

Journal Pre-proof

Health risk assessment of exposure to polycyclic aromatic hydrocarbons in household indoor environments

Tames Maria Florencia , Tavera Busso Ivan ,
Carreras Hebe Alejandra

PII: S2666-7657(21)00130-7
DOI: <https://doi.org/10.1016/j.envadv.2021.100159>
Reference: ENVADV 100159



To appear in: *Environmental Advances*

Received date: 16 September 2021
Revised date: 20 December 2021
Accepted date: 20 December 2021

Please cite this article as: Tames Maria Florencia , Tavera Busso Ivan , Carreras Hebe Alejandra , Health risk assessment of exposure to polycyclic aromatic hydrocarbons in household indoor environments, *Environmental Advances* (2021), doi: <https://doi.org/10.1016/j.envadv.2021.100159>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2021 Published by Elsevier Ltd.
This is an open access article under the CC BY-NC-ND license
(<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

Title: Health risk assessment of exposure to polycyclic aromatic hydrocarbons in household indoor environments

Authors: Tames, Maria Florencia ^{1,3*}; Tavera Busso, Ivan ^{2,4}; Carreras, Hebe Alejandra ^{2,4}.

¹ Atmospheric and Environmental Studies Group (GEAA), National Council for Scientific and Technical Research (CONICET), Argentina.

² Instituto Multidisciplinario de Biología Vegetal (IMBiV), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina.

³ National Technological University (UTN), Mendoza Regional Faculty (FRM), Argentina.

⁴ Departamento de Química, Facultad de Ciencias Exactas, Físicas y Naturales, Universidad Nacional de Córdoba, Córdoba, Argentina.

*Corresponding Author

Maria Florencia Tames, Ph.D.,

Coronel Rodríguez 273, M5500 Mendoza, Argentina.

TE +54 0261 524-4500 – mtames@mendoza-conicet.gob.ar

Highlights

- PAH levels were particularly high in all PM fractions collected during summer.
- Larger particles ($PM_{>2.5}$) had a higher proportion of PAHs compared to smaller ones ($PM_{<1}$).
- None of the calculated health risks exceeded the levels recommended by the Environmental Protection Agency of the United States.
- Indoor environments could be significant exposure scenarios for PAHs.

Abstract:

Airborne particles are able to transport the potentially mutagenic and carcinogenic compounds adsorbed to their surfaces, such as polycyclic aromatic hydrocarbons (PAHs). As a result, they can affect human health and, consequently, the quality of life. In the present paper, we analyzed household airborne particles and estimated the human health risk due to PAH inhalation. Households from Cordoba city (Argentina) were selected for collecting weekly samples of total suspended particles, fine particles ($> 2.5 \mu\text{m}$) and submicron particles ($< 1 \mu\text{m}$) during a one-month period in both winter and summer. We found differences in the PAH composition among the three particle sizes, with the PAH levels being particularly high during summer for all three fractions, probably due to pollutants coming from outside or the persistence of pollutants inside homes. In addition, urban households had higher PAH levels than suburban houses. However, the calculated health risks due to the inhalation of particles never exceeded the levels recommended by the Environmental Protection Agency of the United States (< 1 in 10,000) for any age group. Our results, despite the relatively small number of houses included in the study, provide an indication of the likely exposure range of the population in urban environments of developing countries.

Keywords:

Particulate matter; Human health; Polycyclic aromatic hydrocarbons; Indoor air; Health risk assessment.

Acknowledgments

This work received partial support from Agencia Nacional de Promoción de la Investigación, el Desarrollo Tecnológico y la Innovación, Fondo para la Investigación Científica y Tecnológica (Grants PICT 2015# 3139 and PICT 2018 #03805). We thank Dr. Paul Hobson, native speaker, for revision of the manuscript.

Journal Pre-proof

1. Introduction

Atmospheric particles (PM) are a complex mixture of extremely small particles and liquid droplets made up of a carbonaceous fraction and inorganic constituents (Rogula-Kozłowska, 2016). These can affect human health and the quality of life, as small particles can enter the lungs, reach the *alveoli* and be distributed in the human body by means of the circulatory system. In addition, they can transport potentially mutagenic and carcinogenic compounds, such as polycyclic aromatic hydrocarbons (PAHs), which are adsorbed to their surfaces (Agudelo-Castañeda et al., 2017). PAHs are organic compounds with a low vapor pressure, which allows them to partition between the gaseous and particle phases of air. Based on the number of aromatic rings, they can be classified as low molecular weight PAHs (LMW, < 4 rings) or high molecular weight PAHs (HMW, ≥ 4 rings) (Hussain et al., 2018). The more benzene rings that form the PAH, the greater the carcinogenic and mutagenic capacities of the compound are (Abdel-Shafy and Mansour, 2016).

Some PAHs are pro-carcinogenic, carcinogenic or mutagenic, and can also affect the immune and cardiovascular systems, thereby constituting a human health risk (Lawal, 2017). Consequently, the United States Environmental Protection Agency (US EPA) has recognized 16 PAHs as being priority pollutants (US EPA, 1993), and the IARC (International Agency for Research on Cancer, World Health Organization, 2010) has classified some PAHs as being probably carcinogenic to humans (Group 1, 2A or 2B). In recent decades, the impact of inhalable suspended particles on human health has been widely explored (e.g.: Abdel-Shafy and Mansour, 2016; Agudelo-Castañeda et al., 2017), with most of these studies having focused on the influence of outdoor particles on respiratory and cardiovascular diseases. However, less attention has been paid to indoor particle exposure compared to outdoor studies, even though most people spend up to 90 % of their time indoors, mainly in households (Cattaneo et al., 2016; Tong et al., 2016). Moreover, during last year, the healthy population worldwide spent more time indoors than usual due to the COVID-19 pandemic (Domínguez-Amarillo et al., 2020).

Indoor air pollution may arise from smoking, cooking, heating combustion processes, the use of pesticides, and also from the inflow of outdoor air pollutants (Lawal et al., 2017). Previous studies have shown that building characteristics, in addition to activities carried out indoors, are more important for LMW PAHs, while the input of air from the outside is the main emission source of HMW PAHs (Cattaneo et al., 2016). Moreover, most of these pollutants have been reported to accumulate in indoor environments, with this being related to a lack of sunlight and inappropriate ventilation, thereby impairing the photolytic process and increasing the indoor residence time of the PAHs (Liu et al., 2018).

There are few studies that have been carried out in the region regarding indoor air quality and residential homes (e.g.: Colman Lerner et al., 2018). Thus, in the present study, we assessed human exposure to indoor PAHs by analyzing household airborne particles and estimated the human health risk due to inhalation. In this way, we were able to provide detailed information on the occurrence and concentration of PAHs adsorbed to different fractions of PM in residential homes.

2. Materials and Methods

2.1 Sample Site

The study area was the city of Cordoba, which is located in the center of Argentina (31°24' S, 64°11' W, ~400 m.a.s.l.) and has approximately 1.3 million inhabitants (Instituto Nacional de Estadística y Censo, 2010). It has a concave topography that reduces air circulation and causes frequent thermal inversions during the cold periods. Automobiles are the main outdoor air pollution source in Cordoba city, although there is also some contribution from the metallurgic and mechanical industries. Previous studies reported that, during wintertime, several days exceeded by 2.5 and 2.8 times the European Union Air Quality Guideline values for PM₁₀ and PM_{2.5}, respectively (Mateos et al., 2019). In addition, Carreras et al. (2015) reported a positive relationship between PM levels and hospital admissions due to respiratory diseases.

The city is divided into two zones: an urban zone including the city's downtown area, characterized by scarce vegetation and intense vehicular traffic; and a suburban zone with a low population density area, characterized by abundant natural vegetation and little vehicular traffic (Figure 1).

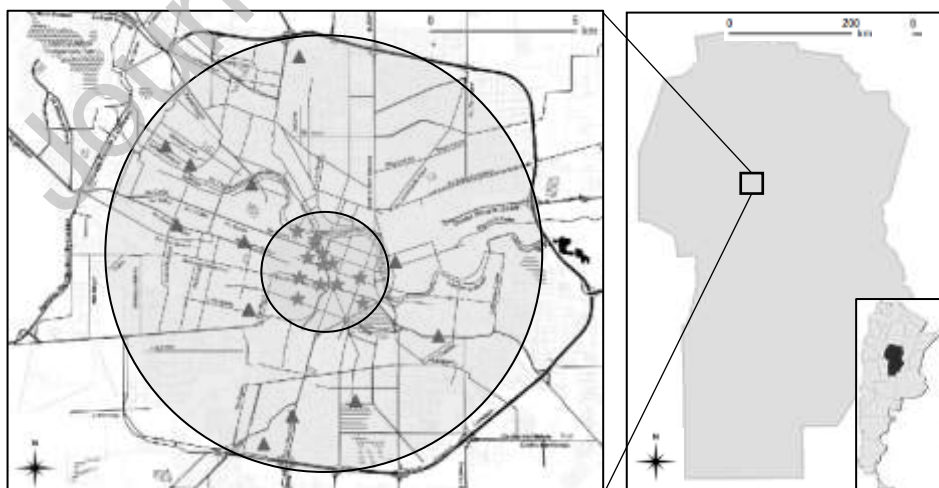


Figure 1. Study area in Cordoba city and sampling points in the urban (stars) and suburban (triangles) areas.

2.2 Sampling method

Only households were selected, with buildings used for offices or shops excluded. In addition, because smoking had been proven to be the main indoor source of PM PAHs (Niu et al., 2021), only non-smokers' homes were considered. Table SM-1 displays the general characteristics of the selected homes. Sampling was performed during one month in both winter (from 6/5/2015 to 6/8/2015) and summer (from 21/10/2015 to 30/12/2015).

