

*Full Length Research Paper*

# Monitoring the levels of toxic air pollutants in the ambient air of Freetown, Sierra Leone

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The ambient air quality in Freetown, Sierra Leone was investigated for the first time for toxic air pollutants. We investigated the levels of polycyclic aromatic hydrocarbons (PAHs), suspended particulate matter (SPM) and carbon monoxide (CO) and considered the implication of air quality and health risks. Particulate samples for PM<sub>2.5</sub> and PM<sub>2.5 to 10</sub> fractions were collected from four sites, and analyzed by HPLC/FLD. SPM and CO were monitored by realtime monitors. The annual average concentrations of total PAHs for PM<sub>2.5</sub> and PM<sub>2.5 to 10</sub> fractions for the various sites were found to be 37.18 and 6.24 ng/m<sup>3</sup>. The average concentration of SPM was 216.3 count per min (cpm) and the 8-h average concentration of CO was 10 ppm. Higher concentrations of PM<sub>2.5</sub> and PM<sub>2.5 to 10</sub> PAHs were found in dry season compared with wet season. The annual carcinogenic potential of PAHs was high in PM<sub>2.5</sub> fraction while the levels of SPM and CO were high enough to raise concern of health risks. The ambient air quality in Freetown was judged to be poor and in view of human exposure, large portion of urban residents are exposed to high levels of toxic air pollutants which is recognized to be a public health risk.

**Key words:** Air pollution, polycyclic aromatic hydrocarbons, suspended particulate matter, carbon monoxide, African countries.

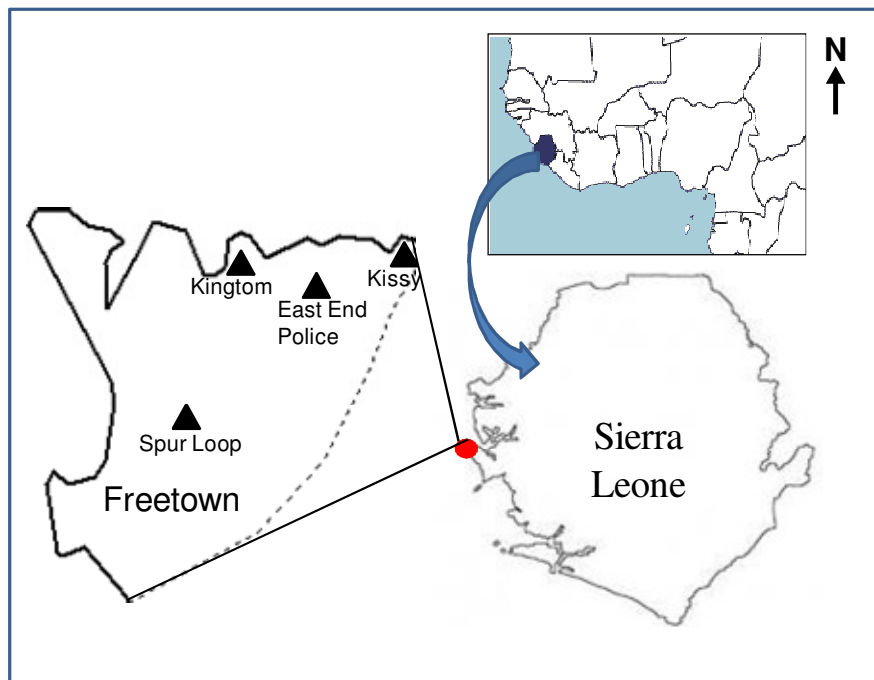
## INTRODUCTION

Urban air pollution is an environmental problem in developing countries. The sources of urban air pollution emanate mostly from combustion activities originating mainly from automobiles and industry. These combustion activities release numerous air pollutants that are toxic to humans. Among the many air pollutants released are, polycyclic aromatic hydrocarbons (PAHs), suspended particulate matter (SPM) and carbon monoxide (CO). PAHs are ubiquitous, carcinogenic, mutagenic and toxic compounds in the environment with cancer being the likely endpoint (IARC, 2010). Benzo(a)pyrene (BaP) the widely studied PAH is classified as group 1 human carcinogen (IARC, 2010), and the 4<sup>th</sup> Daughter Directive (OJEC, 2004) has established a maximum permissible risk level of 1 ng/m<sup>3</sup> of BaP based on the carcinogenic

potential of inhaled particulate PAHs in ambient air. SPM is a collection of tiny droplets of solid or liquid particles in air, and those with particle size less than 10 µm have been the widely studied air pollutant, given that it has been strongly associated with respiratory and cardiovascular diseases (Choudhury et al., 1997; Lanki et al., 2006; Peel et al., 2005; Wanyi et al., 2011). As particle sizes (less than 10 µm) is small enough to be breathed into human lungs, makes it a public health risk. Ambient air quality guideline for annual or 24-h has been set up for particulate matter so as to protect human health. CO is a toxic non irritating gas with high affinity for oxygen, which has been linked to cardiovascular diseases.

Despite the global advancement to address key environmental problems, much improvement has not been made in developing countries where the problems are pervasive. Outdoor air pollution continues to be one of the many environmental problems that need attention in many African countries. This is the case in Sierra Leone where no information of outdoor air pollution exists. Therefore, it is necessary to monitor the exposure

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**Figure 1.** Map of study area indicating sampling sites.

levels of toxic air pollutants in the outdoor air environment in order to establish a baseline data because such monitoring has never been done in the study area. In spite of the paucity of studies on outdoor air pollution in many cities around Africa, a handful of studies have been conducted and reported ambient levels of pollutants (Abu-Allaban et al., 2002; Dionisio et al., 2010; Fanou et al., 2006; Lindén et al., 2008; Muendo et al., 2006; Olajire et al., 2011). The concern of urban air quality in developing countries especially in Africa continues to rise because of direct consequences of combustion activities. These include: wide spread open pit burning of household and commercial wastes, residential wood and charcoal burning ovens in open air, unregulated leaded gasoline vehicles and industrial emissions. Acknowledging the many similarities that exists in the conventional sources of urban air pollution in many countries around the world, many African countries including Sierra Leone differs, because over 70% of the urban population utilizes biomass for cooking in simple open stoves (Smith et al., 2004). Understanding the extent to which humans are exposed to toxic air pollutants requires a sound knowledge of their concentrations in the environment, and the health risks they pose but the lack monitoring data in Sierra Leone makes it difficult to develop a reliable control strategy. This is a broader study that investigated the levels of outdoor and indoor air pollution with the goal of examining the health effects associated with exposure to air pollutants. However, the study was not conducted on a large scale or long duration, but was seen as the first step to assess the environment in Sierra

Leone. In the current paper, we report the preliminary levels of air pollution, and the other components in the wider study will be reported elsewhere. We measured the levels of toxic air pollutants in Freetown, the capital of Sierra Leone to investigate the environmental state and health risks with the view to address environmental problems. Thus, the levels of PAHs, SPM and CO were monitored in the ambient air of Freetown.

