

ASSESSMENT OF SOME HEAVY METALS AND POLYCYCLIC AROMATIC HYDROCARBONS IN SOOT FROM THE EXHAUST OF STANDBY GENERATORS

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ABSTRACT

Instabilities in electric power supply create the need for alternative power sources. Generators have become the major alternative for backup power supply. Exhaust emissions (gases and particles) from these generators contain various pollutants which negatively influence the ecosystem. The focus of this work was to evaluate the level of heavy metals and polycyclic aromatic hydrocarbons (PAHs) in soot from the exhaust of standby generators sampled from University of Ghana, Legon campus. Heavy metals (Cd, Cr, Cu, Fe, Pb and Mn) and PAHs were determined from twenty (20) generators using Atomic Absorption Spectrophotometer and Gas Chromatograph – Mass Spectrometer (GC-MS) respectively. Iron gave the highest mean concentration of 9.20 mg/kg while Lead showed the lowest mean concentration of 0.11 mg/kg. With the exception of Chromium, the concentrations obtained for the other heavy metals were far above the World Health Organization maximum acceptable limits for air and water reception and therefore represent a possible health hazard. Using GC - MS, 15 out of 17 PAHs were identified based on their retention times. They were quantified using their peak areas. Benzo (g,h,i)perylene recorded the highest mean concentration of 384.0 ng/g. Four significant molecular diagnostic PAH ratios were used to determine the major source of PAH contamination in the soot.

KEYWORDS: Heavy Metals, Polycyclic Aromatic Hydrocarbon, Soot, Standby Generator, University of Ghana, Legon Campus

Article History

Received: 11 Mar 2019 | Revised: 08 Apr 2019 | Accepted: 30 Apr 2019

INTRODUCTION

The ever increasing population and the rural-urban drift in search of better economic prospects are causing rapid expansion of cities and towns. This has resulted in the emergence of industries and high demand for energy which has led to air pollution being one of the most hazardous environmental problems in developing countries.

One of the main sources of these air pollutants in present day can be traced to soot generated via the engine exhaust system during combustion. The by-products of this combustion process contain significant amount of heavy metals

and polycyclic aromatic compounds which persist in the environment and tend to bioaccumulate with time. These pollutants are known to have adverse effects on the environment and human health (WHO, 2007). Several epidemiological studies have shown a direct association between heavy metals found in soot and people's health (Tchounwu *et al.*, 2003). Exposure to increased levels of Lead (Pb), Cadmium (Cd), Chromium (Cr), Copper (Cu) and Manganese (Mn) shows a high connection with rise in brain and kidney damage, holes and ulcers in the nasal septum, impaired motor function, brain damage and cardiovascular ailment (Baker *et al.* 1979, Dockery *et al.* 1993, Harrison and Yin 2000). The presence of heavy metals in fuels may be ascribed to additives as previously reported by Mayer *et al.*, (1999). Reports indicating the size, morphology and elemental composition of soot particles have been carried out (Meij, 2000).

Polycyclic Aromatic Hydrocarbons (PAHs) are a large group of organic contaminants, characterized by the presence of at least two fused aromatic rings (Ramírez *et al.*, 2011). PAHs have been classified as priority pollutants by both the U.S. Environmental Protection Agency (EPA 1994) and the European Environment Agency (1999). Ingestion and inhalation are quantitatively the main route for PAH human exposure because of their ubiquitous presence in the environment (Ramírez *et al.*, 2011). Health effects of PAH have been widely studied, primarily because of their potential carcinogenic and mutagenic properties. The level of health effects of PAHs exposure depends on the dose, the duration of exposure, and the individual's characteristics such as age, sex, nutritional status, family traits and life style (ATSDR, 1995). In general, the carcinogenic properties of PAHs increase with the number of aromatic rings (Ramírez *et al.*, 2011). Several toxicological studies in animals [World Health Organization-International Programme on Chemical Safety (WHO-IPCS), 1998] and occupational studies in humans (Armstrong *et al.* 2004) demonstrate an excess risk of lung cancer associated with PAH inhalation.

Many Ghanaians, however, still live in territories with hazardous levels of fine particle pollution that surpass national and international health standards. Power plants, heavy duty trucks and automobiles are the nation's largest industrial and domestic sources of air pollution. These emissions undoubtedly fuel global warming and cause other environmental issues.

Instabilities in electricity power supply have necessitated the procurement of alternative power sources. Generators are the most convenient and widely patronized alternative for backup power in facilities such as educational institutions, hotels, hospitals, factories, shopping centres, prisons and official buildings where continuous power is needed. A significant amount of emissions is discharged during their operation because they are fuel powered.

A university campus hosts a diversity of activities such as education, workshops, conferences, seminars and other operational tasks. As a result of its large area and consistent utilization of energy and materials, a university campus may be considered a small community that interacts in various ways with the surrounding community. In recent times, sustainable power supply is increasingly becoming a serious challenge in many universities found in developing countries including the University of Ghana, Legon. This has called for the installation of new generators in many halls of residence, hostels and departmental facilities. With the increasing number of these standby generators installed, it has become very important to monitor their levels of emission and performance. The present study aims at providing a base-line data for monitoring the levels of polycyclic aromatic hydrocarbons (PAHs) and heavy metals concentrations in soot samples from standby generators within the University of Ghana, Legon campus. The objectives are to determine some physicochemical parameters (pH, bulk density and conductivity), quantitatively measure the levels of heavy metals, carcinogenic and non-carcinogenic nature of PAHs in the soot sampled and also to characterize and identify PAHs and heavy metal emission

sources using molecular diagnostic ratios and Pearson correlation tools.

