Occurrence, distribution and health risk from polycyclic aromatic compounds (PAHs, oxygenated-PAHs and azaarenes) in street dust from a major West African Metropolis

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Abstract

Scientific evidence suggests that the burden of disease on urban residents of sub-Saharan African Countries is increasing, partly as a result of exposure to elevated concentrations of toxic environmental chemicals. However, characterization of the levels, composition pattern and sources of polycyclic aromatic compounds (PACs) in environmental samples from African cities is still lacking. This study measured the PAHs, oxygenated-PAHs (OPAHs) and azaarene (AZAs) content of street dusts collected from Kumasi, Ghana (a major metropolis located in the tropical forest zone of West Africa). The $\sum$ Alkyl+parent-PAHs, $\sum$ OPAHs and $\sum$ AZAs concentration in street dust averaged 2570 ng g^{-1} (range: $181\text{-}7600 \text{ ng g}^{-1}$), 833 ng g^{-1} ($57\text{-}4200 \text{ ng g}^{-1}$) and 73 ng g^{-1} ($3.3\text{-}240 \text{ ng g}^{-1}$), respectively. The concentrations of $\sum$ Alkyl+parent-PAHs were strongly correlated ($n = 25$) with $\sum$ OPAHs ($r = 0.96$, $p < 0.01$) and $\sum$ AZAs ($r = 0.94$, $p < 0.01$). The $\sum$ OPAHs concentrations were also strongly correlated with $\sum$ AZAs ($r = 0.91$, $p < 0.01$). Concentrations of individual PAHs in these street dusts were enriched at between 12 and 836 compared to their average concentrations in background soils from same city, demonstrating the high influence of traffic emissions. Several individual OPAHs and AZAs had higher concentrations than their related and often monitored parent-PAHs. The estimated incremental lifetime cancer risks due to the parent-PAHs in street dusts was $> 10^{-6}$ indicating high risk of contracting cancer from exposure to street dust from Kumasi. The contribution of OPAHs, AZAs, and alkyl-PAHs in street dust to cancer risk could not be quantified because of lack of toxicity equivalency factors for these compounds; however this could be significant because of their high concentration and known higher toxicity of some polar PACs and alkyl-PAHs than their related parent-PAHs.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) and their more polar derivatives such as oxygenated PAHs (OPAHs) and nitrogen heterocyclic PAHs (azaarenes, AZAs) are mainly formed from incomplete combustion of fossil fuels and biomass (Wilcke, 2000; Bleeker et al., 2002; Lundstedt 2007; Vicente et al., 2015). Some polycyclic aromatic compounds (PACs) are also constituents of crude oil, refined petroleum products and industrial chemicals, hence transportation, industry, power plant, waste incineration and household activities (e.g. cooking) are major sources of PACs into the urban environment (Boström et al., 2002; Vicente et al., 2015). Besides their direct emissions from these anthropogenic sources, OPAHs are also formed from transformation of PAHs by photolysis, photochemical, thermochemical reactions and biological oxidation (Lundstedt et al., 2007; Walgraeve et al., 2010). Several PAHs, OPAHs and AZAs are classified as priority pollutants and human carcinogens by National Regulatory Agencies and the International Agency for Research on Cancer (IARC) because they are persistent, bioaccumulative and toxic (carcinogenic, mutagenic & estrogenic) (Lundstedt et al., 2007; IARC 2010, 2013; Grosse et al., 2011; Bandowe et al., 2014a, Andersson and Achten, 2015). Some of the OPAHs and AZAs are direct acting toxicants with the adverse effects of some being higher than their regulated PAHs (Jung et al., 2001; Xue and Warshawsky, 2005; Lundstedt et al., 2007; Knecht et al., 2013). Toxicological analysis of fractionated extracts from particulate matter (PM), dusts, soils, sediments frequently show that fractions containing polar PACs elicit higher adverse effects (Machala et al., 2001; Xia et al., 2004; Misaki et al., 2007; Umbuzeiro et al., 2008; Wang et al., 2011; Andrysik et al., 2011).

Urban street dust is a complex mixture of particles that originate from vehicle exhausts, brake wears, tire debris, soil, plant materials, building demolitions, construction sites, asphalt

/pavement cracks, atmospheric aerosols that are enriched in PAHs, OPAHs, AZAs and nitrated-PAHs (Rogge et al., 1993; Amato, 2011; Mujumdar et al., 2012; Wei et al., 2015). Street dust bound PACs can enter the atmosphere (by re-suspension, volatilization), can be deposited on plant surfaces, and also transported as runoff into the aquatic environment (Krein and Schorer, 2000; Martuzevicius et al., 2011; Mujumdar et al., 2012). Street dusts can therefore be a route by which air, soil, vegetation, crops and the aquatic environment can be contaminated with PACs and serve as a route of exposure to urban populations to these toxic chemicals (Mujumdar et al., 2012).

