



Determination of semi-volatile and particle-associated polycyclic aromatic hydrocarbons in Stockholm air with emphasis on the highly carcinogenic dibenzopyrene isomers



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HIGHLIGHTS

- Determination of PAH levels in the gas phase and various particle size fractions.
- Focus on the seldom determined but highly carcinogenic dibenzopyrene isomers.
- PM₁₀ PAH levels in the order street level > urban background > rural background.
- Higher PAH levels in PM₁ than in PM₁₋₁₀.
- Benzo[*a*]pyrene and dibenzopyrene levels highly correlated.

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ABSTRACT

The concentrations of polycyclic aromatic hydrocarbons (PAHs) have been determined in the gaseous phase and in various particulate matter (PM) size fractions at different locations in and outside of Stockholm, Sweden, representative of street level, urban and rural background. The focus has been on the seldom determined but highly carcinogenic dibenzopyrene isomers (DBPs) dibenzo[*a,l*]pyrene, dibenzo[*a,e*]pyrene, dibenzo[*a,i*]pyrene and dibenzo[*a,h*]pyrene. PAHs with 3 rings were found to be mainly associated with the vapor phase (>90%) whereas PAHs with 5–6 rings were mostly associated with particulate matter (>92%) and the 4-ringed PAHs partitioned between the two phases. PAH abundance was determined to be in the order street level > urban background > rural background with the PM₁₀ street level 2010 mean of benzo[*a*]pyrene (B[*a*]P) reaching 0.24 ng/m³, well below the EU annual limit value of 1 ng/m³. In addition, higher PAH concentrations were found in the sub-micron particle fraction (PM₁) as compared to the super-micron fraction (PM₁₋₁₀) with the abundance in PM₁ varying between 57 and 86% of the total PAHs.

The B[*a*]P equivalent concentrations derived for DB[*a,l*]P and total DBPs exceeded 1–2 and 2–4 times, respectively, that of B[*a*]P at the four sampling sites; therefore underestimation of the cancer risk posed by PAHs in air could be made if the DBPs were not considered in risk assessment using the toxic equivalency approach, whilst the high correlation ($p < 0.001$) found in the relative concentrations supports the use of B[*a*]P as a marker substance for assessment of the carcinogenic risk associated to PAHs. However, the big difference in concentration ratios of B[*a*]P and the DBPs between the present study and some literature data calls for further research to evaluate the temporal and spatial invariance of the B[*a*]P/DBP ratios.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) constitute a vast group of omnipresent environmental pollutants formed primarily by incomplete combustion of organic matter (Kim et al., 2013). PAHs are present in ambient air both in the gaseous phase and associated with particulate matter (PM). The partitioning between the different phases is depending on factors such as vapor pressure of the compound, precipitation, temperature, humidity and the nature and amount of the PM present (Baek et al., 1991; Srogi, 2007). As a rule of thumb, generally two and three ringed PAHs are mostly found in the gas phase whereas five-ringed or larger PAHs are mainly associated with air PM (Baek et al., 1991; Srogi, 2007). PAHs are considered to potentially play a significant role in the adverse human health outcomes of exposure to air pollution (Boström et al., 2002; De Kok et al., 2006; Kim et al., 2013). Benzo[*a*]pyrene (B[*a*]P) is the most studied PAH and the only one that has been classified by the International Agency for Research on Cancer (IARC) as carcinogenic to human beings (IARC, 2010). However, other PAHs are known to be animal carcinogens and some are suspected to be carcinogenic to humans (IARC, 2010). Recently, attention has been focused on the four dibenzopyrene isomers (DBPs) dibenzo[*a,l*]pyrene (DB[*a,l*]P), dibenzo[*a,e*]pyrene (DB[*a,e*]P), dibenzo[*a,i*]pyrene (DB[*a,i*]P) and dibenzo[*a,h*]pyrene (DB[*a,h*]P) due to their high carcinogenic activities in animal experiments (IARC, 2010). This is especially relevant for DB[*a,l*]P, which is the PAH that has displayed the highest cancer potency in rodent models (Luch, 2005). Even though the DBPs have shown to be strong carcinogens, very few studies have been published on their concentrations in air. Although most toxic PAHs are associated with the particulate phase (such as B[*a*]P and the DBPs), some PAHs occurring in the gaseous phase are also of concern for human health. Phenanthrene (Phe), methylated phenanthrenes/anthracenes, pyrene (Py) and fluoranthene (Fl) are suggested to be measured in air as they are present at relatively high concentrations (Boström et al., 2002). Fl exhibits experimental carcinogenicity, and it has been suggested as an indicator complementary to B[*a*]P to assess the carcinogenic risk of PAHs in ambient air (Boström et al., 2002). Furthermore, anthracene, Phe, Fl and Py are listed as Priority Pollutants by the United States (US) Environmental Protection Agency (EPA) and are considered in the Toxicological Profile for PAHs by the Agency for Toxic Substances and Disease Registry (ATSDR) at the US Department of Health and Human Services (ATSDR, 1995; USEPA, 2013). The assessment of the relative cancer risk of each PAH compared to B[*a*]P can be made by using the so called toxic equivalency factor (TEF) approach in which the concentration of a PAH in air is multiplied with its cancer potency relative to B[*a*]P (TEF value) to obtain the B[*a*]P equivalent concentration (B[*a*]Peq). Another method for risk assessment is to use B[*a*]P as a marker substance for the carcinogenicity of the complex PAH mixture in urban air (Boström et al., 2002; Pufulete et al., 2004). The European Union (EU) has adopted this strategy and set a limit value of 1 ng/m³ as annual mean in the PM₁₀ fraction (EU, 2004).

