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Levels, potential sources and human health risk of polycyclic aromatic hydrocarbons (PAHs) in particulate matter (PM₁₀) in Kumasi–Ghana

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Abstract

Airborne particulate samples were collected on quartz filters to determine the concentrations, sources and health risks of polycyclic aromatic hydrocarbons (PAHs) in air in Kumasi, Ghana. A total of thirty two air samples were collected in Kwame Nkrumah University of Science and Technology campus (KNUST) (pristine site) and city centre (CC). Samples were extracted with 1:2 v/v acetone:hexane mixture prior to GC–MS analyses. The sum of concentrations of 17 PAHs in air ranged from 0.51–16 (KNUST) and 19–38 ng/m³ (CC). The concentration of Benzo[a]Pyrene, BaP, ranged from below detection limit to 0.08 ng/m³ (KNUST) and 1.6 to 5.6 ng/m³ (CC). Chemical mass balance model showed that PAHs in air in Kumasi were mainly from fuel combustion. The total BaP toxic equivalent concentration (BaPeq) in CC was 18 times higher compared to KNUST; based on the European Legislation, Swedish and United Kingdom Standards for BaP in air, CC could be classified as highly polluted. Estimated carcinogenicity of PAHs in terms of BaPeq indicated that BaP was the principal PAHs contributor in CC (70%). Health risk of adults and children associated to PAHs inhalation was assessed by taking into account the lifetime average daily dose and corresponding incremental lifetime cancer risk (ILCR). The ILCR was within the acceptable range (10^{-6} to 10^{-4}) indicating low health risk to residents.

Keywords Airborne particulate; PAHs; Kumasi; BaP toxic equivalent; Incremental lifetime cancer risk; Chemical mass balance

47

48 **Introduction**

49 Polycyclic aromatic hydrocarbons (PAHs) are compounds whose structure consist of two or
50 more fused benzene rings in linear, angular or cluster arrangements. PAHs are ubiquitous
51 environmental pollutants affecting the air, soil, stream, sediment, water and food. They are found
52 naturally in coal, crude oil and in emissions from forest fires and volcanoes. Nevertheless, most
53 PAHs entering the environment are formed unintentionally during burning of fossil fuel, biomass,
54 wood etc. (Manoli et al. [2000](#)).

55 Exposure to PAHs takes place mainly by inhalation of contaminated air or ingestion of soil,
56 food and drinking contaminated water (Barranco et al. [2004](#); Dissanayake et al. [2004](#)). PAH
57 exposure to particular work or areas has been explored. These studies have provided many
58 valuable insights on the potential threat of PAHs to human health. Cases include on-duty traffic
59 policemen (Ruchirawat et al. [2002](#); Liu et al. [2007](#)), incense smoke in vehicle (Kuo et al. [2003](#)),
60 fixed site with heavy traffic (Ho and Lee [2002](#)), urban site, vegetation area, forest area
61 (Vasconcellos et al. [2003](#)), bus station and traffic tunnel (Pereira et al. [2002](#)), outdoor air
62 (Velasco et al. [2004](#)), roadside air (Chetwittayachan et al. [2002](#); Marr et al. [2004](#)), and ambient
63 traffic site (Lodovici et al. [2003](#)).

64 Due to their ubiquitous occurrence, persistence, suspected carcinogenicity and mutagenicity,
65 PAHs are included in the US Environmental Protection Agency (EPA), Environmental
66 Monitoring Assessment and the European Union priority lists of pollutants. The US EPA fixed
67 16 parent PAHs as priority pollutants (Mastral and Callén [2000](#); Magi et al. [2002](#); Szolar et al.
68 [2002](#); Schubert et al. [2003](#)).

As one of the most industrialized and economically significant cities in Ghana, Kumasi has been subjected to heavy anthropogenic impacts due to rapid economic development and urbanization. The population and number of vehicles has drastically increased, during the past decade and many fuel filling stations are located in this region leading to greater fuel combustion rate. All of these have led to fuel leakages, smoke production from exhaust of automobiles and as a result high levels of PAHs are released into the environment. Other pollution sources in the Kumasi metropolis, Ghana, are the garbage, wood, and paper burning (Bortey-Sam et al. 2014). According to available literature, no studies on PAHs have been made before in this city.

The objectives of this study were: i) to determine the concentrations of 21 PAHs in particulate matter (PM₁₀) in the Kumasi metropolis; ii) to identify the possible sources of these PAHs; and iii) to determine the toxic potential and possible health risk implications associated with them.