METHODOLOGY

Study Area

The study was conducted on the University of Ghana, Legon campus in the Accra Metropolis of the capital of Ghana (defined by latitudes $5^{\circ}46' - 5^{\circ}28'N$ and longitude $0^{\circ}24' W - 0^{\circ}2'E$), Figure 1. The Accra metropolis consists of ten Sub Metropolitan Districts made up of 72 communities and covers an area of 139.674 square kilometres and with a population of 1,665,086 in 2010 (GSS, 2012). The University of Ghana is the oldest and largest university in Ghana which is about twelve (12) kilometres northeast of the centre of Accra. The generators sampled were chosen from the University of Ghana, Legon campus because of the increasing use of these generators on campus due to the recent power cuts in the region. Twenty different generators were selected for the collection of soot samples. The average temperature at the sampling sites was $30^{\circ}C$.

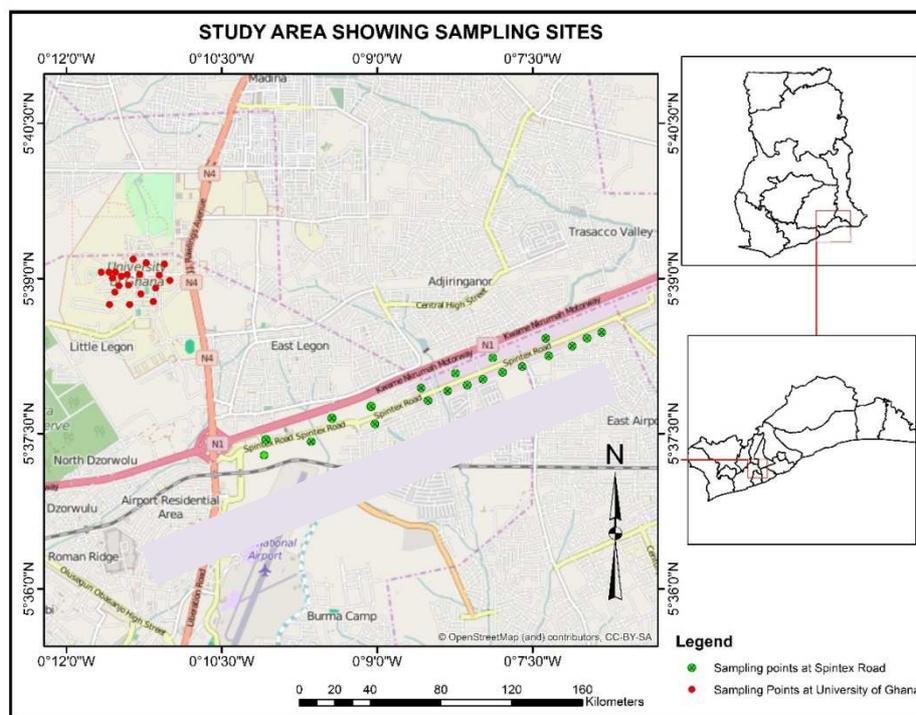


Figure 1: Map Showing Sampling Sites within the Accra Metropolis

Sampling

Soot samples were collected from the exhaust of diesel powered electric generators. Particulate soot emitted from burning of fuel which accumulated in the exhaust of the generators were gently scraped by the use of a soft bristle brush and collected on weighed filter papers (Whatman, $0.3 \mu m$). Samples were stored in plastic sampling tubes to prevent adsorption. The samples were subsequently stored in a desiccator to eliminate moisture and to maintain a constant weight. The mass of the particles were determined gravimetrically. The particulate soot were then transferred and stored in tight fitting sampling tubes. The samples were stored in the dark until extraction and analysis for heavy metals, polycyclic aromatic hydrocarbons (PAHs) and the determination of other physicochemical parameters.

Chemicals and Reagents

All chemicals and reagents used in this study were of analytical grade. Reagents used comprised the following: n-hexane (95 + % purity, Sigma-Aldrich), acetone (99.5 + %, BDH, England), Sodium sulphate (Aldrich- Chemie, Germany), Activated Charcoal, Silica (SiO₃), ethyl acetate (95 + % purity, Sigma-Aldrich), hydrochloric acid (HCl 36% from Fluka), nitric acid (HNO₃, 69%, Suprapure from Fluka), tetraoxosulphate (VI) acid (H₂SO₄, 70%) were used. De-ionized water and Whatman filter paper (No 42) and a PAH custom standard of product code CUS-9059 and Lot number CD3298, containing 100 g/mL each of the analytes were used.

Analytical Procedure

Apparent (bulk) density was determined by filling a 10-mL tube with dry soot collected. The tubes were capped, tapped to a constant (minimum) volume and weighed. The apparent density of soot was calculated by ...

$$\text{Apparent Density (g/cm}^3\text{)} = \frac{\text{Weight of dry sample (g)}}{\text{Volume of packed dry Material (cm}^3\text{)}} \quad (1)$$

Suspensions of soot samples in water (1% w/w) were heated to 90 °C and subjected to continuous stirring for 20 mins then cooled to room temperature. The pH and conductivity of the suspension was subsequently determined with a pH meter (Mettler Toledo MP 220) and conductivity meter (Phywe 13701.93) respectively (ISO, 2002a).

