INDOOR-OUTDOOR RELATIONSHIPS OF CARCINOGENIC POLYCYCLIC AROMATIC HYDROCARBONS IN PORTUGUESE PRESCHOOLS

OLIVEIRA M.[1], SLEZAKOVA K.[2], DELERUE-MATOS C[1]., PEREIRA M.C.[2] and MORAIS S.[1]

[1] REQUIMTE, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Rua Dr. António Bernardino de Almeida 431, 4200-072 Porto, Portugal, [2] LEPABE, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
E-mail: sbm@isep.ipp.pt

ABSTRACT

Children represent one of the most vulnerable groups in society. The detailed characterization of pollution (both indoors and outdoors) of schools is of great importance, since it may allow preventing potential risks to children health. Yet the information related to carcinogenic compounds, such as some polycyclic aromatic hydrocarbons (PAHs) in child educational settings is very limited. Thus the aim of this work was to assess indoor and outdoor levels of PAHs at Portuguese preschools (3–5 years old children) in urban areas with emphasis on carcinogenic compounds, and to identify the main sources of indoor PAHs.

Eighteen PAHs (16 considered by USEPA as priority pollutants, and dibenzo[a,l]pyrene and benzo[j]fluoranthene, the latter recommend EU Directive 2008/50/EC) were collected during 45 days of spring 2013 at two preschools (PS1, PS2) situated in two different (and distant from each other) urban areas in north of Portugal. Nine carcinogenic PAHs were included: benzo[a]pyrene (known carcinogen) and other 8 probable (benz[a]anthracene, dibenz[a,h]anthracene, dibenzo[a,l]pyrene) or possible (naphthalene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene and indeno[1,2,3-c,d]pyrene) carcinogens. PAHs in $PM_{2.5}$ (particulate matter with aerodynamic diameter < 2.5 μm) were simultaneously collected both indoors (classroom, playrooms) and outdoors (playground and preschool yards). Quantification of PAHs was performed by microwave-assisted extraction combined with liquid chromatography with fluorescence and photodiode array detection. Total levels of 18 PAHs (ΣPAHs) were 2.6 and 3.2 higher in indoor and outdoor air of PS1 than at PS2. Compositional profiles were though similar at both preschools with 5–6 ring PAHs being the most abundant. Dibenz[a,h]anthracene and benzo[b]fluoranthene (both class 2A carcinogens) were the predominant individual PAHs at both preschools. Nine carcinogenic compounds ($\Sigma PAHs_{carc}$) accounted for 73 and 74% of indoor particulate PAH content at PS1 and PS2, respectively; outdoors the corresponding $\Sigma PAHs_{carc}$ composed 66% and 71% of ΣPAHs. Analysis of I/O ratios of $\Sigma PAHs_{carc}$ suggested that outdoor emissions were a significant contributor to indoor carcinogenic PAHs at both schools. $\Sigma PAHs_{carc}$ exceeded the recommended EU guideline value of 1 ng m^{-3} (100% of days at PS1, both indoors and outdoors; >65% samples at PS2) for the total content in PM_{10} averaged over a calendar year. Therefore, in order to prevent risks to children health it necessary to establish and implement target values of carcinogenic components in indoor particles of smaller sizes (i.e. $PM_{2.5}$).

Keywords: air, preschools, indoor/outdoor, PAHs, carcinogens, $PM_{2.5}$, microwave-assisted extraction (MAE), liquid chromatography (LC).

1. Introduction

According to World Health Organization (WHO) in 2012 4.3 million people died world-wide due to the effects of indoor air pollution (WHO, 2014). The potential health consequences of exposure to indoor pollution indicate the need for further studies in order to fully comprehend the respective health consequences. This is especially relevant for vulnerable groups of society,

such as young children who are particularly susceptible to air pollution. Children spend around 30% of their time (8-9 h/day) at schools which raises an interest in better understanding of air pollution in these environments. Despite the current concerns about indoor pollutants there is lack of information on polycyclic aromatic hydrocarbons (PAHs) in indoor and outdoor air of educational settings.

PAHs are ubiquitous environmental pollutants that are released from various combustion sources (Slezakova *et al*., 2013b). Some PAHs are potent carcinogens and previously reported findings indicated that high molecular weight PAHs (toxicity increases as their molecular weight increases) are predominantly found in fine fraction of air particulate matter (i.e. $PM_{2.5}$). The exposure to carcinogenic PAHs found in air occurs mainly via inhalation of these particles. PAHs occur as complex mixtures, the composition of which may vary greatly. Because of their potential health impacts (DNA damage, mutagenicity and carcinogenicity) PAHs are considered among the relevant indoor air pollutants (WHO 2010). The aim of this work was to assess indoor and outdoor levels of 18 particulate PAHs (16 considered by USEPA as priority pollutants, and dibenzo[a,l]pyrene and benzo[j]fluoranthene) at Portuguese preschools (3–5 years old children) in urban areas with emphasis on nine carcinogenic compounds, and to identify the main sources of indoor PAHs.

