Air Quality, Atmosphere & Health
https://doi.org/10.1007/s11869-025-01694-8

Health risk assessment of the levels of Persistent Organic Pollutants in ambient air around urban dumpsites in Nigeria

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Received: 7 January 2024 / Accepted: 14 January 2025

Abstract

Open dump disposal is the commonly used means of disposing Municipal Solid Waste (MSW) in Nigeria, just like in various other developing and underdeveloped countries. The environment (land, air, and water) has become contaminated due to this unwholesome practice of uncontrolled dumping of MSW. Notable among the contaminants are persistent organic pollutants (POPs). This study measured polycyclic aromatic hydrocarbon (PAH) and polychlorinated biphenyls (PCB) concentrations of the Igbatoro and Federal University of Technology, Akure (FUTA) dumpsites' ambient air within 30 days (October 2021). The air samples were collected following the standard operating procedures prescribed by the UNEP (2017) and evaluated using gas chromatography-mass spectrometry (GC–MS). The results obtained revealed that considerable levels of PAH and PCB are found at the dumpsites. The summation of the concentration levels of PAH $\left(\sum \text{PAH}\right)$ for FUTA and Igbatoro dumpsites were 3.55×10^{-5} and 5.51×10^{-5} μ/m^3 while $\sum$ PCBs are 1.00 and 0.99 ng/m^3. Cancer risk values of 1.10×10^{-5} and 1.23×10^{-5} obtained for FUTA and Igbatoro dumpsites respectively are within the acceptable limits of 1×10^{-6} to 1×10^{-4}. The inhalation rate analysis values of 1.53×10^{-6} ng TEQ kg^{-1} day^{-1}(1.53 fg TEQ/kg per day) and 3.38×10^{-6} ng TEQ kg^{-1} day^{-1} (3.38 fg TEQ/kg per day) obtained for adults and children respectively at these dumpsites are below the permissible threshold. Despite, being a short-term risk level assessment for the dumpsites, this study highlights the need for effective waste management strategies and the enforcement of environmental regulations to reduce the release of harmful pollutants into the atmosphere, ultimately safeguarding public health and the environment. However, a long-term assessment (annual) of the PAH compounds and PCB congeners within and around the selected dumpsites is recommended for an effective and reliable evaluation of the dumpsite risk, especially concerning ambient air.

Keywords Developing countries · Dumpsites · Environment · Air · Polycyclic aromatic hydrocarbon · Polychlorinated biphenyls · Risk

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Introduction

Municipal solid wastes are disposed of through bioreactors or sanitary/engineered landfills in developed countries, but the crudest and least hygienic – open dumping method—is still rampant in Nigeria and other developing countries. The fact that Abuja – the Nigerian Federal Capital Territory does not have organized engineered landfill sites/ sanitary landfills points to the worrisome state of waste disposal in Nigeria (Aderoju et al. 2020; Chimereze et al. 2016). Open dumping is an unhygienic method of disposing of waste that is characterized by the absence of regulatory control (Ayodele and Alo 2020). Factors including nonchalance, deficient policy formulation and implementation, inefficient and inadequate laws, political meddling, and lack of man, machine, and money power, have engendered the choice and practice of open dumping, proliferating the core business district and

Published online: 08 April 2025

outskirts of major towns in Nigeria (Idowu et al. 2019; Ojuri et al. 2018).

One of the anthropogenic practices that contribute greatly to groundwater and surface water contamination, soil contamination, and air pollution or contamination is open dumping. Air pollution emanating from open dumping yards (open dumpsites) is a result of the toxic pollutants inherent in the MSW particularly after degradation (Akinluyi 2019). The deliberate burning and spontaneous combustion of dumped MSW also contribute to the pollutant load and types found around dumpsites (Adetona et al. 2020; Ayodele and Alo 2020). The pollutants from the open dumpsite in the form of landfill gas, airborne particulates, trace metals, and persistent organic pollutants pose a great public health concern (Adesina et al. 2021; dos Muchangos and Tokai 2020; Vaccari et al. 2018), as they affect human health, the environment, and life quality and ultimately the economy of a nation (Adesina 2021). Specifically, the uncontrolled/unconventional burning (at a lower temperature compared to incineration) of garbage, recyclables, electronics, and other household/consumer products in dumpsites generates particulate matters such as trace metals, dioxins, polybrominated diphenyl ethers (PBDEs), and polychlorinated biphenyls (PCBs) (Adetona et al. 2020; ISWA 2015).

PAH is a toxic compound that significantly impacts human health mostly due to its carcinogenic, mutagenic, and bio-accumulative properties (Patel et al. 2020). On the other hand, PCBs are classified as POPs and have the potential to negatively influence human health (Adetona et al. 2020; Beddaa et al. 2020; Pozo et al. 2017). The impacts of PCBs on human health include death, systemic, cancer, genotoxic, reproductive, neurological, immunological, and lymphoreticular effects, etc. (ATSDR 2000; Igbo et al. 2018; Petrovic et al. 2018). PAH found in the environment could emanate from pyrogenic, petrogenic, and biological sources. Pyrogenic PAH emerges when organic compounds undergo thermal decomposition at elevated temperatures in environments characterized by limited oxygen availability or complete absence thereof. The PAH that arises as a result of the maturation of crude oil and comparable geological processes is commonly referred to be petrogenic. PAH can be generated through biological synthesis by specific plants and microorganisms, as well as being synthesized during the decomposition process of vegetative matter (Loremikan et al. 2020). It has been reported that when one kilogram of domestic waste is burnt openly, especially at low temperatures, about 45 mg of PAH and 0.126 mg of PCBs are generated (Rajan et al. 2021). A common source of PAHs is the plastic cover of some electronic products that are also found on dumpsites (Essienubong et al. 2019).

Studies abound on the concentrations of PAH and PCB from dumpsites. The effects of these compounds have been assessed on the environment globally and in Nigeria particularly. Many of these studies concentrated mainly on soil, especially in Nigeria (Adedosu et al. 2015; Adesina et al. 2020; Ekpete et al. 2019) and sparsely on air and water (Igbo et al. 2018; Inam et al. 2016; Ololade et al. 2021; Petrovic et al. 2018). There is a dearth of information on the ambient air quality of the study areas. Also, little attention has been given to the risk level of the dumpsites, particularly the PAH and PCB loads. The risk level assessment conducted on the Igbatoro dumpsite using an integrated risk-based approach (IRBA) by Ojuri et al. (2018) did not cover air quality while the ecological risk conducted on the FUTA dumpsite by Oluwatuyi et al. (2020) considered trace metals of soils (chromium, iron, manganese, nickel, and zinc).

However, Idowu et al. (2019) reiterated the need to constantly monitor the environment and even isolate the immediate environment from the impact of pollutants generated from unsafe disposal methods, especially in developing countries. Hence, this study is conducted to provide necessary data regarding the dumpsites' PAH and PCB concentration and evaluate the health risks associated with the pollutants emitted from the current waste disposal method. This would engender planning and formulation of effective MSW management policy.

Materials and method

Study areas

There are two study areas and the two dumpsites are located in Akure, Ondo State, Nigeria. Figure 1 shows the study areas. Figure 1a and b show FUTA dumpsite, while Fig. 1c and d show Igbatoro dumpsite. The windrose diagram of the dumpsites is shown in Fig. 2. The Igbatoro dumpsite (Fig. 1c and d), is the biggest and the most active in the State, and it is an open semi-controlled dump yard, owned by the Ondo State Government. The Igbatoro dumpsite is a fenced yard with limited control of the reception of solid waste but the wastes are dumped on the ground for burning. Although, it receives liquid waste too; especially abattoir wastewater from the state-owned semi-mechanized abattoir site, the dumpsite receives solid waste of more than 100,000 metric tons of waste per year (Ojuri et al. 2018).