Developing countries such as Ghana (West Africa) are experiencing rapid urbanization that is leading to rapid increases in the burden of disease (such as cancers, cardiovascular diseases) partly as a result of increasing exposure to environmental chemicals emitted into the urban environment (Baumbach et al., 1995; McCormack and Schüz, 2012; Hashim and Boffetta, 2014). This is because such rapid urbanization, and growth in urban economic activities are often accompanied by an increasing use of old vehicles, and motor-bikes, traffic jams, increased open burning of municipal waste, use of obsolete generators (to produce electricity), all consequentially leading to increased emissions of PACs and exposure (Baumbach et al., 1995; McCormack and Schüz, 2012; Amegah and Jaakkola, 2014; Feldt et al., 2014; Garcia et al., 2014; Hashim and Boffetta, 2014). Residents of West African cities are exposed to higher levels of traffic related environmental chemicals because of the above factors and the high number of citizens whose residencies and businesses (shops) are located at close proximity to streets, the ever present issue of street vendors, selling of food near streets and gardens near streets (Baumbach et al., 1995; Amegah and Jaakkola, 2014; Proietti et al., 2014). Extracts of PM sampled from several West African cities induced adverse effects in human lung cells. Residents

of the West African city of Cotonou, Benin showed high levels of biomarkers (of PAH exposure) in their blood and urine samples (Fanou et al., 2006; Ayi-Fanou et al., 2011; Dieme et al., 2012; Cachon et al., 2014). The biomarker concentrations in residents of these African cities were in several cases much higher than in samples from residents of rural areas (in the same country) and higher than in residents of the developed Western European cities (Tuakuila et al., 2013; Val et al., 2013; Feldt et al., 2014). Enhanced toxicity of PM from African cities and higher biomarkers in samples from urban dwellers of African cities could be a result of higher concentrations or a different composition pattern of the PACs in the environmental samples from African urban areas compared to the rural areas and Western locations. Higher concentrations and different composition patterns could be because of differences in emission sources/characteristics or because of tropical environmental factors (more intense sunlight, heat and microbial activity) causing enhanced post emission transformation of the PAHs into more toxic derivatives such as OPAHs and nitrated-PAHs (Smith et al., 1995; Panther et al., 1999; Bandowe et al., 2014 b, c). The few studies that has characterized PACs in street dusts, PM, and soils from urban areas of sub-Saharan African Countries have concentrated on PAHs (mostly US-EPA PAH) (Ayi-Fanou et al., 2011; Dieme et al., 2012; Cachon et al., 2014; Botey-Sam et al., 2014; Bortey-Sam et al., 2015) and hence do not fully characterize the range of toxicologically relevant PACs (Bandowe et al., 2014 a,b,c; Andersson and Achten, 2015).

The objectives of this study are:

1. To characterize the PAHs, OPAHs and AZAs content of street dust from a major West African metropolis
2. To use the concentration and composition pattern to identify the sources of PAC contamination in this urban area
3. Determine the role of traffic by studying the enrichment of PACs in road dust relative to soil from same city
4. Compare the ratios OPAH/parent-PAH,

azaarene/parent-PAH) from this tropical city to other published values in the literature 5. Estimate the cancer risk to the urban population due to the PAC content of street dust in this city. The study site for this project is Kumasi which is a major and historic West African Metropolis, the seat of the Ashanti Kingdom and the capital of the Ashanti Region of Ghana. Kumasi is the second largest metropolis in Ghana. It is centrally located on the map of Ghana (Figure 1) and acts as nodal city with major arterial routes linking it to other parts of the country and the West African sub-region (Kumasi Metropolitan Assembly, 2015). Kumasi is a major commercial centre in Ghana and the West African Sub-region. Kumasi occupies a land surface area of 254 km² with total human population 2,035,064 in 2010 (Ghana Statistical Service, 2012; Ministry of Food & Agriculture, Ghana, 2015). The climate of Kumasi is described as tropical wet and dry (with sub-equatorial rainfall pattern). The average minimum and maximum temperature is 21.5°C and 30.7°C, respectively. The average relative humidity of 84.16 % at 0900 GMT and 60 % at 1500 GMT; and double peak rainfall in June (214.3 mm) in and September (165.2 mm) (Kumasi Metropolitan Assembly, 2015, Ministry of Food & Agriculture, Ghana, 2015).

Figure 1

2. Materials and Methods

2.1 Sampling

Sampling sites were randomly chosen from the 10 sub-metros (districts) within the Kumasi metropolis. Classification of sites, according to the main activity (such as commercial, recreational, residential, bus terminal, education institution and garage for sale auto spare parts, is shown in Table 1. The GPS coordinates (Table 1) for sampling sites were taken and have been shown in Figure 1.

Table 1

The Random sampling technique was adopted in this study. Street dust was sampled using a brush and a pan. Approximately 20 g of the dust particles accumulated on impervious surfaces of the pavement and road within a 5 m radius circle were collected using plastic brushes and dustpans by gentle sweeping motion to collect fine particulates. After each sampling, brushes and dustpans were cleaned with paper towels. Stones, fibers, leaves and other large particles were physically removed from the sampled street dust. All samples were stored in paper bags wrapped with solvent-rinsed aluminum foil and then sealed in polyethylene bags (Ziploc) for transport to the laboratory. The samples were air dried to constant weight and sieved through a 250 μm mesh.