Nitric acid (HNO₃) and tetraoxosulphate (VI) acid (H₂SO₄) were used as solvents for the digestion of soot samples for heavy metal analysis. Approximately 0.25 g of soot sample was weighed into the pre-treated beaker and 6 mL of 0.1M HNO₃ was added to the sample. The mixture was left to stand for about 24 hours in a fume chamber. The purpose of this was to dissolve the organic matter that was present in the soot. After 24 hours, 2 mL of 0.1M H₂SO₄ was then added to the mixture. The mixture was again left to stand in the fume chamber for another 24 hours for further digestion. After this the mixture was then filtered with Whatman (No 42) filter paper into a pre-treated 30 mL volumetric flask. It was then made to the 30 mL mark with de-ionized water. The volumetric flask together with the content was sonicated to form a uniform mixture.

The solutions obtained after acid digestion were analysed using Atomic Absorption Spectrophotometer (AAS) [Spectrophotometer: S Series 71239 v 1. 27]. Six (6) elements; Lead (Pb), Cadmium (Cd), Copper (Cu), Manganese (Mn), Iron (Fe), and Chromium (Cr) were identified and quantified in each sample solution. Samples were analysed automatically and measurements were performed in triplicate to minimise random error and ensure reproducibility. Concentrations of metals and other elements are expressed as mg/kg (mean ± SD, n = 3).

Particulate soot from generators were separated with filters and dried to constant weight in an oven and stored in a desiccator. Samples were extracted with n – hexane and acetone for the determination of seventeen polycyclic aromatic hydrocarbons (PAHs) using GC – MS. The extraction was done by sonicating approximately 1 g of the sample with 25 mL n-hexane and 25 mL acetone for 20 minutes at room temperature.. The extracted solution was filtered twice with a Whatman filter paper (No. 42) and decolorized. A clean-up step was done to remove more polar substances and decolorize the extract. This was performed using activated charcoal, silica and anhydrous Na₂SO₄. A column was filled with approximately 4 g of silica (to remove debris) followed by 2 g anhydrous Na₂SO₄ (to remove excess water) then 2 g of activated charcoal to decolorize the solution. The packed column was filled with 10 mL, n - hexane for conditioning. The extract was then transferred onto the column with a disposable Pasteur pipette from an evaporating flask. The crude extract

was eluted from the column with the wide opening of the stopcock. The eluate was collected into an evaporating flask and rotary evaporated to dryness. The dry eluate was then dissolved in 2 mL ethyl acetate for Gas Chromatographic analysis.

The seventeen (17) polycyclic aromatic hydrocarbons (PAHs) which were selected for determination by GC – MS in particulate soot emission were: naphthalene, 1 – methylnaphthalene, 2 – Methylnaphthalene, acenaphthylene, acenaphthene, anthracene, benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, benzo(g,h,i)perylene, fluoranthene, fluorene, indeno(1, 2, 3-c, d)pyrene, phenanthrene and pyrene. The analysis was done using a Varian CP – 3800 GC – Saturn 2200 coupled with a CP – 8400 Auto sampler mass spectrometer and operating in a splitless mode. The column used is a SLB5TM - MS fused capillary column (30 m long ×0.25 mm ×0.25µm film thickness), coated with a nonpolar stationary phase (HP-5MS, 5% phenyl methyl polysiloxane). The operation conditions were as follows: The oven temperature was set initially at 50°C (1 min hold), increased to 180 °C. At 180 °C, temperature increased at a rate of 25 °C/min to 220 °C and then to 300 °C at a rate of 5 °C/min (10 min hold).

Helium (99.999 % purity) and air, were used as carrier gases at a constant flow of 1.0ml/min for the gas chromatography (GC). The inlet temperature was held at 50 °C with a pressure of 231.2 Kpa and a total flow of 208 mL/min. The detector heater was also held at 300 °C with He/air flow at 35 and 300 mL/min, respectively. Flow rate was 4 mL/min. Injections of 4 µL of sample each were performed in the splitless mode with a ratio of 50:1, and the split valve was opened after 2 min. Identification of PAHs in the samples was based on comparison of the retention times with those in a standard solution, and quantification was based on the corresponding peak areas of the respective chromatograms.

$$Conc \left(ppb \text{ or } \frac{ng}{g} \right) = \frac{Conc (RF) \times 2ml}{Amount \text{ of Sample Taken } (g)} \quad (2)$$

Diagnostic Isomer Ratio

Diagnostic isomer ratios which are indices associating different isomer ratios of PAHs to possible sources, however, was used in this identification (Dickhut et al. 2000, Soclo et al., 2000; Yunker et al., 2002).

Four significant PAH diagnostic ratios shown in *Table.1* were drawn from correlation factor tables and were calculated for the studied samples: [ANT / ANT + PHE], [FLU / FLU +PYR], [B(a)A / B(a)A + CHY] and [I(cd)P / I(cd)P + B(ghi)P] where ANT = Anthracene, PHE = Phenanthrene, FLU = Fluorene, PYR = Pyrene, CHY = Chrysene, B(a)A = Benz(a)anthracene, I(cd)P = Indeno(1,2,3-cd)pyrene, B(ghi)perylene.