2. Materials and methods

2.1. Sampling

Sixteen PAHs considered by USEPA as priority pollutants, dibenzo[a,l]pyrene and benzo[j]fluoranthene (the latter recommended by EU Directive 2008/50/EC) were collected in $PM_{2.5}$ for 45 consecutive days (April – June) of 2013 at two preschools (i.e. education establishment for 3- to 5-year-old children) situated in urban zones in north of Portugal. Preschool PS1 was in the urban area of Chaves. This preschool was located next to a large shopping center. A petrol station next to preschool and vehicular traffic were the major emission sources. The second preschool (PS2) was situated in Oporto Metropolitan Area; previously it was demonstrated that traffic emissions were the main contributor to air pollution in this area (Slezakova *et al*., 2013a, b). The sampling equipment was placed indoors in a common room that was used throughout day both for educational and entertaining activities as well as for physical exercising. $PM_{2.5}$-bound PAHs were collected on polytetrafluoroethylene (PTFE) membrane filters with polymethylpentene support ring (2 μm porosity, Ø47 mm, SKC Ltd., United Kingdom) by constant flow sampler (model Bravo H2; TCR TECORA, Italy) combined with sampling head and using an air flow rate of 38 L min^{-1}. The 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. To better understand the impacts of outdoor PAH emissions to an indoor preschool environment, the levels of PAHs were concurrently measured in outdoor air (i.e. school yards and playgrounds) in a safe distance from areas with children's intense activity. The samplers were positioned in open area avoiding any obstacles and barriers (trees, bushes walls, and fences) that could interfere with data collection. PM masses were determined gravimetrically according to Slezakova *et al*. (2014). After the sampling filters were stored in a freezer (–20 °C) before consequent chemical analysis. Indoor temperature (T) and relative humidity (RH) were measured by Testo mini data-logger (model 174H; Testo AG, Lenzkirch, Germany), which operated continuously 24 h with a logging interval of 10 min.

2.2. Extraction and chromatographic analysis of PAHs

The extraction of PAHs from $PM_{2.5}$ was performed by previously validated analytical procedure (Castro *et al*., 2009, 2011). Briefly, filters were microwave-assist extracted (30 mL of acetonitrile for 20 min at 110 ºC); and extracts were analysed by liquid chromatography (LC) with photodiode array (PAD) and fluorescence (FLD) detectors (Castro *et al*., 2009, 2011). Each compound was detected at its optimum excitation/emission wavelength pair: 260/315 nm (naphthalene, acenaphthene and fluorene), 260/366 nm (phenanthrene), 260/430 nm (anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b+j]fluoranthene,

benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[ghi]perylene and dibenzo[a,l]pyrene), and 290/505 nm (indeno[1,2,3–cd]pyrene). Acenaphthylene, which shows limited fluorescence, was analysed at 254 nm in the PAD. Each analysis was performed at least in triplicate. Limit of detections between 1.0 pg m^{-3} (for anthracene, benzo[k]fluoranthene, chrysene, benz[a]anthracene, phenanthrene and indeno[1,2,3-cd]pyrene) and 148 pg m^{-3} (for acenaphthylene) were obtained.

3. Results and discussion

Over the sampling period, the levels of $PM_{2.5}$ in indoor air ranged between 5.8 and 28.1 μg m^{-3} (mean of 14.2 μg m^{-3}) at PS1 and from 11.3 to 26.1 μg m^{-3} (mean of 19.4 μg m^{-3}) at PS2. The corresponding outdoor levels were 8.6–22.6 μg m^{-3} (mean of 15.2 μg m^{-3}) at PS1 and 11.2–39.9 μg m^{-3} (mean of 19.3 μg m^{-3}) at PS2. The statistical analysis of the results indicates that at both preschools indoor $PM_{2.5}$ were not significantly different from the outdoors ones ($P<0.05$). In addition, indoor mean concentrations obtained at both PS1 and PS2 were lower (0.8–1.7 times) than the limit value of 25 μg m^{-3} set for $PM_{2.5}$ by Portuguese legislation on indoor air (Decreto Lei 118/2013).

The concentrations of PAHs in indoor and outdoor $PM_{2.5}$ at the selected preschools are presented in Table 1 as sums of individual compounds according to the number of aromatic rings. The total levels of 18 PAHs (ΣPAHs) in indoor air ranged from 1.74 to 7.57 ng m^{-3} at PS1 whereas it was from 0.74 to 2.25 ng m^{-3} at PS2. The corresponding levels of ΣPAHs in outdoor air were slightly higher (2.77–10.3 ng m^{-3} at PS1; 0.84–1.79 ng m^{-3} at PS2). Overall, levels of 18 PAHs were higher (2.6 times for indoors; 3.2 times for outdoor ones) at PS1 probably due to the busier vehicular transport in streets surrounding PS1.

Table 1: Levels of $PM_{2.5}$–bound PAHs (ng m^{-3}) at two preschools (PS1 and PS2). Concentrations are presented as sums of individual compounds according to the number of aromatic rings, i.e. groups with 2, 3, 4, 5 and 6 rings.