Materials and methods

Study area and sampling

Two sampling sites were selected for this study. They were located at Kwame Nkrumah University of Science and Technology campus, KNUST, (pristine site) and city centre, CC, (which is densely populated and host a number of vehicles, fuel stations and small scale industries). Airborne particulate samples (PM_{10}) were collected on quartz filters using a Sibata Low Volume Pump air sampler (SL-30; Shibata; Saitama, Japan). The sampling sites were selected using Global Positioning System (GPS). The GPS coordinates at KNUST site were N06°40'24.7", W001°34'04.8" and that of CC were N06°41'51.6", W001°37'23.6''. A total of 20 samples were collected in KNUST (5 samples were collected each month) whilst 12 samples were collected in CC (3 samples were collected each month).

Air sampling was carried out for 8 h each day at a flow rate of 30 L/min. Thirty two air samples were collected in total from June to September, 2011. The air inlet was located 1.5 m above ground level to simulate the breathing zone. Samples/filters were wrapped in aluminum foil, double packed in zip-lock bags and stored at -20°C in the Department of Chemistry, KNUST, Ghana. Finally, samples were transported to the Laboratory of Toxicology, Hokkaido University, Japan where they stored at -30°C prior to analysis.

From June to September, the northern and central regions of Ghana receive 150–250 mm of rain per month; this period is the coldest and wettest in the year (McSweeney et al. 2013). Variations in temperature both annually and daily are quite small and the minimum temperature is around 23°C (73°F).

Sample extraction and clean-up

Extraction of PAHs in air samples (quartz filters) was done by soxhlet extractor (Soxtherm Gerhardt Variostat; Soxtherm V7.5, Germany) using 170 mL acetone/hexane (1:2; v/v) for 6 h after spiking with 25 μ L of 1 mg/L PAH internal standard (acenaphthene_ d_{10} , phenanthrene_ d_{10} , chrysene_ d_{12} , and perylene_ d_{12}). The extracts were dehydrated by filtering through anhydrous sodium sulfate (Kanto Chemical Co., Inc, Tokyo, Japan). The dehydrated extracts were collected into a round bottom flask. It was then concentrated to approximately 1.5 mL on a rotary evaporator and transferred into a test tube. The dehydrated extract in the test tube was further concentrated to 0.3 mL under a gentle N₂ stream.

The extracts were cleaned-up to remove other contaminants that may have been extracted with PAHs. Clean-up was done using column packed with 5% water content silica gel (Kanto Chemical Co., Inc, Tokyo, Japan). It was then eluted with 100 mL of diethyl ether/hexane mixture in the ratio 1:4, v/v. The eluate was further concentrated to 2 mL using a rotary evaporator. 300 μ L of n-decane was added to the extract and was further concentrated to 0.3 mL using a gentle N₂ stream. All solvents used (Kanto Chemical Co., Inc, Tokyo, Japan) were of analytical grade.

PAHs analysis

PAHs analyses were carried out using Auto Sampler 3000 Gas Chromatograph (Focus GC) coupled with a Thermo scientific Mass Selective Detector (DSQ II MS, Kanagawa, Japan) operating in the electron impact mode (GC-MS). The selective ion monitoring mode was used for quantification. A FactorFour capillary column, VF-Xms, 30 m, 0.25 mm inner diameter, 0.25

µm film thickness (Varian Inc., Lake Forest, CA, USA) was used for separation. Helium gas was used as the carrier gas at a constant flow rate of 1.2 mL/min. Injector and mass transfer line temperatures were 260 °C and 280 °C, respectively. Temperature programming for the column were as follows, initial temperature of 90 °C held for 1 min, ramped to 280 °C at 10 °C/min and finally to 320 °C at a ramp rate of 5 °C/min and held for 10 min. 1 µL sample was injected in the splitless mode for analysis.

Concentrations of 21 individual PAHs (AccuStandard, New Haven, USA) including 16 USEPA priority pollutants (naphthalene (Nap), acenaphthylene (Acl) acenaphthene (Ace), fluorene (Fle), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IDP), dibenz[a,h]anthracene (DBahA), benzo[g,h,i]perylene (BghiP), perylene (Peryl), benzo[e]pyrene (BeP), methylene phenanthrene (Methy-Phe), 1-methyl phenanthrene (Me-Phe) and retene (Ret)) were measured in each sample. Difficulties were often associated with the GC separation of BbF and BkF and since benzo[j]fluoranthene (BjF) co-eluted with BbF (Pietrogrande et al. 2014), the sum of these isomers was used as an abbreviation, BbF + BjF + BkF. All results were expressed in ng/m³.