Table 1: Molecular Diagnostic Ratios and Possible PAH Sources

PAHs (Isomer Ratio)	Ratio	Possible Source
[ANT / ANT + PHE]	< 0.10 > 0.10	Petroleum Dominance Of Combustion
[FLU / FLU +PYR]	< 0.50 > 0.50 0.41 – 0.49 0.20 – 0.58	Petroleum Kerosene, coal and wood combustion Fossil Fuel and Crude Oil Combustion Diesel Exhaust
[B(a)A / B(a)A + CHY]	< 0.20 0.20 – 0.35 > 0.35	Petroleum Petroleum or Combustion Combustion
[I(cd)P / I(cd)P + B(ghi)P]	< 0.50 > 0.50 0.24 – 0.40	Combustion product of gasoline, kerosene, diesel and crude oil Grass and wood combustion Vehicle emissions

RESULTS AND DISCUSSIONS

Physicochemical Parameters

pH is a measure of the hydrogen ion concentration in a solution. It is mathematically defined as $-\log_{10} [\text{H}_3\text{O}^+]$. This implies that a low pH value shows high hydrogen ion concentration. Generally, pH of the soot samples analysed from all the generators, Table 2, were acidic with values ranging from 3.23 to 5.13. Consequently, the samples were ranked based on the pH values obtained in ascending order. The generator soot pH followed the order GE18 > GE19 > GE10 > GE14 > GE13 with GE01 recording the lowest pH value. The low value of pH is however an indication of the presence of heavy metals.

Bulk Density is a measure of strength/attrition of any material for example soot. In this analysis all the values obtained were less than 1 g/cm^3 (values between $0.15\text{-}0.43\text{g/cm}^3$). This indicates that the soot under study can be easily spread by air current to the environment. Fairly low values were obtained for the samples as shown in Table 2. These values range between 0.15 g/cm^3 for GE 02 and 0.43 g/cm^3 for GE14.

Conductivity is a measure of the relative ease with which ions in solution migrate. Conductivity values obtained from the study are shown in Table 2. These values range from $87 \mu\text{S/cm}$ to $2003 \mu\text{S/cm}$ and are indicative of the presence of metal ions.

Table 2: pH, Electrical Conductivity and Bulk Density for Soot Samples from Generators on University of Ghana Campus

Sample	pH \pm SD	Conductivity \pm SD ($\mu\text{S/cm}$)	Bulk Density \pm SD (g/cm^3)
GENERATORS			
SOGE01	3.23 ± 0.02	87.0 ± 4.0	0.17 ± 0.01
SOGE02	3.46 ± 0.01	97.0 ± 1.0	0.15 ± 0.03
SOGE03	3.70 ± 0.01	107.0 ± 3.0	0.16 ± 0.01
SOGE04	3.34 ± 0.01	142.0 ± 0.7	0.23 ± 0.01
SOGE05	4.02 ± 0.01	92.0 ± 3.0	0.40 ± 0.01
SOGE06	4.52 ± 0.01	93.0 ± 3.0	0.32 ± 0.02
SOGE07	4.43 ± 0.01	90.0 ± 1.0	0.33 ± 0.02
SOGE08	4.12 ± 0.01	107.0 ± 2.0	0.22 ± 0.02
SOGE09	4.00 ± 0.02	122.0 ± 2.0	0.21 ± 0.01
SOGE10	5.03 ± 0.01	163.0 ± 3.0	0.18 ± 0.01
SOGE11	3.55 ± 0.01	106.0 ± 2.0	0.31 ± 0.02
SOGE12	4.22 ± 0.01	97.0 ± 4.0	0.31 ± 0.01
SOGE13	4.59 ± 0.02	203.0 ± 3.0	0.38 ± 0.01
SOGE14	4.71 ± 0.02	141.0 ± 2.0	0.43 ± 0.01
SOGE15	3.65 ± 0.01	172.0 ± 4.0	0.42 ± 0.01
SOGE16	4.08 ± 0.01	94.0 ± 3.0	0.19 ± 0.01
SOGE17	4.21 ± 0.01	92.0 ± 4.0	0.20 ± 0.02
SOGE18	5.13 ± 0.01	105.0 ± 0.7	0.41 ± 0.01
SOGE19	5.07 ± 0.01	111.0 ± 3.0	0.34 ± 0.01
SOGE20	3.56 ± 0.00	89.0 ± 3.0	0.26 ± 0.01

SO – Soot, GE – Generator, - Sample I.D, SD – Standard deviation

Heavy Metals

Six elements namely Lead, Cadmium, Iron, Manganese, Copper and Chromium were determined, Table 3. These elements were randomly selected due to their toxicity. Lead gave the least concentrations of $0.11 \pm 0.01 \text{ mg/Kg}$, while Iron had the highest value of $9.20 \pm 1.00 \text{ mg/Kg}$. The overall order of decreasing elemental concentration is $\text{Fe} > \text{Mn} > \text{Cd} > \text{Cu}$

> Pb. Chromium was found to be below the detection limit of the spectrophotometer, Figs 2 and 3. The high concentration of iron could be due to the materials used in making the exhaust or tail pipe. Manganese is known to be an essential element for human survival, but toxic when present in high concentration (Santos-Burgoa *et al.*, 2001). Manganese concentrations as recorded from the soot analysis had the second highest value after Iron. Manganese-based fuel additives (Methyl cyclopentadienyl Manganese Tricarbonyl) may be responsible for this value. However, manganese concentrations in the soot were all above the maximum acceptable limits for air and water.

The values obtained for Lead range from 0.09 to 0.16 mg/Kg. In comparison to acceptable standard limits, these values which are far above the recommended emission standards (WHO, 2007) for both air and water could be attributed to the source of the fuel.

The observed concentrations of cadmium in the samples were between 0.42 and 2.88 mg/Kg. This element however, is not biodegradable and over exposure could ultimately lead to bioaccumulation in humans and the environment.

