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Research article

Characterization and risk assessment of polycyclic aromatic hydrocarbons from the emission of different power generator

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ABSTRACT

Epileptic power supply in Sub-Saharan countries of Africa has warranted the use of power generators as an alternative source of power supply. Exhaust emission from these generators is associated with Polycyclic Aromatic Hydrocarbon (PAHs). Hence, this study focused on the determination of levels of PAHs in the emission of different brands of power generators used in Nigeria. Exhaust emissions of different power generators were sampled using a filter-sorbent sampling system with polyurethane foam (PUF) as an adsorbent material. Analysis of PAHs was carried out using a Gas Chromatograph coupled to a mass selective detector (GC- MS) operated on Electron Ionization (EI) mode. The results showed the $\sum$ PAHs range 14.91–26.0 μg m^{-3}. Bap was the most abundant of all the compounds with a concentration of 2.6 μg m^{-3} with a range of 2.08–3.07 μg m^{-3}. The Incremental Life Cancer Risk (ILCR) values of all the generator's emission sampled are higher than 10^{-4} for both children and adult which indicate a high potential cancer risk from inhalation of emission from these generators while Hazard Quotient (HQ) values from all the power generating set in this study are all above 1 which indicated high associated non-carcinogenic. The study revealed the levels of PAHs associated with the emission of power generators in Nigeria.

1. Introduction

One of the problems of developing countries of Africa such as Nigeria is the epileptic power supply. The Nigerian power sector operates well below its optimal capacity with power outages being a frequent occurrence [1,2]. Data have shown that only 10% of rural households and 40% of the country's total population have access to electricity [3]. Even the households connected to the grid only receive an average of 7 h or less of electricity per day, forcing them to turn to alternative energy sources. Given these many Nigerian households depend on power generators, and also bear the associated costs of fueling them.

Nigeria is currently the leading importer of power generators in Africa and one of the highest importers globally, with an annual import cost of US$ 112 million [4,5]. The huge demand for electric power in the country, mainly from the residential and industrial sectors, has resulted in the mass importation of these power generators to the country. Many households in Nigeria make use of power generators as the source of their power and these power generators are place in close proximity to the house and as such pollute the

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indoor environment. There are many instances in the country where whole family died from the emission of the generator [6]. In view of these there is a need to characterize pollutants presents in the emission of the common generators used by the citizen of the country. Apart from the Criteria Air Pollutants, PAHs are important air pollutants that are emitted from the exhaust of the generators and contribute to the ambient levels concentrations of these compounds [7]. Characterization of their concentration in the environment is important to assess its risks and forecast suitable management practices [8,9].

Polycyclic aromatic hydrocarbons PAHs are multiplex hydrocarbon compounds with a joined ring structure, containing at least two benzene rings [10–12]. PAHs are known to be very common environmental pollutants generated mainly during the partial combustion of organic materials, domestic heating traffic emissions, industrial activities, agricultural waste and biomass burnings and forest fires and fossil fuels combustion [13–15]. There are various routes through which human beings can absorb PAHs such as inhalation, dermal contact, and ingestion [16]. The effects of PAHs on human health and the environment are a global issue of concern. The ecotoxic studies of PAHs show that they are potentially genotoxic, carcinogenic, and mutagenic to humans. They are also related to susceptible health challenges such as reduced immune function, and breakdown of blood cells and are thus named among the organic pollutants of public health concern [17–20].

Only a few studies are available on emissions from the exhaust of generators. Sadiktsis et al. [21], studied the particulate-associated polycyclic aromatic hydrocarbon exhaust emissions from a portable power generator, and Tsai et al. [22], worked on size distributions of PM, carbons, and PAHs emitted from a generator using blended fuels containing water. To the best of our knowledge, no data is available on PAH emissions from different power generators used in sub-Saharan African countries such as Nigeria.

Health risk assessment is very crucial to a risk management program [12,23]. It is usually used determine short and long health risk associated with the human exposures to pollutants [24]. Many health indexes have been in the literature the commonest are Incremental Life Cancer Risk (ILCR) which determined associated carcinogenic risk and non-carcinogenic associated risk, Hazard quotient (HQ) [25,26]. Hence this study focused on the characterization of PAHs from different power generators in Nigeria. The study also carries out risk assessment associated with human contact with the emission from the generators. This study will however provide data for policy maker on the emission of this pollutants from power generator in order to put in place mitigation measure to reduce the emission of this pollutants.

2. Materials and methods

2.1. Study area

The generator samples used for this study were sought out within Ado-Ekiti, Ekiti State, South Western Nigeria. The different household power generators commonly used in the country were conveyed from their various location to Afe-Babalola University Ado-Ekiti where emissions from the exhaust were sampled and analyzed. The generators used for the study were powered by Premium Motor Spirit (PMS).