Quality control and quality assurance

Quantitation was performed using internal standard calibration method (five-point calibration), the correlation coefficients (r^2) for the calibration curves were all greater than 0.995. Analytical methods were checked for precision and accuracy. Limits of detection (LODs) were calculated based on 3SD/S (SD is the standard deviation of the response of seven replicate standard solution

measurements and S is the slope of the calibration graph). LODs of PAHs were in the range of 0.02–0.67 ng/m³.

Prior to extraction, four internal standards (acenaphthene- d_{10} , phenanthrene- d_{10} , chrysene- d_{12} , and perylene- d_{12}) were added to air samples for recovery assessment. Recoveries in spiked air samples were as follows, acenaphthene- d_{10} , $90 \pm 1.6\%$, phenanthrene- d_{10} , $89 \pm 2.1\%$, chrysene- d_{12} , $93 \pm 0.88\%$ and perylene- d_{12} , $91 \pm 1.0\%$. The final PAH concentrations were not corrected from the recoveries of the internal standards.

For each batch of 6 samples, a method blank (solvent), a spiked blank (internal standards spiked into solvent), and a matrix spike (internal standards spiked into pre-extracted air sample) were analyzed. The average recoveries in spiked blanks and matrix spikes varied from 85–102% for PAHs (21 components). Blanks that were run periodically contained no detectable amount of target analyte. The coefficients of variation of PAHs concentration in duplicate samples were less than 15%.

Health Risk Characterization

Health risk estimation can be calculated using PAH exposure through one of the following exposure pathways: ingestion, inhalation, or dermal exposure (USEPA 2005). In this study, inhalation of air particles contaminated with PAHs was considered. Health risk assessment of carcinogenic PAHs cannot be related to the sole total concentration, rather each PAH has a different carcinogenic potential. For this purpose, toxicity equivalency factors (TEFs) are used, which allow to quantify the carcinogenic potential of other PAHs, relative to BaP, and estimate BaP-equivalent concentration (BaP_{eq}) (Nadal et al. 2004). Nonetheless, usually the health risk associated with inhalatory PAH uptake is estimated on the basis of the sole BaP, which was the

principal contributor in every studied site (Halek et al. 2008). In our study, the list of TEFs compiled by Tsai et al. (2004) was adopted (see Table 3), and the total PAH-associated carcinogenicity was calculated through the formula:

$$\text{BaP}_{\text{eq}} = \sum (C \times \text{TEF})$$

The Incremental Lifetime Cancer Risk, ILCR, in humans can be determined by calculating the Lifetime average daily dose (LADD) of PAHs according to the USEPA guidelines (USEPA, 2013). The equation for estimating LADD and ILCR were as follows:

$$\text{LADD (mg/kg/d)} = \frac{Cs \times IR \times ET \times EF \times ED}{BW \times AT} \times CF$$

$$\text{Cancer risk (ILCR)} = \text{LADD} \times \text{cancer slope factor (CSF)}$$

Where LADD is the amount of intake per kg of body weight per day of a chemical suspected of having adverse health effects when absorbed into the body over a long period of time. Cs represents the average concentration of particular PAH (ng/m³); IR is the intake rate (IR_A = 0.83 m³/h for adults and IR_C = 0.5 m³/h for children up to the age of six); ET is the exposure time (21 hrs/day), EF is the exposure frequency (350 days/year), ED represents the exposure duration, the value of which is ED_A = 70 years (adults) and ED_C = 6 years (children); CF is the unit conversion factor (CF = 10⁻⁶). BW is the average body weight (it was assumed that BW_A = 70 kg for adults and BW_C = 15 kg for children), AT is the average timing, which was AT_A = 25550 days (70 × 365) for adults and AT_C = 2190 days (6 × 365) for children (Bozek et al. 2009). The USEPA (1992) and WDNr (1997) CSF values for carcinogenic PAHs were adopted for this study (Table 4). Estimated LADD values of the measured PAHs for human adults and children were calculated and listed in Table 4, and the ILCR values for (7 carcinogenic PAHs by IARC

2006) human adults and children were also listed alongside. It was assumed that the concentration of pollutant would remain approximately constant in that period of time.