The average concentration of copper is 1.30 ± 0.30 mg/Kg, Table 3, Figs 2 and 3. Copper compounds are added to engine oils to reduce wear and oxidation. These might be responsible for the levels of copper observed.

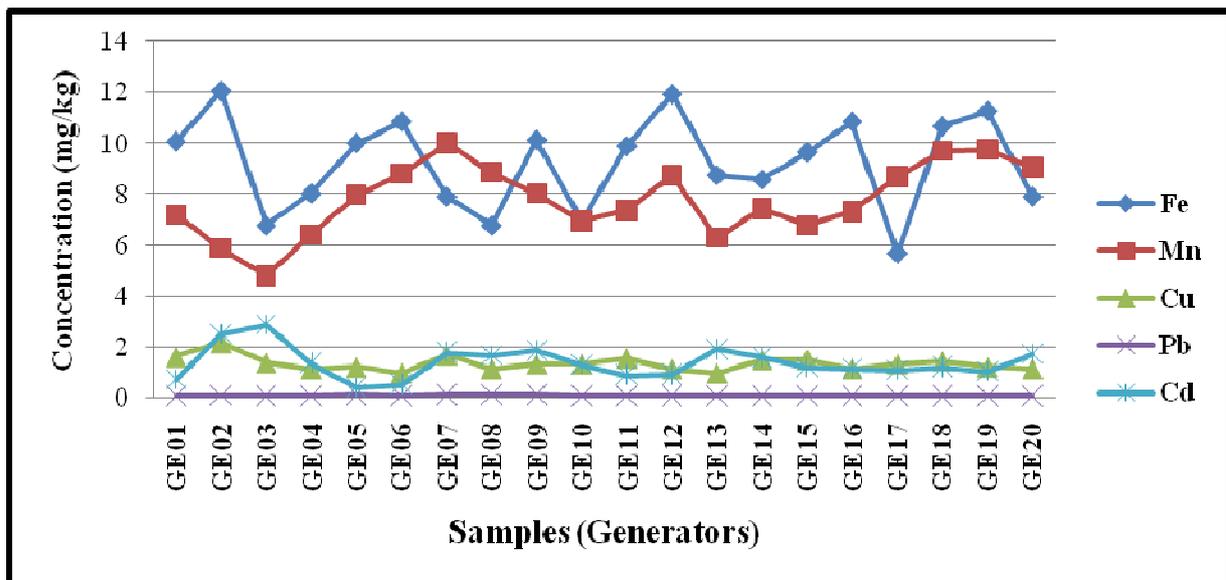


Figure 2: Distribution of Heavy Metals in Standby Generators on University of Ghana, Legon Campus

Table 3: Total Mean Elemental Concentration in Generator Soot

Elements	Mass Concentration / (mg/kg)				Air Quality Limit value/ $\mu\text{g}\text{m}^{-3}$
	Mean	SD	Max	Min	
GENERATOR					
Iron (Fe)	9.20	1.00	12.06	5.70	1.60
Manganese (Mn)	7.80	1.00	10.02	4.80	0.15
Copper (Cu)	1.30	0.30	2.16	0.96	0.01
Lead (Pb)	0.11	0.01	0.16	0.09	0.05
Cadmium (Cd)	1.40	0.60	2.88	0.42	0.01
Chromium (Cr)	BDL		BDL	BDL	0.0025

Minimum detection limits for the metals are 0.1mgkg^{-1} for Cr, Fe and Pb, 0.2mgkg^{-1} for Cd, Mn and Cu.

Max – Maximum Min – Minimum

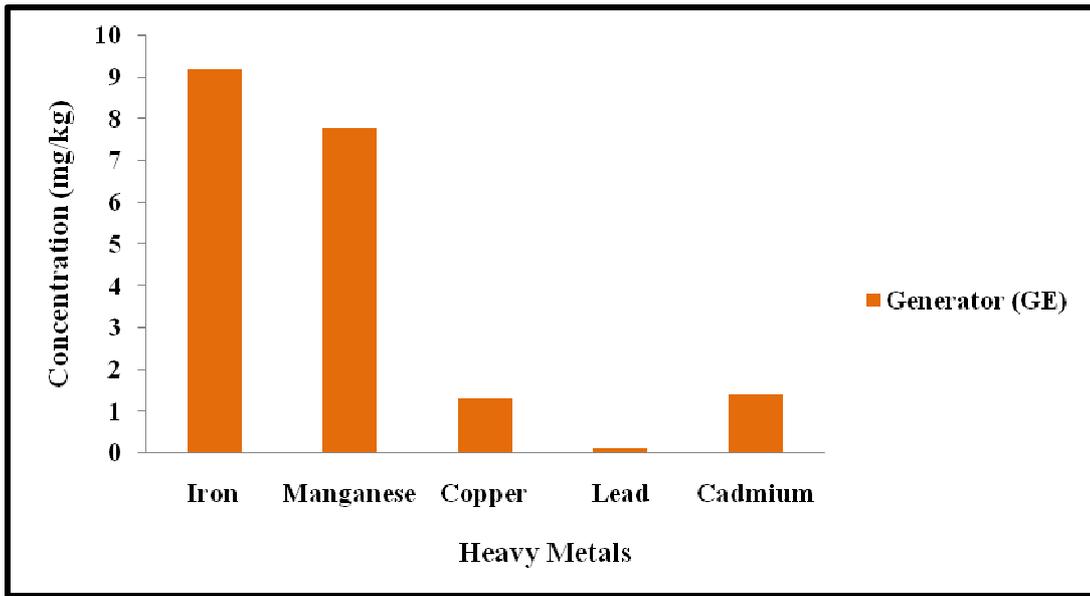


Figure 3: Bar chart showing the Mean Concentration (mg/kg) of Heavy Metals in Soot Samples

Sources of Individual Metals

Table 4 summarizes the correlation factors or coefficients (*R*) for the metals analysed. The correlation coefficients were low which indicates weak correlation with each other. This low linear positive correlation exists between Cu and Fe, Mn and Fe, Pb and Cu, Cd and Cu, Pb and Mn, suggesting there is very little or no relationship. However, Cd and Mn exhibited a fairly high and negative correlation which suggests that the two are not from the same source.