2.2. Reagents and equipment

Dichloromethane (Sigma–Aldrich), Alumina gel (200–400 mesh, Zico-Tech), Silica (200–400 mesh, Zico-Tech), n-Hexane (Sigma–Aldrich). Rotary evaporator (Infitex Co. Ltd). Gas chromatograph (Agilent Model 7890A) coupled to a mass selective detector (Varian 3800/4000 GC–MS) (Agilent Technologies, Pato Alto, CA). PAHs Standard (Sigma–Aldrich).

2.3. Emission sampling

A filter-sorbent sampling system was used to collect particulate plus vapor-phase PAHs using modified European standard stationary source emission and determination of concentration method (EN- 1948 –SS) with polyurethane foam (PUF) as an adsorbent material. Filter sorbent sampling system is an established system for sampling air pollutant especially persistent organic pollutants, the sample train involves the pump that suck in the air to the filter to trap the particulate phase PAHs and PUF to trap the gas phase PAHs. The PUF is chosen as an adsorbent because it is readily available and it is very easy to use. Studies like Adesina et al. [25,27] have effectively used the procedure for sampling. Samples were isokinetically withdrawn from the exhaust emission of each of the generators and collected into the train of a sample probe, a filter, and a packed column consisting of absorbent material. The Filter and PUF were wrapped in aluminum foil and taken to the laboratory for analysis.

2.4. Extraction and samples analysis

PAHs in PUF were extracted into Dichloromethane (DCM) using a Soxhlet extractor placed on the heating mantle, the temperature was set to $60^{\circ}C$ and extraction was done for 7 h. The extracts were then subjected to a Clean-up procedure using conventional liquid-solid adsorption chromatograph in open glass columns at atmospheric pressure. The column was prepared by adding about 10 to 15-mm plug of glass wool to a chromatograph column and alumina and silica were added to the column in the ratio (1:2). The sample extracts were decanted into the column and eluted with 40 mL 1:1, DCM: Hexane [27]. The extracted samples were then concentrated using a rotary evaporator which was later analyzed for PAHs.

2.5. PAHs quantification

The analysis of PAHs was done using GC-MS/MS 4000/3800 gas chromatograph (Agilent Technologies, Pato Alto, CA) of 1 μm column 60 m × 0.32 mm and a stationary phase thickness using selected ion monitoring mode with Nitrogen as the carrier gas. The GC-MS was calibrated by standard solutions containing all 16 target compounds at concentrations of 0.5–50 pg/μl (PAHs standard). Second-order calibration curves were fitted to this data using the least-squares method. 2.0 μl of sample extract was injected into the gas chromatograph using the splitless mode at a temperature of 250^{O}C. The initial column temperature was 70^{O}C, at 10^{O}C min^{-1} to 260^{O}C. It was increased to 300^{O}C min^{-1} and for 8 min. The solvent delay was 7 min, dwell time of 0.1 s was used for each m/z value [25]. The MS transfer line was maintained at 250^{O}C, and quantification was based on calibration with the standard analyte using the mass spectrometer in selective ion monitoring (SIM) mode. The obtained concentrations of the different PAH constituents were subjected to source identification and diagnosis using the appropriate mathematical ratios. Quantitative analysis was performed using calibration data from the PAH standard, which contained the sixteen PAHs specified by the EPA and NIST-SRM was used to confirm the accuracy of PAHs [25].

2.6. Quality assurance/quality control (QA/QC)

Replicates and laboratory blanks were obtained and treated along with the samples. Limit of detection (LOD), limit of quantification (LOQ), recovery (%), relative standard deviation (RSD, %) were calculated to ensure the integrity of the data obtained. LOD and LOQ values for PAHs determined based on the ratio value of the signal-to-noise baseline (S/N) for the reference peaks of each of compound and analyzed to the lowest calibration standard concentration converted to S/N = 3 and S/N = 10, respectively. Values for Limit of detection (LOD), limit of quantification (LOQ), recovery (%), relative standard deviation (RSD, %) are shown in Table 1.