FUTA dumpsite (Fig. 1a and b) is a relatively small-sized open dumpsite that receives an average of about 5,000 metric tons of waste per year from about 15,000 people within and around the university. The study area is characterized by two distinct seasons (rain and dry), with annual rainfall ranging from 1405 to 3500 mm. The atmospheric temperature is between 25 °C and 32 °C and the mean relative humidity annually is approximately 80% (Ajibade et al. 2014; Ojuri et al. 2018). The geology of the study area indicates that

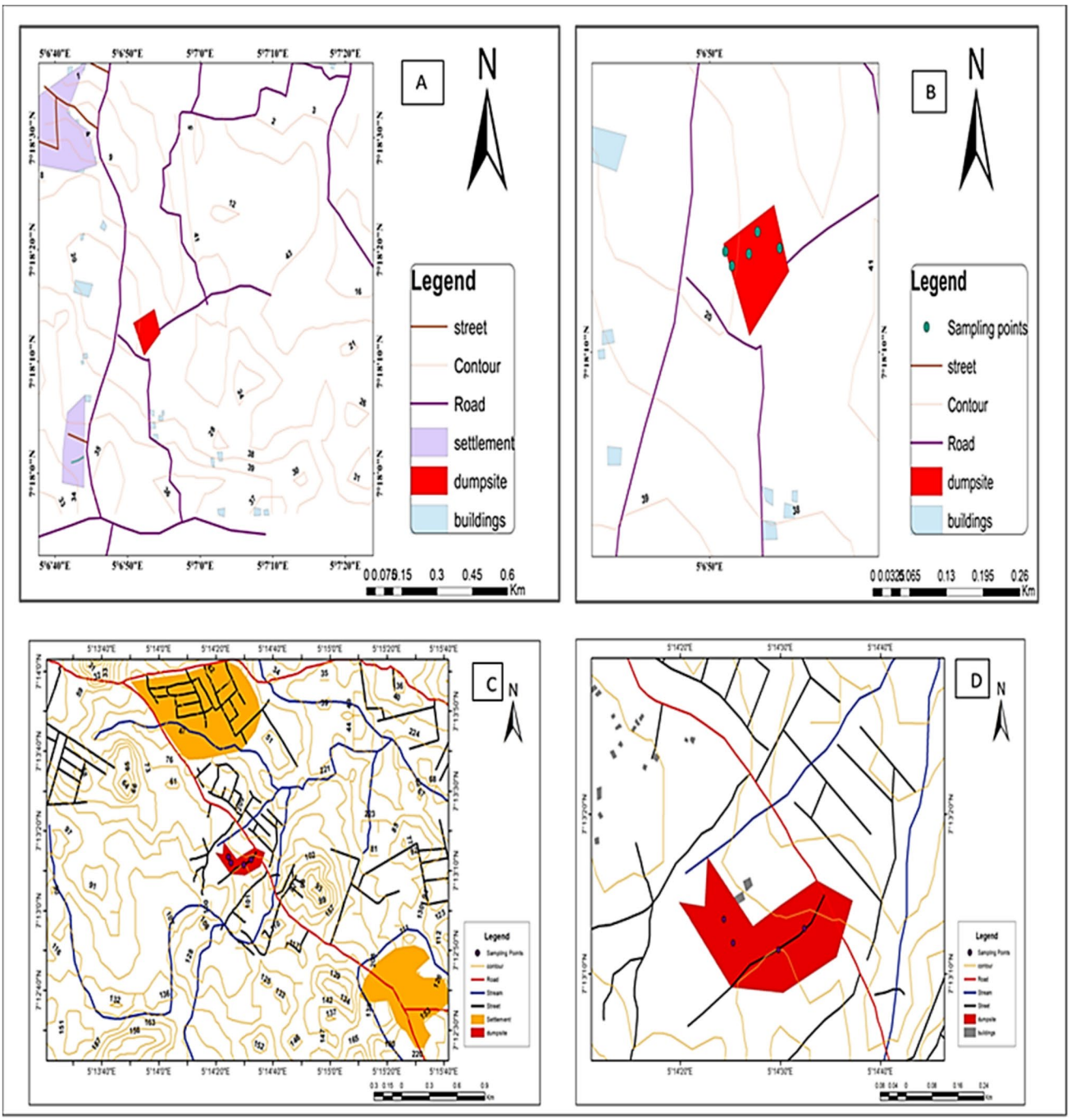

Fig. 1 **A** Map showing the existing FUTA dumpsite **B** Map showing the existing dumpsite and sampling points **C** Map showing the existing Igbatoro dumpsite **D** Map showing the Igbatoro dumpsite and sampling points

dumpsites' soil's main parent material is crystalline basement complex rocks, made up of ferruginous tropical soils.

Sampling (preparation and collection)

14 cm diameter and 1.35 cm thick Polyurethane foam (PUF) disks installed in a passive air sampler placed at 1.5 m above ground level were used in the two selected dumpsites in Akure. Five sampling locations (FTD1: 7.3038 N, 5.1147 E, FTD2: 7.3037 N, 5.1150 E, FTD 3: 7.3037 N, 5.1145 E, FTD4: 7.3037 N, 5.1141 E, and FTD5: 7.3035 N, 5.1142 E) were considered in FUTA and four sampling locations (IGD W: 7.2199 N, 5.2216 E, IGD S: 7.2202 N, 5.2423 E, IGD E: 7.2204 N, 5.2401 E, and IGD O: 7.2200 N, 5.2404