2.2 Analysis of PAHs, OPAHs and AZAs

Between 1 to 2 g of each sample of street dust was weighed and mixed with about 8-10 g bulk sorbent (Isolute HM-N, Biotage, Upsalla, Sweden) before being transferred into 33 mL extraction cells of an accelerated solvent extractor (ASE 200, Dionex, Sunnyvale, CA, USA). Each street dust sample, reference material or blank weighed into the ASE cell, was then spiked with 750 ng of deuterated-PAH mixture (75 μL of 10 $\mu\text{g mL}^{-1}$ of naphthalene- D_8 , acenaphthene- D_{10} , anthracene- D_{10} , pyrene- D_{10} , chrysene- D_{12} , and benzo[g,h,i]perylene- D_{12}), 75 μL of 20 $\mu\text{g mL}^{-1}$ deuterated OPAH mixture (benzophenone- D_5 , 9,10-anthraquinone- D_8) and 75 μL of 20 $\mu\text{g mL}^{-1}$ carbazole- D_8 as internal standard for PAHs, OPAHs and AZAs, respectively. Each sample was extracted in 2 cycles by pressurized liquid extraction with the ASE-200. The instrumental parameters of the ASE used during the extraction were temperature: 120°C, heating time: 6 mins, pressure: 14 MPa; static extraction time: 5 mins; flush volume: 60%; purging time: 1.5 mins;

purging gas: N₂. The first extraction cycle was with dichloromethane (DCM) and the second was with acetone (AC): DCM: 1% trifluoroacetic acid, 250:125:1 v/v/v). The extraction solvents and instrumental parameters of the ASE were same as used in earlier work (Bandowe and Wilcke, 2010; Bandowe et al., 2011; Lundstedt et al., 2014).. The two extracts from each sample were combined, filtered through Na₂SO₄ to dry and partially clean them. Hexane (10 mL) was added to each extract, and rotary evaporated (at 35 °C and 250 MPa) to < 1 mL. Glass columns (8 mL) filled with 3 g of silica gel (10 % deactivated), were prepared and rinsed with 10 mL hexane. Each extract was then transferred onto a separate column for further purification and fractionation. The columns were sequentially eluted with [i] 15 mL hexane: DCM (5:1, v/v) and [ii] 20 mL DCM. The eluates [i] and [ii] from each sample were combined and concentrated to about 500 µL after adding 3 drops of toluene as keeper. Fluoranthene-D₁₀ (25 µL of 20 µg mL⁻¹) was spiked to each extract (as recovery standard for deuterated internal standards) before being transferred into a 1.5 mL vials for gas chromatographic-mass spectrometric (GC-MS) measurements.

The concentrations of the following PAHs: naphthalene [NAPH], 2-methylnaphthalene [2-MNAPH], 1-methylnaphthalene [1-MNAPH], biphenyl [BP], 1,3-dimethylnaphthalene [1,3-DMNAPH], acenaphthylene [ACENY], acenaphthene [ACEN], fluorene [FLUO], phenanthrene [PHEN], anthracene [ANTH], 4H-Cyclopenta[def]phenanthrene, 1-methylphenanthrene [1-MPHEN], 3,6-dimethylphenanthrene [3,6-DMPHEN], fluoranthene [FLUA], pyrene [PYR], retene (RET), benzo[a]anthracene [B(A)A], chrysene + triphenylene [CHRY], benzo[b+j+k]fluoranthenes [B(BJK)] benzo[e]pyrene [B(E)P], benzo[a]pyrene [B(A)P], perylene [PERY], indeno [1,2,3-cd]pyrene (IND), dibenzo[a, h] anthracene [DIBE], benzo[g,h,i]perylene [B(GHI)], OPAHs: 1-indanone [1-INDA], 1-naphthaldehyde [NLD], 2-biphenylcarboxaldehyde

[2-BPCD], 9-fluorenone [9-FLO], 1,2-acenaphthenequinone [1,2-ACQ], 9,10-anthraquinone [9,10-ANQ], 4H-cyclopenta[d,e,f]phenanthrenone [CPHENone], 2-methyl-9,10-anthraquinone [2-MANQ], benzo[a]fluorenone [B(A)FLUone], 7H-benzo[d,e]anthracene-7-one [BANTone], benzo[a]anthracene-7,12-dione [7,12-B(A)A], naphthacene-5,12-dione [5,12-NACQ] and 6H-benzo[c,d]pyren-6-one [BPYRone]) and azaarenes: quinoline [QUI], benzo[h]quinoline [BQI], acridine [ACR] carbazole [CBZ]) were measured in each extract of street dusts, reference material and blanks. The concentrations of PAHs, OPAHs and AZAs were measured with an Agilent 7890A gas GC coupled to an Agilent 5975 C MS. One μL of each analyte was injected into the GC-MS in the splitless mode. The MS was operated in the electron impact ionisation mode at 70 eV with selected ion monitoring. A PAC target compound was only deemed to be positively identified in extracts when its retention time was within ± 0.2 min of the standard and the target-to-qualifier ion ratio within 20% of its ratio measured in the calibration standard. The concentrations of PAHs, OPAHs and AZAs are reported on dry weight basis. Further details of GC-MS instrumental parameters are described in earlier papers (Bandowe and Wilcke, 2010; Bandowe et al., 2011, Bandowe et al., 2014 b, c; Lundstedt et al., 2014)