Data analysis

Data were analysed using SPSS version 20.0 for windows (IBM SPSS Statistics., 2011). The PAHs concentrations in KNUST and CC were tested for normality and distribution was considered statistically significant if p value was less than 0.05. Statistical difference of PAHs between the two sample sites was tested using ANOVA. Results were considered significant with p values less than 0.05. Principal component analysis (PCA), was done to determine the distribution pattern of PAHs in air (except for Nap; because concentrations were not detected in most samples from both sites), and was performed using JMP statistical software v. 10 (SAS Institute). The principal components were extracted with eigenvalues > 1 through varimax rotation.

Chemical mass balance version 8 (CMB8) was applied for source identification from both sample sites and source profiles/input were classified as either coal related (power plant, residential or coke oven) or traffic related (gasoline engine, diesel engine or traffic tunnel) (Li et al. 2003). Study by Bortey-Sam et al. (2014) indicated that coke ovens and traffic were the two major sources of PAHs in the area and these have also been considered to be the two most important source categories in many metropolitan areas in the 20th century (Li et al. 2003).

The basic idea of the CMB model is that the measured chemical pollutants in a sample are the sums of the contributions from several sources (Li et al. 2001; Wang et al. 2010). However, only relative compound concentrations in a source or a sample profile (e.g., normalized with BeP, or any other PAH compound) are important (Christensen et al. 1999). The inputs required by the EPA CMB8 include the ambient data and source profiles. In this study, the “ambient” data are

the experimentally measured concentrations, in ng/m^3 , of PAHs in PM_{10} . The key to a successful CMB application is to obtain a set of source fingerprints which is consistent with the measurements at the receptor location. For the purpose of this work, 11 and 17 published PAH source profiles were collected from literature for coal and traffic related sources respectively (Li et al. 2003).

Nap was not included in the modeling, because of the high uncertainties in its source fingerprints and possible evaporative losses during chemical analysis of the samples. Due to the lack of sufficient data for DBahA in many source profiles, this compound was not selected as fitting species in most model runs (Li et al. 2003). Similarly, Methy-Phe, Me-Phe, Ret, and Peryl were not included. The CMB8 model results were evaluated by using several fit indices such as coefficient of determination, $R^2 (\geq 0.85)$, chi-square distribution, $\chi^2 (\leq 3.0)$, percent mass accounted for (72–95%), T-statistics (≥ 3.0), and the residuals and uncertainty ratios (–1.8 to 4.2). The values in parentheses were the statistical parameters obtained from the modelling results.

Results and discussion

PAHs in ambient air in KNUST and CC

From the 21 PAHs analyzed, the more volatile compounds (Nap, Acl, Ace and Fle) were not discussed at each sampling location because these lower ring molecules are present in the gas phase, especially at high ambient temperatures (20–38 °C), which was observed throughout the sampling period. Moreover, their (Nap, Acl, Ace and Fle) concentrations were either undetected or low, which was also observed in studies by Oanh et al. (2000) and Salam et al. (2011).

The sum of concentrations of 17 PAHs (Σ_{17} PAHs) in air samples (PM₁₀) in KNUST ranged from 0.51–16 ng/m³ with mean and median values of 3.3 ± 3.3 and 2.6 ng/m³ respectively. Meanwhile, Σ_{17} PAHs in air samples in CC ranged from 19–38 ng/m³ with mean and median concentrations of 30 ± 4.9 and 30 ng/m³ respectively. The mean concentration of Σ_{17} PAHs in CC was 9 times greater than in KNUST. This may be attributed to the fact that the sampling in Kejetia was performed in a traffic area suffering high exhaust emission and oil seep from vehicles, and hosting handicraft and small industrial activities (e.g., corn milling).

PM₁₀–bound PAH concentrations were compared with recent measurements in other urban areas around the world, including Turkey, Spain and the comparative information is illustrated in Table 1. The concentrations observed in CC was comparable with that of cities in Thailand (Wiriya et al. 2013) (Table 1), but they were lower than those detected in Zonguldak, Turkey (Akyuz and Cabuk 2009) (Table 1). However, Callen et al. (2008) and Pengchai et al. (2009) reported low PAHs concentrations in air (PM₁₀) in Zaragoza (8.8 ± 7.9 ng/m³) and Thailand (0.05–22 ng/m³), respectively (Table 1).

