Chemosphere 155 (2016) 70–85

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Distribution patterns, infiltration and health risk assessment of PM2.5-bound PAHs in indoor and outdoor air in cold zone

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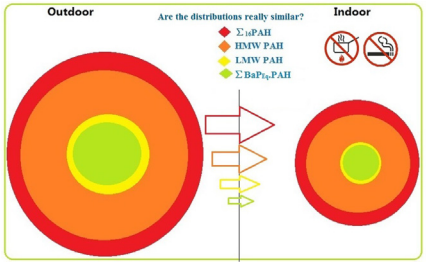
HIGHLIGHTS

- People are exposed to a varying degree to PAHs in different microenvironments.
- Simultaneous measurements of indoor and outdoor PAHs is essential for risk assessment.
- The PAH exposure is negatively influenced by temperature and wind speed.
- Absence of smoking and cooking may lead to similarity in PAH distribution patterns.
- LDA and estimation of outdoor-generated PAHs confirmed each other.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 February 2016
Received in revised form
29 March 2016
Accepted 6 April 2016
Available online 22 April 2016

Handling Editor: Ralf Ebinghaus

Keywords:
Linear discriminant analysis
PAHs' infiltration into indoors
Simultaneous measurements
Particulate phase
Diurnal variability
Cold area

ABSTRACT

In this study we investigated the distribution patterns, infiltration and health risk assessment of PM2.5-bound PAHs in indoor and outdoor air done in Harbin city, northeastern China. Simultaneous indoor and outdoor sampling was done to collect 264 $PM_{2.5}$ samples from four sites during winter, summer, and spring. Infiltration of PAHs into indoors was estimated using Retene, Benzo [*ghi*]perylene and Chrysene as reference compounds, where the latter compound was suggested to be a good estimator and subsequently used for further calculation of infiltration factors (IFs). Modeling with positive matrix factorization (PMF5) and estimation of diagnostic isomeric ratios were applied for identifying sources, where coal combustion, crop residues burning and traffic being the major contributors, particularly during winter. Linear discriminant analysis (LDA) has been utilized to show the distribution patterns of individual PAH congeners. LDA showed that, the greatest seasonal variability was attributed to high molecular weight compounds (HMW PAHs). Potential health risk of PAHs exposure was assessed through relative potency factor approach (RPF). The levels of the sum of 16 US EPA priority PAHs during colder months were very high, with average values of 377 ± 228 ng m^{-3} and 102 ± 75.8 ng m^{-3}, for the outdoors and indoors, respectively. The outdoor levels reported to be 19 times higher than the outdoor concentrations during warmer months (summer + spring), while the indoor concentrations were

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http://dx.doi.org/10.1016/j.chemosphere.2016.04.023

suggested to be 9 times and 10 times higher than that for indoor summer (average 11.73 ± 4 ng m^{-3}) and indoor spring (9.5 ± 3.3 ng m^{-3}). During nighttime, outdoor PAHs revealed wider range of values compared to datytime which was likely due to outdoor temperature, a weather parameter with the strongest negative influence on $\sum_{16}$PAHs compared to low impact of relative humidity and wind speed.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are classes of organic compounds generated mainly by four mechanisms; combustion, pyrolysis and pyrosenthysis of organic materials (Furton and Pentzke, 1998)) and by diagenetic processes (Orecchio et al., 2010). Sixteen of PAHs are classified by US. EPA as priority pollutants (Henry et al., 1995; Furton and Pentzke, 1998; Pergal et al., 2013; Vejerano et al., 2013). Among these priority PAHs, Benzo(a) pyrene (BaP) is considered the main marker for assessing PAH-related cacinogenicity (Boström et al., 2002), therefore, it has received special attention recently (Allen et al., 1998; Chiu et al., 2011; Han et al., 2011; Kong et al., 2012). BaP in the outdoor air is well regulated by European union (BaP in PM10 set at 1 ng m^{-3}) (San José et al., 2013), and in the chinese air quality standards, where the daily mean concentration of BaP was set at 10 ng m^{-3} (Ding et al., 2012). The potential carcenogenicity is most likely to be related to PAHs of high molecular weight (HMW PAHs) mainly in fine particles (PM2.5) rather than low molecular weight (LMW PAHs) commonly detected in high levels in the vapour phase in the atmosphere (Harrison et al., 1996; Allen et al., 1998; Boström et al., 2002; Shen et al., 2013a; Jiang et al., 2014).