For each sampling zone, 10 to 13 households were selected, and samples of total suspended particulate matter (TSP) were collected passively for 28 days, using glass total deposition flasks (Figure 2A) (Bermudez et al., 2012). Simultaneously, samples of $PM_{>2.5}$ (PM with an aerodynamic diameter above $2.5 \mu m$) were actively collected in 5 randomly selected households from each zone for one month, by employing a Harvard Impactor coupled to an air pump at a constant flow of $16.5 \pm 2 \text{ L min}^{-1}$ (Marple et al., 1987; US EPA, 2006) (Figure 2B). The apparatus used was operated according to US EPA (2006) approved standards. The total volume of sampled air was recorded in order to calculate the PAH concentrations. Particles larger than $2.5 \mu m$ were trapped in polyurethane foams (PUF, McMaster-Carr #86195K11 pink) located inside the impactor plate, which were renewed every seven days. This meant that a total of 4 samples of $PM_{>2.5}$ were collected from each household. Particles smaller than $2.5 \mu m$ and up to $1 \mu m$ were trapped from the airstream using polyvinylidene fluoride (PVDF) filters with a $1 \mu m$ pore diameter (Zefluor, Millipore). Finally, particles smaller than $1 \mu m$ and volatile compounds were adsorbed to pro-analytical granular activated charcoal $0.5\text{-}1.0 \text{ mm } \varnothing$ (Tames et al., 2019).

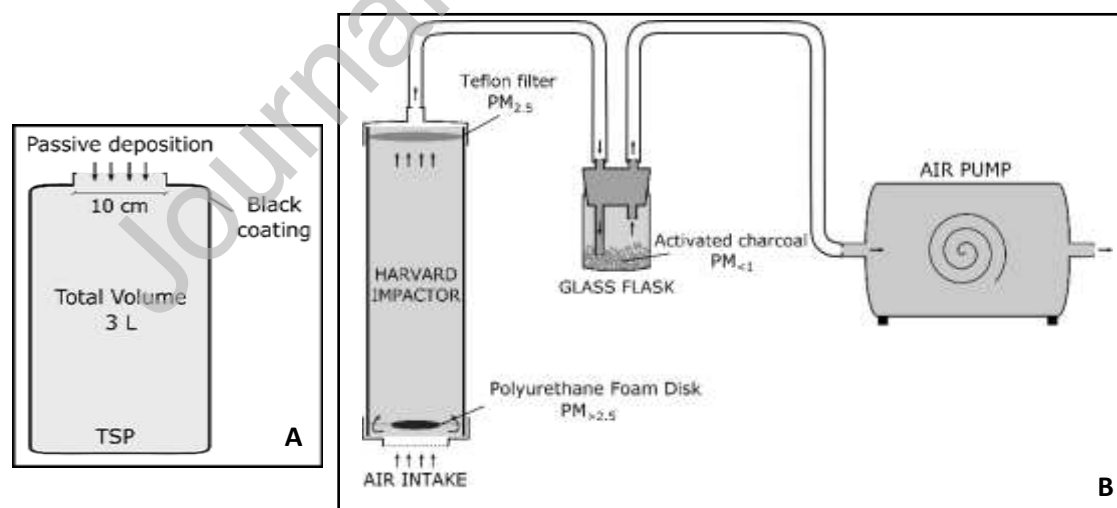


Figure 2. Sampling instruments used for the collection of TSP (A) and samples of $PM_{>2.5}$ and $PM_{<1}$ (B).

2.3 Organic extraction

The organic extraction was carried out following a methodology described by Tames et al. (2019), with some modifications. Briefly, the PAHs bound to the TSP fraction were extracted with 25 mL of dichloromethane (DCM), poured into deposition flasks, gently shaken at room temperature and then transferred to a beaker, with this procedure being repeated twice. For the $PM_{>2.5}$ -bounded PAHs, the PUF disks were sonicated twice with 25 mL of DCM for 30 minutes at room temperature. Finally, the $PM_{<1}$ -bound PAHs were extracted with 25 mL of DCM and then gently shaken for 24 h at room temperature, with this procedure being repeated twice.

All extracts were concentrated in a rotary evaporator to a final volume of 2 mL, filtered with PVDF filters (0.22 μm pore), and resuspended to a final volume of 5 mL. Then, 1 mL of each extract was placed in a previously conditioned 2 mL vial (5 h at 450 °C), dried under an N_2 flow, and resuspended in 0.5 mL of acetonitrile (ACN, HPLC grade).

2.4 PAH determination

The analyses and quantification of PAHs were carried out according to Tames et al. (2019), under strict quality assurance of the analytical procedures. Briefly, concentrations of naphthalene (Nap), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phen), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo(a,h)anthracene (B(ah)A), chrysene (Chry), benzo(b)fluoranthene (B(b)F), benzo(k)fluoranthene (B(k)F), benzo(a)pyrene (B(a)P), dibenzo(a,h)anthracene (DiB(ah)A), indeno(1,2,3-c,d)pyrene (I(123-cd)P) and benzo(g,h,i)perylene (B(ghi)P) were determined by fluorescence through high efficiency liquid chromatography (HPLC, Dionex Ultimate 3000, Thermo Scientific), employing a reversed phase C-18 column (Vydac 201TP 250 mm x 2.1 mm i.d., 5 μm). A five-point PAH curve (0.1 - 25 $\mu\text{g L}^{-1}$) was used for calibration (Supelco, Sigma), and the coefficient of determination (R^2) for all compounds was higher than 0.9991 ($p < 0.005$). Laboratory blanks were measured every 10 samples. Table SM-2 shows the HPLC running conditions, and Table SM-3 gives the retention times, detection, recovery percentages and quantification limits for the PAHs identified.

2.5 Health risk assessment

The health risk indices were calculated by taking into account the inherent toxicity of each compound (US EPA, 2011) and age groups in the population, since differences in exposure time could result in either an over- or underestimation of the risks.

Chemical risks were calculated considering the average daily dose (LADD), expressed as mg (kg day)^{-1} , and a slope factor (SF), expressed as $(\text{kg day}^{-1}) \text{ mg}^{-1}$ (Equation 1). The LADD was calculated by employing the concentration of each compound (CC, mg m^{-3}) and the intake factor (IF, $\text{m}^3 \text{ kg}^{-1} \text{ day}^{-1}$) (Equation 2). The IF was derived from the specific physiological and

exposure parameters of each age group (Equation 3). These parameters included average body weight (BW, kg), a conversion factor ($\mu\text{g mg}^{-1}$), breathing rate (IR_a : expressed as $\text{m}^3 \text{h}^{-1}$, and IR_b : expressed as $\text{m}^3 \text{day}^{-1}$), exposure frequency (EF) given by the number of exposures per year, duration of exposure (ED) expressed in years, exposure time (ET) given by the number of hours per exposure, and average time (AT) obtained from the average exposure time over a lifetime of 70 years (28,489.5 days). In addition, SF was obtained (Equation 4), which represents an estimate of a person's maximum likelihood of developing a cancer as a result of exposure to certain levels of a potential carcinogen over a lifetime (US EPA, 2011). This factor was calculated by considering the inhalation unit risks (IUR), derived from the potential cancer factors corresponding to exposure by inhalation (US EPA, 2005), and physiological parameters obtained from the Office of Environmental Health Hazard Assessment (OEHHA, 2005) and US EPA (2003) (Table SM-5). Finally, we calculated the total carcinogenic risk for each sampling site and for each age group (R) as the sum of the partial risks of the individual pollutants (R_i) (Equation 5).

The US EPA (2011) values, summarized in Table SM-5, were used for the calculations.

$$R = LADD \times SF$$

(1)

$$LADD = CA \times IF$$

(2)

$$IF = IR_a \times EF \times ED \times ET / BW \times AT$$

(3)

$$SF = IUR \times BW \times 1000 / IR_b$$

(4)

$$R_{cum} = \sum R_i$$

(5)

In health risk assessment, a risk of 10^{-6} (when the risk of developing cancer over a human lifetime is 1 in 1,000,000) represents a negligible cancer risk, a value between 10^{-6} and 10^{-4} is defined as a potential cancer risk (US EPA, 2003), while a risk that exceeds 10^{-4} (when the risk of developing cancer over a human lifetime is greater than 1 in 10,000) is a significant cancer risk (Maharjan et al., 2022).

2.6 PAH Diagnostic Ratios (DRs)

The DR method calculates the binary ratios of two PAHs that are frequently found in emissions, with certain values of these ratios indicating specific sources of PAHs (Krugly et al., 2014). The

ratios between some of the analyzed compounds were calculated and compared with values from previous studies (Table SM-6).

2.7 Statistical Analysis

The integrated software Chromeleon 7.2.0.3765 (Dionex, Thermo Scientific) was used to analyze the chromatograms, and the PAH concentrations were expressed in ng m^{-3} .

The descriptive statistics for the PAH concentrations were calculated using InfoStat v.2018e coupled with R 3.6.1, and an ANOVA analysis with LSD Fisher *ad hoc* test was employed to assess differences between zones and sampling periods. Differences with $p < 0.05$ were considered significant.

3. Results and Discussion

3.1 TSP

Even though the TSP level is no longer normally considered for air quality guidelines (US EPA, 2016; WHO, 2005), we decided to collect TSP samples in order to analyze the contribution of all particle fractions. Overall, greater concentrations of individual PAHs were found during the summer than the winter period in TSP, in both sampling zones (Table 1). This could be because windows usually remain closed during wintertime, thereby preventing the entry of outdoors pollutants. In contrast, during summertime, people tend to keep the house ventilated due to the warmer temperatures, thus allowing outdoor pollutants to enter residences. Related to this, indoor levels were considerably higher than those reported for outdoor environments in the same city (Mateos et al., 2019). This fact could be attributed to the sum of contributions from indoor emission sources and the accumulation of outdoor pollutants in indoor environments due to the lack of sunlight and limited ventilation, as already mentioned by Ali (2019). Similarly, Delgado-Saborit et al. (2011) found greater indoor levels of PAHs than outdoor in houses in the United Kingdom, and attributed this difference to the prevalence of high molecular weight and more stable PAHs entering from outdoor sources. Choi and Spengler (2014) found that PAHs of outdoor origin are the predominant contributor to indoor PAH concentrations. Similarly, Cattaneo et al. (2016) also reported that the infiltration of outdoor PAHs into indoor environments was the most important source of PAHs, with a relevant role being played by traffic exhausts as a general source of PAHs.