## MATERIALS AND METHODS

### Study area and sites description

Sierra Leone is situated along the Atlantic Coast of West Africa, boarded by Guinea to the north and Liberia to the South (Figure 1). The commercial capital Freetown, 27 m above sea level is located on the west coast of the country on a mountain peninsula stretching into the Atlantic Ocean. Freetown has a tropical climate with wet season (May to October) and dry season (November to April). Wet season is characterized by precipitation while dry season is characterized by extended sunshine, dust-loaded trade wind coming from the Sahara Desert. Sampling was conducted at four sites in Freetown during September 2010, March 2011 and September 2011, which are: (i) industrial area, (ii) municipal solid waste dumpsite-residential area, (iii) traffic area, and (iv) residential area.

### Industrial area

This site (Kissy) is located from industrial plants, the sea port and main motorway leading to the city center. Extending towards the Atlantic Ocean are illegal settlements that burn biomass and

**Table 1.** Meteorological information of ambient temperature, relative humidity, rainfall, wind direction and wind speed.

Period	Temperature (°C)	Relative humidity (%)	Rainfall (mm)	Prevailing wind direction	Wind speed (km/h)
Wet season (September 2010)	26	89	30	S, SW	18
Wet Season(September 2011)	28	79	19	S, SW	16
Dry season (March 2011)	31	52	0	N, NE	14

Temperature and relative humidity data were obtained by Lascar EL-USB-2 data logger; rainfall, wind direction and wind speed were obtained from BBC weather site <http://news.bbc.co.uk/weather/> and Timeanddate.com at <http://www.timeanddate.com/weather/sierra-leone/freetown>.

domestic wastes in open air, a depot for processing scrap metals for transshipment which also receive other forms of solid wastes. Notably are garages that repair diesel trucks and trailer engines for mining companies. Monitors were deployed about 300 to 400 m away from the closest plant in a residential compound.

#### **Municipal solid waste dumpsite-residential area**

Located in Kingtom, this site is host to the largest municipal waste dump, wood burning ovens (bakeries), and street vendor outlets. Settlements range from middle class to squatting and it is home to two most prominent senior schools in the city. Domestic and commercial forms of solid wastes, plastic materials, car tyres etc are openly and indiscriminately dumped at the waste dump site. Burning of solid wastes is practiced in dry season when little or no precipitation occurs. Samples were collected 300 m from the municipal waste dumpsite in a residential compound.

#### **Traffic area**

Goderich Street/East End Police intersection is located in the central business district of Freetown, characterized by offices, retail shops, vehicular and pedestrian traffic. This intersection serves as major transit point for taxis and mini buses (Poda-Poda), high rising buildings on either side forming street valley. Adjacent to this site is the Annie Walsh Memorial Secondary School that stretches towards the eastern direction. Traffic volumes in the morning period are about 350 to 400 vehicles and 600 to 700 motorcycles per hour. Monitors were deployed and samples collected along the sidewalk 3 m from the main street.

#### **Residential area**

This site (Spur Loop) is located 5 to 6 km from the city center on the outskirts of the city in a valley between two overlooking hills in the west end of the city. Settlements in this area are generally upper class, and the air seems to be clean because of the absence of major roads, industries and solid wastes dumpsite. Abbreviation of sites and total PAHs used in the result and discussion sections are explained thereafter as follow: industry (IND), municipal solid wastes dumpsite-residential (MSWR), traffic (TRF), residential (*RSD*) and total PAHs ( $\Sigma$ PAHs).

#### **Sampling program**

##### **PAHs**

Twenty-four hours simultaneous sampling was carried out in September 2010, while 12-h diurnal sampling was made in March 2011 and September 2011. A sampling height of 2.5 m was

maintained during the monitoring periods. The difference in sampling periods was due to field sampling constraints. Eight samples each from industry, municipal solid wastes dumpsite-residential and traffic areas were collected within seventeen days in wet season (September 2010), and six samples each from the same sites were collected in eight days in dry season (March 2011) for PM<sub>2.5</sub> and PM<sub>2.5-10</sub> fractions of PAHs. Fine [PM<sub>2.5</sub>] and coarse [PM<sub>2.5 to 10</sub>] particles were collected for PAHs on a 20 and 10 mm diameter Teflon coated glass fiber filters using Sibata ATPS-20H dual impactor (Sibata Scientific Technology Limited), although no gravitational determination of particulate matter on the filters were made. A uniform flow rate of 1.5 L/min was maintained during the monitoring periods. Ten samples from traffic and five samples from residential areas were collected within fourteen days in September 2011 for PAHs. Furthermore, samples collected in September 2011 at traffic site were to check whether concentrations of PAHs significantly vary between similar seasons.

At the end of each sampling day, samples were wrapped in aluminum foils and stored below freezing temperature before transportation to Japan for analysis. Prior to sampling, Teflon coated glass fiber filters were baked at 450°C for 5 h to remove traces of organic impurities.