Previous studies have reported the DBPs to make a major contribution to the cancer risk of PAHs in ambient air, concluding that risk assessment using TEFs could underestimate the risk if the DBPs are not included in monitoring studies (Bergvall and Westerholm, 2007; Layshock et al., 2010; Delgado-Saborit et al., 2011; Jia et al., 2011; Slezakova et al., 2011; Wei et al., 2011; Menichini and Merli, 2012; Ahmed et al., 2015). However, most of these studies reports data from only short periods of a year with only two studies presenting yearly average concentrations (Delgado-Saborit et al., 2011; Menichini and Merli, 2012).

Menichini and Merli found the concentrations of B[*a*]P and the DBPs at a street site in Rome over one calendar year to be highly correlated, suggesting that this could indicate.

B[*a*]P to be a suitable marker also for the DBPs should their results be confirmed in other studies at sites affected by various emission sources (Menichini and Merli, 2012).

The aim of this study was to measure the concentrations of semi-volatile and particulate associated PAHs in Stockholm air to assess the gas/particulate partitioning and further to increase the knowledge on the temporal variations of the DBPs over of a year at sites representing street level, urban and rural background and to evaluate the implications of the obtained DBP concentrations for the commonly used carcinogenic risk assessment approaches.

2. Experimental

2.1. Sampling

Sampling was conducted at four different sampling locations: university campus (N 59.36561, E 18.05941), rural background (N 58.80584, E 17.38832), urban background (N 59.31605, E 18.05785) and street level (N 59.31728, E 18.04984).

Collection of semi-volatile PAHs and particulate associated PAHs was performed at the university on the rooftop of the Arrhenius chemistry building at the Stockholm University main campus (ca 4 km North of the city center) from October to December 2012 as well as from May to June and from September to December 2013. The sampling site was previously used for PM collection to measure PAHs (Bergvall and Westerholm, 2007; Jarvis et al., 2013; Umbuzeiro et al., 2014). Two sampling systems were used, each equipped with a filter (upstream in the sampling train) for the collection of the PM (total suspended matter, TSP) followed by PUFs for the collection of the semi-volatile fraction; a flow meter and a pump completed each of the samplers. The sampling volume ranged from 196 to 590 m³ with an average value of 304 m³ and the flow through the pumps was adjusted in order to avoid PAH breakthrough of the PUFs. The filters used were of two types, glass microfibre filters ($\varnothing = 149$ mm, EPM2000, Whatman, UK) or fluorocarbon coated glass fibre filter ($\varnothing = 235$ mm and 149 mm, Fiberfilm Filters, Pallflex, Pall Corporation, Putnam, CT, USA). The sorbent train comprised 3 PUFs ($\varnothing = 70$ mm, $l = 25$ mm, $\rho = 0.023$ g/cm³, Special-Plast Produktion, Vallentuna, Sweden) of polyether type, as recommended by the US EPA in the Method TO-13 A (USEPA, 1999).

PM representing rural background was collected at the Aspveten background station (Tunved et al., 2004). The station is located about 80 km southwest of Stockholm and is representative of the regional background in mid Sweden and not influenced by local anthropogenic activities (Tunved et al., 2003). The Hornsgatan street level sampling station is located on a 24-m wide, four-lane street (ca 30,000 vehicles/day) in the city center of Stockholm (Krecl et al., 2011). The street is a canyon, with 24 m high buildings on both sides. The sampler was located on the north side with the air intake at 3 m height (about 2 m from the façade of the nearest building). The urban background rooftop measurements (25 m above the streets), some 500 m east of Hornsgatan, represents urban background air in central Stockholm (Gidhagen et al., 2005).

Sampling of PM was performed simultaneously at the rural background, urban background and at the street level sampling sites during February to May and August to December 2010 as well as March to May 2011. Sampling was conducted using glass microfibre filters ($\varnothing = 47$ mm, GF/C, Whatman, UK); low volume samplers were used, equipped with PM₁₀ size selective heads and operating at 17 L/min flow rates (Hopke et al., 1997), except for rural background in the 2010 spring campaign, where a high volume device was adopted to collect TSP on glass microfibre filters ($\varnothing = 149$ mm, EPM2000, Whatman, UK) at 500 l/min.

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