Our results were similar to those reported in indoor household air from Saudi Arabia (Ali, 2019). However, higher values were found in schools in Lithuania (Krugly et al., 2014), while lower ones were reported for indoor environments in China (Zhang et al., 2012). These differences could have arisen due to dissimilarities in the intrinsic characteristics of the cities. These might include weather conditions and the presence of outdoor emission sources near the

sampling zones, as well as differences in indoor activities such as cooking or heating (Cattaneo et al., 2016). For instance, Lin et al. (2002) found that the indoor PAH levels in Taiwanese temples were higher than those measured in households or even outdoor environments from the same city, due to the use of candles and incense.

When comparing our study zones, higher concentrations of PAHs were observed in samples from the urban area, probably due to the contribution of outdoor pollutants coming from vehicles. Similar results were previously reported for other cities, such as Taichung in Taiwan, where higher risk values were found for high traffic areas (Chen and Liao, 2006).

Regarding individual PAHs, more than 80 % of the PAHs corresponded to LMW PAHs, i.e., PAHs with less than 4 rings (Figure 3). Nap, a PAH with 2 rings, which is the most abundant PAH in the environment (Tavera Busso et al., 2018), showed the highest concentrations in TSP during warm periods, probably due to its high volatility. This compound is extensively used in the production of plasticizers, resins, insecticides, paints and varnishes. In addition, its frequent occurrence in outdoor and indoor environments has been attributed to the fact that it is a major component of coal-tar products, and is present in a wide variety of preservatives or antiseptics (IARC, 2002). On the other hand, Pyr (4 rings) was the most abundant compound during the cold period. As this compound is a large and heavy molecule that is highly carcinogenic (Ravindra et al., 2008), it is usually the compound that contributes most to the total PAHs in the environment (IARC, 1998).

Table 1. Concentration of individual PAHs in TSP ($\mu\text{g m}^{-2} \text{day}^{-1}$), collected at different sampling areas and periods, and their corresponding health risks.

PAH	Urban						Suburban					
	Summer			Winter			Summer			Winter		
	Mean	SD	Risk	Mean	SD	Risk	Mean	SD	Risk	Mean	SD	Risk
Nap	150.28*	106.27	$1.75 \cdot 10^{-6}$	2.78	2.40	$3.23 \cdot 10^{-8}$	68.44*	76.25	$7.97 \cdot 10^{-7}$	4.09	2.28	$4.76 \cdot 10^{-8}$
Ace+Flu	14.81*	11.33	$5.58 \cdot 10^{-9}$	4.85	3.09	$1.83 \cdot 10^{-9}$	19.79*	15.35	$7.45 \cdot 10^{-9}$	3.32	2.54	$1.25 \cdot 10^{-9}$
Phen	0.28	0.34	$1.07 \cdot 10^{-10}$	1.41	1.68	$5.29 \cdot 10^{-10}$	0.44	0.33	$1.67 \cdot 10^{-10}$	1.14	0.85	$3.23 \cdot 10^{-10}$
Ant	0.31	0.05	$1.19 \cdot 10^{-9}$	0.52	0.38	$1.95 \cdot 10^{-9}$	0.25	0.08	$9.29 \cdot 10^{-10}$	0.63*	0.34	$2.37 \cdot 10^{-9}$
Fla	3.22	0.75	$1.21 \cdot 10^{-9}$	4.08	2.39	$1.54 \cdot 10^{-9}$	3.61	3.24	$1.36 \cdot 10^{-9}$	4.65	2.99	$1.75 \cdot 10^{-9}$
Pyr	9.13	1.93	$3.44 \cdot 10^{-9}$	26.34	47.36	$9.92 \cdot 10^{-9}$	6.40	4.03	$2.41 \cdot 10^{-9}$	11.35	8.18	$4.27 \cdot 10^{-9}$
B(a)A+Chry	3.22*	0.24	$6.67 \cdot 10^{-8}$	0.51	0.37	$1.06 \cdot 10^{-8}$	1.80	1.85	$3.72 \cdot 10^{-8}$	0.87	0.41	$1.80 \cdot 10^{-8}$
B(b)F	0.39	0.23	$1.49 \cdot 10^{-8}$	0.81	0.67	$3.06 \cdot 10^{-8}$	0.70	0.38	$2.62 \cdot 10^{-8}$	0.97	0.25	$3.65 \cdot 10^{-8}$
B(k)F	0.13	0.04	$4.76 \cdot 10^{-9}$	0.33*	0.19	$1.25 \cdot 10^{-8}$	0.27	0.13	$1.03 \cdot 10^{-8}$	0.49*	0.15	$1.86 \cdot 10^{-8}$
B(a)P	0.68	1.18	$2.56 \cdot 10^{-7}$	0.47	0.33	$1.77 \cdot 10^{-7}$	0.33	0.43	$1.26 \cdot 10^{-7}$	0.67	0.40	$2.54 \cdot 10^{-7}$
DiB(ah)A	<DL	-	-	0.04*	0.03	$1.65 \cdot 10^{-8}$	0.16	0.13	$6.39 \cdot 10^{-8}$	0.11	0.08	$4.37 \cdot 10^{-8}$
I(123-cd)P	0.66	0.23	$2.49 \cdot 10^{-8}$	0.90	0.37	$3.39 \cdot 10^{-8}$	0.54	0.19	$2.04 \cdot 10^{-8}$	0.83*	0.20	$3.13 \cdot 10^{-8}$

B(ghi)P	2.64	0.73	$9.94 \cdot 10^{-9}$	1.91	0.90	$7.19 \cdot 10^{-9}$	2.70	3.43	$1.02 \cdot 10^{-8}$	2.05	1.06	$7.71 \cdot 10^{-9}$
Σ PAHs	185.73*	107.56	$2.14 \cdot 10^{-6}$	44.60	46.75	$3.36 \cdot 10^{-7}$	105.33*	86.85	$1.10 \cdot 10^{-6}$	30.37	14.50	$4.68 \cdot 10^{-7}$

Ref.: Values with statistically significant differences between periods in each zone are labeled

with an asterisk ($p < 0.05$).

Ref.: “<DL”, below detection limit.

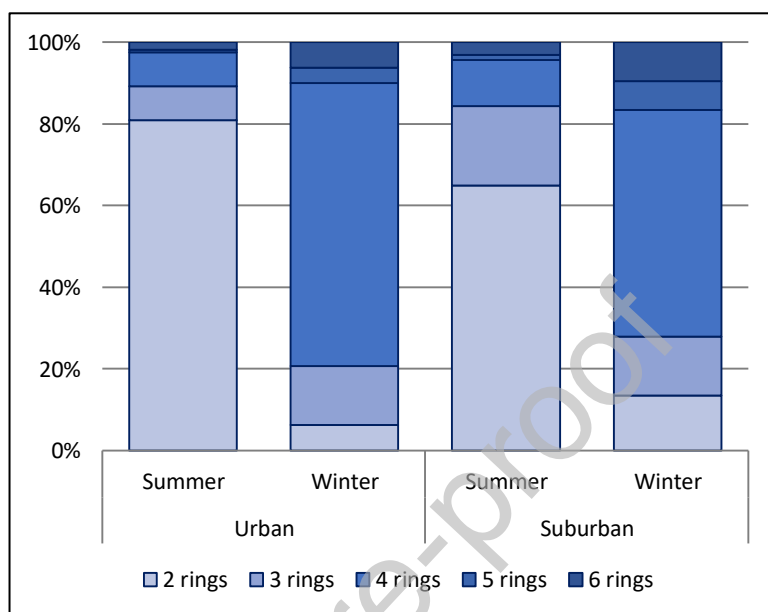


Figure 3. PAHs (%) in TSP collected at different sampling areas and periods, grouped according to the number of rings.

3.2 $PM_{>2.5}$

$PM_{>2.5}$ -bound PAHs showed higher levels in the winter period than in the summer one (Table 2), in contrast with the trend observed in TSP, suggesting that during wintertime $PM_{>2.5}$ particles originate mainly from indoor emission sources. Cattaneo et al. (2016) also found high levels of PAHs in $PM_{2.5}$ from indoor homes during the winter period in the province of Lodi, northern Italy. Colman Lerner et al. (2018) reported similar PM_{10} and $PM_{2.5}$ PAH levels in PM_{10} and $PM_{2.5}$ at different workplaces in La Plata (Argentina). Of the 42 ng m^{-3} of total PAHs found in that study, 34.8 ng m^{-3} corresponded to Pyr, 3.80 ng m^{-3} to B(k)F and 3.40 ng m^{-3} to B(a)P, while the other PAHs were below the detection limit. Although we found lower individual PAHs levels than Colman Lerner et al. (2018), we were able to detect most of the compounds in all the residences. Several authors have reported higher indoor PAH levels than those found in the present study. These include Hassanvand et al. (2015), who quantified PAHs from PM_{10} and $PM_{2.5}$ in a retirement home and in a school dormitory, as well as Wei See et al. (2006) and Li et al. (2005), who measured PAH levels in $PM_{2.5}$ samples collected in Singapore and China,

respectively. Indoor particle levels could be the result of dust resuspension, which is an important particle emission source, especially for particles in the range 0.7-10 μm . Indeed, disturbance of the air-surface boundary layer due to indoor activities can result in a bulk elevation of inhalable particles in the indoor environment (Qian et al., 2014).

The most abundant compound found in $> 2.5 \mu\text{m}$ particles was Nap, in all zones and periods, followed by B(ghi)P.

Table 2. Concentrations of $\text{PM}_{>2.5}$ -adsorbed PAHs (ng m^{-3}) and their corresponding health risks by sampling zones and periods.