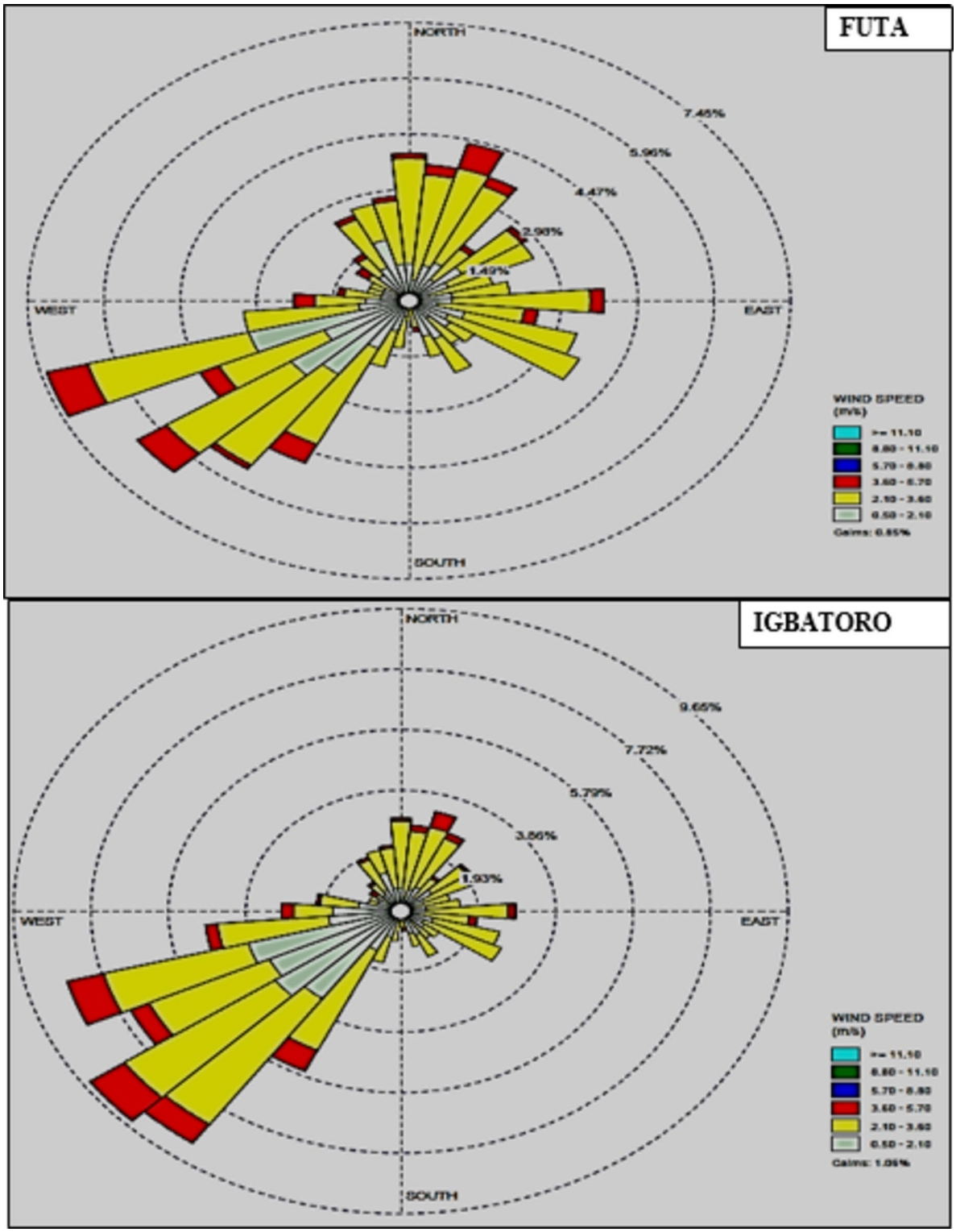

Fig. 2 Windrose diagram of the dumpsites

E) were considered in the Igbatoro dumpsite. The PUFs were first treated and conditioned at the chemical and petroleum laboratory of Afe Babalola University, Ado-Ekiti (ABUAD). The treatment and conditioning followed the procedure prescribed by the UNEP (2017). The PUFs were cleaned, drained, and placed in a Soxhlet for extraction with acetone

for 24 h. Subsequently, the excess acetone in the PUFs was removed and the second extraction was performed using petroleum ether for another 24 h (Adesina et al. 2018; Pozo et al. 2004). The PUFs were dried and wrapped in aluminium foil before being taken to the dumpsites on October 1, 2021, for passive air sampling.

Sample processing and analysis for PCBs

Initially, air samples collected using PUF (polyurethane foam) were spiked with a 100 ng/m^3 concentration of PCB standard prescribed by USEPA (United States Environmental Protection Agency) (2007). Subsequently, the samples were subjected to extraction using dichloromethane in a Soxhlet extractor for 24 h. The air samples were subjected to a clean-up method utilizing a silica gel column with a mass of 5 g. The elution process involved employing a mixture of 40 ml of dichloromethane (DCM) and hexane in a 1:1 ratio. The samples were concentrated using a rotating evaporator while being exposed to a controlled flow of nitrogen gas.

The analysis was conducted with a Varian 3800 gas chromatograph that was fitted with an Agilent mass spectrometer (Varian 4000). The capillary column used for the analysis was an HP-5 fused silica column, with dimensions of 30 m × 0.25 mm and a film thickness of 0.25 µm. Quantification of PCBs was performed using the internal standard technique reported by Adesina (2021). The temperature of the injector was maintained at 250ºC, while the injection volume was set at 1.0 µL in the splitless mode. The oven temperature was initially set at 70ºC and kept for 2 min. Subsequently, the temperature was raised to 150 ºC at a rate of 25ºC per minute. It was then further increased to 200ºC at a rate of 3ºC per minute. Following this, the temperature was elevated to 270ºC at a rate of 8 ºC per minute.

Finally, the temperature was rapidly increased to 290 ºC at a rate of 25ºC per minute and held steady for 5 min. The MS scan ranges between 40–500 Da. The compounds were identified by comparing their retention times to those of authentic compounds and their spectral data to those of the corresponding compounds' data library. Quantities of the compounds are expressed as percentages of relative area derived from the integrator. Two characteristic ions were monitored in Selected Ion Monitoring (SIM) mode to acquire data. The retention durations of the authentic PCB standards and the abundance of the quantification and confirmation ions were used to identify the PCBs in the samples. The procedures of Harner et al. (2013) and Pozo et al. (2009) as reported by Adesina et al. (2021) and Adesina (2021) were adopted in determining the PCB concentrations. No blank correction was done because the field blanks for the two dumpsites were below the detection limit for all targeted compounds.

Sample processing and analysis for PAH

The process of extracting substances from the PUF disks, performing the necessary clean-up procedure, and concentrating the resulting extract followed a methodology identical to that used for PCBs. However, before the extraction step, the samples were spiked with 25 mL of a recovery standard (RS). The sample consists of 20 nanograms (ng) of phenanthrene d10, with a recovery rate ranging from 80 to 90%. The gas chromatograph (Agilent 7890) was connected to a mass spectrometer (Agilent 5975) for analysis. The machines employed electron impact ionization (EI) and were operated in the Selected Ion Monitoring (SIM) mode. The dimensions of the chromatographic column dimension are 30 m × 0.25 mm with an internal diameter × 0.25 µm film thickness.

PAH concentrations were calculated for the analysis by dividing the quantity deposited on the PUF (µg) by the air volume. For the analysis, PAH concentrations were calculated by dividing the amount deposited on the PUF (µg) by air volume. The effective volume of air was calculated using the Global Atmospheric Passive Sampling (GAPS) network template (Harner et al. 2013). The deployment time, the average temperature, and the sampling rate were entered into the template. The sample rate was set to be 4 m^3/day by default. The analysis of PAH in both laboratory and field blanks was conducted, employing the external standard method for quantification of these compounds. No correction was conducted as the field blanks for the two dumpsites exhibited levels of targeted compounds that were below the detection limit.

Health risk assessment

Cancer risk (CR)

The estimation of the CR posed by the dumpsites was estimated using Eq. (1).

$$CR = BaP - TEQ \times IUR \quad (1)$$

where BaP-TEQ is the toxic equivalent quotient of the carcinogenic PAH compounds and IUR is the inhalation unit risk.

The concentration of each of the seven carcinogenic PAH compounds (Benzo [a] Anthracene, Chrysene, Benzo [b] fluoranthene, Benzo [k] fluoranthene, Benzo [a] pyrene, Dibenzo (a,h) anthracene and Indeno [1, 2, 3-cd] pyrene) was multiplied by Relative Potency Factors (RPF) to obtain BaP-TEQ. The resultant BaP-TEQ was then multiplied by an Inhalation Unit Risk (IUR) value of 8.7×10^{-5} suggested by WHO and prescribed by Nadali et al. (2021).

Inhalation Risk Analysis (IRA)

Three (3) PCB congeners, PCB 105, PCB 114, and PCB 118 were considered to estimate the IRA of the dumpsites. The concentrations of these PCBs were used to estimate the IRA for the two (2) dumpsites using Eq. (2).

$$IRA = \frac{V_r C_{air} f_r t_f}{BW} \quad (2)$$

where V_r is the rate of ventilation,

C_{air} is the dioxin-like PCB concentration of air in terms of toxicity equivalence (ρ g TEQ/m3)

f_r is the alveolar fraction retained in the lungs

t_f is the time of exposure

BW is the human body weight

The assumed values for V_r 9.6 m^3/day and 20 m^3/day were adopted for children and adults respectively. The alveolar fraction values were assumed to be 0.75 while the exposure times were 1 for both children and adults. BW of 15 and 69 kg were also assumed, being the values for children and adults respectively. All the assumptions were adapted following Yu et al. (2006), Shalom and Opeyemi (2014), and Francisco et al. (2017).

