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Polycyclic aromatic hydrocarbons: levels and phase distributions in preschool microenvironment

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Running title: PAHs in Portuguese preschool

Abstract

This work aims to characterize levels and phase distribution of polycyclic aromatic hydrocarbons (PAHs) in indoor air of preschool environment and to assess the impact of outdoor PAH emissions to indoor environment. Gaseous and particulate (PM_1 and $PM_{2.5}$) PAHs (16 USEPA priority pollutants, plus dibenzo[a,l]pyrene and benzo[j]fluoranthene) were concurrently sampled indoors and outdoors in one urban pre–school located in north of Portugal for 35 days. The total concentration of 18 PAHs (ΣPAHs) in indoor air ranged from 19.5 to 82.0 ng m^{-3}; gaseous compounds (range of 14.1–66.1 ng m^{-3}) accounted for 85% ΣPAHs. Particulate PAHs (range 0.7–15.9 ng m^{-3}) were predominantly associated with PM_1 (76% particulate ΣPAHs) with 5-ring PAHs being the most abundant. Mean indoor/outdoor ratios (I/O) of individual PAHs indicated that outdoor emissions significantly contributed to PAH indoors; emissions from motor vehicles and fuel burning were the major sources.

Keywords: indoor air, preschools, polycyclic aromatic hydrocarbons (PAHs), indoor/outdoor (I/O), children

Practical Implications

This study fills a gap providing information on levels and phase distribution (gas, and PM_1 and $PM_{2.5}$–bound) of polycyclic aromatic hydrocarbon (PAHs) in preschool educational settings. Despite the current concerns about regulations of indoor pollutants, there is lack of studies on indoor and outdoor PAHs in education settings; in addition no study reported information about PAHs in the finest fractions of particulates (such as PM_1) in schools or preschools. The high proportion of PAHs detected in the gaseous phase clearly demonstrates that adequate assessment of PAHs exposure requires consideration of the gaseous compounds, which are commonly neglected.

1. **Introduction**

Polycyclic aromatic hydrocarbons (PAHs) are organic contaminants characterized by the presence of at least two fused aromatic rings. These compounds are ubiquitous environmental pollutants that are released from combustion sources such as coal burning power plants, diesel– and gasoline–powered vehicles, home heating, and waste treatment (Hanedar et al., 2014; Ravindra et al., 2008; Slezakova et al., 2013b). An important aspect of air quality management is identification of indoor PAH sources. Cooking, secondhand cigarette smoke, as well as the penetration of outdoor particulate and vapour phase PAHs into buildings (through windows, doors, cracks and ventilation system) have been recognised as major contributors to the indoor PAH air pollution (Chen et al., 2012; Qi et al., 2014; Shen et al., 2012; Slezakova et al., 2014). Health effects of PAHs exposure have been widely studied (Annesi-Maesano et al., 2007; Bae et al., 2010; Tuntawiroon et al., 2007), primarily because of their potential carcinogenic and mutagenic properties. Some PAHs are classified as persistent organic pollutants (WHO, 2013) and sixteen of them are regarded as priority pollutants by the U.S. Environmental Protection Agency (USEPA, 2005). Several of the PAHs are referred to as endocrine disrupting chemicals, with the most well-known marker of PAHs being benzo[a]pyrene (WHO, 2013). Benzo[a]pyrene is considered by International Agency for Research on Cancer (IARC) as carcinogenic to humans (group 1) (IARC 2010) whereas several other PAHs are classified as probably and possibly carcinogenic to humans (groups 2A and 2B, respectively).

Benzo[a]pyrene is often used as a surrogate for other carcinogenic PAHs in studies estimating human cancer risks. There have been also efforts to regulate PAHs levels in air. Using benzo[a]pyrene as indicator of carcinogenic PAHs, current European legislation on ambient air (Directive 2004/107/EC) sets annual target value of 1 ng m^{-3} for carcinogenic PAHs in PM_{10}. However, findings about the presence of more potent PAHs, such as dibenzo[a,l]pyrene and dibenz[a,h]anthracene (Okona–Mensah et al., 2005) have raised some questions concerning the suitability of this approach (Pufulete et al. 2004). In that regard the evaluation of PAHs in the smallest particulate fraction, such as PM_1 and $PM_{2.5}$, is health–relevant because of the ability of these particles to deposit deeply in the respiratory airways; the epidemiological evidence indicates that these smaller particles may have a greater potency in causing adverse health effects than larger particles.

The impact of indoor air pollution on child's health is one of the key focuses of many international organisations. Children spend per day approximately 7–8 h of their time (i.e. 30%) at premises of the education settings (i.e. pre-schools and schools) which raises interest in characterizing health relevant pollutants in these environments. Children breathe higher volumes of air relative to their body weights than adults do. As their physiological and immunological systems are not fully developed, in respect to air quality children represent one of the most sensitive groups of the society (Burtscher and Schüepp, 2012; Ginsberg et al., 2008). The studies show that health impact of air pollutants is much higher on pupils than on adults in similar environments (Guo et al., 2010). Thus, children are more likely to suffer the consequences of indoor pollution (Alves et al., 2014). Despite the current concerns about indoor pollutants, there is lack of studies on indoor and outdoor PAHs in educational settings; in addition no study has reported information about PAHs in the finest fractions of particulate matter (such as PM_1) in schools or in preschools. Numerous individual PAH compounds, time–consuming and financially demanding analytical methodology, as well as the complex formation mechanisms have resulted in studies primarily focused on the outdoor air. A better understanding on indoor PAHs may led to further recommendations for air quality improvements and potentially to review existent air quality guidelines. Furthermore, the characterization of particulate and gaseous phase PAHs indoors and outdoors of schools is of great importance, since it may allow lowering health risks for children.

Thus, the aim of this study was to investigate indoor 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) at a preschool in Oporto, Portugal. The phase distribution of indoor PAHs was characterized and the impact of outdoor PAH emissions to indoor environment was assessed. In addition, diagnostic ratios were applied in order to identify possible emission sources of indoor PAHs.

2. Material and methods

2.1 Characterization of the sampling site

Sixteen PAHs considered by USEPA as priority pollutants, plus dibenzo[a,l]pyrene and benzo[j]fluoranthene were sampled in air (gas and particulate phases) for 35 consecutive days during February – April 2011 at one preschool situated in the urban zone of Oporto, Portugal. Preschools are educational establishments that provide education for 3- to 5-year-old children, prior to the beginning of compulsory attendance at primary schools. Specifically in Portugal "preschools" refer to institutions that are directly operated by primary schools. The selected preschool was situated in Oporto Metropolitan Area, in Paranhos district (north of Portugal); previously it was demonstrated that emissions from vehicular traffic contributed the main pollution source in this area (Slezakova et al., 2013a, b). The detailed description of the preschool and its characteristics are shown in Table 1.

