Nap	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acy	0.001	0.02	0.02	0.01	0.00	0.00	0.00	0.00
Acp	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Flr	0.001	0.19	0.03	0.01	0.01	0.01	0.00	0.00
Phe	0.001	0.11	0.03	0.01	0.00	0.00	0.00	0.00
Ant	0.01	0.73	0.13	0.05	0.02	0.02	0.02	0.01
Fit	0.001	0.11	0.01	0.01	0.00	0.01	0.00	0.00
Pyr	0.001	0.13	0.03	0.01	0.00	0.01	0.00	0.00
Chr	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BaA	0.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BbF	0.1	0.96	0.35	0.00	0.00	0.00	0.00	0.00
BkF	0.1	0.35	0.19	0.00	0.00	0.00	0.00	0.00
BaP	1	6.74	3.97	1.68	0.00	0.78	0.00	0.20
IcP	0.1	15.07	5.39	3.26	2.45	0.72	0.99	0.52
DhA	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BgP	0.01	1.31	0.40	0.31	0.27	0.14	0.18	0.10
∑PAHs		25.72	10.56	5.35	2.76	1.70	1.21	0.84

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

CONCLUSION

Ecological risks and toxicity assessment of PAHs in and around a dumpsite in the city of Yenagoa, Bayelsa indicated that some PAHs (Acy, Flr, Phe, Ant, and Pyr) have moderate ecological risks in the dumpsite and distances away from it. The total ecological risk posed by the combined effects of the sixteen (16) PAHs (∑16PAHs) was moderate at the dumpsite while at distances of about 15m away, it appears negligible. The toxicity assessment showed that PAHs concentrations in the dumpsite and beyond were within safe limit. The significant difference between PAHs concentrations in soils of the dumpsite, its proximities and that of the control site however, implicated the contributory role of dumpsite to PAHs in the soil environment. The possibility of further enrichment of PAHs in this soil environment is envisaged because of the nature of PAHs. It is thus, recommended that effort be made to curb unregulated disposal of municipal solid wastes.

REFERENCES

Abdel-Shafy, H.I., Mansour, M.S. (2016). A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. *Egypt. J. Pet.*, 25: 107–123. doi: 10.1016/j.ejpe.2015.03.011

Adeyi, A.A., Oyeleke, P. (2017) Heavy Metals and Polycyclic Aromatic Hydrocarbons in Soil from E-waste dumpsites in Lagos and Ibadan, Nigeria. *J. Health Pollut.*, 7(15), 71- 84.

Ataikiru1, H and Okieimen, F.E. (2019) Risk assessment of trace metals in soils in the vicinity of NPA Expressway Open dump in Warri metropolis, Delta State, Nigeria, *Journal of Environmental Protection*, 10: 562-576 http://www.scirp.org/journal/jep

CCME (2010). Canadian Council of Ministers of the Environment, Canadian Soil Quality Guidelines for Carcinogenic and Other Polycyclic Aromatic Hydrocarbons (Environmental and Human Health Effects). *Scientific Criteria Document* (revised), pp 216

Chokor A.A. (2024a). Polycyclic Aromatic Hydrocarbons in Soils of Open Dumpsites in Warri Metropolis: Concentration and Human Health Risks Assessment, *Arab. J. Chem. Environ.Res.* 11(1): 55-70

Chokor, A. A. and Ediagbonya, T.F. (2024) Profile, health risk assessment and source apportionment of polycyclic aromatic hydrocarbons (PAHs) in terrestrial snails and some aquatic species consumed in parts of Ogbia LGA, Bayelsa, Nigeria, *Ovidius University Annals of Chemistry*, 35(1): 58 – 66, DOI: 10.2478/auoc-2024-0008

Chokor, A.A. (2019). Chemical assessment of heavy metals contaminated soil: A review of evaluation indices, *American Journal of Environmental Protection,* 7(2): 34-40. http://pubs.sciepub.com/env/7/2/1

Chokor, A.A. (2024b) Levels, profiles, and sources of total petroleum hydrocarbons (TPHs) in sediments of the Aba River at Ogbor-Hill Region, South-Eastern, Nigeria, *World Scientific News*, 187, 31- 46

Chokor, A.A**.** and Ogonegbu, A.C. (2023). Assessment of Petroleum Hydrocarbons in Terrestrial Snails (*Achatina achatina*) and Mud Fishes (*Clarias anguillaris*) from some parts of Ogbia LGA, Nigeria, *Arabian Journal of Chemical and Environmental Research,* 10 (2): 92–105

Chokor, A.A.(2022).Distribution and source fingerprinting of total petroleum hydrocarbons in sediments of the River Niger at Okpu and Iyiowa-Odekpe Axes in South-Eastern, Nigeria, *World News of Natural Sciences*, 42: 151-168.

Ekpete, O.A., Edori, O.S., Iyama., W.A. (2019). Concentrations of Polycyclic Aromatic Hydrocarbons from Selected Dumpsites Within Port Harcourt Metropolis, Rivers State, Niger Delta, Nigeria, Int. J, Environ. Sci. Nat. Res., 21(4): 556066. DOI: 10.19080/IJESNR.2019.21.556066

Li, G.L., Lang, Y.H., Yang,W., Peng, P., Wang, X.M. (2014).Source contributions of PAHs and toxicity in reed wetland soils of Liaohe estuary using a CMB-TEQ method. *Sci. Total Environ*. 490: 199–204.

Maioli, O.L.G., Rodrigues, K.C., Knoppers, B.A., Azevedo, D.A. (2011).Distribution and sources of aliphatic and polycyclic aromatic hydrocarbons in suspended particulate matter in water from two Brazilian estuarine systems, *Continental Shelf Research*, 31: 1116-1127.

