Particle-associated polycyclic aromatic hydrocarbons in a representative urban location (indoor-outdoor) from South Europe: Assessment of potential sources and cancer risk to humans.

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Title: Particle-associated polycyclic aromatic hydrocarbons in a representative urban location (indoor-outdoor) from South Europe: Assessment of potential sources and cancer risk to humans.

Short informative title: PAH in an I/O urban location, South Europe

Authors: David G. Madruga[1], Regina M. Ubeda[1], June M. Terroba[1], Saúl G. dos Santos[1], Jesús P. García-Cambero[2]

[1] Department of Atmospheric Pollution. National Center for Environment Health. Health Institute Carlos III. 28220 Madrid

[2] Department of Environment Toxicology. National Center for Environment Health. Health Institute Carlos III. 28220 Madrid

Corresponding author: Dr. David Galan Madruga e-mail address: david.galan@isciii.es

Postal address: Department of Atmospheric Pollution. National Center for Environment Health. Health Institute Carlos III. Ctra. Majadahonda a Pozuelo km 2,2. 28220 Majadahonda. Madrid (Spain)

Telephone: +34 918223507, fax: +34 915097991

Abstract

PM_{10}-bound polycyclic aromatic hydrocarbons (PAHs) levels were monitored at urban locations (outdoor/indoor) within the city of Madrid between May 2017 and April 2018. 14 PAHs congeners were measured, potential emission sources were identified as were potential carcinogenic risks. The ΣPAHs averaged 0.577 and 0.186 ng/m^3 in outdoor and indoor air, with a high linear correlation per individual mean

PAH and month. The largest contributors to the ΣPAHs were the high-molecular weight PAHs. PCA-MLR results showed that emissions from diesel and vehicular processes explained 27% and 23% of the total variance of outdoor and indoor air, while combustion processes accounted for 30% and 25% in ambient and indoor air, respectively. During the cold season, biomass burning plus coal and wood combustion were additional sources of outdoor emissions. The heavy-, medium- and light-molecular weight PAHs originating from outdoor sources accounted for 72%, 80% and ~60% of the indoor levels of the three respective PAH groups. Average BaP concentration was 0.029 and 0.016 ng/m^3 in outdoor and indoor air, respectively. Estimated BaPeq concentration averaged 0.072, 0.035 and 0.027 ng/m^3 for outdoor, indoor and indoor-generated individual PAHs concentrations, respectively. The estimated carcinogenic risk falls within the range of acceptable risk targeted by the US-EPA.

Keywords

PM_{10}-bound PAH, indoor and outdoor sources, indoor-generated concentration, lung cancer risk increment

Practical implications

This work investigated the PAHs levels associated to both indoor/outdoor PM10 particles in an urban environment, providing consistent data on PAH outdoor/indoor distribution, time trend, influence of outdoor emission sources in the indoor PAH levels, and estimates the risk to human health, giving clues for policy guidance regarding indoor air quality by controlling emission sources in outdoor air.

Introduction

Atmospheric pollution is considered the major environmental risk to human health worldwide. According to the World Health Organization (WHO) (http://www.who.int/airpollution/en/), every year, approximately 4.2 million deaths result from exposure to ambient (outdoor) air pollution. An additional 3.8 million deaths are linked to household exposure to smoke from dirty cook stoves and (indoor) fuels. In addition, the International Agency for Research on Cancer (IARC) has classified outdoor air pollution as carcinogenic to humans[1].

Atmospheric pollution include a variety of pollutants, among which ozone (O_3), nitrogen dioxide (NO_2), sulfur dioxide (SO_2) and, mainly, particulate matter (PM) are of the greatest concern for public health given the strong evidence of their deleterious effects. Particulate matter consists of a complex mixture of solid and liquid particles of organic and inorganic substances suspended in the air. The most health-damaging particles are those with a diameter of 10 μm or less, which can penetrate and lodge deep inside of the lungs[2]. Given that polycyclic aromatic hydrocarbons (PAHs) has been shown to be sorbed onto particles with diameters of 10 microns or smaller [3], many authors have attributed the high toxicity of air pollution specifically to these chemicals[4-5].