PAH	Urban						Suburban					
	Summer			Winter			Summer			Winter		
	Mean	SD	Risk	Mean	SD	Risk	Mean	SD	Risk	Mean	SD	Risk
Nap	1.41	0.73	$1.64 \cdot 10^{-8}$	2.49	1.19	$2.89 \cdot 10^{-8}$	1.37	0.37	$1.59 \cdot 10^{-8}$	2.13	1.01	$2.49 \cdot 10^{-8}$
Ace+Flu	0.33	0.20	$1.26 \cdot 10^{-10}$	0.30	0.17	$1.12 \cdot 10^{-10}$	0.37	0.26	$1.38 \cdot 10^{-10}$	0.38	0.19	$1.45 \cdot 10^{-10}$
Phen	0.01	0.002	$1.52 \cdot 10^{-12}$	0.01	0.002	$1.83 \cdot 10^{-12}$	0.12	0.18	$4.36 \cdot 10^{-11}$	0.01	0.003	$2.81 \cdot 10^{-12}$
Ant	0.03	0.02	$1.05 \cdot 10^{-10}$	0.04	0.02	$1.41 \cdot 10^{-10}$	0.03	0.02	$1.06 \cdot 10^{-10}$	0.05	0.03	$2.09 \cdot 10^{-10}$
Fla	0.35	0.14	$1.34 \cdot 10^{-10}$	0.34	0.14	$1.30 \cdot 10^{-10}$	0.52	0.24	$1.97 \cdot 10^{-10}$	0.44	0.18	$1.64 \cdot 10^{-10}$
Pyr	0.38	0.11	$1.45 \cdot 10^{-10}$	0.40	0.19	$1.51 \cdot 10^{-10}$	0.46	0.18	$1.73 \cdot 10^{-10}$	0.43	0.18	$1.62 \cdot 10^{-10}$
B(a)A+Chry	0.09	0.03	$1.98 \cdot 10^{-9}$	0.09	0.04	$1.89 \cdot 10^{-9}$	0.14	0.05	$2.87 \cdot 10^{-9}$	0.13	0.06	$2.77 \cdot 10^{-9}$
B(b)F	0.02	0.03	$8.31 \cdot 10^{-10}$	0.01	0.008	$5.01 \cdot 10^{-10}$	0.02	0.01	$5.90 \cdot 10^{-10}$	0.02	0.01	$8.62 \cdot 10^{-10}$
B(k)F	0.02	0.001	$8.30 \cdot 10^{-11}$	0.01	0.001	$1.16 \cdot 10^{-10}$	0.004	0.002	$1.64 \cdot 10^{-10}$	0.01	0.004	$2.91 \cdot 10^{-10}$
B(a)P	0.06	0.02	$2.24 \cdot 10^{-8}$	0.08	0.04	$2.86 \cdot 10^{-8}$	0.04	0.01	$1.57 \cdot 10^{-8}$	0.13*	0.05	$5.03 \cdot 10^{-8}$
DiB(ah)A	<DL	-	-	<DL	-	-	<DL	-	-	0.01*	0.008	$1.34 \cdot 10^{-9}$
I(123-cd)P	0.02	0.01	$7.36 \cdot 10^{-10}$	0.03	0.01	$9.69 \cdot 10^{-10}$	0.02	0.01	$7.21 \cdot 10^{-10}$	0.04*	0.008	$1.46 \cdot 10^{-9}$
B(ghi)P	0.83	0.29	$3.14 \cdot 10^{-9}$	1.57	0.85	$5.92 \cdot 10^{-9}$	0.41	0.18	$1.55 \cdot 10^{-9}$	1.29*	0.64	$4.85 \cdot 10^{-9}$
Σ PAHs	3.55	1.07	$4.60 \cdot 10^{-8}$	5.35	2.11	$6.74 \cdot 10^{-8}$	3.49	0.52	$3.82 \cdot 10^{-8}$	5.08*	1.38	$8.74 \cdot 10^{-8}$

Ref.: Values with statistically significant differences between periods in each zone are labeled with an asterisk ($p < 0.05$).

Ref.: "<DL", below detection limit.

It was found that LMW PAHs were predominant in both areas and periods (Figure 4). A similar trend was observed in Guangzhou, China (Li et al., 2005), where the PAH distribution was related to housing characteristics such as house type, air exchange rates, household appliances and indoor activities. Similarly, Hassanvand et al. (2015) reported the same trend when studying PAHs in a retirement home and a school dormitory in Tehran (Iran), with the PAH levels being attributed to cooking activities or evaporation from building materials. In contrast, Li et al.

(2005) suggested that indoor PAHs have a predominantly external origin, since they analyzed homes located in close proximity to main streets.

LMW PAHs are considered to be less toxic. Nevertheless, they are highly reactive, and in combination with other pollutants can originate oxygenated, nitro- and dinitro-PAHs, which are much more toxic compounds (Lin et al., 2015). It is also worth mentioning that DiB(ah)A, a potentially carcinogenic PAH (IARC, 2010), was only measured in suburban samples from winter. The fact that DiB(ah)A is mainly released by traffic, which is not intense in the suburban area, suggests that this PAH could have originated from indoor sources (Delgado-Saborit et al., 2011). On the other hand, we found that the proportion of 4, 5 and 6-ring PAHs was higher in samples collected during the cold period compared to the warm period (Figure 4).

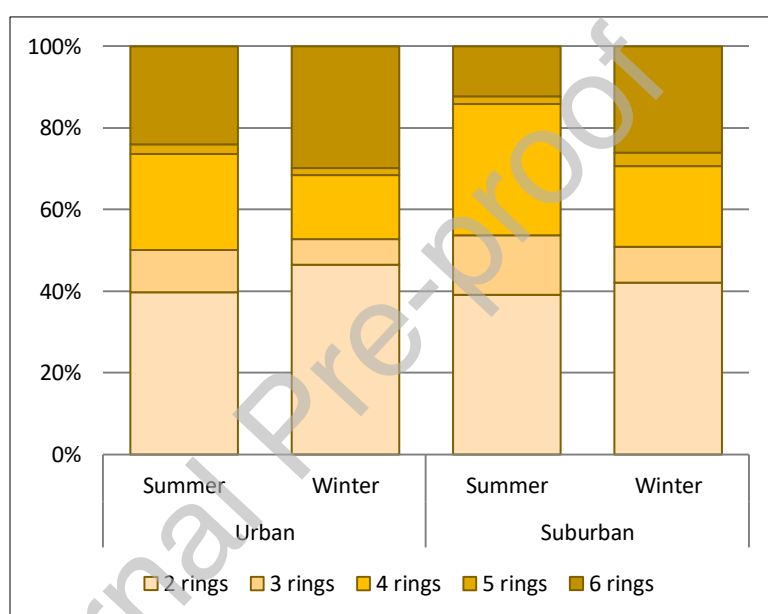


Figure 4. PAHs (%) in $PM_{>2.5}$ for each area and sampling period, grouped according to the number of rings.

3.3 $PM_{<1}$

The highest concentrations of PAHs associated with $PM_{<1}$ were observed during the summer period for both sampling areas (Table 3). In agreement, Sangiorgi et al. (2013) reported that the infiltration of fine particles into indoor environments is higher during the summer than winter months, as long as the ventilation is natural. Thus, the levels of PAHs found in households during the winter period may be the result of mainly internal emission sources, with a small contribution of PAHs from particulate resuspension. Other authors have also pointed out that, during the cold months, internal sources of PAHs such as heating and cooking are more important than outdoor sources (Cattaneo et al., 2016; Gao et al., 2015; Perrino et al., 2016).

Zhang et al. (2019) found higher PAH levels in fine PM from rural households in China than those reported in the present study. This difference may be due to the fact that in Argentina the houses in urban areas use natural gas for cooking and heating, while in rural areas of mainland China, biomass is preferred (Zhang et al., 2019). However, comparing our results with a study that analyzed households with natural gas, Yu et al. (2015) found that PAH concentrations associated with fine particles ranged from 1411.25 and 56221.30 ng m⁻³, which are much higher than the values found in the present study (450 to 2020 ng m⁻³). We can only attribute this difference to the type of cooking, structural characteristics of the houses, or scarce ventilation. On the other hand, the PAH values found in the present study were slightly higher than those reported by Oliveira et al. (2016) in pre-school institutions (PM_{<1}) located in Portugal, but similar to those reported by Sangiorgi et al. (2013) in offices (PM_i) in Milan (Italy). Regarding the proportion of LMW and HMW PAHs, Nap was the most abundant PAH, while the proportion of 4, 5 and 6-ring PAHs tended to increase during wintertime, similar to the trend found for the larger fractions (Figure 5).

Table 3. Concentration of PAHs analyzed in PM_{<1} (ng m⁻³), according to each zone and period, and their corresponding health risk assessment.