To better understand the impacts of outdoor PAH emissions to an indoor preschool environment, the levels of PAHs were concurrently measured in outdoor air.

The traffic densities were estimated for the streets surrounding the preschool (Table 1). During two consecutive days the number of road vehicles, namely passenger cars, trucks/buses, motorbikes and others, was manually counted between 5 a. m. to 12 p. m. during 10 minutes of each hour. These data were used in order to better describe the surroundings of the selected preschool.

2.2 Sample collection

Both gaseous and particulate samples were collected daily for a period of 24 h. During the sampling campaign, 105 daily samples of particulate and gaseous phases were collected. 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. The room layout and its characteristic are shown in Figure 1S and Table 1S of the Supplementary material, respectively. The 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 the floor and minimally 1 m from the walls, without obstructing the normal usage of the rooms. 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. Concurrently, $PM_{2.5}$–bound PAHs were measured in outdoor air at preschool yard, 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. The distance from the main street was 8 m.

The different fractions of particles, i.e. $PM_{2.5}$ and PM_1, were collected on polytetrafluoroethylene (PTFE) membrane filters with polymethylpentene support ring (2 µm porosity, Ø47 mm, SKC Ltd., United Kingdom). Gaseous samples were collected on polyurethane foam (PUF) plugs (75 mm, SKC Ltd., United Kingdom) that were precleaned using the procedure of Castro et al. (2011).

Indoor temperature (T) and relative humidity (RH) were measured by using Testo mini data-logger (model 174H; Testo AG, Lenzkirch, Germany), which operated continuously with a logging interval of 10 min. Other indoor pollutants were also measured (Table 1). The concentrations of carbon monoxide (CO), carbon dioxide (CO_2), total volatile organic compounds (TVOCs), and ozone (O_3) were performed by multi-gas sensor probe (model TG 502; GrayWolf Sensing Solutions, Shelton, USA) that was daily calibrated. The measurements were conducted 2–3 for each school day (both in morning and afternoon), each time for 15 to 20 min (with a logging interval of 30 s). In addition, the levels of formaldehyde were registered with Formaldemeter™ (model htV-M; PPM Technology, Caernarfon, UK) following the same methodology as for other indoor pollutants.

Information on outdoor meteorological conditions, namely T, RH, wind speed (WS), precipitation (P), and solar radiation (SR) were retrieved from the local meteorological stations and are summarized in Table 1.

During sample collection a researcher was present to keep a record of room occupancy, potential source activities, and ventilation system status (door and window positions). During the sampling campaign, the room was extensively ventilated twice per day by opening of all windows: approximately for 15–20 min before children arrivals (around 7:30 a.m.) and at the end of the day when everybody left and room was empty (after 6:0 p.m., for approximately 15 min); throughout the rest of day and during night windows were always kept closed. The doors were always maintained closed during the educational activities (classes) and physical activities; during recesses and periods with recreational activities the they were opened. In addition, teachers and staff were asked daily regarding the occurrence of any additional source or activities that might influence the monitored parameters.

2.3 $PM_{2.5}$ and PM_1 masses

$PM_{2.5}$ and PM_1 masses were determined gravimetrically according to Slezakova et al. (2014). The steps of gravimetric mass determination were the following: 24 h to equilibrate filters before weighing at room temperature (Mettler Toledo AG245 analytical balance weighing with accuracy of 10 µg) followed by weighing during the following 24–48 h. If the measurements for one sample differed more than 10 µg, they were discarded and the filters were repeatedly weighed until three reproducible values were obtained. The filters were then kept in Petri dishes. After the sampling both filters and PUF plugs were stored in a freezer (–20 °C) before consequent chemical analysis.

2.4 Extraction and chromatographic analysis of PAHs

The extractions of PAHs from particles ($PM_{2.5}$ and PM_1) and PUF plugs were performed by previously validated analytical procedure (Castro et al. 2009, 2011). Briefly, filters and PUF plugs were microwave-assist extracted with 30 and 45 mL of acetonitrile, respectively, for 20 min at 110 ºC. After extraction, the vessels were allowed to cool at room temperature; extracts were then carefully filtered through a PTFE membrane filter (0.45 µm) and reduced to a small volume using a rotary evaporator (Buchi Rotavapor, R–200) at 20 ºC. A gentle stream of nitrogen was used to dry the extracts under low temperature; the residue was then dissolved in 1000 µL of acetonitrile immediately before analysis.

To quantify PAHs, extracts were analysed using a Shimadzu LC system (Shimadzu Corporation, Kyoto, Japan) equipped with a LC–20AD pump, DGU–20AS degasser and photodiode array SPD–M20A (PAD) and fluorescence RF–10AXL (FLD) detectors (Castro et al., 2009, 2011). Separation of the compounds was performed in a C18 column (CC 150/4 Nucleosil 100–5 C18 PAH, 150 × 4.0 mm; 5 µm particle size; Macherey–Nagel, Duren, Germany) maintained at room temperature (20 ± 1 ºC). The injected volume was 15.0 µL. A mixture of water and acetonitrile was used as the mobile phase. The initial composition of the mobile phase was 50% of acetonitrile and 50% ultra–pure water, and a linear gradient to 100% of acetonitrile was programmed in 15 min, with a final hold of 13 min. Initial conditions were reached in 1 min and maintained for 6 min before next run. The total run time was 40 min with a flow rate of 0.8 mL min^{-1}. Fluorescence wavelength programming was used to achieve better sensitivity and minimal interference. 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.

2.5 Quality control

The overall MAE-LC procedure for analysis of PAHs in atmospheric particulate samples was previously validated by systematic recovery experiments and analysing the certified reference material SRM 1650b “Diesel particulate matter” (Castro et al., 2009). PAHs were extracted from particles with recoveries ranging from 81.4 ± 8.8% to 112.0 ± 1.1%, for all the compounds except for naphthalene (62.3 ± 18.0%) and anthracene (67.3 ± 5.7%). The validation of MAE procedure for extracting PAHs from PUFs was performed according to Castro et al. (2011). The extraction efficiency was consistent over the entire range of concentrations and the results ranged from 50.2 ± 3.5% (acenaphthylene) to 107.9 ± 1.5% (fluoranthene) for all PAHs. External calibrations with PAHs mixed standards, using at least 6 calibration points, were performed. Calibrations curves were linearly fitted with correlation coefficients always higher than 0.9997 for all PAHs. Limits of detection (LODs) and limits of quantification (LOQs) were calculated as the minimum detectable amount of analyte with a signal-to-noise ratio of 3:1 and

10:1, respectively, (Miller and Miller, 2000). LODs 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, with corresponding LOQs in the range 3.4–492 pg m^{-3}. During each set of MAE extractions, a filter blank or a PUF plug blank was included. The repeatability was evaluated by the relative standard deviations (RSD) of triplicate samples. RSD values ranged from 1.8% (dibenzo[a,l]pyrene) to 9.1% (naphthalene) and from 0.9% (chrysene) to 9.8% (naphthalene) for PAHs extraction from filters and PUFs, respectively. Standards used for calibration were analysed daily and regularly, as well as blank MAE extracts (from filter blank or PUF plug blank), between samples to check instrument performance during PAHs analysis. Each analysis was run at least in triplicate.