Source identification

The source of the measured PAH and PCB was evaluated statistically by adopting a multivariate receptor model analysis also known as Principal Component Analysis (PCA). XLSTAT software was used for the analysis. PCA plot describes the variables such that those with similar sources are confined within proximity while variables with different sources are far apart (Adesina et al. 2018).

Results and discussion

PAH concentration of the dumpsite air

The concentration of the PAH analyzed in the ambient air of the dumpsites is detailed in Tables 1 and 2. The PAH compounds present in the dumpsite ambient air are Naphthalene (Naph), Acenaphthylene (Acey), Acenaphthene (Acen), Fluorene (Fluo), Phenanthrene (Phen), Anthracene (Anth), Fluoranthene (Flan), Pyrene (Pyre), Benzo[a] anthracene (Baan), Chrysene (Chry), Benzo[b]fluoranthene (Bbfl), Benzo[k]Fluoranthene (Bkfl), Benzo[a]pyrene (Bapy), Dibenzo [a, h] anthracene (Daha), Indeno[1,2,3-cd] pyrene (Inpy) and Benzo[ghi]perylene (Bepe). Among the PAH compounds, benz[a]anthracene, chrysene, benzo[b] flouranthene, benzo[a]pyrene, dibenzo [a, h] anthracene, and benzo [ghi] perylene are reported to be among potential human carcinogens by ISWA (2015) and Ololade et al. (2021). The percentage of High Molecular Weight (HMW) PAH (Fluoranthene, Pyrene, Benzo[a]anthracene, Chrysene,

Table 1 PAH concentration of FUTA dumpsite

S/N	PAHs (μg/m^3)	FTD_1	FTD_2	FTD_3	FTD_4	FTD_5	$\overline{X} \pm$ SD
1	Naphthalene	2.89×10^{-6}	2.39×10^{-6}	8.30×10^{-7}	3.56×10^{-6}	3.67×10^{-6}	$2.67\times10^{-6}\pm1.15\times10^{-6}$
2	Acenaphthylene	ND	3.66×10^{-7}	ND	2.25×10^{-7}	4.23×10^{-8}	$2.11\times10^{-7}\pm1.62\times10^{-7}$
3	Acenaphthene	1.56×10^{-6}	2.82×10^{-6}	3.20×10^{-6}	2.56×10^{-6}	1.51×10^{-6}	$2.33\times10^{-6}\pm7.61\times10^{-7}$
4	Fluorene	ND	ND	7.50×10^{-8}	9.63×10^{-7}	ND	$5.19\times10^{-7}\pm6.28\times10^{-7}$
5	Phenanthrene	3.52×10^{-6}	6.48×10^{-8}	1.80×10^{-6}	9.86×10^{-6}	4.81×10^{-7}	$3.15\times10^{-6}\pm3.98\times10^{-6}$
6	Anthracene	1.34×10^{-6}	4.68×10^{-6}	ND	1.60×10^{-6}	4.33×10^{-8}	$1.92\times10^{-6}\pm1.97\times10^{-6}$
7	Fluoranthene	4.07×10^{-7}	6.36×10^{-7}	5.10×10^{-8}	ND	3.31×10^{-7}	$3.56\times10^{-7}\pm2.41\times10^{-7}$
8	Pyrene	1.40×10^{-5}	2.13×10^{-6}	3.30×10^{-6}	1.78×10^{-6}	2.35×10^{-6}	$4.71\times10^{-6}\pm5.22\times10^{-6}$
9	Benzo[a]anthracene	1.60×10^{-6}	6.72×10^{-8}	5.40×10^{-7}	1.60×10^{-7}	1.60×10^{-7}	$5.05\times10^{-7}\pm6.38\times10^{-7}$
10	Chrysene	2.23×10^{-6}	8.40×10^{-8}	7.60×10^{-8}	3.03×10^{-7}	1.18×10^{-7}	$5.62\times10^{-7}\pm9.37\times10^{-7}$
11	Benzo[b]fluoranthene	3.51×10^{-6}	3.43×10^{-6}	4.00×10^{-6}	2.34×10^{-6}	3.94×10^{-6}	$3.44\times10^{-6}\pm6.67\times10^{-7}$
12	Benzo[k]Fluoranthene	3.08×10^{-6}	ND	ND	7.50×10^{-8}	5.83×10^{-8}	$1.07\times10^{-6}\pm1.74\times10^{-6}$
13	Benzo[a]pyrene	4.04×10^{-6}	1.54×10^{-6}	1.70×10^{-5}	8.08×10^{-6}	1.75×10^{-5}	$9.63\times10^{-6}\pm7.34\times10^{-6}$
14	Dibenzo[a,h]anthracene	ND	ND	ND	9.68×10^{-6}	1.3×10^{-5}	$1.13\times10^{-5}\pm2.35\times10^{-6}$
15	Indeno[1,2,3-cd] pyrene	ND	ND	5.00×10^{-8}	ND	ND	5.00×10^{-8}
16	Benzo[ghi]perylene	3.58×10^{-6}	8.92×10^{-7}	1.30×10^{-6}	ND	1.67×10^{-8}	$1.45\times10^{-6}\pm1.52\times10^{-6}$

ND not detected

Table 2 PAH concentration of Igbatoro dumpsite

S/N	PAHs (μg/m^3)	IGD_E	IGD_N	IGD_O	IGD_W	$\overline{X} \pm$ SD
1	Naphthalene	1.78×10^{-6}	1.94×10^{-6}	1.89×10^{-7}	2.78×10^{-6}	$2.10\times10^{-6}\pm4.59\times10^{-7}$
2	Acenaphthylene	9.15×10^{-7}	3.10×10^{-7}	5.92×10^{-7}	9.86×10^{-8}	$4.79\times10^{-7}\pm3.54\times10^{-7}$
3	Acenaphthene	1.67×10^{-6}	2.56×10^{-6}	5.38×10^{-6}	2.13×10^{-6}	$1.15\times10^{-6}\pm8.94\times10^{-7}$
4	Fluorene	1.94×10^{-6}	1.29×10^{-5}	1.38×10^{-5}	2.19×10^{-6}	$7.71\times10^{-6}\pm6.53\times10^{-6}$
5	Phenanthrene	ND	ND	2.69×10^{-7}	ND	2.69×10^{-7}
6	Anthracene	4.59×10^{-7}	8.66×10^{-8}	1.21×10^{-7}	ND	$2.22\times10^{-7}\pm2.06\times10^{-7}$
7	Fluoranthene	8.22×10^{-7}	1.12×10^{-5}	9.66×10^{-6}	5.42×10^{-7}	$5.55\times10^{-6}\pm5.66\times10^{-6}$
8	Pyrene	2.31×10^{-6}	5.5×10^{-6}	1.82×10^{-6}	6.36×10^{-7}	$2.57\times10^{-6}\pm2.08\times10^{-6}$
9	Benzo[a]anthracene	2.61×10^{-7}	7.56×10^{-8}	3.36×10^{-8}	2.61×10^{-7}	$1.58\times10^{-7}\pm1.20\times10^{-7}$
10	Chrysene	1.51×10^{-7}	1.51×10^{-7}	2.27×10^{-7}	6.72×10^{-8}	$1.49\times10^{-7}\pm6.52\times10^{-8}$
11	Benzo[b]fluoranthene	6.96×10^{-6}	3.54×10^{-6}	1.50×10^{-6}	5.17×10^{-6}	$4.29\times10^{-6}\pm2.33\times10^{-6}$
12	Benzo[k]Fluoranthene	8.69×10^{-6}	1.29×10^{-5}	1.16×10^{-5}	4.42×10^{-7}	$8.39\times10^{-6}\pm5.58\times10^{-6}$
13	Benzo[a]pyrene	2.42×10^{-5}	1.08×10^{-6}	1.00×10^{-7}	3.20×10^{-6}	$7.14\times10^{-6}\pm1.14\times10^{-5}$
14	Dibenzo[a,h]anthracene	1.65×10^{-5}	8.79×10^{-6}	9.75×10^{-6}	1.71×10^{-5}	$1.30\times10^{-5}\pm4.38\times10^{-6}$
15	Indeno[1,2,3-cd] pyrene	7.92×10^{-6}	ND	ND	6.83×10^{-7}	$4.30\times10^{-6}\pm5.12\times10^{-6}$
16	Benzo[ghi]perylene	6.67×10^{-8}	ND	8.33×10^{-9}	2.50×10^{-8}	$3.33\times10^{-8}\pm3.01\times10^{-8}$