3. Health implications

3.1. Toxic equivalent

The Toxicity equivalent which is the toxicity potential of individual PAHs is calculated by multiplying PAHs concentration with the toxicity equivalence factor (TEF) (eq. i) [28]. Where C is the individual concentrations of PAHs

$$\text{Toxic Equivalency (TEQ)} = C \times TEF \tag{i}$$

3.2. Incremental Lifetime Cancer Risk and hazard quotient

Incremental Lifetime Cancer Risk (ILCR) from human contact by inhalation of emission from the exhaust of the generator is calculated using eq. ii. Also, the non-carcinogenic risk, Hazard Quotient (HQ) is calculated using eq, iii

$$ILCR_{Inh} = \frac{C \times IR \times ED \times EF \times IUR}{AT \times BW} \tag{ii}$$

$$HQ = \frac{C \times IR \times ED \times EF}{AT \times BW \times RfD} \tag{iii}$$

C is the PAH concentration (μg $m^{-3)}$ IhR is the Inhalation rate (20 m^3/day for adults and 9.6 m^3/day was assumed for children [26,

Table 1
LOD, LOQ, Recovery and RSD values (μg m^{-3}).

Target Compound	LOD	LOQ	Recoveries (%)	RSD
Nap	0.2	0.32	91	9.1
Acy	0.21	0.32	95	8.9
Acen	0.12	0.21	92	8.2
Fln	0.09	0.19	87	7.8
Phe	0.12	0.24	86	7.6
Ant	0.14	0.23	95	8.9
Flt	0.14	0.31	95	8.2
Pyr	0.18	0.21	95	9.2
BaA	0.19	0.25	93	8.6
CHR	0.16	0.31	92	9.1
Bbf	0.21	0.31	95	9.2
Bfk	0.12	0.29	94	8.4
Bap	0.15	0.31	90	8.2
Icp	0.13	0.27	92	9.1
DHa	0.15	0.23	94	9.2
Bgp	0.12	0.31	94	9.2

Table 2
PAHs Concentration in different Power generating set (μg m^{-3}).

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
Naph	2.51	2.47	2.93	2.23	2.44	2.61	2.47	2.16	2.26	2.58	2.40	2.23	2.61	2.54	2.19	2.23	2.30	2.47	2.54	2.69
fln	0.99	2.16	1.91	0.74	0.99	1.10	1.38	1.13	1.48	1.41	1.55	1.77	1.84	2.01	1.94	2.16	2.26	2.05	2.16	2.47
Phe	1.87	0.92	1.52	1.66	1.66	1.94	1.77	1.70	1.87	2.05	2.08	2.26	2.83	2.69	2.58	2.47	2.93	3.11	2.97	3.14
Pyr	2.47	0.64	0.74	2.26	2.61	2.51	2.30	2.19	2.40	1.91	2.19	2.40	2.79	2.65	2.51	2.72	2.79	3.04	2.86	3.00
Flt	1.41	2.65	2.65	1.31	1.45	1.24	1.52	1.66	2.01	2.30	2.37	2.26	2.51	2.30	2.26	2.40	2.65	2.79	2.65	2.86
Ant	1.10	3.04	2.69	0.88	1.13	1.34	1.24	1.45	1.77	1.70	1.70	1.87	2.05	2.01	1.87	2.01	2.23	2.12	1.91	1.84
Bkf	1.84	0.00	0.64	1.52	1.52	1.55	1.66	1.84	2.19	2.12	2.01	2.12	2.23	2.12	2.01	2.19	2.33	2.23	2.12	1.98
Bap	2.65	2.08	2.23	2.51	2.69	2.86	2.69	2.58	2.76	2.86	3.07	2.97	3.04	2.40	2.30	2.40	2.54	2.47	2.40	2.58
BAa	0.00	2.08	1.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Bbf	0.88	1.41	1.31	0.99	1.20	1.13	1.34	1.17	1.59	1.84	1.70	1.66	1.91	1.84	1.70	1.73	2.47	2.30	2.23	2.40
DhA	0.74	0.00	0.00	0.81	1.70	1.63	2.08	2.26	3.00	2.86	2.72	2.93	2.83	3.04	2.83	3.00	2.58	2.69	2.61	2.93

29,30]. ED is exposure duration in years (20 years was adopted, for more than 20 years in Nigeria there has been epileptic power supply in Nigeria), EF is exposure frequency in days yr $^{-1}$ (186 days, people use the generator for at least 12 h in a day). AT is the average exposure time in days, 25,550 was adopted for calculation. IUR is inhalation unit risk (6 $\times 10^{-4}$ for USEPA). BW is body weight (70 kg) and 30 kg for children. RfD is the reference dose of PAHs (2×10^{-3} μg m^{-3}).