#### **SPM and CO**

The level of suspended particulate matter (SPM) was monitored in dry season using a digital LD-3K2 dust monitor (Sibata Scientific Technology Ltd) equipped with a laser that measure the relative concentration of respirable particles in air through the intensity of scattered light. 12 h daytime monitoring of SPM for particles less than 10 µm was conducted for six days in one week in March 2011 across industry, municipal solid wastes dumpsite-residential and traffic sites, respectively. SPM in the current study refer to suspended dust particles in air with 100% of particles having an aerodynamic diameter of less than 10 µm. PM<sub>10</sub> and PM<sub>2.5</sub> fractions largely constitute SPM, and PM<sub>2.5</sub> is mostly considered as the greatest contributor to PM<sub>10</sub> in areas dominated by carbonated materials. The relative concentration measured in this study is expressed as count per min (cpm) which could be expressed as mass concentration (µg/m<sup>3</sup>), if the K factor (factor to calculate mass concentration from relative concentration) is determined. Since the K factor was not determined for PM<sub>2.5</sub>, the relative concentration of SPM is reported. In the case of indoor SPM at school, K factor is approved as 0.0013 (1 cpm = 0.0013 mg/m<sup>3</sup>) (Standard for school environmental sanitation, Japan). CO was monitored in realtime by Lascar EL-USB-CO data logger for the same period as SPM. Meteorological data for the monitoring periods are presented in Table 1.

#### **PAHs extraction and analysis**

All reagents were of chromatographic grade, from WAKO

Pure chemicals (Osaka, Japan). EPA 610 PAHs mixture (Supelco, Bellefonte, PA USA) was used as calibration standard. The sample extraction process is a modified method that has been previously reported (Hayakawa et al., 1996). In brief, PAHs were extracted from the filters with a mixture of benzene/ethanol in the ratio (3:1) in an ultrasonic bath for 50 min in 2 cycles. After centrifugation at 3000 rpm for 10 min, the extracts were filtered, and the filtrates were transferred to a rotary evaporating flask into which 100  $\mu$ l of dimethyl sulfoxide was added for preservation. This was evaporated to about 1 ml using rotary evaporator (BUCHI R-210/R-215 Switzerland), in a water bath at temperature of 55°C and pressure of 180 Torr. This volume was evaporated further to 100  $\mu$ l under a high purity stream of nitrogen. Final volume was adjusted to 1 ml by adding 900  $\mu$ l of acetonitrile, and the sample solution was injected into the following HPLC system. Chromatographic separation and identification of 11 PAHs was enhanced by HPLC system (HP1100; Agilent Technologies) equipped with fluorescence detector supported by diode array detector. A guard column (30  $\times$  4.6 mm, 5  $\mu$ m) for clean up, and an analytical column for PAHs (125  $\times$  4.6 mm, 5  $\mu$ m) were C<sub>18</sub> EnviroSep-PP (Phenomenex). A gradient of water (solvent A) with an increasing acetonitrile content from 55 to 100% (solvent B) over 18 min was used followed by 10 min elapse time to re-establish and wash the column at a flow rate of 1.1 L/ml. Sample volume of 20  $\mu$ l in acetonitrile was injected into the HPLC. Prior to analysis, calibration standard was injected to ensure stability of the column. Quantification of PAHs was standardized by the retention times and peak areas of the calibration standards. Concentrations of 11 PAHs were quantified according to their elution order as follows: phenanthrene [PHE], anthracene [ANT], fluoranthene [FLT], pyrene [PYR], benzo(a)anthracene [BaA], chrysene [CHY] benzo(b) fluoranthene [BbF], benzo(k)fluoranthene [BkF], benzo(a)pyrene [BaP], dibenzo(a,h)anthracene [DBA] and benzo(ghi)pyrene [Bgp].

#### Quality control

Surrogate recoveries and method detection limit procedures were carried out for PAHs to subject the data to strict quality control that would minimize and quantify measurement errors. Recovery analysis was carried out with a reconstituted mixture of three surrogate PAHs standards [phenanthrene-d<sub>10</sub>, pyrene-d<sub>10</sub> and benzo(a) pyrene-d<sub>12</sub>] by spiking 100  $\mu$ l onto laboratory blank filters to examine performance. Mean recoveries and standard deviations were found to be 92% ( $\pm$ 7.3), 85% ( $\pm$ 5.2) and 96% ( $\pm$ 3.7) for phenanthrene-d<sub>10</sub>, pyrene-d<sub>10</sub> and benzo(a) pyrene-d<sub>12</sub>, respectively. Blank filters that accompanied samples to the field were treated as regular samples during the extraction process to determine background contamination during sampling, and results presented were corrected for PHE and PYR which were found in low concentrations in the field blanks.

#### Data analysis

The total concentrations of eleven PAHs ( $\Sigma_{11}$ PAHs) were estimated separately for the individual PM<sub>2.5</sub> and PM<sub>2.5-10</sub> fractions for the different sites. The average concentrations of  $\Sigma_{11}$ PAHs were estimated for PM<sub>2.5</sub> and PM<sub>2.5-10</sub> fractions independently for the different sites. Since total concentration of PAHs (PM<sub>2.5</sub> + PM<sub>2.5-10</sub>) fractions was predominantly in PM<sub>2.5</sub>, the concentration in this size fraction was compared between residential site and the other sites by Dunnett's test. The difference in seasonal concentrations (September 2010 vs. March 2011) for  $\Sigma_{11}$ PAHs (PM<sub>2.5</sub> + PM<sub>2.5-10</sub>) fractions for each site (IND, MSWR, and TRF) was compared by t-test. To determine whether concentration differs between similar seasons for  $\Sigma_{11}$ PAHs (PM<sub>2.5</sub> + PM<sub>2.5-10</sub>) fractions at TRF site, t-test

was used for comparison. To determine the contribution of PM<sub>2.5</sub> and PM<sub>2.5-10</sub> fractions to the concentration of  $\Sigma_{11}$ PAHs for the sampling days across the sites and for the seasons, the percentage compositions were calculated. Health risk assessment of PAHs was conducted for PM<sub>2.5</sub> fraction by utilizing toxic equivalency factors (TEFs) weighting for individual PAHs proposed by (Nisbet and LaGoy, 1992). It was estimated on the basis of benzo(a)pyrene equivalent (BaP<sub>eq</sub>) concentrations. The measured concentrations of individual PAHs were converted to BaP<sub>eq</sub> concentrations by multiplying their corresponding TEFs values. The sum of each BaP<sub>eq</sub> in the mixture expresses the carcinogenicity of the mixture relative to BaP, widely regarded as marker of PAHs. 12-h daytime concentrations of SPM and CO were averaged for six days. Statistical analysis was conducted by using JMP 8 (SAS Institute Inc. 2009).