ND not detected

Benzo[b]Fluoranthene, Benzo[k]Fluoranthene, Benzo[a] Pyrene, Dibenzo [a, h] anthracene, Indeno[1,2,3-cd] Pyrene, and Benzo[ghi]perylene), and Low Molecular Weight (LMW) PAH (Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene) present in the dumpsites are shown in Fig. 3.

Igbatoro dumpsite has 79% HMW and 21% LMW while FUTA dumpsite's HMW and LMW are 72% and 28% respectively. The concentration of the PAH compounds is low compared with the PAH concentration reported in an open dumpsite by Adesina et al. (2020). The low PAH concentration may be due to the deployment days (30 days) and the fact that little or no burning occurred in the dumpsite during the sampling period. The mean PAH concentrations are 3.55×10^{-5} μg/m^3 and 5.51×10^{-5} μg/m^3 for FUTA and Igbatoro dumpsite respectively. The values are lower than 2.0×10^{-4} μg/m^3 (0.2 mg/m^3)—the USA's Occupational Safety and Health Administration (OSHA) recommendation for human health protection—reported by Mumtaz et al. (1996).

The carcinogenic compounds levels are 1.60×10^{-5} μg/m^3 and 3.53×10^{-5} μg/m^3 for FUTA and Igbatoro dumpsite respectively. The concentration of the PAH at the FUTA dumpsite varied by location. Acen, Fluo, Daha, and Inpy were not detected in FTD_1, while Pyre (1.40×10^{-5} μg/m^3), Baan (1.60×10^{-6} μg/m^3), Chry (2.23×10^{-6} μg/m^3), Bkfl (3.08×10^{-6} μg/m^3) and Bepe (3.58×10^{-6} μg/m^3) concentrations were comparatively higher among the five locations. In FTD_2, similar to FTD_1, Fluo, Bkfl, Daha, and Inpy were not detected while Acey (3.66×10^{-7} μg/m^3),

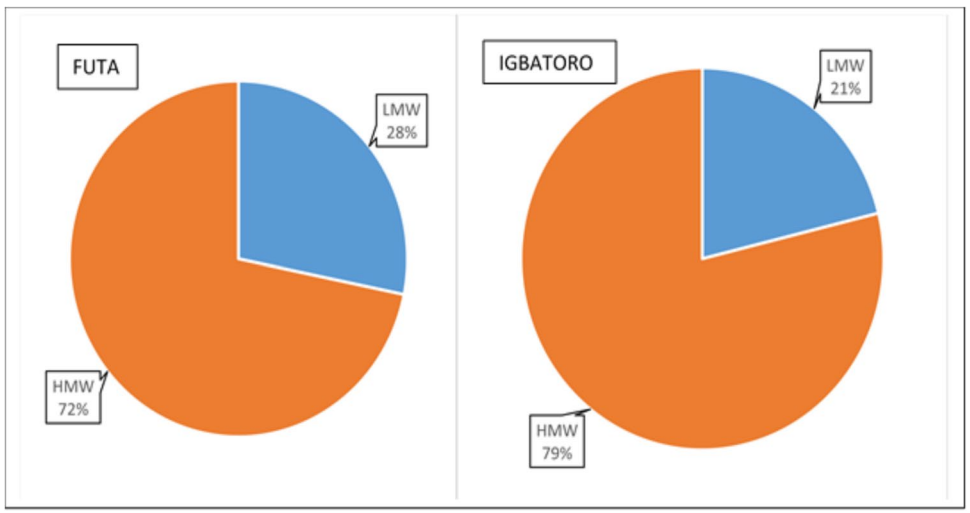

Fig. 3 Percentage distribution of LMW and HMW fraction of the dumpsites PAH

Anth (4.68×10^{-6} µg/m^3), and Flan (6.36×10^{-7} µg/m^3) were comparatively higher among the five locations. Acey, Anth, Bkfl, and Daha were also not detected in FTD_3 while Acen (3.20×10^{-6} µg/m^3), Bbfl (4.00×10^{-6} µg/m^3), and Inpy (5.00×10^{-8} µg/m^3) were comparatively higher among the five locations. Flan, Inpy, and Bepe were not detected in FTD_4 while Fluo (9.63×10^{-7} µg/m^3) and Phen (9.86×10^{-6} µg/m^3) concentrations are comparatively higher among the five locations. In FTD_5, Fluo and Inpy were not detected while Naph (3.67×10^{-6} µg/m^3), Bapy (1.75×10^{-5} µg/m^3), and Daha (1.3×10^{-5} µg/m^3) were comparatively higher among the five locations.

The PAH concentrations of the Igbatoro dumpsite also varied by location. Phenanthrene was not detected at IGD_E, IGD_N, and IGD_W while Indeno [1,2,3-cd] pyrene was also not detected at IGD_N, and IGD_o. Anthracene and Benzo[ghi] perylene were also not detected for IGD_N and IGD_W respectively. The 2.78×10^{-6} µg/m^3 obtained at IGD_W is the highest for Naph in the four locations observed in Igbatoro dumpsite. IGD_E had the highest concentrations for Acey (9.15×10^{-7} µg/m^3), Acen (2.78×10^{-6} µg/m^3), Anth (4.59×10^{-7} µg/m^3), Bbfl (6.96×10^{-6} µg/m^3), Bapy (2.42×10^{-5} µg/m^3), Inpy (7.92×10^{-6} µg/m^3), and Bepe (6.67×10^{-8} µg/m^3). A similar value of 2.61×10^{-7} µg/m^3 was obtained for IGD_E and IGD_W as the highest concentration. At IGD_N, 1.12×10^{-5} µg/m^3, 5.50×10^{-6} µg/m^3, and 1.29×10^{-5} µg/m^3 were obtained as the highest among Igbatoro dumpsite locations for Flan, Pyre, and Bkfl respectively. IGD_O had the highest concentrations for Phen (2.69×10^{-7} µg/m^3) and Chry (2.27×10^{-7} µg/m^3) while IGD_W had 2.19×10^{-5} µg/m^3, 2.61×10^{-7} µg/m^3, and 1.71×10^{-5} µg/m^3 being the highest for Fluo, Baan, and Daha respectively.

Generally for FUTA dumpsite, the PAH concentrations are in this order; Daha > Bapy > Pyre > Bbfl > Phen > Naph > Acen > Anth > Bepe > Bkfl > Chry > Fluo > Baan > Flan > Acey > Inpy while the order for Igbatoro dumpsite is as follows; Daha > Bkfl > Fluo > Bapy > Flan > Inpy > Bbfl > Pyre > Naph > Acen > Acey > Phen > Anth > Baan > Chry > Bepe. The standard deviation obtained for the FUTA and Igbatoro dumpsites' sixteen (16) PAH concentrations evidenced the non-proximity of the values obtained at the different locations.