Most abundant PAHs in air in KNUST and CC

The most abundant PAHs in air (PM₁₀) in KNUST were Phe (21%), BghiP (16%), Ret (15%), and Pyr (11%) (Table 2). Chr was the least abundant with concentration below detection limit in almost all samples (Table 2). Ret (one of the most abundant PAHs in air in KNUST) is a molecular marker of wood combustion (Shen et al. 2012). PAHs profile developed by Harrison et al. (1996) and Ho et al. (2002b) on the types of emission sources suggested that Phe and Pyr in KNUST were typical diesel vehicle markers whereas BghiP, the 2nd most abundant, was indicative of gasoline vehicle emission.

As shown in Table 2, air samples in KNUST was dominated by 3–(44%), 6–(24%), 4–(21%), and 5–ring PAHs (11%). Because only PAHs in the particulate phase were collected, it is expected that some of these 3–ring PAHs will also be in the gas phase and concentrations could be underestimated, especially in KNUST, where 3–ring PAHs showed high contribution. During combustion at low temperatures, the low molecular weight (LMW) PAH compounds (< 4 rings) are abundant (Lake et al. 1979). Whilst at high temperature combustion the high molecular weight (HMW) PAH compounds ($\geq$ 4 rings) are dominant (Laflamme and Hites 1978). According to that, ~55% of PAHs in KNUST were released by high temperature combustion sources.

The most abundant PAHs in air in CC were BghiP, IDP, BeP and BaP (HMW PAHs) (Table 2, $p < 0.001$). Their abundances were 29%, 19%, 14%, 12% respectively (Table 2). Me–Phe were the least abundant PAHs there (0.01 ± 0.04 ng/m³). This pathway has been reported as indicative of vehicle emission (Harrison et al. 1996; Oanh et al. 2000; Jamhari et al. 2014).

Moreover, in CC the PAHs profile was dominated by 6–(48%) ($p < 0.001$), 5–(42%) ($p < 0.001$), 3–(5%) ($p > 0.001$), and 4–ring PAHs (4.5%) ($p < 0.001$) (Table 2). The high percentage

of HMW PAHs (95%) confirmed high temperature processes, such as combustion of fuels in engines, as prevailing sources (Mostert et al. 2010; Tobiszewski and Namiesnik 2012).

PCA was applied to PAHs profiles in KNUST and CC. The PCA revealed that the first principal component (component 1) accounted for 47% of the variation while component 2 accounted for 19% (Fig. 1). As observed from the score plot (Fig. 1a), there was a clear separation between the two sampling sites (K and C). That could depend on the high levels of PAHs in CC compared to KNUST. From the loading plot (Fig. 1b), most of the PAHs (both LMW and HMW) were highly associated/clustered on one side of the component. Another interesting feature observed along the component (Fig. 1) was the clear separation between LMW and HMW PAHs, (Fig. 1b) with the HMW PAHs highly distributed in the CC of Kumasi (Fig. 1).

Levels of BaP in air in KNUST and CC

Concentrations of BaP in air in KNUST ranged from below detection (from most sampling dates) to 0.08 ng/m³. The mean and median concentrations of BaP in KNUST were 0.02 ± 0.03 and 0.01 ng/m³ respectively (Table 3). Since no environmental standard is available for Ghana, the United Kingdom (UK), Swedish Standards and European Legislation were adopted to assess the quality of air. The UK air quality standards, Swedish guideline and European Legislation, values for BaP are equal 0.25, 0.1 and 1 ng/m³ (for the total content in the PM₁₀ fraction averaged over a calendar year), respectively (Dimashki et al. 2001; Bostrom et al. 2002; Directive 2004/107/EC).

The mean concentration of BaP in air in KNUST ($0.02 \pm 0.03 \text{ ng/m}^3$) was 5, 12, and 50 times below the BaP standard set by the Swedish, UK, and European Legislation respectively. Similarly, individual concentrations of BaP in air in KNUST were all below the recommended guideline values. Low concentrations of BaP and Σ_{17} PAHs were recorded in air in KNUST because the sampling site was located within an area with low vehicular movement, low industrial and human activities and therefore PAHs from point sources were negligible.

BaP was the fourth most abundant PAH in air in CC ($p < 0.001$) and concentration ranged from 1.6–5.6 ng/m^3 . The mean concentration of BaP in CC ($3.7 \pm 1.1 \text{ ng/m}^3$) was 187 times higher than in KNUST ($0.02 \pm 0.03 \text{ ng/m}^3$) and exceeded 5 times that found in Taichung Industrial Park, TIP, Taiwan (particles-bound) (0.7 ng/m^3 ; Guor-Cheng et al. 2004). Similarly, the mean concentrations of BaP in CC was higher than Zaragoza, Spain (Callen et al. 2013) and in Amritsar, India (Kaur et al. 2013). On the other hand, the BaP values were comparable with those of Naples, Italy (2.9 ng/m^3) and Seoul, Korea ($2.6 \pm 3.3 \text{ ng/m}^3$) (Caricchia et al. 1999; Park et al. 2002).