Table 4: Correlation Factors between the Heavy Metals Concentrations in the Soot from Generators on University of Ghana Campus

Heavy Metal	Heavy Metals				
	Fe	Cu	Pb	Mn	Cd
Fe	1				
Cu	0.167	1			
Pb	-0.071	0.222	1		
Mn	0.111	-0.218	0.098	1	
Cd	-0.305	0.343	0.148	-0.450*	1

* Correlation is significant at the 0.05 confidence level (2-tailed).

Polycyclic Aromatic Hydrocarbons (PAHs)

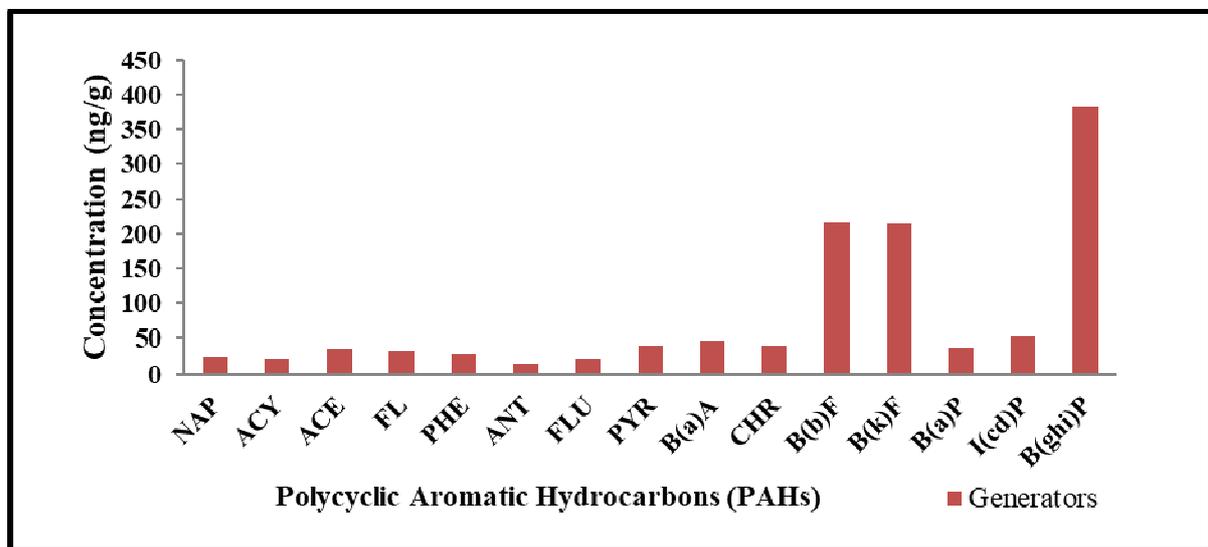
Table 6 shows the mean concentrations of the 15 out of 17 polycyclic aromatic hydrocarbons analysed in the soot samples from the various generators with molecular masses ranging from 152 to 278 g/mol.

Table 5: Mean Concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) in Soot Samples

PAHs	Concentration (ng/g)				Ratio to B[a]P
	Sum	Mean	SD	Max	
Naphthalene	382	25.5	20.0	62	0.7
1 - Methyl-naphthalene	N/D	N/D	N/D	-	-
2 - Methyl-naphthalene	N/D	N/D	N/D	-	-
Acenaphthylene	322	21.5	10.0	40	0.6
Acenaphthene	550	36.7	10.0	58	1.0
Fluorene	482	32.1	10.0	62	0.9
Phenanthrene	440	29.3	10.0	52	0.8
Anthracene	220	15.0	6.0	26	0.4
Fluoranthene	258	22.0	9.0	34	0.6
Pyrene	588	39.2	20.0	66	1.0
Benz(a) anthracene	582	44.8	10.0	64	1.2
Chrysene	356	39.6	20.0	68	1.1
Benzo(b) fluoranthene	3892	216.2	200.0	888	5.8
Benzo(k)fluoranthene	4062	213.8	100.0	654	5.7
Benzo(a) pyrene	564	37.6	10.0	64	1.0
Indeno(1,2,3-c,d)pyrene	838	52.4	50.0	188	1.4
Benzo(g,h,i)perylene	4992	384.0	200.0	860	10.2

N/D – Not detected

1 – Methyl-naphthalene and 2 – Methyl-naphthalene were not detected in the samples. Anthracene having three aromatic rings showed the least mean concentration of 15.0 ± 6.0 ng/g. The total and average mass concentrations of particulate PAHs were 18528 ng/g and 1235.2 ng/g respectively. Pyrene, which recorded a high concentration in the soot, is one of the compounds used as molecular marker for diesel emission (Tsapakis and Stephanou 2003).