At both the Igbatoro and FUTA dumpsites, dibenzo [a, h] anthracene has been indicated to be the most prevalent PAH. The predominant dibenzo [a, h] anthracene present in the emissions could be due to the smoke of food waste, petrol, tobacco, coal tar, and soot. It ranged from 9.68×10^{-6} to 1.30×10^{-5} µg/m^3 for the FUTA dumpsite and 8.79×10^{-6} to 1.71×10^{-5} µg/m^3 for the Igbatoro dumpsite. The concentration of Dibenzo [a, h] anthracene being the highest for the dumpsites agrees with the findings of Adesina et al. (2020). Benzo [a] pyrene, is an indication of the carcinogenic effect of PAH (Ololade et al. 2021) and its concentration in FUTA and Igbatoro dumpsite are 9.63×10^{-6} µg/m^3 and 7.14×10^{-6} µg/m^3 respectively. These values are also low compared with the observed Benzo [a] pyrene concentration levels (0.11 µg/m^3) obtained from a Nigerian dumpsite (Adesina et al. 2020).

However, they are greater than the 8.7×10^{-8} µg/m^3 (8.7×10^{-5} ng/m^3) World Health Organization (WHO) limit value (Hailwood et al. 2001). The observed lower concentration of Benzo [a] pyrene just like other PAH can be attributed to little/no burning of MSW deposited on the dumpsite during the sampling period. The observed PAH concentrations of the dumpsites showed that they do not pose any immediate carcinogenic threat.

PCBs concentration in the dumpsite air

The concentration of the PCBs analyzed in the ambient air of the dumpsite is presented in Table 3. The eleven (11) PCB congeners that were analyzed include; PCB 153, PCB 118, PCB 18, PCB 28, PCB 180, PCB 138, PCB 105, PCB 149, PCB 114, PCB 204, and PCB 110. Only three Dioxin-like PCB congeners (PCB 105, PCB 114, and PCB 118) were found. The $\Sigma PCBs$ concentration of the two dumpsites is very close. The $\Sigma PCBs$ in the FUTA dumpsite is 1.0 ng/m^3 while the Igbatoro dumpsite had its $\Sigma PCBs$ to be 0.99 ng/m^3. These PCB congener levels are lower than the PCB levels reported in and around the Afe Babalola University Ado-Ekiti (ABUAD) open dumpsite by Adesina (2021).

For the FUTA dumpsite, the PCB concentrations are in this order; PCB 110 > PCB 118 > PCB 153 > PCB180 > PCB 138 > PCB 149 > PCB 28 > PCB 105 > PCB 114 > PCB 18 > PCB 204 > PCB 101. The order for the Igbatoro dumpsite almost followed the same trend as PCB 110 > PCB 118 > PCB 153 > PCB180 > PCB 138 > PCB 149 > PCB 28 > PCB 105 > PCB 114. Out of the five FUTA locations, FTD_4 has a total of 1.079 ng/m^3 $\left(\sum \text{PCB}\right)$, the highest while IGD_N had the highest $\left(\sum \text{PCB}\right)$ of 1.084 ng/m^3. The standard deviation obtained for the FUTA and Igbatoro dumpsites' twelve (12) PCB concentrations evidenced the proximity of the values obtained at the different locations.

The PCB congener levels for the two dumpsites are approximately the same except for PCB 101, PCB 18, PCB 180, and PCB 204. Another major disparity in the PCB levels of the dumpsites is that PCB 101 was not detected in Igbatoro dumpsite with about 0.011 ng/m^3 detected in FUTA dumpsite. PCB congeners are either dioxin-like or non-dioxin-like. Out of the 209 PCB congeners, 12 are dioxin-like with the remaining 197 non-dioxin-like congeners (USEPA (United States Environmental Protection Agency) 2003). The more toxic of the dioxin-like PCB congeners are the non-ortho congeners i.e., congeners 77, 81, 126, and 169 (Jia and Smith 2020).

Table 3 PCB concentration of Igbatoro and FUTA dumpsites

S/N	PCBs (ng/m^3)	FUTA Dumpsite						Igbatoro Dumpsite				
		FTD_1	FTD_2	FTD_3	FTD_4	FTD_5	$\overline{X}\pm$ SD	IGD_E	IGD_N	IGD_O	IGD_W	$\overline{X}\pm$ SD
1	1,1'-Biphenyl, 2,2',4,4',5,5'-hexachloro-(PCB 153)	0.125	0.125	0.121	0.140	0.124	0.127 ± 0.008	0.139	0.139	0.122	0.119	0.130 ± 0.010
2	1,1'-Biphenyl, 2,2',4,5,5'-pentachloro-(PCB 101)	ND	ND	ND	0.009	0.012	0.011 ± 0.002	ND	ND	ND	ND	ND
3	1,1'-Biphenyl, 2,3',4,4',5-pentachloro-(PCB 118)	0.158	0.141	0.155	0.169	0.158	0.156 ± 0.010	0.169	0.173	0.138	0.138	0.155 ± 0.019
4	1,1'-Biphenyl, 2,2',5-trichloro-(PCB 18)	0.024	0.025	0.027	0.024	0.026	0.025 ± 0.002	0.024	0.025	0.022	0.022	0.023 ± 0.002
5	1,1'-Biphenyl, 2,4,4'-trichloro-(PCB 28)	0.058	0.064	0.060	0.064	0.060	0.061 ± 0.003	0.063	0.064	0.060	0.058	0.061 ± 0.003
6	1,1'-Biphenyl,2,2',3,4,4',5,5'-heptachloro-(PCB 180)	0.107	0.107	0.106	0.108	0.106	0.107 ± 0.001	0.108	0.111	0.099	0.086	0.101 ± 0.011
7	1,1'-Biphenyl, 2,2',3,4,4',5'-hexachloro-(PCB 138)	0.080	0.080	0.083	0.083	0.082	0.081 ± 0.001	0.083	0.084	0.081	0.082	0.083 ± 0.001
8	1,1'-Biphenyl, 2,3,3',4,4'-pentachloro-(PCB 105)	0.050	0.051	0.047	0.050	0.051	0.050 ± 0.002	0.050	0.050	0.044	0.046	0.047 ± 0.003
9	1,1'-Biphenyl, 2,2',3,4',5',6-hexachloro-(PCB 149)	0.076	0.078	0.079	0.085	0.072	0.078 ± 0.005	0.085	0.085	0.072	0.076	0.079 ± 0.007
10	1,1'-Biphenyl, 2,3,4,4',5-Pentachloro-(PCB 114)	0.024	0.023	0.024	0.048	0.025	0.029 ± 0.011	0.048	0.047	0.016	0.022	0.033 ± 0.016
11	1,1'-biphenyl,2,2',3,4,4',5,6,6'-octachloro-(PCB 204)	0.025	0.021	0.024	0.032	0.019	0.024 ± 0.005	0.032	0.030	0.015	0.026	0.026 ± 0.007
12	1,1'-Biphenyl, 2,3,3',4',6-pentachloro-(PCB 110)	0.263	0.256	0.263	0.277	0.264	0.264 ± 0.008	0.261	0.277	0.232	0.252	0.256 ± 0.019

ND not detected

None of the toxic PCB congeners are found in the dumpsites' air. Although, PCB 114 and PCB 118 were detected in the two dumpsites. The congener levels of PCB 114 and PCB 118 are 0.029 ng/m^3 and 0.156 ng/m^3 for the FUTA dumpsite while they are 0.033 ng/m^3 and 0.155 ng/m^3 for the Igbatoro dumpsite. Although Adesina (2021) did not identify PCB 118 in the open dumpsite, he reported > 1.0 ng/m^3 for PCB 114. The concentration of PCB 114 found in the air sample is lower than 1.0 ng/m^3. The concentration of PCBs 105, 114, and 118 are 0.050 ng/m^3, 0.029 ng/m^3, and 0.156 ng/m^3 respectively for FUTA dumpsite while Igbatoro dumpsite had values of 0.047 ng/m^3, 0.033 ng/m^3, and 0.155 ng/m^3 respectively. Similar to what was obtained for the FUTA dumpsite, a WHO_{2005} -TEQ concentration of 0.00000705 ng/m^3 was obtained for the Igbatoro dumpsite.