## RESULTS

The concentrations of 3 to 6 rings PAHs for PM<sub>2.5</sub> and PM<sub>2.5-10</sub> fractions were investigated. The  $\Sigma_{11}$ PAHs represent the sum of eleven individual PAHs for either PM<sub>2.5</sub> or PM<sub>2.5-10</sub> fractions for the different sites unless stated otherwise. The concentration and standard deviation (SD) of eleven PM<sub>2.5</sub> and PM<sub>2.5-10</sub> bound PAHs and  $\Sigma_{11}$ PAHs for wet and dry seasons are presented in Tables 2 and 3. The concentration of  $\Sigma_{11}$ PAHs for PM<sub>2.5</sub> fraction at IND, MSWR and TRF sites in wet season (September 2010) ranged from 12.89 to 32.94 ng/m<sup>3</sup> with an average of 21.89 ng/m<sup>3</sup>. The concentration of  $\Sigma_{11}$ PAHs for PM<sub>2.5</sub> fraction in dry season at the same sites ranged from 42.13 to 75.95 ng/m<sup>3</sup>, with an average of 62.17 ng/m<sup>3</sup>. Similarly, concentration of  $\Sigma_{11}$ PAHs for PM<sub>2.5-10</sub> fraction at IND, MSWR and TRF sites in wet season (September 2010) ranged from 3.28 to 4.75 ng/m<sup>3</sup> with an average of 3.94 ng/m<sup>3</sup>. In dry season, concentration of  $\Sigma_{11}$ PAHs for PM<sub>2.5-10</sub> fraction at the same sites ranged from 6.04 to 11.74 ng/m<sup>3</sup> with an average of 8.68 ng/m<sup>3</sup>. The concentration of  $\Sigma_{11}$ PAHs for (PM<sub>2.5</sub> + PM<sub>2.5-10</sub>) fractions for the different days at TRF site in wet season (September 2011) ranged from 10.01 to 81.42 ng/m<sup>3</sup> with an average of 45.72 ng/m<sup>3</sup>. Similarly, concentration of  $\Sigma_{11}$ PAHs for PM<sub>2.5</sub> fraction at RSD site in wet season (September 2011) ranged from 1.38 to 8.94 ng/m<sup>3</sup> with an average of 5.43 ng/m<sup>3</sup>. The average annual concentration and standard deviation of  $\Sigma_{11}$ PAHs for PM<sub>2.5</sub> fraction was 37.18  $\pm$  25.12 ng/m<sup>3</sup>, and 6.24  $\pm$  2.93 ng/m<sup>3</sup> for PM<sub>2.5-10</sub> fraction for the sites.

Concentrations of  $\Sigma_{11}$ PAHs for PM<sub>2.5</sub> fraction in wet season (September 2010) were significantly greater at IND site ( $p = 0.0336$ ), TRF site ( $p < 0.0001$ ) but not significantly greater at MSWR site ( $p = 0.3672$ ) compared with RSD site. Similarly, concentrations of  $\Sigma_{11}$ PAHs for PM<sub>2.5</sub> fraction in dry season were significantly greater at IND site ( $p = 0.0137$ ), MSWR site ( $p = 0.006$ ) but not significantly greater at TRF site ( $p = 0.1879$ ) compared with RSD site. Concentrations of  $\Sigma_{11}$ PAHs for PM<sub>2.5</sub> fraction were elevated 3.6 times, 2.3 times, 6.0 times at IND, MSWR, and TRF sites in wet season (September 2010) compared with RSD site. Similarly, concentrations

**Table 2.** Average concentrations and standard deviations of 11 individual PAHs and  $\Sigma$ PAHs (ng/m<sup>3</sup>) in wet seasons.

Compounds	IND (n = 8)		MSWR (n = 8)		TRF (n = 8)		TRF* (n = 10)		RSD* (n = 5)
	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>	PM <sub>2.5</sub>
	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD
PHE	1.70 $\pm$ 0.52	1.18 $\pm$ 0.46	1.66 $\pm$ 0.93	1.37 $\pm$ 0.75	1.67 $\pm$ 0.64	1.35 $\pm$ 0.76	1.64 $\pm$ 2.58	1.27 $\pm$ 1.70	0.17 $\pm$ 0.13
ANT	0.17 $\pm$ 0.11	0.08 $\pm$ 0.05	0.23 $\pm$ 0.28	0.11 $\pm$ 0.12	0.13 $\pm$ 0.08	0.08 $\pm$ 0.07	0.23 $\pm$ 0.25	0.07 $\pm$ 0.08	0.12 $\pm$ 0.02
FLT	1.13 $\pm$ 0.47	0.34 $\pm$ 0.29	0.45 $\pm$ 0.25	0.41 $\pm$ 0.19	0.80 $\pm$ 0.17	0.79 $\pm$ 0.56	1.10 $\pm$ 0.74	0.86 $\pm$ 0.41	0.42 $\pm$ 0.24
PYR	1.77 $\pm$ 0.93	0.32 $\pm$ 0.17	0.34 $\pm$ 0.15	0.18 $\pm$ 0.10	1.12 $\pm$ 0.41	0.51 $\pm$ 0.27	1.48 $\pm$ 1.03	0.51 $\pm$ 0.29	0.41 $\pm$ 0.24
BaA	0.99 $\pm$ 0.67	0.05 $\pm$ 0.07	0.18 $\pm$ 0.17	0.07 $\pm$ 0.09	0.86 $\pm$ 0.85	0.11 $\pm$ 0.08	0.64 $\pm$ 0.43	0.20 $\pm$ 0.30	0.12 $\pm$ 0.11
CHY	1.74 $\pm$ 0.88	0.13 $\pm$ 0.12	0.44 $\pm$ 0.28	0.13 $\pm$ 0.09	1.92 $\pm$ 1.17	0.26 $\pm$ 0.20	1.09 $\pm$ 0.92	0.39 $\pm$ 0.18	0.30 $\pm$ 0.07
BbF	1.98 $\pm$ 0.56	0.59 $\pm$ 0.57	1.94 $\pm$ 1.38	0.08 $\pm$ 0.04	3.91 $\pm$ 2.10	0.17 $\pm$ 0.08	5.79 $\pm$ 3.1	0.63 $\pm$ 0.30	0.56 $\pm$ 0.37
BkF	1.01 $\pm$ 0.37	0.45 $\pm$ 1.01	0.76 $\pm$ 0.54	0.03 $\pm$ 0.02	2.01 $\pm$ 1.11	0.12 $\pm$ 0.05	2.75 $\pm$ 1.63	0.32 $\pm$ 0.14	0.25 $\pm$ 0.13
BaP	2.27 $\pm$ 1.26	0.10 $\pm$ 0.04	1.05 $\pm$ 0.81	0.07 $\pm$ 0.03	4.56 $\pm$ 2.82	0.22 $\pm$ 0.12	4.78 $\pm$ 3.16	0.48 $\pm$ 0.23	0.42 $\pm$ 0.22
DBA	4.18 $\pm$ 0.48	0.28 $\pm$ 0.29	3.41 $\pm$ 1.72	0.40 $\pm$ 0.75	8.55 $\pm$ 4.05	0.63 $\pm$ 0.31	11.53 $\pm$ 5.74	0.62 $\pm$ 0.75	1.44 $\pm$ 1.35
BgP	2.89 $\pm$ 1.43	0.28 $\pm$ 0.19	2.44 $\pm$ 1.31	0.43 $\pm$ 0.51	7.41 $\pm$ 4.65	0.51 $\pm$ 0.24	8.85 $\pm$ 4.38	0.49 $\pm$ 0.39	1.19 $\pm$ 1.11
$\Sigma$ PAHs	19.83 $\pm$ 4.87	3.80 $\pm$ 0.82	12.90 $\pm$ 5.61	3.28 $\pm$ 1.18	32.94 $\pm$ 16.12	4.75 $\pm$ 1.57	39.88 $\pm$ 21.21	5.84 $\pm$ 2.81	5.40 $\pm$ 3.79