2.6 Statistical analysis

For the data treatment, the Student's t-test was applied to determine the statistical significance ($P<0.05$, two tailed) of the differences between the means determined for indoor and outdoor samples or for different phases or particle size fractions.

3. Results and discussion

3.1 PM and indoor gases

The indoor concentrations of $PM_{2.5}$ and PM_1 ranged, respectively, from 2.1 to 106 μg m^{-3} (mean of 27 μg m^{-3}) and 1.1 to 82 μg m^{-3} (mean of 24 μg m^{-3}). On average, a majority of the $PM_{2.5}$ was comprised of PM_1; these particles accounted for 91% of $PM_{2.5}$. Furthermore, the outdoor air exhibited similar levels of $PM_{2.5}$ as indoors, with outdoor concentrations ranging from 5.1 to 113 μg m^{-3} (mean of 29 μg m^{-3}); the estimated indoor and outdoor means were not significantly different ($P<0.05$).

The levels of other indoor pollutants are presented in Table 1. The mean of CO fulfilled the limit of 10 mg m^{-3} set by current Portuguese legislation for indoor air of public buildings (Decreto Lei 118/2013). CO_2 slightly exceeded the limit of 2250 mg m^{-3}. The levels of TVOCs and formaldehyde surpassed (approximately 4.5 and 1.8 times) limit values of 100 and 600 µg m^{-3}, respectively. It is necessary to point out that in 2013 Portuguese legislation on indoor air pollution of public buildings was revised. Whereas the limit values of the these gas pollutants remained the same, the recommend sampling duration was set to 8 h instead the previously suggested 5 min interval (as conducted within this work).

3.2 Indoor PAHs

The levels of indoor PAHs associated with each phase are summarised in Table 2, which shows the indoor mean concentrations (as well as median and interquartile range) of 18 PAHs in $PM_{2.5}$, PM_1, and in the gas phase at the studied preschool. In agreement with the previous studies on indoor air quality in the Oporto Metropolitan Area (Castro et al., 2011; Slezakova et al., 2009) dibenz[a,h]anthracene was the most abundant indoor particle–bound PAH at the studied preschool. This compound reached mean concentrations of 1.7 and 1.4 ng m^{-3} in $PM_{2.5}$ and PM_1, respectively, accounting in both PM size fractions for about 30% of Σ_{PAHs}. The dominance of this compound indicates influence from light-duty gasoline vehicle emissions (Ravindra et al., 2008). The other abundant PAHs in $PM_{2.5}$ and PM_1 were, in descending order, benzo[b+j]fluoranthene (approximately 15%), indeno[1,2,3–cd]pyrene (12–14% in $PM_{2.5}$ and PM_1, respectively) and benzo[ghi]perylene (8% in $PM_{2.5}$, 10% in PM_1). Naphthalene was the least abundant particle–bound PAH (approximately 1%); but, in the gas phase, it was the second most abundant compound (26% of gaseous Σ_{PAHs}) reaching a mean of 7.7 ng m^{-3}. Other abundant gaseous compounds were, in descending order, phenanthrene (33% of Σ_{PAHs}), fluorene (19%), and acenapthylene (13%). These four PAHs accounted in total for 91% of indoor gaseous Σ_{PAHs} at the studied preschool whereas each of the 5–6 ringed compounds accounted approximately for less than 0.5% of gaseous Σ_{PAHs}. Regarding the levels of PAHs in air (i.e. sum of PAH levels in $PM_{2.5}$ and in gas phase; Table 2), the total concentrations of 18 PAHs (Σ_{PAHs}) ranged from 20 to 82 ng m^{-3} with a mean of 35 ng m^{-3}. Specifically, naphthalene reached a mean of 7.8 ng m^{-3} which is below the WHO recommend annual guideline value of 10 µg m^{-3} (WHO, 2010). Krugly et al. (2014) observed naphthalene levels in similar ranges in five elementary schools in Lithuania (medians between 12 and 27 ng m^{-3}). Wilson et al. (2003) reported higher concentrations of naphthalene in indoor air of a preschool (median of 546 ng m^{-3}); still these levels were well below the WHO recommended guideline.

There is relatively very little information on indoor PAHs in educational environments (i.e. in preschools and in schools). The reported levels of all studies available in literature are summarized in Table 3. In general, the levels of $PM_{2.5}$–bound PAHs in this study were similar to those reported from elementary schools in Rome during winter season (Gatto et el., 2013) whereas no information was found on PM_1–bound PAHs in indoor air of schools and/or preschools. Concerning gaseous PAHs, the most similar range of concentrations was observed in primary schools in Lithuania (Krugly et al., 2014). Overall, there were very significant differences among the levels and ranges of PAHs reported in the literature for indoor air of educational environments, ranging from 0.28 ng m^{-3} in Bankok Thailand (Ruchirawat et al., 2006, 2007) to 1040 ng m^{-3} in North Carolina, USA (Wilson et al., 2003). Certainly, geographical and seasonal influences, meteorological conditions, level of urbanization and development of the surrounding area could account for some of the differences. However, it is necessary to point out that study designs varied greatly between the mentioned works, namely in terms of considered indoor environments (preschool, elementary or primary school), particle size fractions (differing between PM_1, $PM_{2.5}$, PM_{10}, TSP, or unspecified), consideration of compounds present in the gas phase, and the number of individual PAHs compounds analysed, which can influence the significance of comparisons across studies.