**Figure 4: Bar Chart Showing Mean Concentrations (ng/g) of PAHs in Soot Samples**

Carcinogenicity and Non-Carcinogenicity of PAHs

To determine the carcinogenicity of PAHs, the PAHs were grouped according to their carcinogenic properties. Non – carcinogenic PAHs include naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, fluoranthene, pyrene, benzo(ghi)perylene and phenanthrene. Carcinogenic PAHs include benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, Chrysene, and indeno(1,2,3-cd)pyrene. The soot samples contained 56% and 44 % carcinogenic and non – carcinogenic PAHs respectively (Table 7). The mean value of Benzo(a)pyrene, classified as a

carcinogenic and mutagenic material (Lijinsky 1991) was found to be 37.6 ± 10.0 ng/g.

Table 6: Mean Concentrations of Carcinogenic and Non Carcinogenic PAHs in Soot Samples

Particulates	GENERATORS					
	Mean Concentration (ng/g)					
	Sum	Mean	S.D	Max	Min	Percentage
PAHs	18528	1235.2	1617.0	4992	220	
PAHs (CARC)	10294	1715.7	1759.1	4062	356	55.6
PAHs (NON-CARC)	8234	914.9	1534.0	4992	220	44.4

$PAH_{(CARC)}$ = Carcinogenic PAHs, $PAH_{(NON\ CARC)}$ = Non Carcinogenic PAHs

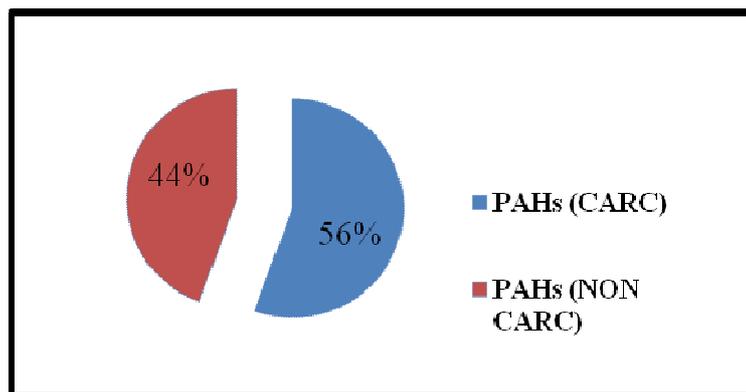


Figure 5: Pie chart showing the Percentage of Carcinogenic and Non Carcinogenic PAHs

Molecular Weights of PAHs

Most of the carcinogenic polycyclic aromatic hydrocarbons fall within the group of the high molecular weights. The average mass concentration of the six genotoxic PAHs (Benz(a)anthracene, Benzo(a)pyrene, Benzo(k)fluoranthene, Benzo(b)fluoranthene, Indeno(1,2,3-cd)pyrene and Chrysene) was observed to be high, Table 6. The volatile PAHs: Naphthalene (NAP), Acenaphthylene (ACY), Acenaphthene (ACE), Fluorene (FLU), Phenanthrene (PHE) and Anthracene (ANT) also contributed on the average 7.15 % of the total mass of the PAH compounds.

To assess PAH homolog distribution for each collected sample, the PAHs were grouped based on molecular weights. The high molecular weight PAHs (228-278 g/mol), include benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, Chrysene, and indeno(1,2,3-cd)pyrene. The medium molecular weights (202 g/mol) are fluoranthene and pyrene and the low molecular weights (152-178 g/mol) include naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene and phenanthrene.

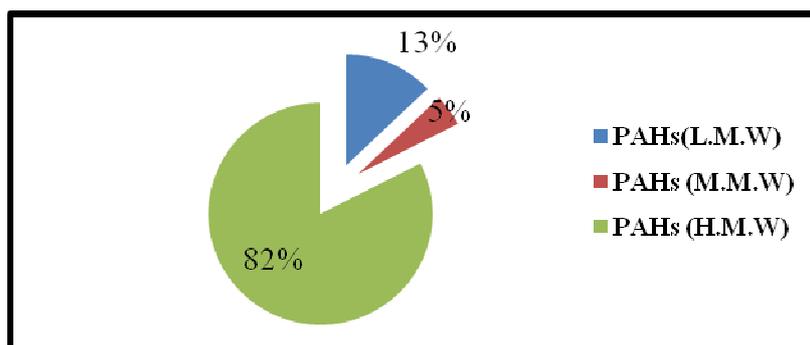
The mean concentrations of Low Molecular Weight PAHs [$PAHs_{(L.M.W.)}$], Medium Molecular Weight PAHs [$PAHs_{(M.M.W.)}$] and High Molecular Weight PAHs [$PAHs_{(H.M.W.)}$] ranged from (220 – 550 ng/g), (258 – 558 ng/g) and (356 – 4992 ng/g) respectively. The High, Medium and Low Molecular Weight PAHs had 82%, 13% and 5 % respectively by weight of PAH compounds in all samples, Fig 6, Table 8. The small contribution by mass of the Low Molecular Weight PAHs was expected because of their small size and high volatility at the high ambient temperatures (28°C - 33°C) during the sampling period (Baek et al. 1991). The presence of HMW polycyclic aromatic hydrocarbons is indicative of deposits by previous pyrolytic processes. Pyrolysis of polycyclic aromatic hydrocarbon residues leads to the formation of additional higher molecular weight polycyclic aromatic hydrocarbons and, consequently increases the PAH concentration in the samples.