\*Represents samples collected in September 2011; IND - industry area, MSWR - municipal solid waste dumpsite- residential area, TRF - traffic area, RSD-residential area. The concentrations of PM<sub>2.5 to 10</sub> bound PAHs at UBS site was not reported because over 70% of individual PAHs had levels below the detection limits.

of  $\Sigma_{11}$ PAHs for PM<sub>2.5</sub> fraction were elevated 12.6 times, 13.9 times, 7.7 times at IND, MWSR and TRF sites in dry season compared with RSD site. Concentrations of  $\Sigma_{11}$ PAHs for (PM<sub>2.5</sub> + PM<sub>2.5-10</sub>) in dry season were significantly greater compared with wet season (September 2010) for IND site ( $p = 0.0198$ ), MSWR site ( $p = 0.0078$ ) but not significant for TRF site ( $p = 0.0818$ ). The concentrations of  $\Sigma_{11}$ PAHs for (PM<sub>2.5</sub> + PM<sub>2.5-10</sub>) fractions for samples collected in September 2010 and September 2011 were not different ( $p = 0.7944$ ) at TRF site.

The percentage composition of PM<sub>2.5</sub> and PM<sub>2.5-10</sub> fractions in  $\Sigma_{11}$ PAHs for sites in wet seasons (September 2010 and September 2011), were found to be in the range of 66.8 to 92.9% and 7.1 to 33.2% with an average of 83.3 and 16.7% for

PM<sub>2.5</sub> and PM<sub>2.5 to 10</sub> fractions, respectively. Similarly, the percentage composition of PM<sub>2.5</sub> and PM<sub>2.5-10</sub> fractions  $\Sigma_{11}$ PAHs for sites in dry season were found to range from 78.1 to 93.5% and 6.5 to 21.9% with an average of 86.2 and 13.8% for PM<sub>2.5</sub> and PM<sub>2.5-10</sub> fractions, respectively. The site with the highest percentage composition of PM<sub>2.5</sub> fraction in wet season (September, 2010) was TRF with 86.1% while MSWR had the highest with 88.2% in dry season. In pursuit of identifying potential sources of air pollution, the following compounds DBA, BgP, BaP BbF, PHE were identified as markers of PAHs across the sites and for the seasons. DBA, BgP, BaP and BbF were the greatest contributor to PM<sub>2.5</sub> bound PAHs across the sites constituting 71.3% in wet seasons (September 2010 and

September 2011); while PHE, DBA, BgP, BbF and BaP were in dry season contributing 69.7%.

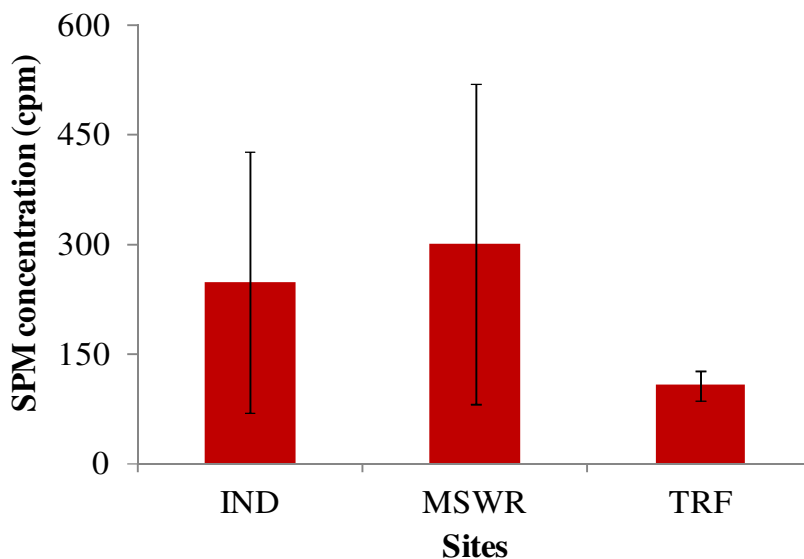
The 12-h average concentrations and standard deviations of SPM for the different sites are presented in Figure 2. The concentrations across IND, MSWR and TRF sites ranged from 107 to 300.5 cpm. In the same way, the 12-h average concentrations and standard deviations of CO for the different sites are presented in Figure 3. The concentrations across IND, MSWR and TRF sites ranged from 6 to 10 ppm. When the 8h average concentrations from the data were extracted for the sites, the average was 10 ppm. MSWR had the highest average and CO concentrations across the different sites.