Figure 1 shows the distribution of PAHs between particle and gas phases in the indoor air of the studied preschool. The distribution of PAHs between the two phases predominantly depends on the physical characteristics of the compounds as well as on the physical conditions of the studied environments such as temperature and relative humidity (Ravindra et al., 2008). Typically, PAHs with higher molecular weight (5 and more aromatic rings) are mostly associated with the particle phase, whereas compounds with 2 to 3 rings are predominantly found in the gas phase (Guo et al., 2011). As demonstrated in Figure 1, the phase–distribution of PAHs in indoor air of the studied preschool was in agreement with findings of other studies (Possanzini et al., 2004). Compounds with 2 and 3 aromatic rings, namely naphthalene, acenapthlylene, fluorene, phenanthrene were almost entirely present in the gas phase (i.e. more than 99%). On the contrary, PAHs with 5 rings, namely benzo[b+j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, were predominantly bound to particles (i.e. more than 90%). Compounds with 6 aromatic rings such as dibenzo[a,l]pyrene and indeno[1,2,3–cd]pyrene were entirely present in particles. Finally, PAHs with 4 rings that included fluoranthene, pyrene, benz[a]anthracene and chrysene were distributed between the two phases with the proportions in the gas phase ranging between 13 and 71%. In that regard, it is necessary to point out that acenapthene (3 aromatic rings) exhibited unexpected high distribution in the particle phase (i.e. 19%). No reason was identified which could justify this abundance in PM, though unlike other individual PAHs acenapthene was detected only in 51% of the existent particulate samples and this might contribute to the apparent inconsistency. Overall, the PAH phase distribution of the studied preschool was similar to those of primary schools reported by Krugly et al. (2014); other studies available in literature that included characterization of PAHs in air (i.e. assessment of both gaseous and particulate phases) in educational settings (Table 3) did not specifically report these findings.

In total, the gaseous PAHs accounted for 85% of Σ_{PAHs}. This high proportion of PAHs in the gas phase clearly demonstrates that adequate assessment of PAHs exposure requires consideration of the gaseous compounds, which have commonly been neglected in prior studies.

The results in Table 2 and Figure 1 also demonstrate that particulate PAHs were associated with particles of smaller sizes, i.e. PM_1. For all 18 individual compounds, the proportion in PM_1 (in comparison with $PM_{2.5}$) ranged between 65% (pyrene) and 95% (fluoranthene). On average, PM_1–bound PAHs accounted for 76% for particulate Σ_{PAHs} whereas PAHs on particles bigger than 1 μm (i.e. $PM_{1-2.5}$) accounted for 14% of PAH particulate content. Overall, these results confirmed the previously reported findings that particulate-bound PAHs are predominantly found in smaller fractions of PM (Klejnowski et al., 2010; Ladji et al., 2014). Due to their ability to deposit deep in the lower airways, the smaller classes of PM are more apt to cause respiratory toxicity and dysfunction. Furthermore, various chemical compounds bound to these small particles, such as PAHs, may eventually enhance (or at least contribute to) the PM–induced adverse health effects (Kim et al., 2013; Saravia et al., 2013).

Out of 18 analysed PAHs, naphthalene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]luoranthene, benzo[a]pyrene, dibenzo[a,l]pyrene, dibenz[a,h]anthracene and indeno[1,2,3–cd]pyrene were reported as carcinogenic ones (possible, probable) (IARC, 2002, 2010). The mean concentrations of these ten carcinogenic PAHs (i.e. $\Sigma_{PAHscarc}$) in indoor PM, gas phase, and in indoor air are reported also in Table 2. Dibenz[a,h]anthracene, a strong carcinogen with a toxic equivalency factor (TEF) 5 times higher than benzo[a]pyrene (Okona-Mensah et al., 2005), was the most abundant carcinogen and accounted for 40% of $\Sigma_{PAHscarc}$. Considering the protection of public health, it is important to stress that dibenz[a,h]anthracene exhibited the highest concentrations of all 18 PAHs in both $PM_{2.5}$ and PM_1 in indoor air of the studied preschool, being followed by other carcinogens: benzo[b+j]fluoranthene (20% of $\Sigma_{PAHscarc}$) and indeno[1,2,3–cd]pyrene (16 and 18% of $\Sigma_{PAHscarc}$ in PM_1 and $PM_{2.5}$, respectively). Finally, benzo[a]pyrene, the most studied and characterized carcinogen (IARC, 2010), was the fifth most abundant particulate (and the fourth most abundant carcinogenic) PAH, contributing 8% of $\Sigma_{PAHscarc}$ in both PM size fractions. Concerning the gas phase, naphthalene was the predominant carcinogenic gaseous PAH (94% of gaseous $\Sigma_{PAHscarc}$) as the content of other carcinogenic compounds was much less significant (i.e. 0.5–2% of gaseous $\Sigma_{PAHscarc}$).

The total concentration of the carcinogenic PAHs in indoor air of the studied pre-school was 12.8 ng m^{-3}. The obtained results showed that 64% of $\Sigma_{PAHscarc}$ existed in the gas phase whereas 36% was particle–bound. Despite this distribution, carcinogenic PAHs accounted for 27% of the gaseous PAH content whereas it was 74% of Σ_{PAHs} in both $PM_{2.5}$ and PM_1; similarly Jyethi et al. (2014) reported that carcinogenic PAHs accounted for approximately 75% of the particulate PAH content. Finally, in agreement with the findings on the distribution of PAHs (Figure 1), carcinogenic particulate PAHs were predominantly associated with PM_1 (76%).

3.3 Outdoor PAHs and source identification

The levels of PAHs in $PM_{2.5}$ measured outdoors in the preschool yard are presented in Table 4. Overall, concentration levels of outdoor particulate PAHs were similar to those reported in earlier studies (Castro et al., 2011; Slezakova et al., 2013a,b). The levels registered in ambient air of the selected preschool were much higher compared to other Portuguese and Italian cities (Alves et al., 2014; Cirillo et al., 2006). On the contrary, in close proximity of schools situated in Asian countries authors reported much higher concentrations of particle–bound PAHs (Jyethi et al., 2014; Ruchirawat et al., 2006, 2007) compared to this study. In general, the observed concentrations of outdoor particulate PAHs were higher than the indoor ones, but the compositional profiles were similar. The most abundant compounds were (in descending order): dibenz[a,h]anthracene (25% of ΣPAH_{scarc}), benzo[b+j]fluoranthene (approximately 15%), indeno[1,2,3–cd]pyrene (9%) and benzo[ghi]perylene (8%). Finally, ten carcinogenic PAHs accounted for 78% of the particulate PAHs, being similar percentage as indoors.

3.3.1 Indoor–to–outdoor ratios

Indoor–to–outdoor concentration ratios (I/O) of individual PAHs can provide some clues about pollutant's origin. I/O ratios of all 18 $PM_{2.5}$–bound PAHs are presented in Figure 2. The mean I/O ratios of all 18 PAHs were lower than unity suggesting that outdoor air is the dominant contributor to indoor PAH levels at this site. However, on some occasions all 18 PAHs exceeded unity, indicating contributions from indoor sources. Krugly et al. (2014) reported I/O ratio higher than unity for low molecular weight PAHs in indoor air of schools; these authors suggested an indoor origin due the respective activities of the occupants and/or volatilization from building materials. The potential indoor sources registered during the sampling in the studied preschool that could have resulted in elevated PAH content included combustion sources (candles on birthday cake during several occasions; Derudi et al., 2013), children artistic activities during classes (i.e. painting, sculpturing, wax melting, and other arts and crafts activities) and classroom cleaning (wood polishing) (Morawska et al., 2013).