	PS1				PS2			
	indoor		outdoor		indoor		outdoor	
	mean	SD	mean	SD	mean	SD	mean	SD
2–rings	0.142	0.136	0.070	0.050	n.d.	n.d.	n.d.	n.d.
3–rings	0.507	0.295	0.974	0.927	0.081	0.036	0.057	0.021
4–rings	0.320	0.128	0.640	0.610	0.191	0.140	0.399	0.113
5–rings	1.83	1.51	2.28	2.00	0.862	0.283	0.764	0.243
6–rings	0.682	0.650	0.787	0.750	0.194	0.061	0.242	0.074
$\Sigma PAHs_{carc}$	2.50	2.22	3.14	3.01	0.978	0.358	1.03	0.31
ΣPAHs	3.44	2.34	4.74	3.20	1.33	0.51	1.46	0.38

Compounds with 5 (dibenz[a,h]anthracene, benzo[k]fluoranthene, benzo[a]pyrene and benzo[b+j]fluoranthene) and 6 (dibenzo[a,l]pyrene, benzo[g,h,i]perylene, indeno[1,2,3-c,d]perylene) aromatic rings were the most abundant particulate PAHs. Indoors they accounted, respectively, for 73 and 80% of ΣPAHs at PS1 and PS2, whereas it was 65 and 69% of outdoor ΣPAHs at PS1 and PS2, respectively. The abundances of PAHs with 3–4 rings were also similar at both preschools (indoors: 24 and 20% of ΣPAHs at PS1 and PS2; 31–34 % of ΣPAHs outdoors). These results demonstrate that even though the levels of PAHs were significantly higher at PS1 ($P<0.05$), compositional profiles of indoor PAHs (as well as outdoor ones) were similar at both preschools.

Nine carcinogenic compounds ($\Sigma PAHs_{carc}$) accounted for 73 and 66% of indoor and outdoor ΣPAHs at PS1. The contribution of carcinogenic PAHs at PS2 was very similar, $\Sigma PAHs_{carc}$ composing 74 and 71% of the indoor and outdoor particulate PAHs content, respectively. In addition, it is worth mentioning that out of 18 compounds the most abundant individual PAH

were dibenz[a,h]anthracene and benzo[b+j]fluoranthene, both class 2A carcinogens. At PS1 dibenz[a,h]anthracene accounted, respectively, for 27 and 25% of ΣPAHs indoors and outdoors; at PS2 it was 48 and 30% of indoor and outdoor ΣPAHs. The dominance of this PAH indicates an influence from light-duty gasoline vehicle emissions (Ravindra *et al*., 2008). Benzo[b+j]fluoranthene accounted at PS1 13% of both indoor and outdoor ΣPAHs; at PS2 these compounds contributed 11-16% of indoor and outdoor ΣPAHs. Finally, the levels of benzo[a]pyrene, the most studied PAH (class 1 carcinogen; IARC, 2010) ranged indoors between 116 and 848 pg m^{-3} and between 24 and 88 pg m^{-3} at PS1 and PS2, respectively. The corresponding outdoor levels of this compound were 137–967 pg m^{-3} at PS1 and 43–112 pg m^{-3} at PS2. In order to minimize the harmful effects on human health and environment European Union defined the target value for benzo[a]pyrene in ambient air being 1 ng m^{-3} for the total content in PM_{10} averaged over a calendar year (Directive 2008/50/EC). At PS1 $\Sigma PAHs_{carc}$ exceeded the recommended guideline value during all days both indoors and outdoors, whereas at PS2 more than 65% of indoor and outdoor samples were higher than 1 ng m^{-3}.

Indoor–to–outdoor concentration ratios (I/O) of individual PAHs were assessed in order to provide some understanding about pollutant's origin. The mean I/O ratios of $\Sigma PAHs_{carc}$ were lower than unity suggesting that outdoor air was the dominant contributor to indoor carcinogenic PAH levels at both schools. However, on some occasions some individual PAH ratios exceeded unity, indicating contributions from indoor sources. Previous studies reported an indoor origin due to activities of the respective occupants and/or volatilization from building materials (Krugly *et al*., 2014). The potential indoor sources registered during the sampling in PS1 and PS2 that could have resulted in elevated PAHs content were: combustion sources (candles on birthday cakes; Derudi *et al*., 2013), children activities during classes (i.e. painting, wax melting) and classroom cleaning (wood polishing).

4. Conclusions

During the entire period of the sampling campaign, the total concentrations of $PM_{2.5}$-bound PAHs (both indoors and outdoors) exceeded the ambient target limit established for PM_{10}. Despite the current concerns about regulations of indoor pollutants, there is a lack of studies in educational settings especially concerning carcinogenic compounds such as PAHs. The findings obtained in the present study demonstrate that it is necessary to establish and implement target values of carcinogenic components in particles of smaller sizes (i.e. $PM_{2.5}$ or PM_1), both for indoor and outdoor air. As far as it is known, these targets have not been established in anywhere in the world yet. A better understanding of indoor pollution may allow further recommendations for air quality improvements and potentially to review existent air quality guidelines.

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