The total concentration of BaP<sub>eq</sub> for each site and season is presented in Table 4. The

**Table 3.** Average concentrations and standard deviations of 11 individual PAHs and  $\Sigma$ PAHs ( $\text{ng}/\text{m}^3$ ) in dry season.

Compounds	IND (n = 6)		MSWR (n = 6)		TRF (n = 6)	
	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>
	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD
PHE	17.71 $\pm$ 14.51	3.99 $\pm$ 1.96	11.90 $\pm$ 7.37	2.86 $\pm$ 1.46	2.25 $\pm$ 0.82	1.31 $\pm$ 1.16
ANT	0.56 $\pm$ 0.56	0.29 $\pm$ 0.17	0.72 $\pm$ 0.43	0.21 $\pm$ 0.07	0.41 $\pm$ 0.27	0.24 $\pm$ 0.06
FLT	2.29 $\pm$ 1.73	2.35 $\pm$ 1.79	1.72 $\pm$ 0.67	1.20 $\pm$ 0.52	1.48 $\pm$ 0.21	1.41 $\pm$ 0.58
PYR	4.47 $\pm$ 3.87	1.18 $\pm$ 0.75	2.05 $\pm$ 1.16	0.69 $\pm$ 0.43	2.01 $\pm$ 1.37	0.66 $\pm$ 0.24
BaA	6.22 $\pm$ 7.26	0.84 $\pm$ 0.98	6.39 $\pm$ 6.61	0.45 $\pm$ 0.40	0.79 $\pm$ 0.49	0.10 $\pm$ 0.11
CHY	5.72 $\pm$ 5.94	0.77 $\pm$ 0.44	10.86 $\pm$ 8.98	0.80 $\pm$ 0.44	2.23 $\pm$ 0.74	0.40 $\pm$ 0.12
BbF	6.12 $\pm$ 3.29	0.63 $\pm$ 0.55	9.00 $\pm$ 6.44	0.39 $\pm$ 0.23	4.49 $\pm$ 1.32	0.73 $\pm$ 0.85
BkF	2.72 $\pm$ 2.04	0.46 $\pm$ 0.54	3.80 $\pm$ 2.38	0.35 $\pm$ 0.23	2.07 $\pm$ 0.52	0.26 $\pm$ 0.34
BaP	5.63 $\pm$ 5.12	0.49 $\pm$ 0.27	7.41 $\pm$ 4.71	0.44 $\pm$ 0.27	4.15 $\pm$ 1.48	0.36 $\pm$ 0.12
DBA	10.68 $\pm$ 5.42	0.39 $\pm$ 0.18	13.69 $\pm$ 6.7	0.57 $\pm$ 0.33	12.14 $\pm$ 2.41	0.26 $\pm$ 0.16
BgP	6.31 $\pm$ 2.97	0.35 $\pm$ 0.14	8.41 $\pm$ 4.82	0.31 $\pm$ 0.17	10.11 $\pm$ 2.17	0.31 $\pm$ 0.17
$\Sigma$ PAHs	68.43 $\pm$ 46.28	11.74 $\pm$ 5.46	75.95 $\pm$ 43.54	8.27 $\pm$ 3.48	42.13 $\pm$ 9.44	6.04 $\pm$ 1.25

IND - industry area, MSWR - municipal solid waste dumpsite-residential area, TRF - traffic area.



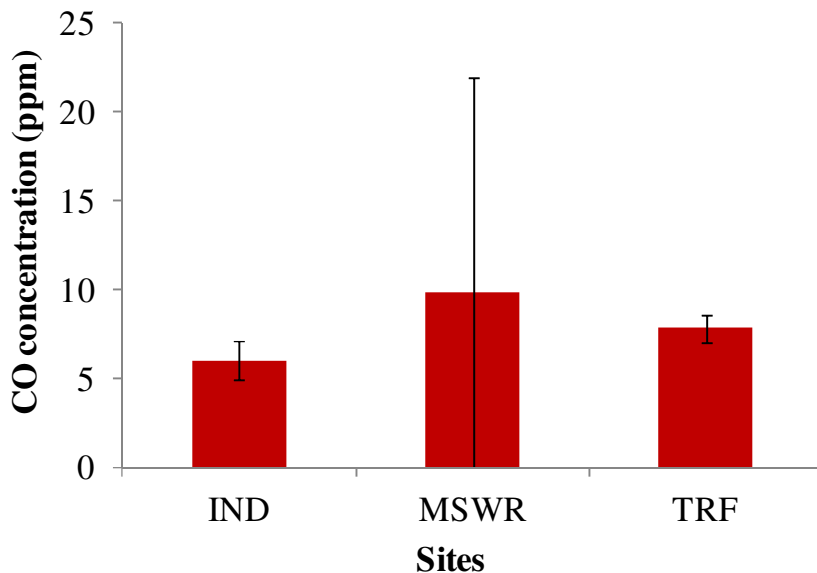
**Figure 2.** 12-h average (box) and standard deviation (vertical bar) of SPM concentrations for the different sites represented as IND-industry area, MSWR-municipal solid wastes dumpsite-residential area, TRF-traffic area in dry season (March 2011). Error bars represent one standard deviation from the mean.

concentrations of BaPeq in each site, and for the seasons were averaged to represent the annual concentration of BaPeq. The annual average concentration of BaPeq was estimated to be  $12.90 \text{ ng}/\text{m}^3$ . Comparing the concentration of BaPeq at *RSD* site relative to the other sites revealed elevated concentrations at the different sites and for the seasons. For instance, in wet season (September 2010), the concentration of BaPeq at *RSD* site was 3.5, 2.4 and 7.0 times lower compared with IND, MSWR and TRF sites,

respectively. Similarly, in dry season, the concentration of BaPeq at *RSD* site was 9.1, 11.7, and 8.7 times lower compared with IND, MSWR and TRF sites, respectively.