3.3.2 Diagnostic ratios

The ratio values of individual PAH concentrations were used as diagnostic tools to identify the possible origin of the PAHs. The diagnostic ratios were calculated based on the same particulate fraction ($PM_{2.5}$) for both indoor and outdoor PAHs and means are presented in Table 5. It is necessary to point out that such ratios are crude indicators of possible sources and need to be used with caution; it is often difficult to distinguish between different sources (Galarneau, 2008). Furthermore, their values can be altered due to the reactivity of some PAH species with other atmospheric species (such as ozone and/or oxides of nitrogen; Ravindra et al., 2008). Diagnostic ratios of the total concentration of 2 and 3–rings PAHs ($\Sigma PAHs_{LMW}$) to 4 and 6–ring PAHs ($\Sigma PAHs_{HMW}$) indicate if the origin of PAHs is pyrogenic or petrogenic. In case of ratio bigger than 1, a possible source of PAHs is petrogenic; otherwise the source may be considered as pyrogenic (Krugly et al., 2014; Zhang et al., 2008). In the studied preschool, these diagnostic ratios in both indoors and outdoors were lower than 1, indicating a pyrogenic origin of the PAHs as reported in previous studies; Slezakova et al. (2013b) identified emissions from vehicle road transport as the main sources of PAHs in Oporto. The road traffic was the most likely source of PAHs at the studied preschool; in agreement, the ratio of benzo[a]anthracene to chrysene was lower than 0.35, indicating combustion of fuel and/or vehicular emissions (Krugly et al., 2014). The ratio value of fluoranthene to (fluoranthene plus pyrene) suggests potential origin from vehicular traffic (Kavouras et al., 1999; Yunker et al., 2002; Zencak et al., 2007) but also possibly from coal combustion (Krugly et al., 2014). Similarly, the ratio indeno[1,2,3–cd]pyrene/(indeno[1,2,3–cd]pyrene+benzo[ghi]perylene), with values in range 0.35 to 0.70, indicates influence by diesel emissions (Kavouras et al. 2001; Rogge et al. 1993a; Sicre et al. 1987), as close to 0.56 it might suggest origin from coal combustion (Grimmer et al., 1983; Pio et al., 2001). Other ratios that were applied to the obtained PAHs levels in the studied preschool were indicative of vehicular influence. Ravindra et al. (2008) reported a ratio of benzo[a]pyrene to (benzo[a]pyrene plus chrysene) to distinguish between diesel (0.5) and gasoline (0.73) vehicle emissions. In addition, benzo[b]fluoranthene to benzo[k]fluoranthene ratios higher than 0.5 (Ravindra et al., 2008) and benzo[ghi]perylene/benzo[a]pyrene with values between 1.2 and 2.2 (Rogge et al., 1993a) also indicate diesel emissions. The comparison of the data in Table 5 with values of these three ratios, but also with ratios of benzo[b+k]fluoranthene and benzo[ghi]perylene shows that diesel motor emissions were a source of particulate PAHs at the studied preschool. These findings are in agreement with patterns of fuel consumption in Portugal: diesel is the most used car fuel – in 2011 it accounted for 78.4% of the total national car fuel consumption (National Institute of Statistics, 2013). The ratio of fluorene/(fluorene+pyrene) is typically also used to differentiate between diesel and gasoline exhausts. Whereas values > 0.5 indicates contribution from diesel emissions, ratios < 0.5 indicate gasoline emissions (Ravindra et al., 2008; Rogge et al., 1993a); the present result shows very low values of this diagnostic ratio thus suggesting some presence of gasoline emissions. Finally, phenanthrene/(phenanthrene+anthracene) ratio exhibited values higher than 0.7, which are characteristic of contributions from lubricant oils and fossil fuels (Mirante et al., 2013). In general it is possible to conclude that most of the observed PAH diagnostic ratios indicated traffic (with a predominant contribution of diesel) and fossil fuel (with contribution of coal) combustion as the main sources of PAHs in the studied preschool.

4. **Conclusions**

This study fills a gap providing information on the PAH levels and phase distribution in indoor air in a preschool environment. Little information was available for school or for preschool facilities especially with regard to gaseous compounds or PAHs bound to the finest PM. In total, the gaseous PAHs accounted for 85% of Σ_{PAHs}. This high proportion of PAHs in the gaseous phase clearly demonstrates that adequate assessment of PAHs exposure requires consideration of the gaseous compounds, which are in the most of the studies neglected. Particulate PAHs were predominantly associated with PM_1 (76% particulate ΣPAHs) with 5 rings PAHs being the most abundant. The use of various diagnostic ratios determined two main sources of indoor PAHs: traffic emissions and the combustion of fossil fuel, as a consequence of penetration of outdoors into the indoor air.

Children represent one of the most vulnerable groups in society. In order to provide a better information for the protection of their health, the future work should focus on the characterizing PAH exposure of children, also considering various school microenvironments.

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Figure Captions

Figure 1 Distribution of PAHs between particulate and gaseous phases in indoor air of the studied preschool. The particle phase is further divided into PM_1 and $PM_{1–2.5}$ fractions (particles with aerodynamic diameter between 1.0 and 2.5 μm).

Figure 2 Indoor to outdoor (I/O) $PM_{2.5}$–bound PAH ratios at the studied preschool. Midpoints represent average values; whiskers are 25th and 75th percentiles.

Table 1

Characterization of the studied preschool, meteorological and indoor and outdoor air pollution conditions during the sampling campaign

General description	Built in 1940
	Private school
	Two-floors building
	173 enrolled students: 3-5 years old
Location	Urban - traffic
	Situated on moderately trafficked streets
Traffic density	Mean: 16 cars min^{-1}
	Peak hours: 8:30h (27 cars/min)
	18:30h (25 cars/min)
Indoor parameters	Temperature: 18.2 ± 1.1 ºC
	Relative humidity: 58.7 ± 9.0 %
Indoor pollutants levels (mg m^{-3})	[a]
Mean (Min – Max)	TVOCs: 2.67 (0.601 – 4.51)
	CO_2: 2340 (1360 – 3400)
	CO: 1.01 (n.d – 2.84)
(µg m^{-3})	Formaldehyde:184 (n.d.– 479)
	Ozone: 0.128 (8.97×10^{-2} – 0.180)
Outdoor meteorological parameters	

Mean ± SD	Temperature: 13.0 ± 2.4 ºC
	Relative humidity: 73.0 ± 15.6 %
	Wind speed: 4.5 ± 2.4 km h^{-1}
	Precipitation: 2.9 ± 3.02 mm
	Solar radiation: 162 ± 53 W m^{-2}
Outdoor pollution parameters (µg m^{-3})	
Mean (Min – Max)[b]	PM_{10}: 33 (6–80)
	NO: 148 (30–1369)
	CO: 981 (314–1559)

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[a] Total volatile organic compounds (TVOCs), carbon dioxide (CO_2), and carbon monoxide (CO).