PAH	Urban						Suburban					
	Summer			Winter			Summer			Winter		
	Mean	SD	Risk	Mean	SD	Risk	Mean	SD	Risk	Mean	SD	Risk
Nap	1.46*	0.92	1.70 10 ⁻⁸	0.34	0.2	2.76 10 ⁻⁹	0.98	0.93	1.15 10 ⁻⁸	0.69	0.51	8.09 10 ⁻⁹
Ace+Flu	0.34*	0.16	1.27 10 ⁻¹⁰	0.04	0.01	1.19 10 ⁻¹¹	0.22*	0.09	8.27 10 ⁻¹¹	0.04	0.02	1.64 10 ⁻¹¹
Phen	0.03	0.02	1.13 10 ⁻¹¹	0.01	0.01	6.23 10 ⁻¹²	0.02	0.02	8.16 10 ⁻¹²	0.07	0.08	2.49 10 ⁻¹¹
Ant	0.001	0.001	3.95 10 ⁻¹²	0.003*	0.001	9.49 10 ⁻¹²	0.001	0.001	4.26 10 ⁻¹²	0.01*	0.003	2.26 10 ⁻¹¹
Fla	0.002	0.001	8.03 10 ⁻¹³	0.01*	0.005	5.22 10 ⁻¹²	0.004	0.004	1.47 10 ⁻¹²	0.03*	0.01	9.63 10 ⁻¹²
Pyr	0.005	0.001	1.79 10 ⁻¹²	0.02*	0.005	1.62 10 ⁻¹¹	0.01	0.01	4.61 10 ⁻¹²	0.03*	0.01	1.30 10 ⁻¹¹
B(a)A+Chry	0.001	0.001	2.41 10 ⁻¹¹	0.004	0.004	2.75 10 ⁻¹⁰	0.002	0.002	4.13 10 ⁻¹¹	0.01*	0.004	1.54 10 ⁻¹⁰
B(b)F	0.02	0.02	8.51 10 ⁻¹⁰	0.02	0.01	4.90 10 ⁻¹⁰	0.05	0.06	1.85 10 ⁻⁹	0.02	0.01	7.63 10 ⁻¹⁰
B(k)F	0.01	0.003	2.31 10 ⁻¹⁰	0.004	0.001	4.88 10 ⁻¹⁰	0.01	0.02	5.64 10 ⁻¹⁰	0.005	0.002	1.96 10 ⁻¹⁰
B(a)P	0.01	0.01	4.97 10 ⁻⁹	0.004	0.002	1.39 10 ⁻⁹	0.03	0.07	1.24 10 ⁻⁸	0.01	0.005	3.10 10 ⁻⁹
DiB(ah)A	0.003	0.001	1.10 10 ⁻⁹	0.001	0.001	3.99 10 ⁻¹⁰	0.001	0.002	5.57 10 ⁻¹⁰	0.001	0.001	3.73 10 ⁻¹⁰
I(123-cd)P	0.18	0.35	6.66 10 ⁻⁹	0.005	0.001	1.38 10 ⁻¹⁰	0.01	0.0001	4.58 10 ⁻¹⁰	0.01	0.002	2.47 10 ⁻¹⁰
B(ghi)P	0.003	0.001	1.22 10 ⁻¹¹	0.01*	0.002	2.32 10 ⁻¹¹	0.004	0.002	1.44 10 ⁻¹¹	0.01*	0.003	3.02 10 ⁻¹¹
Σ PAHs	2.02*	0.83	3.10 10 ⁻⁸	0.45	0.21	6.01 10 ⁻⁹	1.35	0.94	2.75 10 ⁻⁸	0.9	0.59	1.30 10 ⁻⁸

Ref.: Values with statistically significant differences between periods in each zone are labeled with an asterisk ($p < 0.05$).

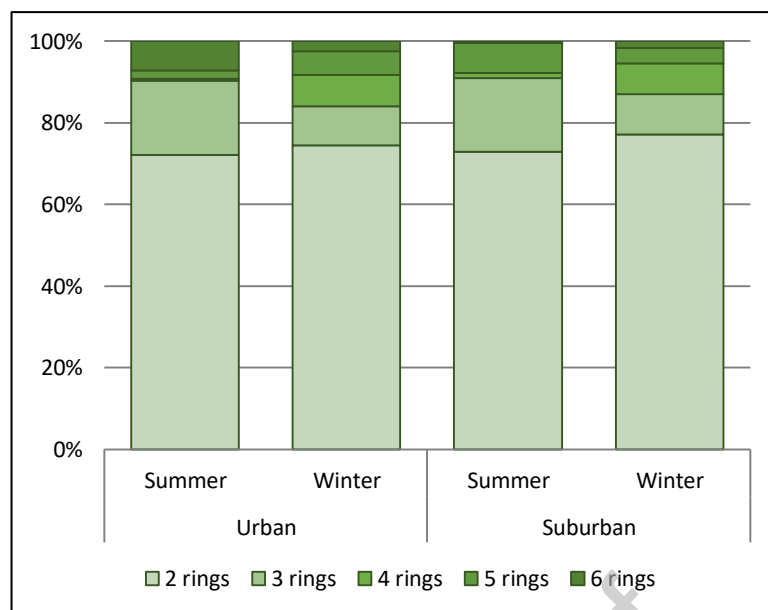


Figure 5. PAHs (%) in PM_{2.5} for each area (urban and suburban) and sampling period (summer and winter), grouped according to the number of rings.

3.4 Health Risk Assessment

Individual compounds adsorbed to TSP were not high enough to be a significant risk, although when combined, together they became a potential cancer risk during the summer period, at both sampling zones. Nap had a relatively high health risk because of its abundance, despite its low toxicity (Table 4). B(a)P had the highest cancer potency factor value (Table SM-4), but it did not represent a significant risk because of its very low concentrations.

The risks associated to PM_{2.5} were overall lower than those for TSP in all seasons, due to their lower concentrations of PAHs. Nap was the most abundant compound of these particles and had the highest health risk value. Despite the high concentrations of B(ghi)P, its contribution to the total health risk was relatively low, because this compound has not yet been classified as carcinogenic by IARC (2010). However, it is suspected of being both carcinogenic and mutagenic (ATSDR, 1995).

The risk due to PAHs adsorbed to PM_{2.5} was higher in samples collected during summertime. Related to this, Zhang et al. (2019) indicated that indoor emission sources were the main contribution to air PAHs in kitchens and bedrooms during the summer period, rather than outdoor sources. The two compounds that contributed the most to the risk were Nap, due to its high concentration, and B(a)P, due to its high IUR (Table 4). In fact, B(a)P is listed as a carcinogenic compound by IARC (2010), and its presence indoor could be due to cooking activities, since it has been found in grilled meats and charbroiled food (Zhu and Wang, 2003).

Table 4. Health risk assessment for each PAH individually adsorbed in TSP, PM_{>2.5} and PM_{<1}, respectively.

PM fraction	PAH	Urban		Suburban	
		Summer	Winter	Summer	Winter
TSP	Nap	1.75 10 ⁻⁶	3.23 10 ⁻⁸	7.97 10 ⁻⁷	4.76 10 ⁻⁸
	Ace+Flu	5.58 10 ⁻⁹	1.83 10 ⁻⁹	7.45 10 ⁻⁹	1.25 10 ⁻⁹
	Phen	1.07 10 ⁻¹⁰	5.29 10 ⁻¹⁰	1.67 10 ⁻¹⁰	3.23 10 ⁻¹⁰
	Ant	1.19 10 ⁻⁹	1.95 10 ⁻⁹	9.29 10 ⁻¹⁰	2.37 10 ⁻⁹
	Fla	1.21 10 ⁻⁹	1.54 10 ⁻⁹	1.36 10 ⁻⁹	1.75 10 ⁻⁹
	Pyr	3.44 10 ⁻⁹	9.92 10 ⁻⁹	2.41 10 ⁻⁹	4.27 10 ⁻⁹
	B(a)A+Chry	6.67 10 ⁻⁸	1.06 10 ⁻⁸	3.72 10 ⁻⁸	1.80 10 ⁻⁸
	B(b)F	1.49 10 ⁻⁸	3.06 10 ⁻⁸	2.62 10 ⁻⁸	3.65 10 ⁻⁸
	B(k)F	4.76 10 ⁻⁹	1.25 10 ⁻⁸	1.03 10 ⁻⁸	1.86 10 ⁻⁸
	B(a)P	2.56 10 ⁻⁷	1.77 10 ⁻⁷	1.26 10 ⁻⁷	2.54 10 ⁻⁷
	DiB(ah)A	-	1.65 10 ⁻⁸	6.39 10 ⁻⁸	4.37 10 ⁻⁸
	I(123-cd)P	2.49 10 ⁻⁸	3.39 10 ⁻⁸	2.04 10 ⁻⁸	3.13 10 ⁻⁸
B(ghi)P	9.94 10 ⁻⁹	7.19 10 ⁻⁹	1.02 10 ⁻⁸	7.71 10 ⁻⁹	
PM _{>2.5}	Nap	1.64 10 ⁻⁸	2.89 10 ⁻⁸	1.59 10 ⁻⁸	2.49 10 ⁻⁸
	Ace+Flu	1.26 10 ⁻¹⁰	1.12 10 ⁻¹⁰	1.38 10 ⁻¹⁰	1.45 10 ⁻¹⁰
	Phen	1.52 10 ⁻¹²	1.83 10 ⁻¹²	4.36 10 ⁻¹¹	2.81 10 ⁻¹²
	Ant	1.05 10 ⁻¹⁰	1.41 10 ⁻¹⁰	1.06 10 ⁻¹⁰	2.09 10 ⁻¹⁰
	Fla	1.34 10 ⁻¹⁰	1.30 10 ⁻¹⁰	1.97 10 ⁻¹⁰	1.64 10 ⁻¹⁰
	Pyr	1.45 10 ⁻¹⁰	1.51 10 ⁻¹⁰	1.73 10 ⁻¹⁰	1.62 10 ⁻¹⁰
	B(a)A+Chry	1.98 10 ⁻⁹	1.89 10 ⁻⁹	2.87 10 ⁻⁹	2.77 10 ⁻⁹
	B(b)F	8.31 10 ⁻¹⁰	5.01 10 ⁻¹⁰	5.90 10 ⁻¹⁰	8.62 10 ⁻¹⁰
	B(k)F	8.30 10 ⁻¹¹	1.16 10 ⁻¹⁰	1.64 10 ⁻¹⁰	2.91 10 ⁻¹⁰
	B(a)P	2.24 10 ⁻⁸	2.86 10 ⁻⁸	1.57 10 ⁻⁸	5.03 10 ⁻⁸
	DiB(ah)A	-	-	-	1.34 10 ⁻⁹
	I(123-cd)P	7.36 10 ⁻¹⁰	9.69 10 ⁻¹⁰	7.21 10 ⁻¹⁰	1.46 10 ⁻⁹
B(ghi)P	3.14 10 ⁻⁹	5.92 10 ⁻⁹	1.55 10 ⁻⁹	4.85 10 ⁻⁹	
PM _{<1}	Nap	1.70 10 ⁻⁸	2.76 10 ⁻⁹	1.15 10 ⁻⁸	8.09 10 ⁻⁹
	Ace+Flu	1.27 10 ⁻¹⁰	1.19 10 ⁻¹¹	8.27 10 ⁻¹¹	1.64 10 ⁻¹¹
	Phen	1.13 10 ⁻¹¹	6.23 10 ⁻¹²	8.16 10 ⁻¹²	2.49 10 ⁻¹¹
	Ant	3.95 10 ⁻¹²	9.49 10 ⁻¹²	4.26 10 ⁻¹²	2.26 10 ⁻¹¹
	Fla	8.03 10 ⁻¹³	5.22 10 ⁻¹²	1.47 10 ⁻¹²	9.63 10 ⁻¹²
	Pyr	1.79 10 ⁻¹²	1.62 10 ⁻¹¹	4.61 10 ⁻¹²	1.30 10 ⁻¹¹
	B(a)A+Chry	2.41 10 ⁻¹¹	2.75 10 ⁻¹⁰	4.13 10 ⁻¹¹	1.54 10 ⁻¹⁰

