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Assessment of exposure to polycyclic aromatic hydrocarbons in preschool children: Levels and impact of preschool indoor air on excretion of main urinary monohydroxyl metabolites

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HIGHLIGHTS

- Children PAHs exposure was assessed by environmental monitoring and biomonitoring;.
- Total levels of PAHs in preschools were higher indoors than outdoors;.
- Indoor sources affected mainly levels of lighter compounds (2–3 rings);.
- Combined level of 1OH-Naph and 1OH-Ace was predominant among urinary metabolites;.
- Significant correlations were found among urinary OH-PAH excretion and inhaled PAHs.

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ABSTRACT

The present work aimed to assess exposure of preschool children to polycyclic aromatic hydrocarbons (PAHs) by environmental monitoring (eighteen compounds in air) and biomonitoring (six urinary biomarkers of exposure (OH-PAHs)). The impact of preschool indoor air on excretion of urinary monohydroxyl metabolites was also evaluated. Gaseous and particulate-bound PAHs were simultaneously collected indoors and outdoors in two Portuguese preschools. PAHs and OH-PAHs were quantified by high-performance liquid chromatography with fluorescence and photodiode array detection. Total air (gaseous + total suspended particles) levels of PAHs (ΣPAHs) were higher indoors than outdoors. Gaseous phase (composed by ≥98% of 2–3 rings compounds) and particulate-bound PAHs (90–99% of 5–6 rings) accounted for 93–95% and 5–7% of ΣPAHs in indoor air, respectively. Total (including probable/possible) carcinogenic PAHs represented 26–45% of ΣPAHs; naphthalene and dibenz[a,h]anthracene were the strongest contributors. A similar distribution profile was observed between airborne PAHs and urinary OH-PAHs. Urinary 1-hydroxynaphthalene + 1-hydroxyacenaphthene represented more than 78% of ΣOH-PAHs, being followed by 2-hydroxyfluorene, 1-hydroxypyrene, and 1-hydroxyphenanthrene. 3-hydroxybenzo[a]pyrene (PAH biomarker of carcinogenicity) was not detected. Results suggest that children had preschool indoor air as their major exposure source of naphthalene and acenaphthene, while no conclusion was reached regarding fluorene, phenanthrene and pyrene.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous and persistent compounds formed during pyrolysis or incomplete combustion of organic matter, with air and food as major routes of exposure [1,2]. Man-made sources of PAHs include motor-vehicle exhausts, emissions from industry, commercial and residential heating using coal, wood or other biomass fuels, and indoors tobacco smoke [3–6]. US Environmental Protection Agency listed 16 PAHs as priority compounds [7] since some compounds are toxic and present mutagenic and/or carcinogenic properties [8,9]. Benzo[a]pyrene is the only known carcinogen (group 1, International Agency for Research on Cancer (IARC) [8]), while naphthalene, benz[a]anthracene, benzo[b]fluoranthene,

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benzo[j]fluoranthene, benzo[k]fluoranthene, chrysene, and indeno[1,2,3-cd]pyrene are considered as possible carcinogen to humans (group 2B, IARC) [8,9]. Dibenzo[a,l]pyrene and dibenz[a,h]anthracene (group 2A-probable carcinogens to humans) have been also under scrutiny due to their higher carcinogenic potency than benzo[a]pyrene [10–12]. PAHs are also classified as endocrine disrupting chemicals [13], with some of them causing neuro-, immuno-, hemato-, cardio-, reproductive and developmental toxicities in humans and laboratory animals [14].

Children are more susceptible to environmental pollutants because their immune and respiratory systems are still developing and due to their higher inhalation rates than adults [15]. Typically, children spend up to $^1/_3$ of the time (i.e. around 7–8 h) at education institutions such as preschools, primary or elementary schools. Therefore, understanding the exposure to health relevant pollutants in these places has become a priority to the scientific community [16,17], as well as to international organisations. Incorporating exposure biomarkers into studies is particularly relevant in children because absorbed dose for a given external exposure level may be very different from that of an adult due to different behaviours (playing on the floor and hand-to-mouth activity), physiology, and metabolism [18]. Among the many different elimination routes of PAH metabolites, urine is the easiest, cheapest and less invasive matrix. 1-hydroxypyrene (1OHPy) and 3-hydroxybenzo[a]pyrene (3OHBaP) are the more widely used biological indicators of exposure to total and carcinogenic PAHs, respectively [19,20] Acenaphthene, fluorene, and phenanthrene are common PAHs in different matrices [11,21–23], being 1-hydroxyacenaphthene (1OHAce), 2-hydroxyfluorene (2OHFlu), and 1-hydroxyphenanthrene (1OHPhen) their major metabolites, respectively. Concerning naphthalene, 1-hydroxynaphthalene (1OHNaph) and 2-hydroxynaphthalene are the main metabolites [24]. Regarding PAHs, among the available information in educational settings [11,21–23,25–40], only eight works focused on preschools [11,22,23,27,37–40]. Studies that assessed simultaneously environmental PAH levels and urinary concentrations of OH-PAHs in preschool children (3–6 years old) are even scarcer [23,27,37,38], with very limited information concerning European countries (only one study performed 15 years ago in Czech Republic [27]) and other compounds besides 1OHPy. Furthermore, no report that also differentiates between genders in preschool children was found.