[b] Figures in parenthesis represent concentration ranges of 24–h means during the sampling campaign as settled in EU air quality legislation (Directive 2008/50EC).

Table 2

Indoor levels of PAHs in $PM_{2.5}$, PM_1, gas phase, and in air (i.e. total) at the studied preschool (ng m^{-3})

Indoor	Particulate phase								Gas phase				Air			
Compound	$PM_{2.5}$				PM_1											
	Mean	25th	Median	75th	Mean	25th	Median	75th	Mean	25th	Median	75th	Mean	25th	Median	75th
Naphthalene	0.14	3.5×10^{-2}	4.9×10^{-2}	0.16	n.d.	n.d.	n.d.	n.d.	7.7	4.6	5.9	12.6	7.8	4.4	5.6	11
Acenaphthylene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.8	2.0	2.8	4.6	3.8	2.0.	2.8	3.9
Acenaphthene	0.23	0.13	0.26	0.33	n.d.	n.d.	n.d.	n.d.	0.96	0.39	0.59	1.4	1.1	0.20	0.67	1.2
Fluorene	2.5×10^{-2}	1.2×10^{-2}	2.0×10^{-2}	2.9×10^{-2}	2.5×10^{-2}	1.0×10^{-2}	1.9×10^{-2}	2.8×10^{-2}	5.6	3.1	4.9	6.7	5.6	2.9	4.7	6.5
Phenanthrene	0.13	6.1×10^{-2}	0.11	0.17	0.11	5.5×10^{-2}	7.7×10^{-2}	0.17	9.6	7.5	8.6	11	9.8	7.3	8.7	11
Anthracene	4.2×10^{-2}	1.7×10^{-2}	2.7×10^{-2}	5.8×10^{-2}	3.6×10^{-2}	1.1×10^{-2}	2.7×10^{-2}	5.5×10^{-2}	0.15	4.3×10^{-2}	0.16	0.20	0.20	0.13	0.18	0.21
Fluoranthene	0.37	0.20	0.34	0.46	0.35	0.23	39×10^{-2}	0.44	0.52	0.48	0.54	0.56	0.88	0.70	0.78	0.89
Pyrene	0.29	0.12	0.24	0.40	0.19	6.2×10^{-2}	9.9×10^{-2}	0.34	0.72	0.45	0.64	0.92	1.0	0.60	0.94	1.1
Benz[a]anthracene	0.12	4.2×10^{-2}	9.9×10^{-2}	0.16	8.5×10^{-2}	2.3×10^{-2}	3.5×10^{-2}	0.13	1.7	1.1×10^{-2}	1.6×10^{-2}	2.0×10^{-2}	0.13	6.1×10^{-2}	9.4×10^{-2}	0.16
Chrysene	0.31	0.16	0.25	0.44	0.24	0.14	0.25	0.32	9.9×10^{-2}	5.3×10^{-2}	9.6×10^{-2}	0.13	0.41	0.17	0.32	0.56
Benzo[b+j]fluoranthene	0.96	0.44	0.76	1.1	0.69	0.25	0.38	0.91	0.13	8.9×10^{-2}	0.12	0.16	1.1	0.60	0.79	1.2
Benzo[k]fluoranthene	0.20	0.10	0.16	0.24	0.15	5.9×10^{-2}	9.5×10^{-2}	0.19	2.3×10^{-2}	1.7×10^{-2}	2.1×10^{-2}	2.4×10^{-2}	0.24	0.13	0.18	0.25
Benzo[a]pyrene	0.36	0.17	0.26	0.40	0.29	0.11	0.16	0.39	8.9×10^{-2}	4.9×10^{-2}	6.5×10^{-2}	0.11	0.45	0.28	0.32	0.48
Dibenzo[a,l]pyrene	6.4×10^{-2}	2.1×10^{-2}	5.8×10^{-2}	0.11	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6.4×10^{-2}	2.1×10^{-2}	5.8×10^{-2}	0.11
Dibenz[a,h]anthracene	1.73	0.84	1.40	2.4	1.4	0.79	0.98	1.92	2.9	8.2×10^{-2}	0.14	0.24	1.9	0.93	1.5	2.2
Benzo[ghi]perylene	0.50	0.25	0.39	0.58	0.46	0.21	0.25	0.52	5.5×10^{-2}	7.5×10^{-2}	0.11	0.12	0.59	0.30	0.51	0.67
Indeno[1,2,3-cd]pyrene	0.72	0.47	0.58	0.92	0.65	0.50	0.62	0.85	n.d.	n.d.	n.d.	n.d.	0.72	0.47	0.58	0.92
Σ_{PAHs}	6.2	3.0	4.6	7.6	4.7	1.9	3.5	6.0	30	17	25	36	35	24	30	40
$\Sigma_{PAHscarc.}$	4.6	2.2	3.6	5.9	3.5	1.0	2.5	3.7	8.2	5.2	6.1	13	13	7.6	9.8	15

Table 3

PAH levels (mean ± SD or range, expressed as ng m^{-3}) reported in indoor and outdoor air of educational environments: comparison with existent studies