2.3 Quality control and quality assurance

Solvents used during the analytical procedure were of pesticide residue or HPLC grade. All non-volumetric glassware and metallic lab ware were machine washed, and baked at 250°C for 24 hrs. Baked glasswares were rinsed several times with appropriate solvent before use. Several blanks ($n = 3$) made of inert bulk sorbent (Isolute HM-N) were extracted and treated in same way as samples. Their PAC content was also measured and their average mass was subtracted from the mass of PACs obtained in samples in order to correct for contaminations during sample

preparation. The recovery of the internal standards spiked to the samples (before extraction) was determined as further indicator of the accuracy of the analytical method. The average recovery of the deuterated internal standards used to quantify the polar PACs was 74 % (carbazole-D₈), 80 % (benzophenone-D₅) and 86 % for 9,10-anthraquinone-D₈. The average recoveries of deuterated PAHs ranged from 48% (naphthalene-D₈) to 67 % (benz[g,h,i]perylene-D₁₂). The relative standard deviation [RSD, %] of the replicate analysis of street dust (from Cathedral, n = 2) was 0.2 % for $\sum$ PAHs while those of individual PAHs were mostly < 10 %, except for perylene that showed a RSD of 22%, indicating high precision of the analytical procedure. The RSD for the $\sum$ OPAHs and $\sum$ AZAs concentrations in replicate street dust analyses were < 3 %. The RSD of individual OPAHs for the replicate analyses of street dust averaged 7% (range: 1-22%) and 6% (1-7%) for the AZAs. We extracted and analysed aliquots (n = 2) of a certified reference material (ERM-CC013a: Polycyclic Aromatic Hydrocarbons in Soil) obtained from the Federal Institute of Materials Research and Testing [BAM], Berlin Germany. The values obtained from our analyses were within the certified and indicator values provided by BAM. The recoveries of the sum of the concentrations of PAHs measured with our procedure were 98 % of the certified and indicator values. The measured concentrations of individual PAHs averaged 96 % (range: 53 – 152 %) of their individual certified and indicator values.

2.5 Calculations and data evaluation

The sum of the concentrations of all analysed PAHs, non-alkylated PAHs, 16 US-EPA PAHs, non-alkylated PAHs with 2-3 benzene rings, non-alkylated PAHs with 4-6 benzene rings, OPAHs and AZAs are referred to as $\sum$ alkyl+parent-PAHs, $\sum$ parent-PAHs, $\sum$ US-EPA PAHs, $\sum$ LMW-PAHs, $\sum$ HMW-PAHs, $\sum$ OPAHs, $\sum$ AZAs, respectively. The sum of B(A)A, CHRY, B(BJK),

B(E)P, B(A)P, IND, DIBE, B(GHI), COR, in each sample is referred to as the sum of combustion PAHs (Σ COMB-PAHs).

Concentration data were log (x+1) transformed to improve their normal distribution before statistical analyses were done. All statistical analysis was done with SPSS 19.0 (IBM Corp., Armonk, NY, USA). Statistical tests were deemed to be significant if $p < 0.05$.

The benzo[a]pyrene equivalent concentration $\Sigma[B(A)P]_{eq}$ due to PAHs in urban dust with toxicity equivalency factors (TEFs) was calculated using equation 1 below.

$$\Sigma B(A)P_{eq} = \sum_i (C_i \times TEF_i) \dots\dots\dots[1]$$

Where C_i (ng g⁻¹) is the concentration of the ith PAH in the street dusts. TEF_i of individual PAHs were taken from Nisbet and Lagoy, 1992. The Incremental lifetime cancer risk (ILCR) to the residents of Kumasi resulting from exposure to PACs bound to street dust taken from the three uptake routes (ingestion, dermal uptake and inhalation) was estimated using formulas below (equations 2, 3 and 4), which have been applied in previous studies (Wang et al., 2011; Tuyen et al., 2014; Wei et al., 2015).

$$ILCRS_{ingestion} = \frac{(\Sigma B(A)P_{eq}) \times (CSF_{ingestion} \times \sqrt[3]{\frac{BW}{70}}) \times IR_{ingestion} \times EF \times ED}{BW \times AT \times 10^6} \quad [2]$$

$$ILCRS_{dermal} = \frac{(\Sigma B(A)P_{eq}) \times (CSF_{dermal} \times \sqrt[3]{\frac{BW}{70}}) \times SA \times AF \times ABS \times EF \times ED}{BW \times AT \times 10^6} \quad [3]$$

$$ILCRS_{inhalation} = \frac{(\Sigma B(A)P_{eq}) \times (CSF_{inhalation} \times \sqrt[3]{\frac{BW}{70}}) \times IR_{inhalation} \times EF \times ED}{BW \times AT \times PEF} \quad [4]$$

Where carcinogenic slope factor (CSF) (mg/kg/day)⁻¹ is with values of 7.3, 25 and 3.85 for $CSF_{ingestion}$, CSF_{dermal} and $CSF_{inhalation}$ respectively. Body weight (BW in kg), exposure frequency (EF in day year⁻¹), exposure duration (ED in year), average life span (AT in year), inhalation rate

($IR_{\text{inhalation}}$ in $\text{m}^3 \text{ day}^{-1}$), dust ingestion rate ($IR_{\text{ingestion}}$ in mg day^{-1}), dermal exposure area (SA in cm^2), dermal adherence factor (AF in mg cm^{-2}), dermal adsorption fraction (ABS, unitless) and particle emission factor (PEF in $\text{m}^3 \text{ kg}^{-1}$). Calculations were made separately for Adults and Children using the parameters as specified in Table S1. The total ILCR is the sum of ILCR from the three routes of uptake.