4. Results and discussion

The samples were analyzed for 16 EPA priority PAHs, however compounds observed in the samples were naphthalene (Naph), fluorene (Fln), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DhA), benzo[ghi]perylene (BgP). While PAHs compounds such as acenaphthalene (Acy), acenaphthene (Ace), indeno [1,2,3-cd] pyrene (IcP), and chrysene (CHR) were below the limit of detection. Table 2 shows the concentrations of PAHs observed in different power generators. BaA has only been observed in two of the power generators' emissions. This could probably be due to the combustion mechanism of the engine and the emission control mechanism of those generators [31]. Table 3 shows the mean, minimum, maximum, and standard deviation of the PAHs observed in the emission of the different power-generating sets. Bap which is usually used as a PAH indicator is the most abundant in all the compounds with a mean concentration of 2.6 μg m^{-3} with the range of 2.08–3.07 μg m^{-3}. BaA has the lowest concentration with the value of 0.18 μg m^{-3} with the range of 0–2.08 μg m^{-3}. Fig. 1 shows the sum of PAHs in the different generators. The results showed that generators Q, R, and T have the highest $\sum$ PAHs with values of 25.09, 25.27, and 26.0 μg m^{-3}, respectively. This could be connected to the type of cycle of the engine, generator Q, R and T are 2-stroke engine generators, and they tend to emit more pollutants than 4-stroke engines. Also, 2-stroke engine generators are the most avoidable type of generator in the country that burn a mixture of oil and gasoline for the operation. This can lead to elevated concentration of PAHs at the exhaust of the generator [32,33]. However, the configuration of the 4-stroke generator engine is different, oil and fuel have different compartments, and this could be the reason lower emission is observed. Generator D which is a 4-stroke generator has the lowest PAHs emission with a concentration value of 14.91 μg m^{-3}. Also, it is observed the age of the generator contributes to the level of PAH emission in the generator emission analyzed. Generators I, J, K, and M have elevated concentration of PAHs may be, due to the age of the generator and poor maintenance, as the emission control mechanism of combustion engines get weaker with the age of the generator.

The Carcinogenic PAHs are (Benzo[a]anthracene, Chrysene, Benzo[b]fluoranthene Benzo[k]fluoranthene, Benzo[a]pyrene, indeno [1,2,3-cd] pyrene and Dibenzo (a,h) anthracene). Fig. 2 shows the distribution of 5 carcinogenic PAHs observed in the generator emission. It is observed that Bap is the most abundant carcinogenic PAH in all the compounds and this is very worrisome as Bap is believed to be the most carcinogenic PAH compound with has high health implication on human [34] Fig. 3 shows the $\sum$ carcinogenic PAHs observed in the different generators, the trend of the concentration is the same as in Fig. 1 where generators Q, R, and T have the highest concentration due to the type of cycle of the engine. This means 2-stroke engines emit high concentrations of carcinogenic PAHs.

The distribution of PAHs based on the number of rings is shown in Fig. 4. 2-ring PAHs (Nap), 3-ring PAHs (Ace, Acy, Flu, Phen, and Anth), 4-ring PAHs (Flt, Pyr, BaA, and Chr), 5-ring PAHs (BbF, BkF, BaP, and DahA), and 6-ring PAHs (BghiP and Ind) (Hassanvand et al., 2015; Rostami et al., 2019; Adesina et al., 2021). 5-ring PAHs have a range of 22–48 % contribution in the emission from the exhaust of the generator studied, this is because combustion of fossil fuel usually emits high concentrations of 5-ring PAHs. The contribution of 4-ring range 26–36 %, the contribution of 3-ring range 16–21 %, while 2-ring PAHs have the lowest contribution of 0–18 %. Classification of PAHs based on their molecular weight is shown in Fig. 5. 2 and 3 rings PAHs are Low molecular weight (LMW), 4-ring PAHs are middle molecular weight (MMW) while high molecular weight (HMW) consist of 5 and 6-ring PAHs [26,35,36]. HMW PAHs are the most dominant in the sample, and these are the compounds with great health implications for human.

4.1. Risk assessment

The toxicity equivalent reveals the toxicity potential of each PAH in the PAH mixture. Fig. 6 shows the mean toxicity equivalent of PAHs in the generator, the Bap has the highest toxic equivalent followed by Dha. The result also revealed that BbF has a moderately

Table 3
Mean concentration of PAHs compounds (μg m^{-3}).

	MEAN	min	max	Std
Naph	2.44	2.16	2.93	0.20
fln	1.67	0.74	2.47	0.50
Phe	2.20	0.92	3.14	0.61
Pyr	2.35	0.64	3.04	0.64
Flt	2.16	1.24	2.86	0.54
Ant	1.80	0.88	3.04	0.53
Bkf	1.81	0.00	2.33	0.58
Bap	2.60	2.08	3.07	0.27
BaA	0.18	0.00	2.08	0.56
Bbf	1.64	0.88	2.47	0.47
DhA	2.16	0.00	3.04	1.01