## DISCUSSION

Toxic air pollutants were monitored in the ambient air of Freetown. The results indicated that concentrations of  $\Sigma_{11}$ PAHs were generally low at *RSD* site compared to



**Figure 3.** 12-h average (box) and standard deviation (vertical bar) of CO concentrations for the different sites represented as IND-industry area, MSWR-municipal solid wastes dumpsite-residential area, TRF-traffic area in dry season (March 2011). Error bars represent one standard deviation from the mean.

other sites irrespective of the season. This suggests the absence of hot spots of air pollution such as, major traffic road, open air burning of biomass, solid wastes disposing sites etc around this site. It was further observed that concentrations of  $\sum_{11}$ PAHs for ( $PM_{2.5} + PM_{2.5-10}$ ) fractions at TRF site did not vary between similar season, implying that traffic volume and emission intensities were largely similar.

From the estimated percentage composition, it was glaringly clear that  $PM_{2.5}$  fraction contributed more to the concentrations of  $\sum_{11}$ PAHs irrespective of the season and sampling sites. This is in agreement with published data (Kume et al., 2007; Manoli et al., 2002; Wang et al., 2008). For instance, 94 to 98% of total PAHs in  $PM_{2.5}$  fraction was reported (Kume et al., 2007), while 76% of total PAHs in the same size fraction was also reported (Manoli et al., 2002). As total concentrations of PAHs were largely found in  $PM_{2.5}$  size fraction across the monitoring sites, demonstrates health risks considering the existing evidence of toxicity (Schwartz, 1996).

One notable aspect of our results was the higher concentrations of PAHs at MSWR and IND sites relative to TRF site in dry season. This bizarre observation was attributed to strong local influence of sporadic combustion from, domestic refuse, car tyres, metal scraps (growing commercial trade for scrap metals) and domestic fires in open stoves. These combustion activities affected the concentrations around these areas which are considered major sources of atmospheric PAHs. Nevertheless, concentration of  $\sum_{11}$ PAHs for ( $PM_{2.5} + PM_{2.5-10}$ ) fractions at TRF site is greater than a previous study in Japan (Kume et al., 2007), but much lower than earlier studies

in two African countries, Benin (Fanou et al., 2006) and Kenya (Muendo et al., 2006), although the last two studies collected air particulate matter without consideration of size fractions. Even though the traffic volume was estimated to be 350 to 400 vehicles of different kinds an hour, yet concentrations were high. This is an indication of poor combustion efficiency of vehicles, usually without catalytic converters, coupled with the use of low quality fuels that often emit black plumes of smoke from vehicle exhausts. Providing qualitative information on the profile of PAHs is useful to confirm sources of air pollution based on existing studies. DBA, BgP, BaP BbF and PHE contributed 85% to the concentration of  $\sum_{11}$ PAHs for  $PM_{2.5}$  fraction for the different sites and seasons. These homologs are reported to contain fingerprints of gasoline, diesel, wood and solid wastes combustion (Guo et al., 2003; Kulkarni and Venkataraman, 2000; Ruokojarvi et al., 1995). DBA, BgP, BaP and BbF were largely the major components of PAHs mixture in wet season (September 2010), and these fingerprints could be associated with gasoline and diesel emissions.

However, PHE was one of the main components in the mixture of PAHs in dry season at IND and MSWR sites, and this observation could be associated with combustion of metal scraps, plastics, car tyres, domestic refuse, etc on the basis of our field observations. It should be noted that combustion of car tyres were merely to unearth the spiral wires from the latex to make domestic cook stove for charcoal use. An earlier study reported that PHE was a major component in landfill fires which is an indication that combustion of different forms of solid wastes could

**Table 4.** Benzo(a)pyrene equivalent (BaP<sub>eq</sub>) concentrations using Nisbet and LaGoy's (1992) TEFs.

PAHs	TEF	BaP <sub>eq</sub> concentration (ng m <sup>-3</sup> )							
		IND		MSWR		TRF		TRF*	UBS*
		Wet season	Dry season	Wet Season	Dry season	Wet season	Dry season	Wet season	Wet season
PHE	0.001	0.0017	0.01771	0.00166	0.0119	0.00167	0.00225	0.00164	0.00017
ANT	0.01	0.0017	0.0056	0.0023	0.0072	0.0013	0.0041	0.0023	0.0012
FLT	0.001	0.00113	0.00229	0.00045	0.00172	0.0008	0.00148	0.0011	0.00042
PYR	0.001	0.00177	0.00447	0.00034	0.00205	0.00112	0.00201	0.00148	0.00041
BaA	0.1	0.099	0.622	0.018	0.639	0.086	0.079	0.064	0.012
CHY	0.01	0.0174	0.0572	0.0044	0.1086	0.0192	0.0223	0.0109	0.003
BbF	0.1	0.198	0.612	0.194	0.90	0.391	0.449	0.579	0.056
BkF	0.1	0.101	0.272	0.076	0.38	0.201	0.207	0.275	0.025
BaP	1.0	2.27	5.63	1.05	7.41	4.56	4.15	4.78	0.42
DBA	1.0	4.18	10.68	3.41	13.69	8.55	12.14	11.53	1.44
BgP	0.01	0.0289	0.0631	0.0244	0.0841	0.0741	0.1011	0.0885	0.0119
Σ BaP <sub>eq</sub>		6.90	17.97	4.78	23.23	13.89	17.15	17.33	1.97
Annual average BaP <sub>eq</sub>						12.90			

TEFs -Toxic Equivalency Factors; IND - industry area, MSWR - municipal solid waste dumpsite-residential area, TRF - traffic area, RSD-residential area. \*Denotes samples collected in wet season (September 2011).

be considered major source of air pollution (Ruokoijarvi et al., 1995). Quantifying the volume of the already mentioned solid wastes that are combusted is difficult to ascertain due to the widespread burning practice.