Thus, the present work aimed to assess exposure of Portuguese preschool children to PAHs by environmental monitoring (18 compounds in air: 16 USEPA priority PAHs, dibenzo[a,l]pyrene, and benzo[j]fluoranthene recommended by EU Directive 2004/107/EC [41]) and biomonitoring (six urinary biomarkers of exposure: 1OHNaph, 1OHAce, 2OHFlu, 1OHPhen, 1OHPy, and 3OHB[a]P). Potential sources of PAHs in preschool environments were investigated and the contribution of outdoor emissions to indoors assessed. In addition, the impact of preschool indoor air on excretion of urinary monohydroxyl metabolites was explored for the first time taking into consideration differences between genders.

2. Materials and methods

2.1. Characterization of the sampling sites

Preschool one (PS1) was situated in Paranhos (41°10′36.12N; 8°36′50.54W), Oporto Metropolitan Area (2nd largest Portuguese city) where main emission sources of PAHs include vehicular traffic, an international shipping port, petrochemical complex with oil refinery situated nearby, and an incineration unit [12]. The second preschool (PS2) was located 150 km north–east of Oporto (41°44′29; 7°28′19W), in city of Chaves (municipality with 2nd highest population in Vila Real district). PS2 was located directly next to a road which is the major thoroughfare to city center. A mall and gas station (both being in direct vicinity of PS2) resulted in consistent vehicular traffic throughout the day. Further characterization of preschools is presented in Table 1S (Supplementary material).

2.2. Sample collection

2.2.1. Air

PAHs in gas phase and in total suspended particulate matter (TSP) were simultaneously sampled in indoor air and outdoors of PS1 and PS2. A total of 152 samples (88 and 64 at PS1 and PS2, respectively) were collected between May-June 2015 during a 8 h period when children were present at premises of preschools (9 a.m. till 5 p.m.). Collection of indoor samples was performed at classrooms that were consistently occupied throughout day for educational and entertaining activities of preschool children; detailed descriptions of places are presented in Table 1S. Ambient air sampling was conducted in preschool yards where children daily played. TSP samples were collected on polytetrafluoroethylene membrane disks (Ø47 mm, SKC Ltd., UK) whereas gaseous PAHs were trapped in pre-cleaned polyurethane foam (PUF) plugs (75 mm, SKC Ltd., UK) according to the method USEPA TO13A [42] and previous studies [43,44]. The validated conditions of the method [42] are 24 h sampling time with total sample volume up to 300 m^3; the total volume used in the present work was 18–20 m^3. Thus it was not necessary to use a second (a back-up) PUF in series. Both phases were simultaneously collected by constant low-flow (38.3 L min^{-1}) pumps (models Bravo H2; TCR TECORA, Italy) connected to specific PM EN LVS sampling heads. Indoors, the inlets were positioned at 1.3 m above the floor and about 1 m from the walls, without obstructing the normal usage of the rooms. Outdoors, the collectors were positioned in open areas avoiding any barriers (such as fences, walls, vegetation that might interfere with data collection). Samples were kept at −20 °C before chromatographic analysis.

2.2.2. Urine

A total of 43 children (3–5 years old) participated in this study (Table 2S). A structured questionnaire that was adapted from validated questionnaires [45,46] was filled out by parents. The questionnaire collected information on gender, age and factors associated with PAH exposures, namely families' smoking habits, and the most consumed meals (boiled, roasted, and grilled) at home during the two days before urine collection. Since the majority of children lunched at preschools, all daily meals were registered. Children were not exposed to tobacco smoke.

USEPA recommends the collection of 24-h urine void for daily evaluation of total exposure to toxic substances that are primarily eliminated in the urine [47]. However, it is burdensome and almost impossible in young children. Thus parents were asked to collect two spot-urine specimens of their child: one in the morning immediately after the subject woke up (first-morning) and the other at night before the subject went to bed (last-night) according to previous studies [27,37,48,49]. Triplicate campaigns were performed. Urine samples were collected in sterilized polycarbonate containers and frozen at −20 °C until analysis.

2.3. PAHs and OH-PAHs chromatographic analysis

Extraction and determination of airborne PAHs, as well as urinary OH-PAHs were performed by previously validated analytical procedures [43,50–52]. Detailed information is presented in Supplementary material (section 2.3S and Fig. 1S).

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