Anyway, the BaP concentrations in CC were 37, 15, and 4 times higher, respectively, than the air quality standards of Sweden, UK, and European Legislation. Therefore, the CC air was classified as heavily polluted.

Determination of sources of PAHs in air

Chemical mass balance (CMB) model

In general, the contributions appeared similar in both cases. Fuel contributions from diesel and gasoline engines were higher from both sites. From Fig. 2, 15.3% of PAHs in KNUST was contribution from coal related sources i.e. coke oven and 84.7% from traffic related sources (Fig.

2). Of this 84.7%, 42.5% were emissions from diesel engines and the other 42.2% from roadway traffic (Fig. 2). Similarly 85% of PAHs in CC were from traffic related sources out of which 78.4% was contribution from gasoline engines and 6.3% from roadway traffic (Fig. 3).

The overall CMB results clearly showed that gasoline and diesel engines were the two major sources of PAHs in air samples (PM_{10}) in the Kumasi metropolis.

Air toxicity assessment (CC)

In Kumasi (CC), PAHs including human carcinogenic compounds (BaA, BbF, BkF, BaP, Chr, DBahA, and IDP) (IARC, 2006) were at high concentrations (Tables 2 and 3). The mean concentration of these compounds were IDP (5.8 ± 1.2), BaP (3.7 ± 1.1), BbF + BjF + BkF (3.2 ± 0.98), DBahA (0.5 ± 0.16) BaA (0.29 ± 0.08) and Chr (0.15 ± 0.06) ng/m^3 (Table 3).

WHO (2000) stated that the BaP equivalent concentration producing an excess lifetime cancer risk of 1/10,000 is approximately $1.2 ng/m^3$. The mean concentrations of BaP alone in CC ($3.7 \pm 1.1 ng/m^3$) exceeded this threshold. The toxic equivalent concentration (BaPeq) in air of carcinogenic PAHs was $0.3 ngBaPeq/m^3$ in KNUST and $5.2 ngBaPeq/m^3$ in CC (Table 3). Thus BaPeqs in CC were, on the average, 18 times higher than in KNUST.

According to BaPeqs of individual PAHs, BaP was the predominant contributor to toxicity in CC. In comparison of the BaPeq's of PAHs in air with other conducted studies in PM_{10} , the BaPeq values of 16 USEPA PAHs in CC ($5.3 ng/m^3$; Table 3) was found to be higher than similar work done in Christchurch, New Zealand ($1.4 ng/m^3$; city) (Brown et al. 2005; assigned same TEF values as this study except for DBahA, which was assigned a value of 5); Dunedin, New Zealand ($0.006 ng/m^3$; city) (Brown et al. 2005); Taiwan ($3.7 ng/m^3$; urban), (Chang et al. 2006); Chiang Mai, Thailand (sub-urban, 0.18–3.7) (Wiriya et al. 2013). The BaPeqs from this

study were however lower than similar study from traffic site (particle phase; 13 ng/m³) in Japan (Chang et al. 2006).

To assess the health risk for humans, adults and children were assumed to be exposed to airborne PAHs through inhaling PM₁₀. The estimates were made by considering LADD and the corresponding ILCR.

The LADD PAH values ranged from 2.5E-9 to 2.1E-6 for adults (average 4.4E-7) and 6.9E-8 to 5.8E-6 for children (average 1.3E-6). According to that, ILCR associated to carcinogenic PAHs (IARC 2006) ranged from 2.2E-10 to 5.4E-6 (adults) and 6.1E-10 to 1.5E-5 (children). The mean ILCR for adults (1.2E-6) and children (3.3E-6) were within the acceptable limit of 10⁻⁶ to 10⁻⁴ as acknowledged by regulatory agencies (USEPA 2005). The acceptable risk distribution is expressed as a constraints-based percentile and must be ≤ 10⁻⁶ to 10⁻⁴ using upper-bound factors, which represents the increase of cancer by one in the group of million of people (USEPA 2005).