3. Results and Discussion

3.1 Alkyl and parent-PAHs in street dusts

The Σ Alkyl+parent-PAHs concentration in street dusts averaged 2570 ng g^{-1} (range: $181\text{-}7600 \text{ ng g}^{-1}$), with the lowest concentrations in KNUST campus (campus of a University) and Ahinsan estate (gated residential area), and the highest concentrations in samples from Aboabo (a major road) and Suame magazine (minor street), (Figure 2, Table 1, Table S2).

Figure 2

The concentrations of individual PAHs ranged between 4 and 320 ng g^{-1} (Table S2). The finding that KNUST campus samples have the lowest concentrations could be attributed to the confined nature of the place and the less vehicular traffic that it is exposed to. The level of PAHs is consistent with previous works that measured concentrations of PAHs in soils and particulate matter (PM_{10}) sampled from several locations of Kumasi. Hence KNUST campus is classified as background (in terms of PAH contamination levels) in comparison to other locations in the city of Kumasi (Sam-Bortey et al., 2014; Sam-Bortey et al., 2015). We therefore calculated the enrichment in concentrations of PAHs in street dusts relative to the concentrations in background soils (as reported in Bortey-Sam et al., 2014) from Kumasi. Individual PAHs and some sums

(Figure 3) were enriched in street dust comparative to soils by magnitudes between 12 and 863 confirming traffic as a significant source of contamination of PAHs in the street dust. Furthermore this shows that compared to soils and even PM₁₀, street dust in Kumasi remains a significant source of exposure of the urban populations to potentially carcinogenic PAHs.

Figure 3

Samples from other gated areas like the Baba Yara Stadium (BYS) and the Kumasi High School (KHS) also had relatively low concentrations of PAH though slightly higher than that of KNUST (Figure 1 & 2). The high PAH concentration observed for the street dust from Suame Magazine (SMM) (Figure 1 & 2), can be attributed to the fact that a village for artisanal engineering in Ghana and the single largest cluster of artisans in the sub-Saharan Africa and artisans are involved in the sale of spare parts, vehicular repairs, maintenance, metal fabrication, welding, spraying etc. (Adeya, 2008). It was also observed that samples from residential areas collected from lanes or minor roads such as Pataase Estates (PAE), Asuoyeboah (ASY) and Ahinsan Estates (AHI) had lower PAH concentrations compared to a sample taken from the Danyame-Miklin Hotel (DMH) which is a major road connecting the residency to other parts of the city (Table 1). The highest level of total PAH observed for Aboabo (ABO), a major urban road connecting to other parts of the city and also other part of the region. It is one of the busiest roads in the metropolis experiencing huge vehicular traffic from the early hours (08:00 – 12:00) of the day to lunch time and after work (16:00). There also exists a wide range of economic activities on the roadside. Many previous studies have demonstrated that the PAH concentration of street dust are influenced by differences in source characteristics (eg. traffic density, type of cars, characteristics of neighbourhood where street is located, nature of road, speed of vehicles (Table 1;

Marr et al., 2004; Boonyatumanond et al., 2007; Lee and Dong, 2010, Wei et al., 2015). The results of the PAH and polar PAH (see later discussion) distribution in Kumasi is in-line with previous studies.

The PAHs concentration measured in Kumasi street dust samples is similar to those from cities in developing and tropical countries (eg Bangkok-Thailand, Lahore-Pakistan, Delhi-India, and Bangalore-India, Hanoi-Vietnam) but lower than those in China, Japan, North America and European Countries (Table 2).

Table 2

A possible explanation for higher concentration of PAHs in road dusts from cities in more industrialized temperate countries compared to the less industrialized mostly tropical countries might be a result of extra PAH contaminated particles deposited onto the roads by industries, household heating and higher intensity of traffic. Due to better public transport, more efficient traffic movement, use of newer more efficient automobiles, better vehicle emission control standards and better streets in the cities of developed countries of Europe, North America and Japan, it could be envisaged that traffic emissions (exhaust and non-exhaust vehicular) of PACs into street dust should be lower than those in cities of developing countries like Ghana. Hence the higher levels of PAHs in the street dust from developed Western countries as compared to the developing countries like Ghana (Table 2) might be explained by more intense household heating, industrial emissions current and legacy industrial production in these developed countries. Furthermore tropical climatic conditions in Kumasi are known to more intensively reduce the concentrations of emitted PAHs by photo degradation, thermal degradation and

photolysis and vaporization and long-range atmospheric transport (Smith et al., 1995; Panther et al., 1999; Mujumdar et al., 2012; Wei et al., 2015).

The alkyl and parent-PAH mixtures in street dust were dominated by PHEN, PYR, B(BJK), and NAPH with average contribution to the Σ alkyl+parent-PAHs of 12%, 11%, 11% and 8%, respectively (Figure 3). The HMW-PAH/LMW-PAHs averaged 2.5 (range: 1.5-6.1) suggesting the slight to major dominance of pyrogenic sources (originating from exhaust emissions of vehicles) on the PAH composition of street dusts.