Health risk assessment

Cancer risk assessment

The cancer risk estimates are shown in Table 4. The cancer risk estimates computed from the seven (7) carcinogenic PAH are 1.10×10^{-5} and 1.23×10^{-5} for FUTA and Igbatoro dumpsite respectively. These risk estimates are within the acceptable range of 1×10^{-6} to 1×10^{-4} reported by Nadali et al (2021). In addition, the cancer risk values are even lower than the acceptable limit when the California Environmental Protection Agency (CAL. EPA) value of 1.1×10^{-6} IUR (Jia and Smith 2020) was used. However, these risk estimates are greater than reported estimates of the United States National-scale Air Toxics Assessment (NATA) of 0.18×10^{-6}, 1.62×10^{-6}, $1.52\times10^{-}6$, and 0.36×10^{-6} for the year 1999, 2002, 2005 and 2011 respectively (Jia and Smith 2020). These results infer that the gaseous ambient air concentration does not pose a cancer risk to human health. The low cancer risk estimates may be due to the short duration (30-day sampling period) and the probable no/low burning activities on the dumpsite during the sampling duration.

Inhalation risk analysis

The risk associated with inhaling PCBs can be measured by assessing inhalation exposure. Drawing from the computation of PCBs and other adopted parameters, the inhalation risk analysis (IRA) of the two dumpsites is determined to be 1.53×10^{-6} ng TEQ kg^{-1} day^{-1} (1.53 fg TEQ kg^{-1} day^{-1}) and 3.38×10^{-6} ng TEQ kg^{-1} day^{-1} (3.38 fg TEQ kg^{-1} day^{-1}) for adult and children respectively. The results infer that children are more than twice as exposed to inhalation of PCBs as adults. The disparity in the IRA for adults and children is due to the varied values of body weight (Francisco et al. 2017). These values are lower than the reported values of Yu et al. (2006) as well as Adesina (2021). However, inhalation

Table 4 Cancer risk estimates of the dumpsites

S/N	PAH (μg/m^3)	RPF*	Concentration (μg/m^3)		BaP_{eq}	
			FTD	IGD	FTD	IGD
1	Benzo[a]anthracene	0.2	5.05×10^{-7}	1.58×10^{-7}	1.01×10^{-7}	3.15×10^{-8}
2	Chrysene	0.1	5.62×10^{-7}	1.49×10^{-7}	5.62×10^{-8}	1.49×10^{-8}
3	Benzo[b]Fluoranthene	0.8	3.44×10^{-6}	4.29×10^{-6}	2.76×10^{-6}	3.43×10^{-6}
4	Benzo[k]Fluoranthene	0.03	1.07×10^{-6}	8.39×10^{-6}	3.21×10^{-8}	2.52×10^{-7}
5	Benzo[a]Pyrene	1	9.63×10^{-6}	7.14×10^{-6}	9.63×10^{-6}	7.14×10^{-6}
6	Dibenzo[a,h]anthracene	10	1.13×10^{-5}	1.30×10^{-5}	1.13×10^{-4}	1.30×10^{-4}
7	Indeno[1,2,3-cd] pyrene	0.07	5×10^{-8}	4.3×10^{-6}	3.5×10^{-9}	3.01×10^{-7}
					$BaP\text{-}TEQ_{FTD}=1.26\times10^{-4}$	$BaP\text{-}TEQ_{IGD}=1.42\times10^{-4}$
					$CR=1.10\times10^{-5}$	$CR=1.23\times10^{-5}$

Relative Potency Factors (RPF)* [31]

exposure obtained for both adults and children are higher than the ones reported during spring (September – November) for the rural area of Sao Paulo, Brazil by Francisco et al. (2017). Generally, the inhalation exposure is still lower than the minimum threshold—a tolerable daily intake of 1000 fg I-TEQ/kg (WHO (World Health Organization) 1998).

Source identification

The PCA plot of the PAH in FUTA and Igbatoro dumpsite is shown in Fig. 4. For FUTA dumpsite, factor 1(F1) accounts for 47.22% of total variability, and factor 2 (F2) accounts for 25.37% of total variance. The factors 1 and 2 for Igbatoro dumpsite are 31.67% and 57.60% respectively, totaling