B(b)F	8.51 10 ⁻¹⁰	4.90 10 ⁻¹⁰	1.85 10 ⁻⁹	7.63 10 ⁻¹⁰
B(k)F	2.31 10 ⁻¹⁰	4.88 10 ⁻¹⁰	5.64 10 ⁻¹⁰	1.96 10 ⁻¹⁰
B(a)P	4.97 10 ⁻⁹	1.39 10 ⁻⁹	1.24 10 ⁻⁸	3.10 10 ⁻⁹
DiB(ah)A	1.10 10 ⁻⁹	3.99 10 ⁻¹⁰	5.57 10 ⁻¹⁰	3.73 10 ⁻¹⁰
I(123-cd)P	6.66 10 ⁻⁹	1.38 10 ⁻¹⁰	4.58 10 ⁻¹⁰	2.47 10 ⁻¹⁰
B(ghi)P	1.22 10 ⁻¹¹	2.32 10 ⁻¹¹	1.44 10 ⁻¹¹	3.02 10 ⁻¹¹

To analyze further the health risk of total PAHs on the population, we considered different age groups. From the age of 21 onwards, the risks found for TSP were less than 10⁻⁵ during the warm periods for all ages (Table 5). These values are considerably lower than 10⁻⁴, which is considered to represent a high potential risk according to US EPA (2003). Despite this, adults have longer exposure periods than children, resulting in a higher risk of being affected by PAHs via inhalation (Ali, 2019; Chen and Liao, 2006; Hu et al., 2012). Nevertheless, our results were lower than some risk values reported for some other cities in Saudi Arabia and Taiwan (Ali, 2019; Chen and Liao, 2006). The risk for PM_{>2.5}-adsorbed PAH exposure did not exceed the established limit of 10⁻⁶ in any age group, with our values being lower than those reported by Colman Lerner et al. (2018) for different workplaces in La Plata, Argentina. Each PAH has a different relative importance in the calculation of the health risk. Therefore, although the sum of PAHs in the present study was similar to the one informed by these authors, the differences in PAH composition resulted in different risk indexes. In fact, Colman Lerner et al. (2018) reported high levels of high carcinogenic power PAHs, which resulted in the risk indices being higher than the ones we calculated for the adult groups. We observed the highest potential cancer risks in adults and the lowest in infants, in agreement with Morakinyo et al. (2020). Finally, despite the fact that PAHs adsorbed to PM_{<1} never exceeded the suggested upper limit in any age group (Table 5), their levels are concerning since several authors have demonstrated that most carcinogenic PAHs are particularly associated with fine particles (Agudelo-Castañeda et al., 2017). Thus, PAHs associated to submicron particles (i.e.: PM₁) may increase the exposure risk, especially for respiratory diseases including bronchitis and pneumonia (Agudelo-Castañeda et al., 2017).

Table 5. Health risk assessment for PAHs adsorbed in TSP, PM_{>2.5} and PM_{<1} respectively, according to each age group.

PM fraction	Age groups (years old)	Urban		Suburban	
		Summer	Winter	Summer	Winter
TSP	< 1	3.15 10 ⁻⁸	4.95 10 ⁻⁹	1.62 10 ⁻⁸	6.88 10 ⁻⁹
	1 - < 6	1.93 10 ⁻⁷	3.03 10 ⁻⁸	9.95 10 ⁻⁸	4.21 10 ⁻⁸
	6 - < 11	4.21 10 ⁻⁷	6.62 10 ⁻⁸	2.17 10 ⁻⁷	9.21 10 ⁻⁸

	11 - < 16	6.63 10 ⁻⁷	1.04 10 ⁻⁷	3.42 10 ⁻⁷	1.45 10 ⁻⁷
	16 - < 21	8.57 10 ⁻⁷	1.35 10 ⁻⁷	4.42 10 ⁻⁷	1.88 10 ⁻⁷
	21 - < 61	2.16 10 ⁻⁶	3.40 10 ⁻⁷	1.12 10 ⁻⁶	4.73 10 ⁻⁷
	61 - < 71	4.30 10 ⁻⁶	6.75 10 ⁻⁷	2.22 10 ⁻⁶	9.39 10 ⁻⁷
	71 - < 81	4.98 10 ⁻⁶	7.83 10 ⁻⁷	2.57 10 ⁻⁶	1.09 10 ⁻⁶
	≥ 81	5.63 10 ⁻⁶	8.85 10 ⁻⁷	2.91 10 ⁻⁶	1.23 10 ⁻⁶
	< 1	6.78 10 ⁻¹⁰	9.93 10 ⁻¹⁰	5.62 10 ⁻¹⁰	1.29 10 ⁻⁹
	1 - < 6	4.15 10 ⁻⁹	6.08 10 ⁻⁹	3.44 10 ⁻⁹	7.88 10 ⁻⁹
	6 - < 11	9.07 10 ⁻⁹	1.33 10 ⁻⁸	7.53 10 ⁻⁹	1.72 10 ⁻⁸
	11 - < 16	1.43 10 ⁻⁸	2.09 10 ⁻⁸	1.18 10 ⁻⁸	2.71 10 ⁻⁸
PM_{>2.5}	16 - < 21	1.84 10 ⁻⁸	2.70 10 ⁻⁸	1.53 10 ⁻⁸	3.50 10 ⁻⁸
	21 - < 61	4.66 10 ⁻⁸	6.83 10 ⁻⁸	3.87 10 ⁻⁸	8.85 10 ⁻⁸
	61 - < 71	9.25 10 ⁻⁸	1.35 10 ⁻⁷	7.67 10 ⁻⁸	1.75 10 ⁻⁷
	71 - < 81	1.07 10 ⁻⁷	1.57 10 ⁻⁷	8.90 10 ⁻⁸	2.04 10 ⁻⁷
	≥ 81	1.21 10 ⁻⁷	1.78 10 ⁻⁷	1.00 10 ⁻⁷	2.30 10 ⁻⁷
	< 1	4.56 10 ⁻¹⁰	8.85 10 ⁻¹¹	4.04 10 ⁻¹⁰	1.92 10 ⁻¹⁰
	1 - < 6	2.79 10 ⁻⁹	5.42 10 ⁻¹⁰	2.48 10 ⁻⁹	1.17 10 ⁻⁹
	6 - < 11	6.11 10 ⁻⁹	1.18 10 ⁻⁹	5.41 10 ⁻⁹	2.57 10 ⁻⁹
	11 - < 16	9.62 10 ⁻⁹	1.86 10 ⁻⁹	8.52 10 ⁻⁹	4.04 10 ⁻⁹
PM_{<1}	16 - < 21	1.24 10 ⁻⁸	2.41 10 ⁻⁹	1.10 10 ⁻⁸	5.22 10 ⁻⁹
	21 - < 61	3.14 10 ⁻⁸	6.09 10 ⁻⁹	2.78 10 ⁻⁸	1.32 10 ⁻⁸
	61 - < 71	6.23 10 ⁻⁸	1.21 10 ⁻⁸	5.52 10 ⁻⁸	2.62 10 ⁻⁸
	71 - < 81	7.23 10 ⁻⁸	1.40 10 ⁻⁸	6.40 10 ⁻⁸	3.04 10 ⁻⁸
	≥ 81	8.16 10 ⁻⁸	1.58 10 ⁻⁸	7.23 10 ⁻⁸	3.43 10 ⁻⁸

The reported health risks may have been underestimated in some studies because exposure via inhalation of the air gaseous phase or food or water consumption could also be significant exposure scenarios for PAHs as well as other carcinogenic compounds. In the present study, the inhalation of PM PAHs was the only kind of exposure assessed. Furthermore, we did not consider any chemical interactions or synergistic effects between compounds, which could be other sources of potential errors. Indeed, the assessment of PAHs alone is likely to underestimate the carcinogenic potential of PAH mixtures because other co-occurring substances may be carcinogenic.

3.5 PAH diagnostic ratios (DRs)

Table SM-7 shows the results of the DR calculated for PAHs quantified in PM_{<1}. In general, these PAHs originated from vehicular traffic and incomplete combustion of gasoline or diesel, but the LMW PAH values also showed a contribution of PAHs from food cooking. Significant

contributions from heavy traffic were observed in all areas, as determined by the proportion of PAHs derived from combustion (CHAPs) in relation to total PAHs.

The DR calculated with the PAHs measured in $PM_{>2.5}$ suggest that the main source of emissions are fossil fuels and lubricating oils, i.e., vehicle traffic (Table SM-8). Especially important is the use of gasoline as a source of Flu and Pyr, and diesel as a source of B(a)A and Chry. The values of CHAPs related to total PAHs indicate the presence of vehicles with catalytic converters in the vehicle emissions, especially during the summer period.

The DRs calculated for PAHs quantified in TSP indicate a significant contribution of vehicular emissions, especially from vehicles using gasoline as fuel, considering the DR that correlates Flu with Pyr (Table SM-9). In addition, the values of CHAPs related to total PAHs indicate the presence of heavy traffic in all the areas and periods analyzed.

Different approaches based on PAH DR have been used to evaluate potential emission sources of PAHs (Madruga et al., 2019). In the main, these indices are used for the source analysis of PAHs collected in outdoor environments, although some studies have also used them in indoor environments (Krugly et al., 2014).

Taken together, the ratios calculated in the present study indicate that vehicular emissions are the main source of PAHs in the indoor environments, in particular, emissions from heavy traffic. During the winter, DRs indicating diesel and heavy traffic as well as cooking were the most important, especially for the smaller particulate fraction, as observed by Krugly et al. (2014). This could be due to the low natural ventilation of houses during low temperature periods, as suggested by Oliveira et al. (2017) and Madruga et al. (2019).