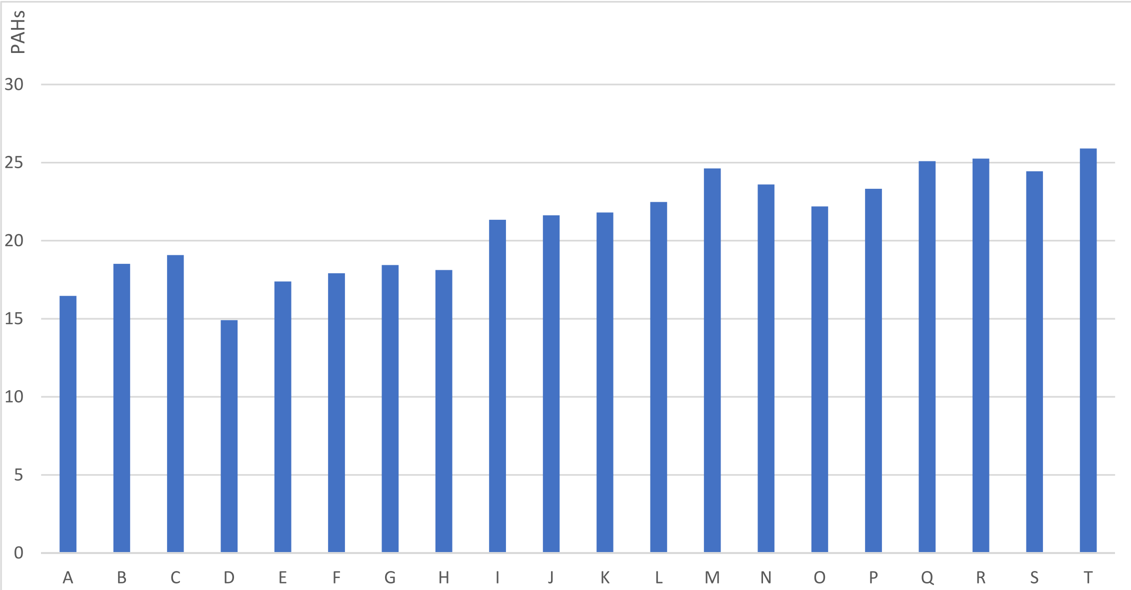

Fig. 1. Sum of PAHs in different generator (μg/m^3).

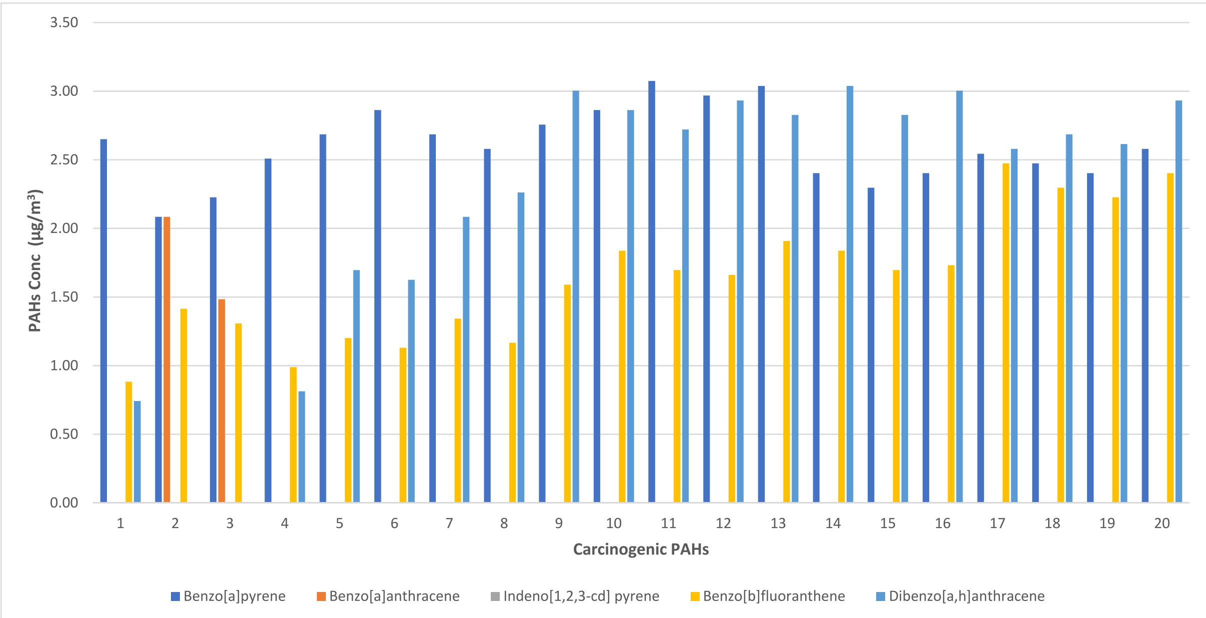

Fig. 2. Distribution of carcinogenic PAHs in the generator emission.