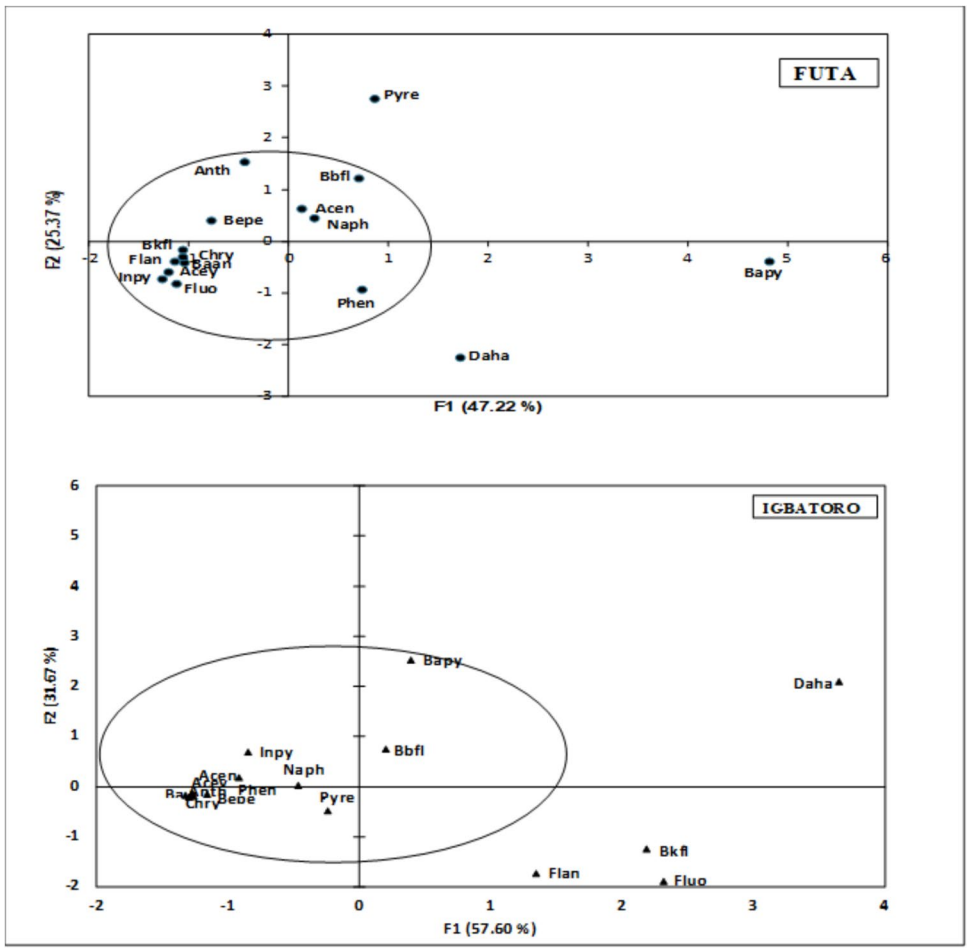

Fig. 4 PCA plot of the dumpsites PAH

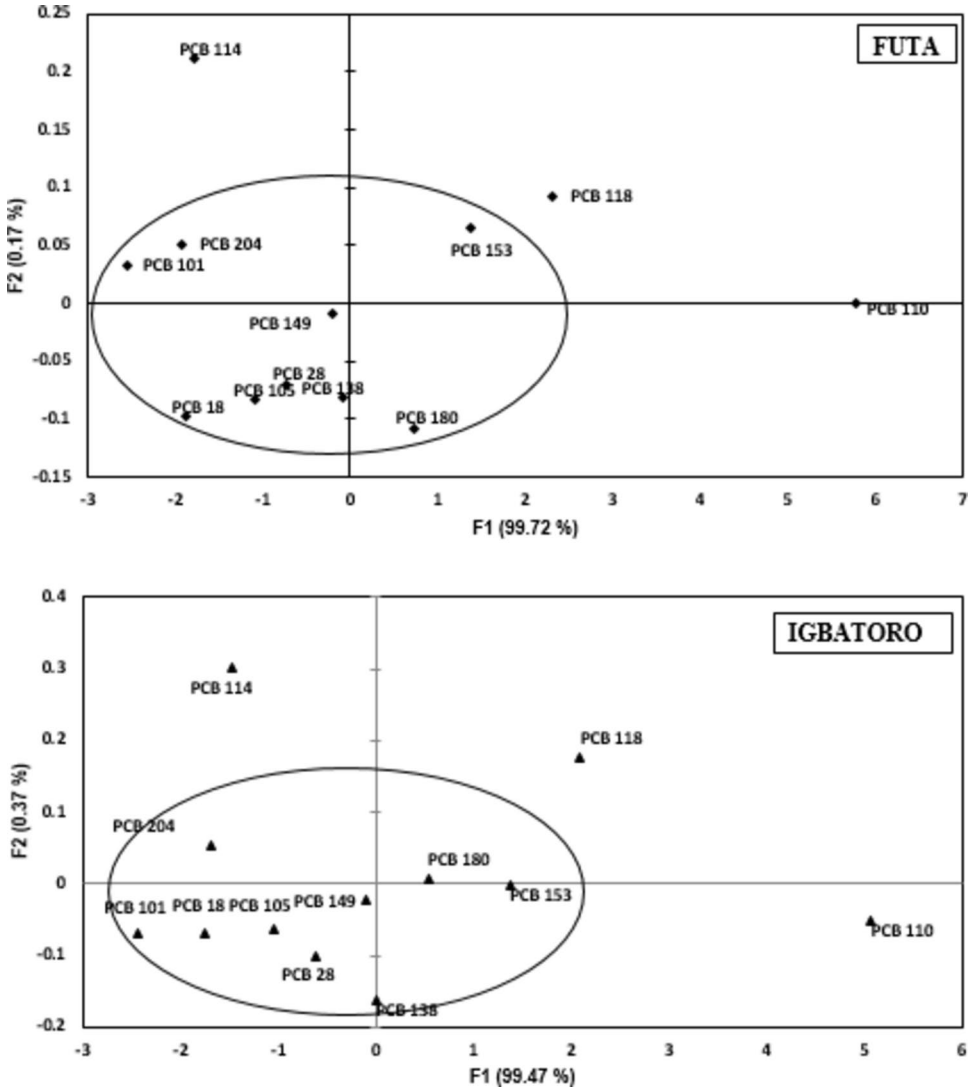

Fig. 5 PCA plot of the dumpsites PCBs

89.27% which explains the variability of Igbatoro dumpsite's PAH. The total of 72.59% and 89.27% suggests that the variability of PAH concentrations can be explained. The observation of the cluster in the FUTA dumpsite showed that except Pyrene, Benzo[a]pyrene and Dibenzo [a, h] anthracene, all other PAH may have been generated from the same source. However, similar to FUTA dumpsite's, Benzo[a]pyrene, Dibenzo [a, h] anthracene, and other different three PAH namely; Fluoranthene, Fluorene, and Benzo[k] Fluoranthene seem to share a source, different from the remaining eleven (11) PAH which shared the same source as observed from the cluster. The sources of the pyrene, Benzo [a] pyrene and Dibenzo [a, h] anthracene, Fluoranthene, Fluorene, and Benzo [k] Fluoranthene may have been from other sources around the dumpsites' environs (Adesina 2021).

The PCA plot of the PCBs in FUTA and Igbatoro dumpsite are shown in Fig. 5. For the FUTA dumpsite, Factor 1(F1) accounts for 99.72%, and factor 2 (F2) accounts for 0.17% of the total variability of 99.89. Factors 1 and 2 for Igbatoro dumpsite are 99.47% and 0.37% respectively, totaling 99.84% which explains the variability of Igbatoro dumpsite's PCBs. The total of 99.89% and 99.84% suggests that the variability of PCB concentrations can be explained. The observation of the clusters in FUTA and Igbatoro dumpsites showed that except for PCB 114, PCB 118, and PCB 110, all other PCBs may have been generated from the same source. The sources of the PCB 114, PCB 118, and PCB 110 may have been from other possible sources around the dumpsites' environs (Adesina 2021).

Conclusions

This study evaluated the PAH and PCB profiles of two selected dumpsites in the Akure metropolis. The PAH and PCB concentrations are very low because little or no burning of MSW took place during the study period. Dibenzo [a, h]

anthracene had the highest concentration in both dumpsites while Benzo[ghi]perylene had the lowest concentration for the PAH compound analyzed. The summation of the PAH compound of the dumpsites also showed low composition. This trend was also observed in the summation of PCB congeners within and around the dumpsites. The low values obtained from the PAH compounds and PCB congeners are responsible for the values obtained for cancer risk and inhalation rate analysis. The inhalation rate analysis values of 1.53×10^{-6} ng I-TEQ kg^{-1} day^{-1} and 3.38×10^{-6} ng I-TEQ kg^{-1} day^{-1} for adults and children respectively obtained in the dumpsites are below the permissible threshold. However, cancer risk values of 1.10×10^{-5} and 1.23×10^{-5} for FUTA and Igbatoro dumpsite respectively are greater than the reported cancer risk estimates of previous findings. The current study is a short-term risk level assessment of the dumpsites. Therefore, a long-term assessment of the PAH compounds and PCB congeners within and around the selected dumpsites is recommended for an effective and reliable evaluation of the dumpsite risk, especially concerning ambient air.

Acknowledgements The authors are grateful for the support received from the Chemical and Petroleum Engineering Department, ABUAD. The technical assistance offered by Mr. D. Ewere, Dr. O. A. Adesina, and Dr. J. A. Adeniran is greatly appreciated.

Author contributions All authors contributed to the manuscript revision and read and approved the submitted version. F.O. Ayodele: Data accusation, methodology, field experiments, first to final draft writing; O.O. Ojuri: Conceptualization, supervision, review, and editing; J.K. Ogunjobi and B.D. Oluyemi-Ayibiowu: Co-supervision and review; O.O. Esuola: Laboratory experimental analyses & editing; I. Nakouti: Validation, review & editing.

Funding The authors declare that no funds or grants were received during the preparation of this manuscript.

Data availability The datasets generated during and/or analysed during the current study shall be publicly available upon the publication of this manuscript. Further information can be obtained from the corresponding author.

Declarations

Ethics approval Not applicable.

Consent to participate Not applicable.

Consent to publish Not applicable.

Competing interests The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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