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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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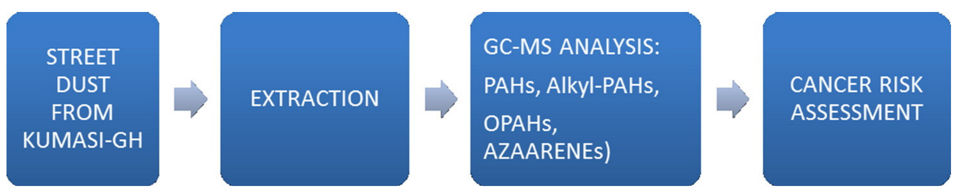
HIGHLIGHTS

- Polycyclic aromatic compounds in street dusts of Kumasi, Ghana are characterized
- Oxygenated PAHs and azaarenes are strongly correlated with PAHs
- PAHs are highly enriched in street dust compared to background soils
- Concentrations of several oxygenated PAHs and azaarenes are higher than related PAHs
- Incremental lifetime cancer risk due to PAHs in street dust is $>10^{-6}$

GRAPHICAL ABSTRACT



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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: 181–7600 ng g^{-1}), 833 ng g^{-1} (57–4200 ng g^{-1}) and 73 ng g^{-1} (3.3–240 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.

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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 et al., 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; Lundstedt et al., 2007; Misaki et al., 2007; Umbuzeiro et al., 2008; Wang et al., 2011a, 2011b; Andrysik et al., 2011; Lübcke-von Varel 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; Oda et al., 2001; Amato et al., 2011; Majumdar et al., 2012; Pant and Harrison, 2013; 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 run-off into the aquatic environment (Krein and Schorer, 2000; Martuzevicius et al., 2011; Majumdar et al., 2012; Pant and Harrison, 2013). 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 of urban populations to these toxic chemicals (Majumdar 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 venders, 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 (Ayi 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 (Tukuila 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., 2014b, 2014c). 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; Bortey-Sam et al., 2014; Bortey-Sam et al., 2015) and hence do not fully characterize the range of toxicologically relevant PACs (Bandowe et al., 2014a, 2014b, 2014c; 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 identity 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 (Fig. 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 km^2 with total human population 2,035,064 in 2010 (Ghana Statistical Service, 2012; Ministry of Food, and 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, and Agriculture, Ghana, 2015).

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 Fig. 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