PAHs are generally emitted from a wide range of sources such as coal, oil, biomass (Orecchio et al., 2016) combustion (Orecchio, 2011) and natural sources (Shakya and Griffin, 2010; Gupta et al., 2011). During the last 30 years, biomass burning followed by on-road vehicle emissions suggested to be the greatest contributors to PAHs in the air (Shen et al., 2013b). The incomplete combustion of fossil fuel and biomass could increase the atmospheric levels of PAHs (Usenko et al., 2010; Zhang et al., 2011; Shen et al., 2013a, 2013b). PAHs are also found naturally in some materials such as coal and oil (Barnes et al., 2012). Weather parameters such as ambient temperature, solar radiation, relative humidity, and wind are all considered essential factors influencing the trends of PAHs in the atmosphere (Barrado et al., 2012; Melymuk et al., 2014; Kim et al., 2015).

On the national scale, there has been a growing concern in China about PAHs' emissions from burning of agricultural wastes (Liu et al., 2007; Zhou et al., 2008; Yang et al., 2010; Chiu et al., 2011; Zhu et al., 2014), household combustion of wood (Orecchio et al., 2016), and coal for cooking (Liu et al., 2007; Yang et al., 2010; Han et al., 2011; Wang et al., 2011b). In Northeast China, results of previous studies showed elevated levels of ∑PAHs bound to atmospheric particle in winter than in other seasons that attributed mainly to weather conditions that lead to accumulation of pollutants in the air, and to biomass burning and the nationwide use of coal in heating, power generation (Feng et al., 2007; Guo et al., 2009; Wang et al., 2011b; Zhu et al., 2014). For other parts of China, the seasonal trends of particle-bound ∑PAHs are different than that for north China, with overall lower PAHs concentrations compared northern China (Zhou et al., 2008; Yang et al., 2010; Chiu et al., 2011; Hu et al., 2012).

Studying indoor and outdoor PAHs through simultanous measurments is suggested to be essential for several reasons. Firstly, during the last three decades (1984–2014), critical review of studies on indoor levels of PAHs (Ma and Harrad, 2015) showed that, indoor sources emit less carcinogenic PAHs as compared to outdoor sources, and that no substantial decrease in the benzo[a] pyrene toxicity equivalents (BaP_{eq}) was observed during the same time period, with overall indoor/outdoor (I/O) ratios of BaP_{eq} being lower than that for ∑PAHs. However, higher carcinogenicity due to indoor PAHs was also reported, implying importance of studying indoor PAHs(Oliveira et al., 2016). Secondly, although the indoor concentrations are usually lower than the corresponding outdoor levels (Masih et al., 2010; Sangiorgi et al., 2013; Romagnoli et al., 2014), the simultanous measurments of indoor and outdoor PAHs are necessary for exposure assessment and source assignment, particularly when we consider the heterogeneity among studies in modeling data of indoor exposure (Choi and Spengler, 2014; Romagnoli et al., 2014; Gariazzo et al., 2015; Zhu et al., 2015a). Last but not least, it has been suggested that, indoor particulate matter could lead to accumulation of HMW PAHs that considered more carcinogenic than LMW PAHs(Minguillón et al., 2012). The major aims of the current study are to describe the indoor and outdoor distribution patterns of the 16 US EPA priority PAHs, to estimate the infiltration of outdoor-generated PAHs into indoors, to determine emission sources, and to estimate potential health risk of the PAHs exposure.

2. Materials and methods

2.1. Study area and sampling

This study was conducted in Harbin city, Northeast China (44°04′N - 46°40′N and 125°42′E - 130°10′E), see Fig. 1. The city is characterized by great annual temperature differences that range from −30 °C to +30 °C (Wan-Li et al., 2009; Liu et al., 2013). Wintertime which last for six months (November to April), is characterized by extremely low temperature, an average value around (−15 °C). Central heating systems are commonly operated from Nov.20 to Apr.20 each year. Simultaneous indoor and outdoor sampling was done, during winter, summer and spring seasons on 12-h basis, first to determine the daytime and nighttime variations, then to calculate the 24-h averaged concentrations. A medium flow rate (100 l/min) aerosol sampler (model: *Laoying, 2030 intelligent flow, qingdao laoshan,* Applied Technology Research Institute, China) was used to collect the PM2.5 samples on Quartz filters. The sampling sites included an office and three residential households (nonsmoking and non-cooking during sampling days). These two types of microenvironments (i.e. offices and residential buildings) were chosen for the sampling under the assumption that people spend more than 90% of their time indoors (Bronsema et al., 2004), mostly either in their living or at work. A total of 264 $PM_{2.5}$ samples were collected for the entire period, on a basis of 22 samples from each site collected each season. Prior to sampling, filter samples and blank samples were baked into oven (at 450 °C degree, for 6–8 hours), then, were taken to desiccators for neutralization under lab controlled condition (25 ± 5 °C and 35 ± 5 relative humidity) for 24–48 hours before the gravimetric analysis in sensitive balance. Twenty-six (26) blanks were collected and analyzed along with the