Figure 4

The dominance of HMW-PAHs over LMW-PAHs, and individual PAHs like PHEN and PYR in street dusts has been observed in many previous studies on street dusts and their source materials (Rogge et al., 1993; Boonyatumanond et al., 2007; Liu et al., 2007; Tuyen et al., 2014; Yu et al., 2014; Wei et al., 2015). Non exhaust sources such as brake wear, asphalt, petroleum and oil emissions (originating from automobiles, motorbikes) might contain higher percentage of low molecular weight alkylated-PAHs while those originating from exhaust pipe emissions will contain higher percentage of higher molecular weight PAHs (Majumdar et al., 2012). The strong contribution of LMW-PAHs such as PHEN, 1-MPHEN and NAPH could therefore be an indication that other non-exhaust sources makes strong contributions to the overall PAH content in the street dust (Rogge et al., 1993; Boonyatumanond et al., 2007).

3.2 OPAHs and AZAs in street dusts

The $\sum$ OPAHs in street dust averaged 833 ng g^{-1} (range: 57- 4200 ng g^{-1}) with the KNUST again showing the lowest concentration and the highest from Aboabo (Major road), which is similar to the trend shown by the alkyl and parent-PAHs (Figure 5, Table S3).

Figure 5

The similar spatial trends of the concentrations of OPAHs and alkyl+parent-PAHs is further confirmed by their strong and significant positive correlation between $\sum$ OPAHs and $\sum$ Alkyl+parent-PAHs ($r = 0.96$, $p < 0.01$). Such spatial correlations have been previously reported in street dusts and particulate matter samples from Xi'an, China, and soil samples from Bratislava (Slovakia), Xi'an (China), Angren (Uzbekistan), Bangkok (Thailand) and even in background soils from North-South of Argentina (Bandowe et al., 2010, Bandowe et al., 2011; Bandowe et al., 2014 b, c; Wei et al., 2015). Such relationships are a strong indication of the co-emission of OPAHs together with PAHs from the various combustion sources (vehicular emissions) and non-exhaust sources. Their co-sorption to sorbents in the street dust and similar post emission fates is other explanation of their strong spatial correlations. The strong correlation between OPAHs and Alkyl+parent-PAHs might also suggest that a low proportion of OPAHs in street dust are formed from secondary transformation of PAHs or that the secondary transformation of PAHs to OPAHs is a 1:1 reaction. Both scenarios could lead to the strong positive correlations observed in this study (Alam et al., 2013; Wei et al., 2015). The drivers of the spatial distribution of OPAHs in Kumasi street dust are similar to that of PAHs.

The $\sum$ OPAHs concentrations in Kumasi street dust was again much lower than in street dusts from Xi'an (China, mean: 10620 ng g⁻¹, range: 2799-7824 ng g⁻¹), but similar to the average value of 3800 ng g⁻¹ measured street dust from Pasadena, USA (Rogge et al., 1993; Wei et al., 2015). Yu and Baumann, 1995 measured two OPAHs in street dust from various cities and highways in Germany (Table 2) with the sum of the two OPAHs averaging 2828 ng g⁻¹ (range: 68-23600 ng g⁻¹). The individual concentrations of the OPAHs measured in Kumasi street dust (Table S3) were in general lower than the concentrations of same compounds measured in Xi'an, and various cities and higher in Germany (Yu and Bauman, 1995). The composition pattern of OPAHs in Kumasi street dust was dominated by 9,10-ANQ (mean: 35%, range: 21-55%), B(A)FLUone (19%, 7-25%) and 9-FLO (16%, 4-42%) (Figure 6A). The dominance of 9,10-ANQ and 9-FLO in soils, urban dusts, atmospheric particulate matter and diesel particles (Walgraeve et al., 2010; Layshock et al., 2010; Bandowe et al., 2010, 2011, Wei et al., 2015).

Figure 6

The $\sum$ AZA concentrations averaged 73 ng g⁻¹ (range: 3-240 ng g⁻¹). The concentrations of $\sum$ AZA showed similar spatial distribution as the PAHs and the OPAHs (Figure 1 & 5, Table S3). The close spatial relationship is demonstrated by the strong positive correlation of $\sum$ AZAs with $\sum$ alkyl+parent-PAHs ($r = 0.94$, $p < 0.01$) and $\sum$ OPAHs ($r = 0.91$, $p < 0.01$). This again demonstrates that AZAs in street dust of Kumasi are of similar sources as PAHs and OPAHs. They are also co-sorbed together in street dust particulates making their fate and transport linked together hence their strong spatial correlations. The concentrations in Kumasi street dust are lower than those from Xi'an, China (Table 2). The AZA composition pattern in Kumasi street dust was dominated by CBZ (59%, 0-85%) followed by BQI (19%, 0-17%) (Figure 6 B), which

is different from the pattern in Xi'an street dust which was dominated by QUI followed by CBZ (Wei et al., 2015). However the dominance of CBZ is similar to the pattern observed in Bangkok urban soils (Bandowe et al., 2014b). The differences in composition pattern maybe determined by source differences.

The ratio of individual OPAHs to their related parent-PAH is a relevant parameter to assess the relative importance of OPAHs to their related parent-PAHs in environmental samples. Furthermore, this parameter can be a useful parameter to elucidate the role of secondary formation of OPAHs from their parent-PAHs (Alam et al., 2013; Wei et al., 2015). We found that 5 out of the 7 OPAH/parent-PAH ratios > 1 (range; 2-6) while CBZ/FLUO was the only AZA/parent-PAH with ratio > 1 (i.e. 1.8, Figure 7).