PAHs consist of two or more fused aromatic rings made up of carbon and hydrogen atoms. These chemicals are generated from the incomplete combustion of organic material and are ubiquitous contaminants in ambient air. The sources of PAHs in urban air are usually associated with anthropogenic activities, such as those related to industrial activity, gas/coal heating systems and vehicle emissions[6]. Thus, PAHs are widely distributed in the atmosphere as free volatile compounds or adhered to

PM. Given their potential to be inhaled by humans, these compounds have received special consideration as they have been identified as carcinogenic, teratogenic and genotoxic[7].

European legislation establishes air quality standards for outdoor environments. For the PAH group, the annual average target of 1 ng/m^3 for benzo(a)pyrene (BaP) was set by Directive 2004/107/EC. Nevertheless, current EU legislation does not specify standards for indoor environments, despite the estimation that people spend approximately 90% of their time indoors[8]. In this sense, in order to accurately assess the air quality of indoor environments, internal sources of pollution must be considered together with external sources.

External sources of pollution, which can be influenced by factors such as the urban context, the nature of the pollution source and the meteorological contour, contribute to the infiltration rate of particles to indoor environments[9]. Therefore, the identification of external sources, and their distribution, plays a crucial role in assessing the air quality of indoor environments and may inform air quality policies and building techniques that aim to control the infiltration of external air pollutants into indoor environments. This aspect is especially relevant in urban indoor environments due to the numerous outdoor emission sources of pollutants (e.g. heavy traffic, more industries and the higher use of heating systems), and their potential transference to indoor environments.

In the present study, PM_{10} particles (thoracic fraction PM) were systematically and simultaneously sampled at both an indoor and an outdoor location of an urban environment (Madrid, Spain). The main objectives were to (i) investigate PAHs levels associated with PM_{10} particles and their seasonal trend, (ii) identify potential external

and internal emission sources and estimate the influence of these sources on PAHs levels in the indoor location and (iii) evaluate the potential risk of lung cancer in humans posed by the monitored levels of PAHs.

Materials and Methods

Description of sampling point and sample collection

This work was conducted in the capital city of Madrid, Spain, which is located in the center of the Iberian Peninsula. The city consists of 21 districts and 128 neighborhoods. Madrid has over 3 million inhabitants and a surface area of approximately 600 km^2 (Figure S1).

For PM_{10} sampling, an outdoor (40º25'43.08''N-3º40'18.37''W) and an indoor (40º25'43.75''N-3º40'18.92''W) location was established in an urban background environment (non-industrial). Sampling was conducted over a 12-month period between May 2017 and April 2018. Information about both sampling locations is provided in Text S1.

Monitoring of PAH levels was carried out following regulation[10], implemented in the laboratory and accredited, according to the EN ISO/IES 17025:2005 standard, by the National Entity of Accreditation[11]. PM_{10} particles were collected using reference high-volume samplers (EN 12341:2014 standard) equipped with quartz fiber filters (150 mm in diameter) that were previously cleaned by thermal treatment for 12 h. The flow rate was set at 30 m^3/h, the sampling time was 24 h and the sampling frequency was once every three days. The monthly samples (10 samples per month) were combined in one composite sample by location.

Sample extraction and analysis

PM_{10} samples collected at the indoor and outdoor locations were stored in the dark at 4 ºC. Prior to the extraction process, each collected quartz fiber filter was spiked with the internal standards benzo(a)pyrene-D12 and benzo(a)anthracene-D12. Collected samples were extracted by accelerated solvent extraction, concentrated using a nitrogen flow and cleaned using BakerBond extraction cartridges. Finally, they were analyzed and quantified by gas chromatography (capillary column DB – 5MS, 30 m x 0.25 m x 0.25 µm id) coupled with a mass spectrometer detector. Details of the extraction procedures and analysis are provided in Text S2. The PM_{10}-bound PAHs analyzed in the present work are shown in Table S1.

Statistical treatment

Statistical analysis of the dataset was performed using the software IBM SPSS Statistics v22.0 (IBM Corp Armonk, NY, USA). Kolmogorov-Smirnov and Levene tests were performed to test for normal distribution and homogeneity of variance, respectively. ANOVA or Kruskal–Wallis tests were conducted on normally or non-normally distributed data, respectively. Values of significance lower than 0.05 were considered statistically significant.

Meteorological parameters

Daily temperature (meteorological station: Barajas, Madrid, Spain, 40°27'00.06"N 3°33'00.01'W) and relative humidity (datalogger Testo 175-H) were monitored in both locations. In addition, daily rainfall (Barajas meteorological station) was measured in the outdoor location. Multiple linear regressions (MLR) were performed to assess the relationship between meteorological conditions and monthly ΣPAHs levels.