Conclusions

BaP concentrations in air samples (PM₁₀) in KNUST varied from below detection to 0.08 ng/m³ and 1.69 to 5.66 ng/m³ in CC. The mean concentrations of BaP in air was 0.02 ± 0.03 (KNUST) and 3.7 ± 1.1 ng/m³ (CC) respectively. By the Swedish, UK air quality standards and European Legislation value for BaP in air, CC is polluted with BaP. CMB model showed that PAHs in air in KNUST and CC were emissions from diesel and gasoline engines respectively. 78% of PAHs in CC originated from gasoline combustion. The estimated carcinogenicity of PAHs in terms of BaP_{eq} confirmed that BaP was the dominant PAHs contributor (70%). Estimated probabilistic

366 health risk for human adults and children was within the acceptable levels (10^{-6} to 10^{-4}),
367 suggesting low health risk to residents in Kumasi.

368

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558 **Figure captions:**

559 **Fig. 1** Distribution patterns of PAHs in PM₁₀ in KNUST and CC characterized by PCA; (a) score
560 plot (b) loading plot (K: pristine site; C: city centre; LMW: low molecular weight PAHs; HMW:
561 high molecular weight PAHs)

562 **Fig. 2** Chemical mass balance source apportionment of PAHs in air (PM₁₀) in KNUST

563 **Fig. 3** Chemical mass balance source apportionment of PAHs in air (PM₁₀) in CC

564

565 **Table 1** Concentrations of PAHs in air (ng/m³) (PM₁₀) in different sites/countries

City/Country	Σ PAHs			Reference
	Nos.	Range	Average	
KNUST, Ghana	17	0.51–16	3.3 ± 3.3	This study
City centre, Kumasi, Ghana	17	19–38	30 ± 4.9	This study
Chiang Mai, Thailand [#]	16		25 ± 10	Wiriya et al. (2013)
Zonguldak, Turkey ^{##}	14	–	94 ± 122	Akyuz and Cabuk (2009)
Thailand [#]	16	0.05–22	–	Pengchai et al. (2009)
Zaragoza, Spain ^{###}	18	0.4–30	8.8 ± 7.9	Callen et al. (2008)

566 Nos.: indicates, number of PAHs measured

567 #: indicates, Nap, Acl, Ace, Fle, Phe, Ant, Flu, Pyr, BaA, Chr, BbF + BkF, BaP, DBahA, IDP,
568 BghiP

569 ##: indicates, Ace, Fle, Phe, Ant, Pyr, Flu, BaA, Chr, BbF, BkF, BaP, DBahA, IDP and BghiP

570 ###: indicates, Phe, Ant, 2+2/4–methyl phe, 9-methyl phe, 1–methyl phe, 5–dimethyl phe, Flu,
571 Pyr, BaA, Chr, BbF, BkF, BeP, BaP, IDP, DBahA, BghiP and Coronene

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574 **Table 2** Abundance of PAHs in air samples in KNUST and CC

KNUST				CC	
PAHs	Abbreviation	Ring No.	% Abundance	% Abundance	<i>p</i> value
Phenanthrene	Phe	3	21	2.6	0.56
Anthracene	Ant	3	3.6	0.91	0.15
Methylene phenanthrene	Methy–Phe	3	3.3	0.20	0.67
1–methyl phenanthrene	Me–Phe	3	1.2	0.03	0.29
Fluoranthene	Flu	4	8.1	1.3	0.07
Pyrene	Pyr	4	11	1.7	0.30
Retene	Ret	3	15	1.2	0.64
Benz[a]anthracene	BaA	4	1.5	0.96	0.00
Chrysene	Chr	4	0.0	0.49	0.00
Benzo[b+j+k]fluoranthene	BbF + BjF + BkF	5 + 5	0.9	11	0.00
Benzo[e]pyrene	BeP	5	1.5	14	0.00
Benzo[a]pyrene	BaP	5	0.6	12	0.00
Perylene	Peryl	5	1.2	3.1	0.00
Dibenz[a,h]anthracene	DBahA	5	6.9	1.6	0.00
Indeno[1,2,3–cd]pyrene	IDP	6	7.8	19	0.00
Benzo[g,h,i]perylene	BghiP	6	16	29	0.00

575 Bold values: means data are statistically significant (ANOVA)

576

577 **Table 3** Mean Concentrations, standard deviations of PAHs in air (ng/m³), toxic equivalence
578 factor (TEF), BaP equivalence (BaPeq) in Kumasi metropolis