Another important finding is the low proportion of emissions from vehicles equipped with catalytic converters, as reflected in the ratios between B(a)A and Cri and between CHAPs and total PAHs. This technology transforms the toxic compounds produced by the exhaust system into CO_2 and water vapor, thereby reducing the quantity of harmful compounds that escape through the exhaust pipe (Lin et al., 2019). Nevertheless, these converters should be replaced every 80,000 to 100,000 km, as once the optimal period of operation has elapsed, this equipment no longer operates optimally. Although many new vehicles in Cordoba are equipped with catalytic converters, it is not the usual procedure to replace them.

Cordoba is the province with the second largest circulating fleet of vehicles in Argentina, representing 9.97 % of a total of 13,302,670 units (AFAC, 2017). Out of this total number of vehicles, approximately 77.9 % are less than 20 years old. Considering the city's population (1,438,492 inhabitants; INDEC, 2010), there is one vehicle for every 1.67 people on average, reflecting the sharp increase in the vehicle park in only ten years, when the ratio was one vehicle for every three inhabitants. These details concerning vehicles support the hypothesis of the

infiltration of PAHs from outdoors, especially during the warm period, when homes keep their doors and windows open the most.

4. Conclusions

In the present work, we report on the PAH values found inside urban households during two different seasons. To the best of our knowledge, this is the first study to describe the composition of PAHs within family homes in Argentina and present an estimate of the health risk due to inhalation of different PM fractions.

We found that indoor environments could be significant PAH exposure scenarios, although the calculated health risks never exceeded the upper levels recommended by the US EPA. Nevertheless, as the overall health risk in the population should be calculated by considering the contribution of both outdoor and indoor particles, the risk values presented here are just a portion of the total exposure risk. Indeed, this additive effect is worse for people living in the city center compared to the residential area, and also with increasing age.

The PAH levels were found to be particularly high during summer, due to pollutants coming from outside and/or due to the permanence of pollutants inside homes. We also found that larger particles ($PM_{>2.5}$) had a higher proportion of PAHs compared to smaller ones ($PM_{<1}$). This probably occurs since even though PAHs are released in the environment in the gas phase, they immediately tend to aggregate and/or condensate into the particulate phase. In addition, the proportion of LMW PAHs (2 and 3-rings) was much higher in smaller particles than in the larger ones.

The results of this exploratory study need to be validated with further studies. However, these results make a significant contribution to the knowledge of indoor pollution in developing countries, given the small number of studies available on indoor compared to outdoor environments. Moreover, we used a low-cost methodology to collect different particulate fractions in indoor environments, which could be easily employed in developing countries. Our findings also provide an indication of the likely exposure range of the population in urban environments in developing countries.

Declarations of interest

The authors declare no conflicts of interest.

References

Abdel-Shafy, Hussein I, Mansour, M.S.M., 2016. A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. Egypt. J. Pet. 25, 107–123.

- Abdel-Shafy, H.I., Mansour, M.S.M., 2016. A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. *Egypt. J. Pet.* 25, 107–123. <https://doi.org/10.1016/j.ejpe.2015.03.011>
- AFAC. Asociación Argentina de Fábricas de Componentes, 2017. En Argentina En Argentina. AFAC.
- Agency for Toxic Substances and Disease Registry, 1995. Toxicological profile for polycyclic aromatic hydrocarbons. United States Department of Health and Human Services, Public Health Service, Atlanta, USA.
- Agudelo-Castañeda, D., Teixeira, E., Schneider, I., Lara, S.R., Silva, L.F.O., 2017. Exposure to polycyclic aromatic hydrocarbons in atmospheric PM_{1.0} of urban environments: Carcinogenic and mutagenic respiratory health risk by age groups. *Environ. Pollut.* 224, 158–170. <https://doi.org/10.1016/j.envpol.2017.01.075>
- Ali, N., 2019. Polycyclic aromatic hydrocarbons (PAHs) in indoor air and dust samples of different Saudi microenvironments; health and carcinogenic risk assessment for the general population. *Sci. Total Environ.* 696, 133995. <https://doi.org/10.1016/j.scitotenv.2019.133995>
- Bermudez, G.M.A., Jasan, R., Plá, R., Pignata, M.L., 2012. Heavy metals and trace elements in atmospheric fall-out: their relationship with topsoil and wheat element composition. *J. Hazard. Mater.* 213, 447–456.
- Carreras, H., Zanobetti, A., Koutrakis, P., 2015. Effect of daily temperature range on respiratory health in Argentina and its modification by impaired socio-economic conditions and PM₁₀ exposures. *Environ. Pollut.* 206, 175–182. <https://doi.org/10.1016/j.envpol.2015.06.037>
- Cattaneo, A., Fermo, P., Urso, P., Perrone, M.G., Piazzalunga, A., Tarlassi, J., Carrer, P., Cavallo, D.M., 2016a. Particulate-bound polycyclic aromatic hydrocarbon sources and determinants in residential homes. *Environ. Pollut.* 218, 16–25. <https://doi.org/10.1016/j.envpol.2016.08.033>
- Cattaneo, A., Fermo, P., Urso, P., Perrone, M.G., Piazzalunga, A., Tarlassi, J., Carrer, P., Cavallo, D.M., 2016b. Particulate-bound polycyclic aromatic hydrocarbon sources and determinants in residential homes. *Environ. Pollut.* 218, 16–25.
- Chen, S.C., Liao, C.M., 2006. Health risk assessment on human exposed to environmental polycyclic aromatic hydrocarbons pollution sources. *Sci. Total Environ.* 366, 112–123. <https://doi.org/10.1016/j.scitotenv.2005.08.047>
- Choi, H., Spengler, J., 2014. Source attribution of personal exposure to airborne polycyclic aromatic hydrocarbon mixture using concurrent personal, indoor, and outdoor measurements. *Environ. Int.* 63, 173–181. <https://doi.org/10.1016/j.envint.2013.11.007>
- Colman Lerner, J.E., Elordi, M.L., Orte, M.A., Giuliani, D., de los Angeles Gutierrez, M.,

- Sanchez, E.Y., Sambeth, J.E., Porta, A.A., 2018. Exposure and risk analysis to particulate matter, metals, and polycyclic aromatic hydrocarbon at different workplaces in Argentina. *Environ. Sci. Pollut. Res.* 25, 8487–8496. <https://doi.org/10.1007/s11356-017-1101-0>
- Delgado-Saborit, J.M., Stark, C., Harrison, R.M., 2011. Carcinogenic potential, levels and sources of polycyclic aromatic hydrocarbon mixtures in indoor and outdoor environments and their implications for air quality standards. *Environ. Int.* 37, 383–392. <https://doi.org/10.1016/j.envint.2010.10.011>
- Domínguez-amarillo, S., Fernández-agüera, J., Cesteros-garcía, S., González-lezcano, R.A., 2020. Bad air can also kill: Residential indoor air quality and pollutant exposure risk during the covid-19 crisis. *Int. J. Environ. Res. Public Health* 17, 1–34. <https://doi.org/10.3390/ijerph17197183>
- Gao, B., Wang, X., Zhao, X., Ding, X., Fu, X., Zhang, Y., He, Q., Zhang, Z., Liu, T., Huang, Z., 2015. Source apportionment of atmospheric PAHs and their toxicity using PMF : Impact of gas / particle partitioning. *Atmos. Environ.* 103, 114–120. <https://doi.org/10.1016/j.atmosenv.2014.12.006>
- Hassanvand, M.S., Naddafi, K., Faridi, S., Nabizadeh, R., Sowlat, M.H., Momeniha, F., Gholampour, A., Arhami, M., Kashani, H., Zare, A., Niazi, S., Rastkari, N., Nazmara, S., Ghani, M., Yunesian, M., 2015. Characterization of PAHs and metals in indoor/outdoor PM10/PM2.5/PM1 in a retirement home and a school dormitory. *Sci. Total Environ.* 527–528, 100–110. <https://doi.org/10.1016/j.scitotenv.2015.05.001>
- Hu, X., Zhang, Y., Ding, Z., Wang, T., Lian, H., Sun, Y., Wu, J., 2012. Bioaccessibility and health risk of arsenic and heavy metals (Cd , Co , Cr , Cu , Ni , Pb , Zn and Mn) in TSP and PM2 . 5 in Nanjing , China. *Atmos. Environ.* 57, 146–152. <https://doi.org/10.1016/j.atmosenv.2012.04.056>
- Hussain, K., Hoque, R.R., Balachandran, S., Medhi, S., Idris, M.G., Rahman, M., Hussain, F.L., 2018. Monitoring and risk analysis of PAHs in the environment. *Handb. Environ. Mater. Manag.* 1–35.
- IARC Working Group on the Evaluation of Carcinogenic Risks to Humans., 2010. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Lyon, France.
- Instituto Nacional de Estadística y Censo, 2010. Censo Nacional de Población , Hogares y Viviendas 2010 Censo del Bicentenario. Buenos Aires, Argentina.
- International Agency for Research on Cancer. World Health Organization, 2010. Some non-heterocyclic polycyclic aromatic hydrocarbons and some related exposures., IARC monographs on the evaluation of carcinogenic risks to humans.
- International Agency for Research on Cancer. World Health Organization, 2002. Some traditional herbal medicines, some mycotoxins, naphthalene and styrene, IARC

monographs on the evaluation of carcinogenic risks to humans.

