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Assessment of polycyclic aromatic hydrocarbons in indoor and outdoor air of preschool environments (3–5 years old children)

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ABSTRACT

This work characterizes levels of polycyclic aromatic hydrocarbons (PAHs) in indoor and outdoor air of preschool environments, and assesses the respective risks for 3–5-years old children. Eighteen gaseous and particulate (PM_1 and $PM_{2.5}$) PAHs were collected indoors and outdoors during 63 days at preschools in Portugal. Gaseous PAHs accounted for 94–98% of total concentration (Σ_{PAHs}). PAHs with 5–6 rings were predominantly found in PM_1 (54–74% particulate Σ_{PAHs}). Lighter PAHs originated mainly from indoor sources whereas congeners with 4–6 rings resulted mostly from outdoor emissions penetration (motor vehicle, fuel burning). Total cancer risks of children were negligible according to USEPA, but exceeded (8–13 times) WHO health-based guideline. Carcinogenic risks due to indoor exposure were higher than for outdoors (4–18 times).

1. Introduction

Young children represent one of the most susceptible sub-populations with regard to potentially harmful effects induced by air pollution (Pongpiachan and Paowa, 2014; Schüepp and Sly, 2012; WHO, 2010). In their earliest years, children stay mostly indoors where they are exposed to a complex mixture of air pollutants. In comparison with adults, children are more vulnerable to poor indoor air quality due to their still developing physiological and immunological systems, and greater inhaled breath per unit mass (Foos et al., 2008; Burtscher and Schüepp, 2012). Recently, Annesi-Maesano et al. (2013) focused specifically on school environment by reviewing existent literature (until 2012) on indoor air quality (IAQ) and adverse health effects (particularly respiratory outcomes). The authors concluded that IAQ in schools has been much less studied than IAQ in other buildings (offices and other working places) with available data frequently showing severe indoor air problems due to poor building construction and maintenance, poor cleaning and ventilation; in addition, air quality in schools has been associated with a large spectrum of diseases with respiratory health being particularly challenged by air pollutants found in schools. Understanding child exposure is vital to child healthy development (Burtscher and Schüepp, 2012), so the impacts of indoor air pollution on child's health is one of the key focuses of many international organisations. Development of protective guidelines, understanding the complexity of indoor air exposure and the health impacts are also among the priorities of the World Health Organization (WHO) that has defined relevant indoor air pollutants (WHO, 2010), among those being polycyclic aromatic hydrocarbons (PAHs).

PAHs are a large group of organic pollutants characterized by the presence of at least two fused aromatic rings. PAHs are ubiquitously found in environment. Depending on the volatility of the individual compound and meteorological conditions, they are transported either in gaseous form or bound to particles of different sizes over long distances in the atmosphere (Ma et al., 2011; Yan et al., 2015). PAHs are released to ambient air during incomplete combustions from various sources such as vehicular road transport, power plants, coal burning, waste treatment, and shipping emissions (Hanedar et al., 2014; Lu et al., 2008; Pongpiachan et al., 2015a, b; Slezakova et al., 2013a, b). The main indoor sources include

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second-hand cigarette smoke, cooking, as well as the penetration of outdoor particulate and vapour phase PAHs into buildings (through windows, doors, cracks and ventilation system) (Liaud et al., 2014; Pongpiachan, 2015; Pongpiachan et al., 2015a, b; Qi et al., 2014; Shen et al., 2012). However, ventilation, building height and floor level may also influence the levels of PAHs indoors, increasing the respective risks for occupants living in dwellings near the ground levels (Pongpiachan, 2013a, b; Wang et al., 2014). Health effects associated with exposure to PAHs have drawn the scientific attention (Annesi-Maesano et al., 2007; Bae et al., 2010) because of PAH mutagenic and potentially carcinogenic properties; some compounds are classified as persistent organic pollutants (WHO, 2013) with sixteen of them (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene benz[a] anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[(a,h]anthracene, benzo[g,h,i] perylene, indeno[1,2,3-cd]pyrene) being regarded as priority pollutants by the U.S. Environmental Protection Agency (USEPA, 2005). Several of the PAHs are considered as endocrine disrupting chemicals (WHO, 2013), with the most well-known marker of PAHs being benzo[a]pyrene (IARC, 2010).

Because of their potential health impacts, the data concerning PAHs in educational environments have been slowly emerging but the information is far from comprehensive. Up to this date eight studies were conducted in Europe (Alves et al., 2014; Cirillo et al., 2006; Gatto et al., 2013; Jovanović et al., 2014; Krugly et al., 2014; Moshammer and Neuberger, 2003; Oliveira et al., 2015; Romagnoli et al., 2014), four in Asia (Jyethi et al., 2014; Ruchirawat et al., 2006, 2007; Tuntawiroon et al., 2007) and two in USA (Eiguren-Fernandez et al., 2007; Wilson et al., 2003). However, majority of these studies focused on assessment of particulate PAHs only, and were conducted in school environments (i.e. for children 7–12 years old), yet preschools represent the first place for child social activity. Although no definitive proof exists, it might be assumed that preschool students (i.e. 3–5 years old) are more vulnerable to poor indoor air quality than elementary or middle school students because their activities are more diverse, and their immune systems and bodies are less mature (Yoon et al., 2011); yet there is scarce information concerning the levels of PAH exposures and the respective risks in these types of educational environments.