Mojiri, A., Zhou, J.L., Ohashi, A., Ozaki, N., Kindaichi, T. (2019).Comprehensive review of polycyclic aromatic hydrocarbons in water, sources, their effects and treatments, *Science of the Total Environment* 696: 133971.

Nisbet, I.C., LaGoy, P.K. (1992). Toxic equivalency factors (TEFs) for polycyclic aromatic Hydrocarbons (PAHs). *Regulatory Toxicology and Pharmacology* 16: 290-300.

NPC (2006) National Population Census, Details of the breakdown of State provisional population totals, Official Gazette, *Federal Republic of Nigeria.*

Oliveira M., Slezakova K., Delerue-Matos C., Pereira M.C., Morais S. (2019) Children environmental exposure to particulate matter and polycyclic aromatic hydrocarbons and biomonitoring in school environments: A review on indoor and outdoor exposure levels, major sources and health impacts, *Environment International*, 124: 180 – 204.

Olufunmilayo, O.O., Oludare, H.A., Rotimi, A.I. (2015) Determination of polycyclic aromatic hydrocarbons (PAHs) on selected dumpsites in Abeokuta Metropolis, SW, Nigeria, *Applied Environmental Research*, 37(3), 33-48.

Patel, A.B., Shaikh, S., Jain, K.R., Desal, C., Madamwar, D. (2020). Polycyclic aromatic hydrocarbons: sources, toxicity, and remediation approaches, *Frontiers in Microbiology,* 10: 11-24.

Readman, J.W., Fillmann, G., Tolosa, I., Bartocci, J., Villeneuve, J.P., Catinni, C., Mee, L.D. (2002). Petroleum and PAHs contamination of the Black Sea, *Marine Pollution Bulletin*, 44: 48-62

Roy, D., Jung, W., Kim, J., Lee, M., Park, J. (2021). Cancer risk levels for sediment- and soil-bound polycyclic aromatic hydrocarbons in coastal areas of South Korea, *Frontiers Environmental Science*, 9 (2021) 719243, Doi: 10.3389/fenvs.2021.719243

Tobiszewski, M. (2019) Application of diagnostic ratios of PAHs to characterize the pollution emission sources,. In*: Proceedings of the 5th International conference on Environmental Science and Technology*, Sarajevo, Bosnia and Herzegovina, 9–13 October 2019.

USEPA (1992). U.S. Environmental Protection Agency. *Report on the Ecological Risk Assessment Guidelines Strategic Planning Workshop*; EPA 630/R-92-002; Risk Assessment Forum: Washington, DC, USA, 1992.

USEPA (2003). Recommended toxicity equivalence factors (TEFs) for human health risk assessments of 2,3,7,8- Tetrachlorodibenzo-p-dioxin and dioxin-like compounds. U.S. Environmental Protection Agency Risk Assessment Forum; Washington D.C.: 2003. EPA-600-R-10-005

USEPA (2014) United State Environmental Protection Agency, *Priority Pollutant List, 2014*, (40CRF Part 423, Appendix A).

Varjani,S.J., Gnansounou, E., Pandey, A. (2017). Comprehensive review on toxicity of persistent organic pollutants from petroleum refinery waste and their degradation by microorganisms, *Chemosphere*, 188: 280–291.

Wang, D., Ma, J., Hao Li, H., Zhang, X. (2018). Concentration and Potential Ecological Risk of PAHs in Different Layers of Soil in the Petroleum-Contaminated Areas of the Loess Plateau, China, International *Journal of Environmental Research and Public Health*, 15: 1785; doi:10.3390/ijerph15081785

Wang, L.J., Zhang, S.W., Wang, L., Zhang,W.J., Shi, X.M., Lu, X.W., Li, X.P., Li, X.Y. (2018).Concentration and Risk Evaluation of Polycyclic Aromatic Hydrocarbons in Urban Soil in the Typical Semi-Arid City of Xi'an in Northwest China. *Int. J. Environ. Res. Public Health*, 15: 607.

Yuan, H.M., Li, T.G., Ding, X.G., Zhao, G.M., Ye, S.Y. (2014). Distribution, sources and potential toxicological significance of polycyclic aromatic hydrocarbons (PAHs) in surface soils of the Yellow River Delta, China. *Mar. Pollut. Bull*., 83: 258–264.

Yunker, M.B., Perreault, A., Lowe,C.J. (2012). Source apportionment of elevated PAH concentrations in sediments near deep marine outfalls in Esquimalt and Victoria, BC, Canada: is coal from an 1891 shipwreck the source?, *Organic Geochemistry,* 46 :12–37.

Zhao, L., Hou, H., Shangguan, Y.X., Cheng, B., Xu, Y.F., Zhao, R.F., Zhang, Y.L., Hua, X.Z., Huo, X.L., Zhao, X.F. (2014).Occurrence, sources, and potential human health risks of polycyclic aromatic hydrocarbons in agricultural soils of the coal production area surrounding Xinzhou, China. *Ecotoxicol. Environ. Saf.*, 108: 120–128

Zheng T., Ran Y., Chen L. (2014). Polycyclic aromatic hydrocarbons (PAHs) in rural soils of Dongjiang River Basin: occurrence, source apportionment, and potential human health risk. *J. Soils Sediments*. 14: 110

Zhengyu, Z., Hailong, T., Yangsheng, L. (2013). Source and distribution characteristics of polycyclic aromatic hydrocarbons in agricultural soils in Beijing suburbs, *Environ. Chem.,* 32: 874–880