PAHs	TEF	Sampling Sites		BaPeq	
		KNUST (n = 20)	CC (n = 12)	KNUST	CC
		Mean $\pm$ SD	Mean $\pm$ SD	TEF $\times$ Mean conc.	TEF $\times$ Mean conc.
Phe	0.001	0.70 $\pm$ 0.49	0.79 $\pm$ 0.38	7.0E-04	7.9E-04
Ant	0.01	0.12 $\pm$ 0.27*	0.27 $\pm$ 0.31*	1.2E-03	2.7E-03
Flu	0.001	0.27 $\pm$ 0.19*	0.39 $\pm$ 0.14*	2.7E-04	3.9E-04
Pyr	0.001	0.39 $\pm$ 0.35*	0.50 $\pm$ 0.16	3.9E-04	5.0E-04
BaA ^a	0.1	0.05 $\pm$ 0.02	0.29 $\pm$ 0.08	5.0E-03	3.0E-02
Chr ^a	0.01	0.01 $\pm$ 0.01	0.15 $\pm$ 0.06	5.0E-05	1.5E-03
BbF ^a + BjF + BkF ^a	0.1	0.03 $\pm$ 0.02	3.2 $\pm$ 0.98	3.0E-03	3.2E-01
BeP	0.01	0.05 $\pm$ 0.05*	4.1 $\pm$ 1.1	5.0E-04	4.0E-02
BaP ^a	1	0.02 $\pm$ 0.03*	3.7 $\pm$ 1.1	2.0E-02	3.7E+00
Peryl	0.001	0.04 $\pm$ 0.05*	0.94 $\pm$ 0.32	4.0E-05	9.4E-04
DBahA ^a	1	0.23 $\pm$ 0.12*	0.50 $\pm$ 0.16	2.3E-01	5.0E-01
IDP ^a	0.1	0.26 $\pm$ 0.35*	5.8 $\pm$ 1.2*	3.0E-02	5.8E-01
BghiP	0.01	0.53 $\pm$ 1.1*	8.6 $\pm$ 2.3	1.0E-02	9.0E-02
$\sum_{\text{carc}}$ PAHs		0.6 $\pm$ 0.5	14 $\pm$ 3.6	0.28	5.2
$\sum_{16}$ USEPA PAHs		3.0 $\pm$ 3.5	25 $\pm$ 7.9	0.30	5.3
$\sum_{14}$ PAHs		2.7 $\pm$ 3.0	29 $\pm$ 8.7	0.30	5.3

579 PAHs Carc^a: BaA, Chr, BkF, BbF, BaP, DBahA and IDP according to IARC (2006)

580 Bold: indicates the 16 USEPA priority PAHs

581 *: indicates statistical significance with *p* value less than 0.05 (Shapiro–Wilks test for normality)

582 n: number of samples

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586 **Table 4** LADD and ILCR of PAHs in air from in CC

PAHs	LADD		CSF	ILCR	
	Adult	Child		Adult	Child
Phe	1.9E-07	5.3E-07	0.61 ^a 0.0061 ^a 0.061 ^a 6.1 ^a 6.1 ^a 0.61 ^a		
Ant	6.6E-08	1.8E-07			
Methy-Phe	1.5E-08	4.2E-08			
Me-Phe	2.5E-09	6.9E-09			
Flu	9.4E-08	2.6E-07			
Pyr	1.2E-07	3.4E-07			
Ret	8.6E-08	2.4E-07			
BaA	6.9E-08	1.9E-07		4.2E-08	1.2E-07
Chr	3.5E-08	9.9E-08		2.2E-10	6.1E-10
BbF + BjF + BkF	7.6E-07	2.1E-06		4.6E-08	1.3E-07
BeP	9.8E-07	2.8E-06			
BaP	8.9E-07	2.5E-06		5.4E-06	1.5E-05
Peryl	2.3E-07	6.3E-07			
DBahA	1.2E-07	3.3E-07		7.2E-07	2.0E-06
IDP	1.4E-06	3.9E-06		8.4E-07	2.4E-06
BghiP	2.1E-06	5.8E-06			
∑ PAHs	7.1E-06	2.0E-05			
Minimum	2.5E-09	6.9E-09			
Maximum	2.1E-06	5.8E-06			
Average	4.4E-07	1.3E-06		1.2E-06	3.3E-06

^a indicates CSF values (WDNR 1997; USEPA 1992)

Bold: indicates 16 USEPA priority PAHs

Fig. 1

Contribution of the sources

Fig. 2

Contribution of the sources

Fig. 3