Figure 7

The ratio 9-FLO/FLUO and 9,10-ANQ/ANTH averaged 3.8 ± 1.0 and 1.4 ± 0.5 in street dust from Xi'an, China, which is lower than the 5.3 ± 5.1 and 6.3 ± 5.6 in the Kumasi street dust samples. In street dust from several locations in Germany, the 9,10-ANQ/ANTH averaged 5.9 ± 6.3 (Yu and Bauman, 1995). The 9,10-ANQ/ANTH in street dust from Pasadena, USA was 1.3 (Rogge et al., 1993). The average of BQI/PHEN, ACR/ANTH and CBZ/FLUO in Kumasi had values, which were higher than the average of 0.028, 0.10 and 0.81, respectively obtained in samples from Xi'an, China (Wei et al., 2015). The fact that the ratios of OPAHs/parent-PAHs is higher in Kumasi (tropical zone) than in Xi'an, China and Pasadena, USA (temperate zone) might be partly a result of the enhanced transformation of parent-PAHs to OPAHs because of tropical climatic conditions than in temperate zone (Smith et al., 1995; Bandowe et al., 2014b). This higher concentration of OPAHs and AZA relative to their parent-PAH has also been reported in air, soil,

diesel particulate matter samples, (Layshock et al., 2010; Bandowe et al., 2010; Bandowe et al., 2014 b,c) which demonstrate once more the need to include these compounds in monitoring programs. Their observed higher concentration, known higher water solubility, bioavailability and toxicity could lead them to having higher toxic effects, mobility and overall environmental impact than their parent-PAHs and therefore the need to be included in monitoring programs (Andersson and Achten, 2015).

3.3 Cancer risk assessment

The $\Sigma B(A)P_{eq}$ averaged 118 ng g⁻¹ (range: 5-532) with the lowest occurring in KNUST campus samples and the highest occurring in Asawase Methodist (Table 3).

Table 3

These $\Sigma B(A)P_{eq}$ values are higher than the values of 1.2 ng g⁻¹ in KNUST Botanical garden soils but comparable to the 188 ng g⁻¹ for the five most polluted soils in Kumasi Metropolis (Sam-Bortey et al., 2014). This indicates that the street dust serves as a significant source of exposure to carcinogenic PAHs compared to soils. Samples from Xi'an, Guangzhou, and Tianjin all mega cities in China showed mean $\Sigma B(A)P_{eq}$ 1150, 2763, 4554 ng g⁻¹ indicating significantly higher potentially carcinogenic effects from PAHs in street dusts from China, compared to Ghana. The total incremental lifetime cancer risk (ILCR) for an adult resident of Kumasi averaged 2×10^{-4} (range: 9.6×10^{-6} to 9.5×10^{-4}) with the lowest in KNUST and Ahinsan Estate Residential Areas while the highest was Asawase Methodist street dust (Table 3). The total ILCR for children averaged was smaller averaging 8.5×10^{-5} (range: 3.9×10^{-6} to 3.8×10^{-4}). National and international regulatory agencies delineated ILCR value $\leq 10^{-6}$, 10^{-6} to 10^{-4} , and $> 10^{-4}$ as

corresponding to negligible risk, potential risk and high risk of cancer, respectively (Chen and Liao, 2006; Wei et al., 2015). The ILCR values obtained for this work indicate that exposure of both adults and children to urban dust from Kumasi could lead to potential and high cancer risk.

4. Conclusions

The concentrations of PAHs in street dust from Kumasi, Ghana were comparable to those of mega cities in other tropical developing countries but lower than those in cities from developed temperate regions and China. The concentrations of OPAHs and AZAs were strongly correlated with those of PAHs indicating similar sources, fate and co-transport. The concentrations of several individual OPAHs and AZAs were higher than those of their related PAHs indicating potentially higher toxic and environmental effects given the known higher toxicity and mobility of some of the OPAHs and AZAs than their related PAHs. The incremental lifetime cancer risk (ILCR) due to PAH concentrations in street dust of Kumasi was $> 10^{-6}$ in many of the samples indicating a high probability of cancer from exposure to these urban dusts. The concentrations of OPAHs and AZAs in street dust were significant and sometimes higher than the concentrations of parent-PAHs. The OPAHs, AZAs and most alkyl-PAH were not accounted for in the evaluation of cancer risks because they have no TEF values. However, their high concentrations, and higher toxicity (than some parent-PAHs) suggest a significant underestimation of the ILCR from exposure to these street dusts.

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Table 1: Sampling location and characteristics