Location	Type of school (children age)	Note	Analysed phase	No. of PAHs	ΣPAHs indoor	ΣPAHs outdoor	Reference
Porto, Portugal	Preschool (3-5 years)	Urban	PM$_{2.5}$	18	0.72 – 16	1.2 – 33	This study
			PM$_1$		0.53 – 15		
			Gas phase		14 – 66		
			Total air		20 – 82		
Aveiro, Portugal	Primary (n.r.)	City centre	PM$_{10}$	n.r.	0.893 ± 0.650	0.830 ± 0.421	Alves et al., 2014
Linz, Austria	Elementary (7-10 years)		PM$_{2.5}$			1.5 – 174.7	Moshammer and Neuberger, 2003
Campania, Italy	n.r.	Urban	Total air (PM + gas)	16	0.30 – 6.30	0.3 – 3.4	Cirillo et al., 2006
	(7-9 years)	Rural			1.70 – 7.90	0.6 – 1.4	
Rome, Italy	Elementary	Summer	PM$_{2.5}$	8	2.21 – 1.32	0.36 –2.56	Gatto et al., 2013
	(8-11 years)	Winter			1.6 – 16	4.2 – 18.5	
Kaunas, Lithuania	Primary (n.r.)		PM$_{2.5}$	15	20.3 –131	40.7 – 121.1	Krugly et al., 2014
			Gas		35.6 – 80.6	n.r.	
North Carolina, USA	Preschool (2-5 years)		Total air (PM + gas)	18	0.04 – 1044	0.04 – 76.5	Wilson et al., 2003
Thailand		Urban	PM				Ruchirawat et al., 2006
Bangkok	n.r.	Classroom	PM–air particulates		5.06 – 9.39		Ruchirawat et al., 2007
	(9-13 years)	Playground			2.64 – 25.54	12.01 – 99.95	
Bangkok		Rural					
		Classroom			0.28 – 2.31		
		Playground			0.28 – 1.92	0.31 – 2.91	
Thailand, Bangkok	Primary (8-13 years)	Urban	PM	10		2.10 – 25.54	Tuntawiroon et al., 2007
Bangkok		Rural				0.28 – 2.31	

Delhi, India	Primary (n.r.)	Industrial and roadside	PM_{10}	10	n.r.	38.1 – 217.3	Jyethi et al., 2014

n.r. – not reported

Table 4

Concentrations of $PM_{2.5}$–bound PAHs in ambient (i.e. outdoor) air of the studied preschool (ng m^{-3})

Compound	Mean	25th	Median	75th
Naphthalene	0.76	5.5×10^{-2}	6.9×10^{-2}	0.20
Acenaphthylene	0.80	0.40	0.83	1.2
Acenaphthene	0.12	3.3×10^{-2}	4.5×10^{-2}	0.18
Fluorene	5.0×10^{-2}	1.4×10^{-2}	3.1×10^{-2}	3.8×10^{-2}
Phenanthrene	0.27×10^{-2}	0.12	0.17	0.31
Anthracene	7.1	2.7×10^{-2}	5.0×10^{-2}	0.10
Fluoranthene	0.61	0.26	0.45	1.0
Pyrene	0.62	0.28	0.44	0.75
Benz[a]anthracene	0.25	7.1×10^{-2}	0.13	0.27
Chrysene	0.60	0.27	0.33	0.76
Benzo[b+j]fluoranthene	1.3	0.39	0.86	1.7
Benzo[k]fluoranthene	0.29	0.11	0.18	0.33
Benzo[a]pyrene	0.49	0.15	0.31	0.57
Dibenzo[a,l]pyrene	9.8×10^{-2}	5.7×10^{-2}	8.2×10^{-2}	0.12
Dibenz[a,h]anthracene	2.2	0.88	1.5	2.50
Benzo[ghi]perylene	0.70	0.32	0.42	0.76
Indeno[1,2,3-cd]pyrene	0.79	0.20	0.54	0.94
Σ_{PAHs}	8.9	4.0	5.5	13
$\Sigma_{PAHscarc}$	6.8	2.8	4.2	10

Table 5

Diagnostic ratios for PM$_{2.5}$–bound PAHs at the studied preschool

Ratio	This study		Value	Source	Reference
	Indoor	Outdoor			
$^{a}\Sigma PAHs_{LMW}/\Sigma PAHs_{HMW}$	0.24	0.57	> 1 < 1	Petrogenic Pyrogenic	Zhang et al., 2008
Benzo[a]anthracene/Chrysene	0.38	0.42	> 0.35	Fuel combustion	Krugly et al., 2014
Fluoranthene/(Fluoranthene + Pyrene)	0.54	0.50	0.40-0.5 >0.5 0.42, 0.52	Vehicular traffic Coal combustion Road dust	Kavouras et al., 1999; Yunker et al., 2002; Zencak et al., 2007; Rogge et al., 1993a; Oda et al., 2001
Indeno[1,2,3-cd]pyrene/(Indeno[1,2,3-cd]pyrene + Benzo[ghi]perylene)	0.59	0.52	0.21–0.22 0.35–0.70 0.56 0.62 0.36	Gasoline cars Diesel emissions Coal combustion Wood combustion Road dust	Guo et al., 2003; Grimmer et al., 1983; Gogou et al., 1996; Kavouras et al., 2001; Khalili et al.,1995; Ravindra et al., 2008; Rogge et al., 1993a; Pio et al., 2001;
Benzo[a]pyrene/(Benzo[a]pyrene + Chrysene)	0.54	0.45	0.5 0.73	Diesel Gasoline	Ravindra et al., 2008
Benzo[b]fluoranthene / Benzo[k]fluoranthene	4.72	4.64	>0.5	Diesel	Ravindra et al., 2008
Benzo[ghi]perylene / Benzo[a]pyrene	1.38	1.44	1.2–2.2 2.5–3.3 0.86, 0.91	Diesel cars Gasoline cars Road dust	Rogge et al.,1993a,1993b ; Oda et al., 2001
Benzo[a]anthracene/(Benzo[a]anthracene + chrysene)	0.27	0.30	0.40, 0.38–0.64 0.76 0.43	Diesel Gasoline Wood combustion	Manoli et al., 2004; Sicre et al., 1987; Li and Kamens, 1993
Benzo[b+k]Fluoranthene/Benzo[ghi]perylene	1.36	1.75	1.60 0.33 2.18	Diesel cars Gasoline cars Wood combustion	Li and Kamens, 1993
Fluorene/(Fluorene + Pyrene)	0.08	0.07	>0.5 <0.5	Diesel Gasoline	Ravindra et al., 2008

Phenanthrene/ (Phenanthrene+ Anthracene	0.75	0.79	>0.7	Lubricant oils and fossil fuels	Mirante et al., 2013

[a] Total concentration of 2– and 3–ring PAHs (ΣPAHs$_{LMW}$), and 4– and 6–ring PAHs (ΣPAHs$_{HMW}$)