Thus the main aim of this study was to investigate levels of particulate (PM_1 and $PM_{2.5}$) and gaseous PAHs (16 considered by USEPA as priority pollutants, and dibenzo[a,l]pyrene and benzo[j] fluoranthene; the latter recommended by EU Directive 2004/107/EC (2005)) at preschool environments. The phase distribution of indoor PAHs was characterized and the impacts of outdoor PAH emissions to indoor environments were assessed. The diagnostic ratios were applied in order to identify possible emission sources of indoor PAHs. Furthermore, the risks of 3–5 years old children to PAHs in preschool environments were assessed by toxicity equivalency factors (TEF) and according to the methodology recommended by USEPA (USEPA, 2015).

2. Material and methods

2.1. Characterization of the sampling sites

Sixteen PAHs considered by USEPA as priority pollutants, dibenzo[a,l]pyrene (toxicity equivalency factor of 100), and benzo [j]fluoranthene were sampled in air (gas and particulate phases) for 63 consecutive days of April–June 2013 at two preschools situated in north of Portugal. Preschools represent an educational establishment that, prior to the beginning of compulsory attendance at primary schools, provides education for 3–5 years old children. Specifically in Portugal, "preschools" refer to institutions that are directly associated with and operated by primary schools. Preschool PS1 was situated in Oporto Metropolitan Area that is the second largest metropolitan area in the country. The most important air pollution sources of the area include traffic emissions, an oil refinery and a petrochemical complex, a power plant, an incineration unit, and an international shipping port (Pereira et al., 2007). Specifically, PS1 was situated in the zone of Paranhos; previously it was demonstrated that emissions from vehicular traffic are the main pollution source in this area (Slezakova et al., 2013a, b). Preschool PS2 was situated in Chaves (approximately 150 km north–east of Oporto) that represents the second most populous municipality in district of Vila Real (INE, 2014a). This preschool was situated next to the road, which is the main traffic connection to city centre. A petrol station and main city shopping centre are situated directly next to the school complex, which leads to relatively consistent traffic density throughout the day. The detailed descriptions of both preschools and their characteristics are shown in Table 1.

2.2. Sample collection

Both gaseous and particulate samples were collected daily for a period of 24 h. During the sampling period, 204 daily samples of particulate and gaseous phases were collected. At PS1 indoor sampling was conducted in a common room that was used throughout day both for educational and entertaining activities as well as for physical exercising. At PS2, samples were collected in a classroom (also used for educational physical activities). The main characteristics and images of the studied rooms are shown in Fig. 1S and Table 1S, respectively.

Sampling was done by constant flow samplers (model Bravo H2; TCR TECORA, Italy) that were combined with PM EN LVS sampling heads for gaseous and particulate samples (in compliance with norm EN14907 for $PM_{2.5}$, and PM_1); an air flow rate of 2.3 $m^3\ h^{-1}$ was used. The inlets were positioned at 1.5 m above floor and minimally 1 m from walls, without obstructing the normal usage of rooms. Samplers were located as far as possible from windows or doors in order to minimize direct influence of any source. All requirements to maintain child safety were fulfilled. Outdoor (i.e. in ambient air) particulate and gaseous PAHs were measured in preschools yards. The samplers were positioned in open area avoiding any obstacles and barriers.

$PM_{2.5}$ and PM_1 were collected on polytetrafluoroethylene (PTFE) membrane filters with polymethylpentene support ring (2 μm porosity, Ø47 mm, SKC Ltd., United Kingdom). $PM_{2.5}$ and PM_1 masses were determined gravimetrically according to Slezakova et al. (2014). Gaseous samples were collected on polyurethane foam (PUF) plugs (75 mm, SKC Ltd., United Kingdom) that were precleaned using the procedure according to Castro et al. (2011). After sampling both filters and PUF plugs were stored in a freezer (−20 °C) before chemical analysis.

Physical parameters, namely temperature (T) and relative humidity (RH) were measured by multi-gas sensor probe (model TG 502; GrayWolf Sensing Solutions, Shelton, USA).

During sample collection a researcher kept a record of room occupancy, ventilation systems (door and window positions), and potential source activities. In addition, preschool staff was daily inquired regarding the occurrence of an additional source and/or activities.

2.3. Extraction and chromatographic analysis of PAHs

The extractions and quantification of PAHs from particles ($PM_{2.5}$ and PM_1) and PUF plugs were performed by previously validated