- International Agency for Research on Cancer. World Health Organization, 1998. Polynuclear aromatic compounds. Part 1, chemical, environmental and experimental data. Lyon, France.
- Krugly, E., Martuzevicius, D., Sidaraviciute, R., Ciuzas, D., Prasauskas, T., Kauneliene, V., Stasiulaitiene, I., Kliucininkas, L., 2014a. Characterization of particulate and vapor phase polycyclic aromatic hydrocarbons in indoor and outdoor air of primary schools. *Atmos. Environ.* 82, 298–306.
- Krugly, E., Martuzevicius, D., Sidaraviciute, R., Ciuzas, D., Prasauskas, T., Kauneliene, V., Stasiulaitiene, I., Kliucininkas, L., 2014b. Characterization of particulate and vapor phase polycyclic aromatic hydrocarbons in indoor and outdoor air of primary schools. *Atmos. Environ.* 82, 298–306. <https://doi.org/10.1016/j.atmosenv.2013.10.042>
- Lawal, A.T., 2017. Polycyclic aromatic hydrocarbons. A review. *Cogent Environ. Sci.* 3.
- Li, C., Fu, J., Sheng, G., Bi, X., Hao, Y., Wang, X., Mai, B., 2005. Vertical distribution of PAHs in the indoor and outdoor PM_{2.5} in Guangzhou, China. *Build. Environ.* 40, 329–341. <https://doi.org/10.1016/j.buildenv.2004.05.015>
- Lin, T.C., Chang, F.H., Hsieh, J.H., Chao, H.R., Chao, M.R., 2002. Characteristics of polycyclic aromatic hydrocarbons and total suspended particulate in indoor and outdoor atmosphere of a Taiwanese temple. *J. Hazard. Mater.* 95, 1–12. [https://doi.org/10.1016/S0304-3894\(02\)00146-2](https://doi.org/10.1016/S0304-3894(02)00146-2)
- Lin, Y.-C., Li, Y.-C., Shangdiar, S., Chou, F.-C., Sheu, Y.-T., Cheng, P.-C., 2019. Assessment of PM_{2.5} and PAH content in PM_{2.5} emitted from mobile source gasoline-fueled vehicles in concomitant with the vehicle model and mileages. *Chemosphere* 226, 502–508.
- Lin, Y., Qiu, X., Ma, Y., Ma, J., Zheng, M., Shao, M., 2015. Concentrations and spatial distribution of polycyclic aromatic hydrocarbons (PAHs) and nitrated PAHs (NPAHs) in the atmosphere of North China, and the transformation from PAHs to NPAHs. *Environ. Pollut.* 196, 164–170.
- Liu, R., He, R., Cui, X., Ma, L.Q., 2018. Impact of particle size on distribution, bioaccessibility, and cytotoxicity of polycyclic aromatic hydrocarbons in indoor dust. *J. Hazard. Mater.* 357, 341–347.
- Madriga, D.G., Ubeda, R.M., Terroba, J.M., Dos Santos, S.G., García-Camero, J.P., 2019. Particle-associated polycyclic aromatic hydrocarbons in a representative urban location (indoor-outdoor) from South Europe: assessment of potential sources and cancer risk to humans. *Indoor Air* 29, 817–827.
- Maharjan, L., Kang, S., Tripathee, L., Gul, C., Zheng, H., Li, Q., Chen, P., Rai, M., Santos, E., 2022. Atmospheric particle-bound polycyclic aromatic compounds over two distinct sites

- in Pakistan: Characteristics, sources and health risk assessment. *J. Environ. Sci.* 112, 1–15.
- Marple, V.A., Rubow, K.L., Turner, W., Spengler, J.D., 1987. Low flow rate sharp cut impactors for indoor air sampling: design and calibration. *JAPCA* 37, 1303–1307.
- Mateos, A.C., Amarillo, A.C., Tavera Busso, I., Carreras, H.A., 2019. Influence of Meteorological Variables and Forest Fires Events on Air Quality in an Urban Area (Córdoba, Argentina). *Arch. Environ. Contam. Toxicol.* 77, 171–179. <https://doi.org/10.1007/s00244-019-00618-9>
- Morakinyo, O.M., Mukhola, M.S., Mokgobu, M.I., 2020. Concentration levels and carcinogenic and mutagenic risks of PM_{2.5}-bound polycyclic aromatic hydrocarbons in an urban–industrial area in South Africa. *Environ. Geochem. Health* 42, 2163–2178. <https://doi.org/10.1007/s10653-019-00493-2>
- Niu, X., Jones, T., BéruBé, K., Chuang, H.-C., Sun, J., Ho, K.F., 2021. The oxidative capacity of indoor source combustion derived particulate matter and resulting respiratory toxicity. *Sci. Total Environ.* 767, 144391.
- Office of Environmental Health Hazard Assessment, 2005. Air Toxics Hot Spots Program Risk Assessment Guidelines. Part II. Technical Support Document for Describing Available Cancer Potency Factors. Office of Environmental Health Hazard Assessment, Sacramento, California.
- Oliveira, M., Slezakova, K., Delerue-Matos, C., do Carmo Pereira, M., Morais, S., 2017. Assessment of exposure to polycyclic aromatic hydrocarbons in preschool children: levels and impact of preschool indoor air on excretion of main urinary monohydroxyl metabolites. *J. Hazard. Mater.* 322, 357–369.
- Oliveira, M., Slezakova, K., Delerue-Matos, C., Pereira, M.D.C., Morais, S., 2016. Assessment of polycyclic aromatic hydrocarbons in indoor and outdoor air of preschool environments (3-5 years old children). *Environ. Pollut.* 208, 382–394. <https://doi.org/10.1016/j.envpol.2015.10.004>
- Perrino, C., Tofful, L., & Canepari, S., 2016. Chemical characterization of indoor and outdoor fine particulate matter in an occupied apartment in Rome , Italy 558–570. <https://doi.org/10.1111/ina.12235>
- Qian, J., Peccia, J., Ferro, A.R., 2014. Walking-induced particle resuspension in indoor environments. *Atmos. Environ.* 89, 464–481. <https://doi.org/10.1016/j.atmosenv.2014.02.035>
- Ravindra, K., Sokhi, R., Van Grieken, R., 2008. Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. *Atmos. Environ.* 42, 2895–2921. <https://doi.org/10.1016/j.atmosenv.2007.12.010>
- Rogula-Kozłowska, W., 2016. Size-segregated urban particulate matter: mass closure, chemical

- composition, and primary and secondary matter content. *Air Qual. Atmos. Heal.* 9, 533–550. <https://doi.org/10.1007/s11869-015-0359-y>
- Sangiorgi, G., Ferrero, L., Ferrini, B.S., Lo Porto, C., Perrone, M.G., Zangrando, R., Gambaro, A., Lazzati, Z., Bolzacchini, E., 2013. Indoor airborne particle sources and semi-volatile partitioning effect of outdoor fine PM in offices. *Atmos. Environ.* 65, 205–214. <https://doi.org/10.1016/j.atmosenv.2012.10.050>
- Tames, M.F., Tavera Busso, I., Carreras, H.A., 2019. Método optimizado para la determinación de hidrocarburos aromáticos policíclicos asociados a partículas atmosféricas. *Rev. Int. Contam. Ambient.* 35, 387–395.
- Tavera Busso, I., Tames, F., Silva, J.A., Ramos, S., Homem, V., Ratola, N., Carreras, H., 2018. Biomonitoring levels and trends of PAHs and synthetic musks associated with land use in urban environments. *Sci. Total Environ.* 618, 93–100. <https://doi.org/10.1016/j.scitotenv.2017.10.295>
- Tong, Z., Chen, Y., Malkawi, A., Adamkiewicz, G., Spengler, J.D., 2016. Quantifying the impact of traffic-related air pollution on the indoor air quality of a naturally ventilated building. *Environ. Int.* 89–90, 138–146. <https://doi.org/10.1016/j.envint.2016.01.016>
- United States Environmental Protection Agency, 2016. Criteria Air Pollutants [WWW Document]. URL <https://www.epa.gov/criteria-air-pollutants>
- United States Environmental Protection Agency, 2011. Exposure Factors Handbook: 2011 Edition. National Center for Environmental Assessment, Office of Research and Development, Washington DC, USA.
- United States Environmental Protection Agency, 2006. Reference Method for the Determination of Fine Particulate Matter as PM_{2.5} in the Atmosphere, in: Standards for Particulate Matter. Federal References Method, Appendix L to Part 50.
- United States Environmental Protection Agency, 2005. Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities Final This page deliberately left blank.
- United States Environmental Protection Agency, 2003. EPA's Report on the environment. Washington DC, USA.
- United States Environmental Protection Agency, 1993. Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons. Office of Health and Environmental Assessment, US Environmental Protection Agency., Cincinnati, Ohio.
- Wei See, S., Karthikeyan, S., Balasubramanian, R., 2006. Health risk assessment of occupational exposure to particulate-phase polycyclic aromatic hydrocarbons associated with Chinese, Malay and Indian cooking. *J. Environ. Monit.* 8, 369–376. <https://doi.org/10.1039/b516173h>

- World Health Organization, 2005. WHO Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide: Global update 2005. [https://doi.org/10.1016/0004-6981\(88\)90109-6](https://doi.org/10.1016/0004-6981(88)90109-6)
- Yu, K.P., Yang, K.R., Chen, Y.C., Gong, J.Y., Chen, Y.P., Shih, H.C., Candice Lung, S.C., 2015. Indoor air pollution from gas cooking in five Taiwanese families. *Build. Environ.* 93, 258–266. <https://doi.org/10.1016/j.buildenv.2015.06.024>
- Zhang, J. Di, Liu, W.J., Xu, Y.S., Cai, C.Y., Liu, Y., Tao, S., Liu, W.X., 2019. Distribution characteristics of and personal exposure with polycyclic aromatic hydrocarbons and particulate matter in indoor and outdoor air of rural households in Northern China. *Environ. Pollut.* 255, 113176. <https://doi.org/10.1016/j.envpol.2019.113176>
- Zhang, K., Zhang, B.Z., Li, S.M., Wong, C.S., Zeng, E.Y., 2012. Calculated respiratory exposure to indoor size-fractioned polycyclic aromatic hydrocarbons in an urban environment. *Sci. Total Environ.* 431, 245–251. <https://doi.org/10.1016/j.scitotenv.2012.05.059>
- Zhu, L., Wang, J., 2003. Sources and patterns of polycyclic aromatic hydrocarbons pollution in kitchen air, China. *Chemosphere* 50, 611–618.

CRedit author statement

Tames, Maria Florencia: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - Original Draft, Visualization; **Tavera Busso, Ivan:** Methodology, Validation, Formal analysis; **Carreras, Hebe Alejandra:** Methodology, Formal analysis, Writing - Review & Editing, Supervision, Funding acquisition.

Journal Pre-proof

Conflict of interest

The authors declare no conflicts of interest.

Journal Pre-proof