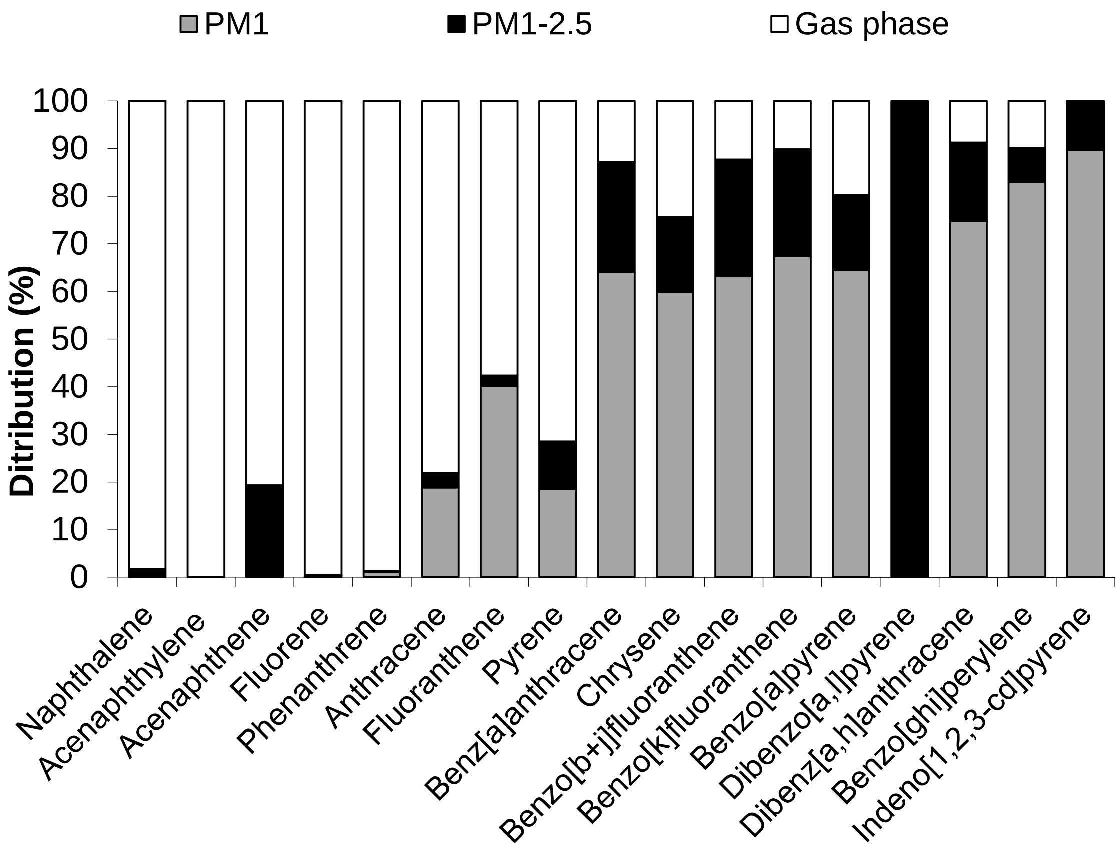
PM1
PM1-2.5
Gas phase
Ditribution (%)
100
90
80
70
60
50
40
30
20
10
0
Naphthalene
Acenaphthylene
Acenaphthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benz[a]anthracene
Chrysene
Benzo[b+j]fluoranthene
Benzo[K]fluoranthene
Benzo[a]pyrene
Dibenzo[a,l]pyrene
Dibenz[a,h]anthracene
Benzo[ghi]perylene
Indeno[1,2,3-cd]pyrene

Figure 1

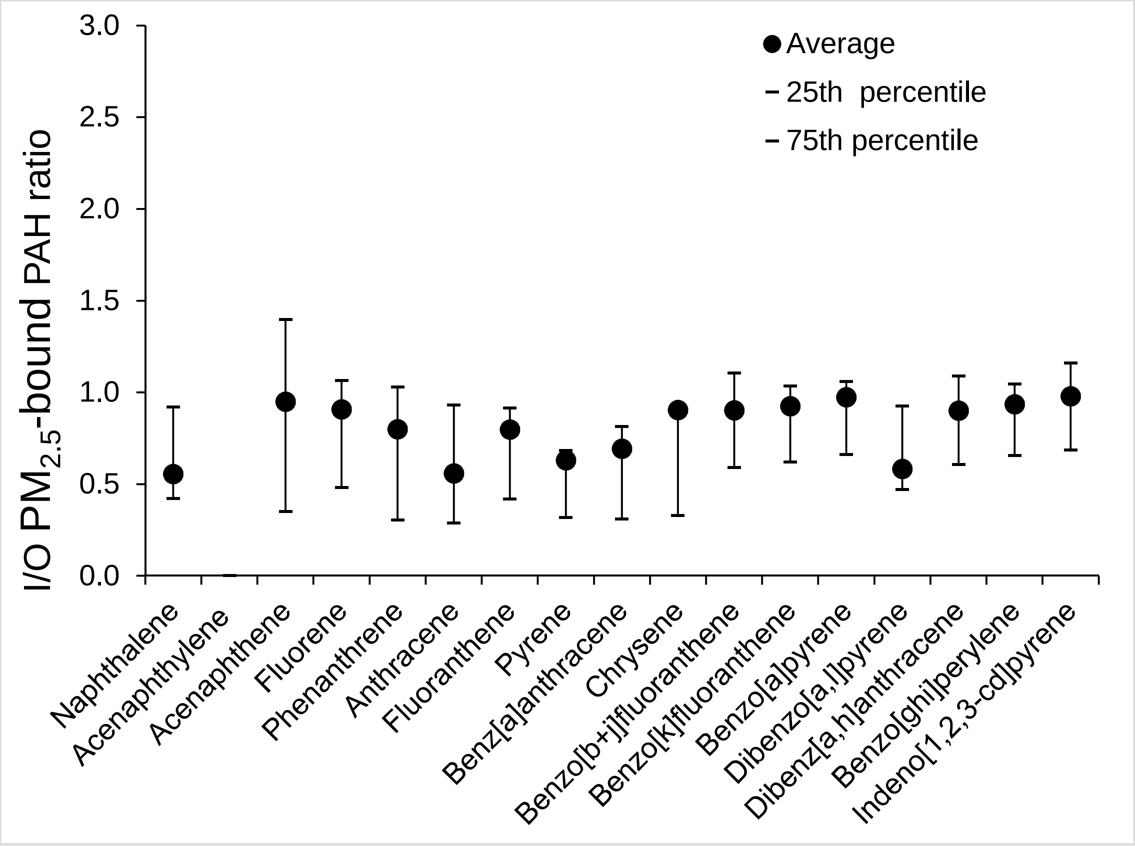
3.0
2.5
2.0
1.5
1.0
0.5
0.0
I/O PM2.5-bound PAH ratio
● Average
- 25th percentile
- 75th percentile
Naphthalene
Acenaphthylene
Acenaphthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benz[a]anthracene
Chrysene
Benzo[b+j]fluoranthene
Benzo[k]fluoranthene
Benzo[a]pyrene
Dibenzo[a,l]pyrene
Dibenz[a,h]anthracene
Benzo[ghi]perylene
Indeno[1,2,3-cd]pyrene

Figure 2