high degree of toxicity. The high toxicity equivalent of BaP is very worrisome as study has shown that Bap has epigenotoxic, neurotoxic, and teratoxic tendencies [37]. Apart from the carcinogenic effect of Dha, Dha has also shown acute health effects on humans such as

Irritation of the nose, throat, and lungs. Fig. 7 shows the total toxicity equivalent of the Generators. Generators, K, L, M, and N have the highest total toxicity equivalent values, this is also related to the high concentration of PAHs in the exhaust of the generators due to the type of the engine as these generators are 2-cycle engines.

The ILCR model is usually used as a tool to assess human cancer risk. The model shows the likelihood of human exposed to the emission to develop cancer in lifetime. Table 4 shows ILCR and HQ from different generators studied. Most regulatory bodies stipulate that an ILCR of more than 10^{-4} shows high potential health risks [38–41]. ILCR values between 10^{-6} and 10^{-4} indicate a potential risk, where safety levels with ILCR are 10^{-6} or less [29,40]. The table reveals the ILCR values of all the generator's emission sampled

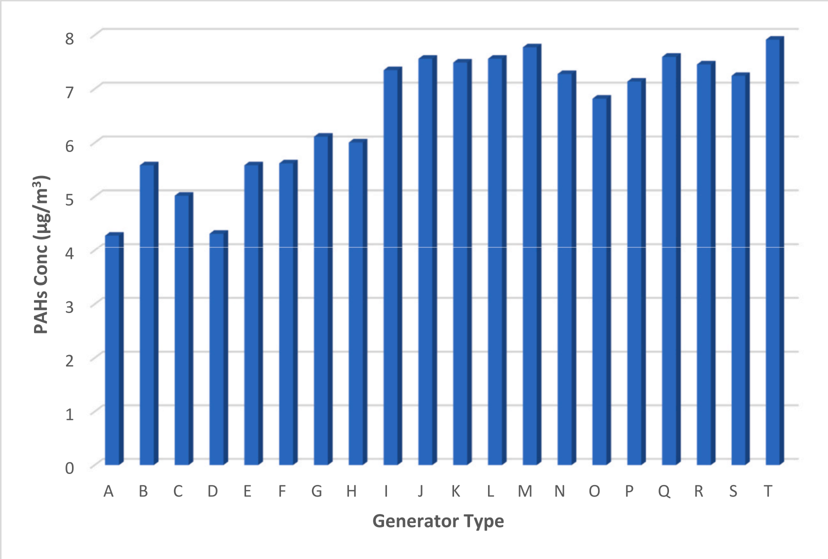

Fig. 3. Sum of carcinogenic PAHs.

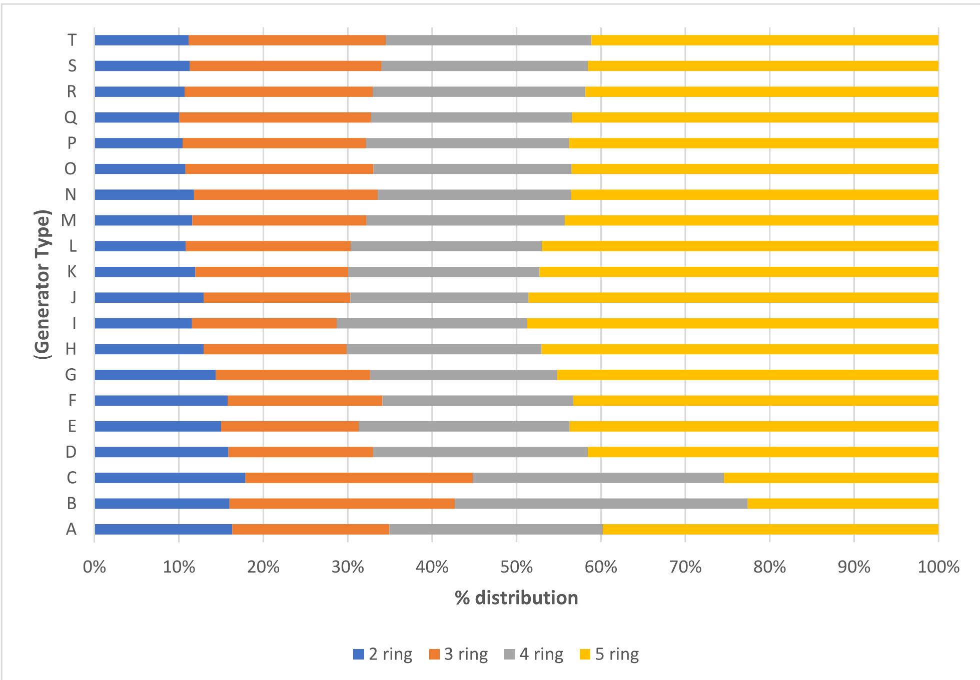

Fig. 4. Distribution of PAHs based on number of rings.

are higher than 10^{-4} which indicate a high potential cancer risk from inhalation of emission from these generators.