Sampling site	Abbreviation	GPS Coordinates	Nature of Street	Activity
Aboabo	ABO	N06°42.058,W001°35.787	Major urban road	Diverse
Ahinsan	AHI	N06°40.017,W001°35.157	Lane	Residential
Ahodwo Melcom	AME	N06°39.762,W001°37.055	Major road	Diverse
Asafo Market	ASM	N06°41.235,W001°36.938	Major	Commercial
Asawase	AMC	N06°42.145,W001°36.445	Minor	Diverse
Asuoyeboa	ASY	N06°41.740,W001°40.277	Minor	Diverse
Ayigya Market	AYM	N06°41.392,W001°34.386	Minor	Diverse
Baba Yara Stadium	BYS	N06°41.005,W001°36.359	Pavement	Recreational
Bantama (Metro bus terminal)	BMT	N06°42.464,W001°38.354	Bus terminal	Bus terminal
Cathedral	CTD	N06°41.711,W001°37.122	Major	Diverse
Central Market	CNM	N06°41.778,W001°37.236	Major	Commercial
Dechemso	DCS	N06°42.799,W001°36.135	Minor	Diverse
KNUST Campus 1	KNU 1	N06°40.434,W001°34.255	Steet in gated compound	University campus
KNUST Campus 2	KNU 2	N06°40.434,W001°34.255	Steet in gated compound	University campus
KNUST Campus 3	KNU 3	N06°40.434,W001°34.255	Steet in gated compound	University campus
Kumasi High School	KHS	N06°39.685,W001°34.785	Steet in gated compound	School
Kwadaso SDA	KWS	N06°41.926,W001°39.535	Steet in gated compound	School
Manhyia	MAH	N06°42.215,W001°36.765	Minor	Diverse
Danyame (Miklin Hotel)	DMH	N06°40.487,W001°38.420	Major	Residential
Old Tafo	OLT	N06°44.330,W001°36.475	Major	Diverse
Patase Estate	PAE	N06°41.316,W001°38.995	Main Street	Residential
Suame Magazine Minor Street	SMS	N06°43.410,W001°37.899	Minor	Garage for sale of auto spare parts
Suame Magazine Front of Shop	SMC	N06°43.437,W001°37.931	Lane	Garage for sale of auto spare parts
Suame water Works	SWW	N06°42.743,W001°37.686	Major	Diverse
Wesley College	WC1	N06°42.854,W001°37.492	Steet in gated compound	College campus

Table 2: Comparison of concentrations of PACs in Kumasi street dust to other locations

Location	Typology	Number of PAHs	Σ PAHs [ng g ⁻¹]	Reference
PAHs				
Kumasi, Ghana	Urban	28	2571 (181-7770)	This study
Birmingham, UK	Urban	16	12560-93700	Smith et al., 1995
Newcastle, UK	Urban, industrial	16	590-46000	Lorenzi et al., 2011
Several cities, Germany	Urban, highways	39	3100-21600	Yang and Baumann, 1995
Pasadena, USA	Urban	23	58680	Rogge, 1993
Tokyo, Japan	Urban	34	1400-26000	Takada et al., 1991
Lahore, Pakistan	Urban	16	120-1000	Smith et al., 1995
Bangkok, Thailand	Urban	10	1100	Boonyatumanond et al. 2007
Dalian, China	Urban	25	7460 (1890-17070)	Wang et l., 2009
Guangzhou, China	Urban	16	4800 (840-12300)	Wang et al., 2011
Tianjin, China	Urban	16	538-34300	Yu et al., 2014
Xi'an, China	Urban	29	15767(10422-26258)	Wei et al., 2015
Hanoi, Vietnam	Urban	22	1900 (530-4700)	Tuyen et al., 2014
Bangalore, India	Urban	22	1100 (670-1800)	Tuyen et al., 2014
New Delhi, India	Urban	22	1100 (650-1700)	Tuyen et al., 2014
Niteroi, Brazil	Urban	21	434-1247	Pereira Netto et al., 2006
OPAHs				
	Typology	Number of OPAHs	Σ OPAHs [ng g ⁻¹]	
Kumasi, Ghana	Urban	10	833 (57-4202)	This study
Several cities, Germany	Urban, highways	2	2828 (68-23600)	Yang and Baumann, 1995
Pasadena, USA	Residential	8	3830	Rogge, 1993
Xi'an, China	Urban	15	10620 (2799-7824)	Wei et al., 2015
AZAs				
	Typology	Number of AZAs	Σ AZAs [ng g ⁻¹]	
Kumasi, Ghana	Urban	4	73 (3-240)	This study
Dubendorf, Switzerland	Urban	23	4610	Wakeham, 1979
Xi'an, China	Urban	4	673 (440-1171)	Wei et al., 2015

Table 3: Estimated incremental lifetime cancer risk due to exposure to street dust from Kumasi

	$\sum B(A)P_{eq}$ [ng g ⁻¹]	ILCR: Child				ILCR: Adult			
		Ingestion	Dermal	Inhalation	Total ILCR	Ingestion	Dermal	Inhalation	Total ILCR
Minimum	5	1.7E-06	2.2E-06	6.7E-12	3.9E-06	3.4E-06	6.1E-06	2.7E-10	9.6E-06
Maximum	532	1.07E-05	2.1E-04	6.6E-10	3.8E-04	3.4E-04	6.1E-05	2.6E-8	9.5E-05
Mean	118	3.8E-05	4.7E-05	1.5E-10	8.5E-05	7.6E-05	1.3E-04	5.9E-9	2.1E-04

Figure Captions

Figure 1: Map of Kumasi indicating sampling locations

Figure 2: Concentrations [ng g^{-1}] of $\sum$ Alkyl+parent-PAHs in street dust from Kumasi, Ghana

Figure 3: Enrichment of Alkyl and parent-PAHs in street dust relative to soils from Kumasi, Ghana

Figure 4: Composition pattern of Alkyl and parent-PAHs mixtures in street dust from Kumasi, Ghana

Figure 5: Concentrations [ng g^{-1}] of $\sum$ OPAHs [A] and $\sum$ AZAs [B] in street dust from Kumasi, Ghana

Figure 6: Composition pattern of OPAH [A] and AZA [B] mixtures in street dust from Kumasi, Ghana

Figure 7: Derivative to their parent-PAH ratios in street dust from Kumasi, Ghana

[illegible]

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7