In the present study, the estimated carcinogenic potential expressed as BaP<sub>eq</sub> concentrations was high. The annual average BaP<sub>eq</sub> concentration was compared with published data, and the estimated concentration was much higher than a previous study in Tarragona, Spain (Ras et al., 2009), but lower than in Liaoning, China (Kong et al., 2010). Recognizing the uncertainties in estimating BaP<sub>eq</sub> concentrations, it would be stated that residents around IND, MSWR, and TRF sites are exposed to large amount of fine particles, containing higher carcinogenic PAHs

which is an indication that human exposure to these environments could increase health risks.

Whilst the average concentration of SPM for the sites was considered high, there was large variability of SPM concentrations at MSWR and IND sites which indicates that there were days with high concentrations of SPM. Similarly, concentrations of CO at MSWR showed marked variability during the monitoring period, suggesting low concentrations among days. The high concentration of SPM and CO at MSWR site was in agreement with the already mentioned combustion sources of PAHs, in addition to resuspension of dusts largely from unpaved alleys around the site. Average concentrations of CO were higher than an earlier study in London (Kaur et al., 2005), but lower than along a traffic road in

Lagos, Nigeria (Olajire et al., 2011). The average concentration of SPM in the present study was considered to be elevated if we consider World Health Organization (WHO) ambient air quality guideline for PM<sub>10</sub> and PM<sub>2.5</sub> fractions which are the main constituents of SPM in environments where combustion activities are dominant. The 8-h average concentration of CO was in excess of WHO air quality guideline which is an indication of health risks. Given the non existence of regulatory guidelines for air quality in Sierra Leone, our data from this preliminary investigation is suggesting that the ambient air quality is poor.

Exposure to chronic levels of particulate matter and carbon monoxide air pollution has been reported to increase the risk of respiratory and cardiovascular diseases. In this study, we referred



to the ambient concentrations of SPM and CO as measures of human exposure to explain the potential health risks based on citations of published epidemiological evidence. Epidemiological studies have linked exposure to particulate matter to respiratory and cardiovascular diseases. A previous study have found positive association between annual mean concentrations of PM<sub>10</sub> to chronic phlegm production and cough (Zemp et al., 1999), and another study associated minimal change in PM<sub>10</sub> concentration to increasing risk of hospitalization for myocardial infarction (Lanki et al., 2006). The average concentration of SPM for the various sites in the present study was higher than the levels of particulate matter found in the referred epidemiological studies which raised the concern with regards to public health. Long term exposure to high levels of particulate matter increase mortality for heart and lung diseases according to the peer reviewed prospective cohort (Pope and Dockery, 2006).

CO is a toxic non irritating gas with high affinity for oxygen and it reduces the oxygen carrying capacity to vital organs in the body. Because the overall 8-h average CO concentration for the sampling sites was marginally above the recommended level set by WHO, an indication of health risks. Recent evidence suggests that exposure to low levels of CO deteriorate lung function in asthmatic adults (Canova et al., 2010). From the aforementioned human responses to air pollution, it is implied that our results would cause similar or severe health responses if epidemiological rudiments were observed, because the concentrations reported in this study are high. Bearing in mind the height at which these pollutants were collected, concentrations of each toxicant reflects personal exposure (Micallef and Colls, 1998). It could therefore be said that a large number of residents in Freetown are exposed to high levels of toxic air pollutants which have the propensity of either short or long term health consequence.

### Seasonal variation of PAHs

Existing studies on seasonal variation have shown that the difference in seasonal concentrations largely depends on the climatic and existing anthropogenic activities. Since the concentration of  $\sum_{11}$ PAHs for (PM<sub>2.5</sub> + PM<sub>2.5-10</sub>) fractions between results of September 2010 and September 2011 (37.69 ng/m<sup>3</sup> vs. 45.73 ng/m<sup>3</sup>) at TRF site was statistically indistinguishable ( $p = 0.7944$ ), we considered results of September 2010 only to explain seasonal variation. It was evident in the results that lower concentrations of  $\sum_{11}$ PAHs for PM<sub>2.5</sub> and PM<sub>2.5-10</sub> fractions were observed in wet season compared with dry season, suggesting that concentrations were affected between seasons. In wet season, the West African Monsoon blow clean oceanic air (south westerly) into the continent and in the process dilute aerosols containing PAHs. In

addition, the occurrence of precipitation which have been reported to decrease concentrations of PAHs in air is thought to have scavenged PAHs due to washing out effect during rainy days (Ligocki et al., 1985; Park et al., 2001), and perhaps the low horizontal dispersion of air pollutants due to high humidity could not be ignored. In dry season, there was a reversal in the Monsoon as the north easterly trade wind blow dusty aerosols to the West African coastline with the possibility of long range transport of PAHs aerosols.

Notwithstanding the meteorological factors, we think that the existing anthropogenic activities that peak in dry season were highly responsible for the difference in seasonal concentrations. The drier ambient conditions increased burning of household and commercial solid wastes, biomass in simple open stoves by roadside vendors, car tyres, and different materials for metal scraps. Furthermore, the prolonged use of generators that run on fossil fuels in offices and industries due to frequent power cut, and the increase in mobility of two stroke engines commonly called *Okada* could not be ignored. The latter have been reported to increase the amount of unburned hydrocarbons such as PAHs (EMEP/CORINAIR, 2007; Ntziachristosa et al., 2006). Consequently, higher concentrations of ambient PAHs in dry season were strongly associated with the aforementioned combustion activities, and are considered as major sources of ambient PAHs that affected seasonal concentrations.

### Conclusion

The ambient air quality in Freetown was investigated for toxic air pollutants for the first time by reporting the concentration levels, health risks and seasonal variation of polycyclic aromatic hydrocarbons. Further reported were the concentration levels of suspended particulate matter and carbon monoxide in dry season with the consideration of ambient air quality and human health. The ambient concentrations of PAHs and CO were high because levels were in excess of WHO guidelines. The levels of SPM though cannot be directly compared with air quality guidelines which are based on 24-h or annual average were high enough to raise concern of health risks. The ambient air quality in Freetown was poor, and in view of human exposure, large portion of urban residents are exposed to high levels of toxic air pollutants which is recognized to be a public health risk.

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