A hazard quotient is used to calculate the noncarcinogenic effects of toxic compounds. HQ less than or equal to **1** indicates that less adverse effects and thus can be considered to have negligible hazard, however. HQs greater than **1** showed the possibility of the pollutant causing hazardous effects [42]. The HQ values from all the power-generating sets in this study are all above 1 indicating possible noncarcinogenic effects of the PAH compounds from the generators. The results of this study reveal the danger associated with exposure of PAHs from emission of fossil fuel powered generator. It is advised that there should the reduction in the usage of these power generating sets. Other sources of energy such as solar should be encouraged. Government as a matter of urgency should stabilize power supply and, in the interim, can heavily subsidize portable solar power generator for the common citizens to reduce the usage of the fossil fuel power generator.

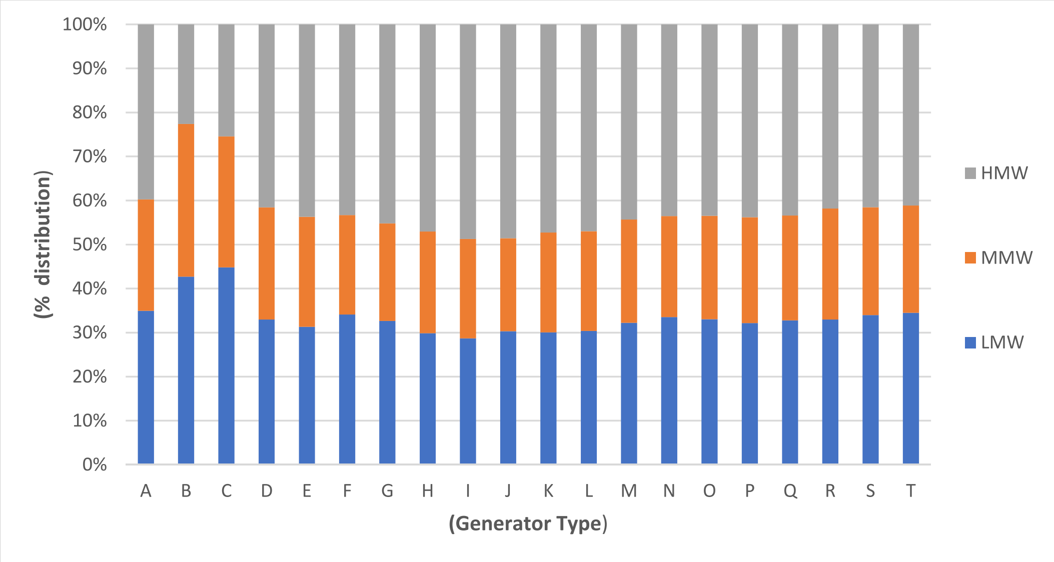

Fig. 5. Distribution of PAHs based on Molecular weight.

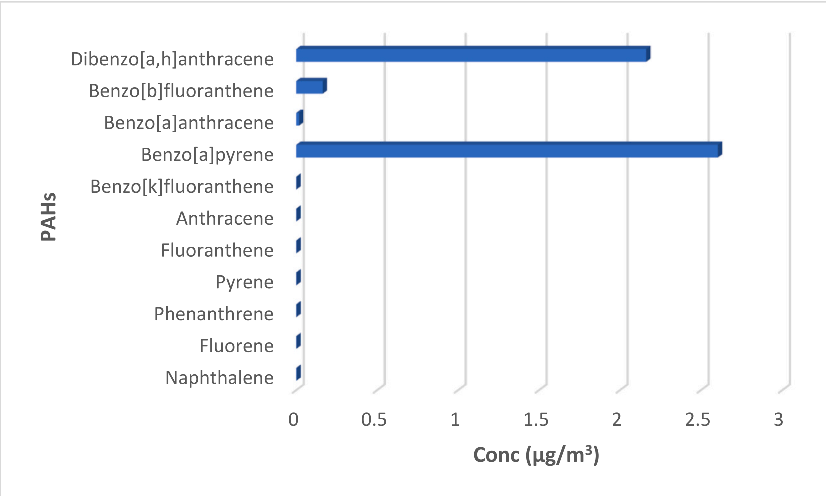

Fig. 6. Mean toxicity equivalent of PAHs in the Generator.