Table 7: Mean Concentrations of Low, Medium and High Molecular Weight PAHs in Soot Samples

GENERATORS (GE)						
Particulates	Mean Concentration (ng/g)					
	Sum	Mean	S.D	Max	Min	Percentage
PAHs _(L.M.W)	2396	399.3	118.0	550	220	12.9
PAHs _(M.M.W)	846	423	233.4	588	258	4.6
PAHs _(H.M.W)	15286	2183.7	2027.9	4992	356	82.5

PAH_(LMW) = Low Molecular Weight PAH PAH_(HMW) = High Molecular Weight PAH

PAH_(MMW) = Medium Molecular Weight PAH

**Figure 6: Pie Chart Showing the Percentage Concentration of PAHs Molecular Weights**

The majority of PAHs originate from pyrogenic or petrogenic sources. Pyrogenic PAHs are produced during the incomplete combustion of carbon, wood, and fossil fuels. They are characterized by compounds with four or more aromatic rings. However, petrogenic PAHs contain only two or three aromatic rings, which are associated with spills of crude and refined oil (Soclo et al., 2000; Deng et al., 2013).

Diagnostic Isomer Ratios and Possible Sources of PAHs

Table 9 shows the diagnostic isomer ratios of all soot sampled from all locations. Comparing results from Table 9 to the diagnostic ratios in Table 1, it can be seen that few of the values vary from the specified rule of having a particular source.

In (ANT / ANT + PHE), the ANT/178 ratio generally varied from 0.14 to 0.47. In fact, phenanthrene and anthracene are two structural isomers. In view of their distinctive physicochemical properties, they could behave differently in the environment and could lead to different values for their ANT / ANT + PHE ratio that would give useful information on the PAH origin. Phenanthrene being more thermodynamically stable than anthracene causes the ratio, to be low on combustion.

The ratio of fluoranthene and pyrene ranged from 0.10 to 0.59. They are often associated during natural matrices analyses and were considered as typical pyrogenic products derived from high-temperature condensation of lower molecular weight aromatic compounds. The results obtained for this study suggest that the sources of these PAHs are diesel exhaust or crude oil combustion. Chrysene and benzo(a)anthracene are derived from processes of organic matter combustion at high temperatures. In contrast, low maturation of organic matter during burial in the sedimentary matrix could lead to an inversion of this tendency (Shreadah et al. 2011). The ratio of CHY and B(a)A ranged from 0.38 to 0.70. This result shows that the source of these PAHs is combustion. Similar to the other mass ratios, [I(cd)P / I(cd)P + B(ghi)P] varied from 0.06 to 0.54. The results indicate the source to be diesel, kerosene and wood combustion. However, the results

suggest that the PAHs originated mostly from pyrogenic sources (combustion of fossil fuels).

Table 8: Some PAHs Isomer Ratios of Sampled Generator (GE) from University of Ghana, Legon Campus

Sample	Isomer Ratio			
	[ANT/ANT+PHE]	[FLU/FLU+PYR]	[B(a)A/B(a)A+CHY]	[I(cd)P/I(cd)P+B(ghi)P]
SOGE01	-	-	-	-
SOGE02	0.26	0.52	0.56	0.08
SOGE03	0.40	0.37	0.48	0.04
SOGE04	0.14	0.53	-	0.06
SOGE05	0.31	0.54	0.48	-
SOGE06	-	-	-	-
SOGE07	0.41	0.44	0.70	0.54
SOGE08	-	-	-	-
SOGE09	-	-	-	-
SOGE10	-	-	-	-
SOGE11	0.38	0.25	0.53	0.13
SOGE12	0.31	0.59	-	-
SOGE13	0.21	0.33	0.63	-
SOGE14	0.28	0.33	0.65	0.13
SOGE15	0.55	0.20	-	0.05
SOGE16	0.45	0.10	-	-
SOGE17	0.22	-	0.58	0.10
SOGE18	0.47	-	0.38	0.11
SOGE19	0.41	-	-	0.08
SOGE20	0.37	0.36	-	0.08

CONCLUSIONS

Generally, engines, especially diesel engines are regulated for smoke capacity, total oxide of nitrogen, total particulate matter and total hydrocarbon. The magnitude of engine emissions depends on fuel consumption. This research considered the assessment of heavy metals and polycyclic aromatic hydrocarbons in particulate emissions in the form of soot which was collected from the exhaust of generators.

The pH of the soot from the generators sampled fell within the acidic range. Conductivity values obtained in this analysis were low. In this analysis all the values obtained for bulk density were less than 1. This implies that the soot can easily be spread by air current to the environment. Soot can sometimes contain toxic heavy metals such as lead, cadmium, iron, copper and manganese which are released into the environment. Correlations between the concentrations of the various metals were relatively low, indicating that the concentrations of the heavy metals in the soot are more or less independent of each other.

Mean concentrations of the 15 out of 17 polycyclic aromatic hydrocarbons analysed in the samples from the various generators with molecular masses ranging from 152 to 278 g/mol were identified and quantified. The High, Medium and Low Molecular Weight PAHs had 82%, 13% and 5% respectively by weight of PAH compounds. The carcinogenic and non - carcinogenic PAHs had 56% and 44% respectively. Most of the carcinogenic polycyclic aromatic hydrocarbons fall within the group of the high molecular weights. However, the results from four diagnostic PAH ratios suggested that the PAHs originated mostly from pyrogenic sources.

ACKNOWLEDGMENT

This research did not receive any specific grant from funding agencies in the government, commercial, or not-for-profit sectors. The authors are particularly grateful to Ms. Emmanuella Ernestina Gyamfi, Ms. Akosua Adutumwaa Boatten, Mr. John Obeng, and Mr. Thomas Mensah for providing language help, writing assistance, and proofreading the article.

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