5. Conclusion

The study determined the levels of PAHs in the emission from commonest types of generators used by common citizen in the country Nigeria which are powered by premium motor spirit. The result showed these generators which are used to power household appliances are associated with considerable level of PAHs emission. Although the limitation of the study includes lack of maintenance history data, the study however showed generator type and age of generator affect the PAHs emission from the generators. The ILCR values of all the generator's emission sampled are higher than 10^{-4} for both children and adult which means continuous exposure to compounds increases the probability of 1 person developing cancer in 10,000 people exposed to these PAHs emissions during their lifetime. HQ values from all the power generating set in this study are above 1, which implies high non carcinogenic risk is associated with the exposure to these emissions. It is recommended that conscious effort should be made by the government to improve power supplies in the country to reduce the usage of these power generator and when used it should not be in close proximity to the living rooms. It also recommended that use of renewable energy for power supply should be encouraged and subsidized by the Goverment.

Data availability

Data was included in the article and referenced in article. The related data are available from the corresponding authors upon

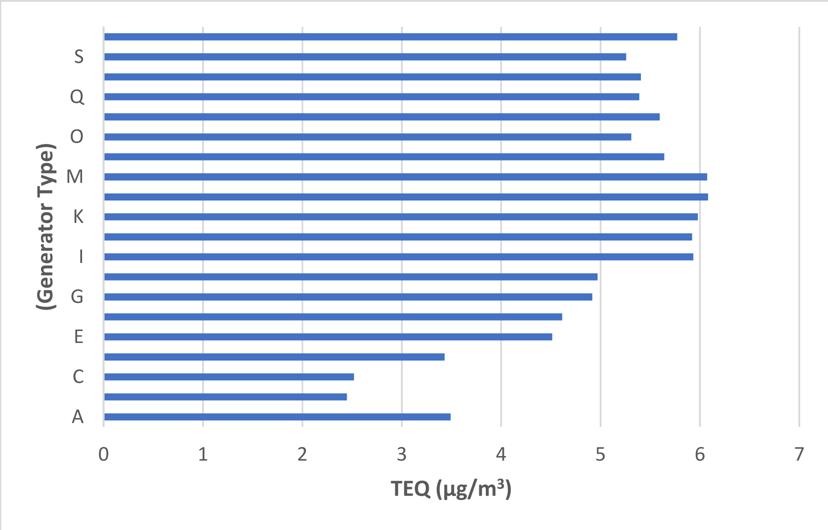

Fig. 7. Total toxicity equivalent of the Generators.

Table 4
ILCR and HQ from different Generator.

Generator	ILCR Adult	Children	HQ Adult	Children
A	0.0004	0.0005	228.3	255.7
B	0.0005	0.0005	256.7	287.6
C	0.0005	0.0005	264.6	296.3
D	0.0004	0.0004	206.8	231.6
E	0.0004	0.0005	241.1	270.0
F	0.0004	0.0005	248.4	278.2
G	0.0005	0.0005	255.8	286.5
H	0.0005	0.0005	251.4	281.5
I	0.0005	0.0006	295.9	331.5
J	0.0005	0.0006	299.9	335.9
K	0.0005	0.0006	302.3	338.6
L	0.0006	0.0006	311.6	349.0
M	0.0006	0.0007	341.5	382.5
N	0.0006	0.0007	327.3	366.6
O	0.0006	0.0006	307.7	344.6
P	0.0006	0.0007	323.4	362.2
Q	0.0006	0.0007	347.9	389.6
R	0.0006	0.0007	350.3	392.4
S	0.0006	0.0007	339.1	379.8
T	0.0006	0.0007	359.2	402.3

request. No restriction was imposed on data security.

CRediT authorship contribution statement

Olusola Adedayo Adesina: Funding acquisition, Formal analysis, Data curation, Conceptualization. **Oluwabusuyi Mattew Kolawole:** Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Mayowa Adeoye Lala:** Writing – original draft, Validation, Supervision, Software, Resources, Methodology, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Mfliah Gbemisola Omofoyewa:** Software, Resources, Methodology, Investigation. **Anslem Iuebego Igbafe:** Writing – review & editing, Writing – original draft, Software, Project administration.

Declaration of competing interest

I am enclosing herewith a manuscript entitled {**LEVELS OF POLYCYCLIC AROMATIC HYDROCARBONS FROM THE EMISSION OF DIFFERENT POWER GENERATOR**}With the submission of this manuscript I would like to undertake that the above mentioned manuscript has not been published elsewhere, accepted for publication elsewhere.

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