Emission sources: Identification, apportionment and their influence on indoor PM_{10}-bound PAHs levels

Emission sources of air pollutants play a crucial role for understanding and controlling their possible impact on the environment and human health. Therefore, different approaches based on PAH molecular diagnostic ratios (DRs)[12] and binary ratios were used to evaluate potential emission sources of PM_{10}-bound PAHs.

Furthermore, a principal component analysis-multiple linear regression (PCA-MLR) technique was used to characterize and quantify the contribution of outdoor and indoor emission sources. For this technique, the dataset derived from the DRs analysis was used as the input and varimax as the rotation method. The factor loadings were extracted with eigenvalues higher than one (extraction criterion for the principal components). Variables with higher factor loadings were regarded as more pertinent, which indicated potential emission sources.

Finally, the influence of both indoor and outdoor emission sources on indoor PAH concentration was estimated in terms of the ratio of indoor-to-outdoor (I/O) concentrations[13].

Carcinogenic potential of PM_{10}-bound PAHs

The carcinogenic risk posed by a mixture of PAHs is based on an assumption of additivity of the individual risks posed by the PAHs. It is well known that benzo(a)pyrene (BaP) is the most carcinogenic PAH, while others such as benzo(a)anthracene or indeno[1,2,3-cd]pyrene have relatively lower potency to produce cancer. In this sense, carcinogenic risk of inhaled PAHs was calculated using the toxic equivalent factor (TEF) of the PM-bound PAH concentrations in environmental samples. The TEFs used in this work were adopted from[14-15], who allocated a TEF of 0.001 for Nap, Acy, Acp, Flr, Phen, Flt and Pyr; 0.01 for Ant, Chr and BghiP; 0.1 for BaA, BbF+ BjF, BkF and IcdP and 1 for BaP and DahA. These

TEFs indicate the carcinogenic potency of each compound relative to BaP, and multiplying the concentration of each PAH by its corresponding TEF yields a concentration for the total PAH mixture that is expressed in terms of an equivalent concentration (with regards to toxicity potency) of BaP.

After BaPeq concentrations were calculated for the different PAH mixtures, the unit risk of lung cancer was estimated according to guidelines established by the World Health Organization. Regional Office for Europe, 1987[16], World Health Organization. Regional Office for Europe, 2000[17] and the Environmental Protection Agency[18]. In addition, to evaluate cancer risk posed by the measured PAH levels, the incremental lifetime cancer risk (ILCR) was calculated following the method described by Xia et al.[19], considering different population groups (i.e. children, adolescents, adults and seniors) (see Table S2).

Results and discussion

PM_{10}-bound PAH concentrations and seasonal trends

A statistical summary of the PM_{10}-bound PAHs analyzed in this work is shown in Table 1.

In ambient air, the average PM_{10}-bound ΣPAHs was 0.577 ng/m^3 for the study period (range 0.080-2.99 ng/m^3). However, the ΣPAHs did not remain constant during the study period. As shown in Figure 1, ΣPAHs were higher in winter 2018 (1.393 ng/m^3), followed by autumn 2017 (0.637 ng/m^3), spring 2017 (May-June 0.279 ng/m^3), spring 2018 (April, 0.202 ng/m^3) and finally summer 2017 (0.118 ng/m^3). Therefore, the lowest values of PM_{10}-bound PAHs were observed in summer, while the highest were observed in winter.

187 The ΣPAHs for the entire study period was 6.918 ng/m^3. As shown in Figure 2, the
188 largest contributors to the total level of PAHs were the high-molecular weight (HMW)
189 PAHs (4.704 ng/m^3, 68% of the total), followed by the medium-molecular weight
190 (MMW) PAHs (1.937 ng/m^3, 28%), and, lastly, the low-molecular weight (LMW) PAHs
191 (0.277 ng/m^3, 4%). However, this ratio was not constant throughout the year, and
192 there seemed to be a cycle for the studied period. The greatest contribution of
193 HMWPAHs was observed in spring (May 2017 and April 2018); the lowest
194 contribution was observed throughout warmer season (June-November 2017). In
195 contrast, higher levels of LMWPAHs were detected during summer (June-September
196 2017) compared to spring (May 2017 and April 2018).

197 In terms of individual PAHs, BbjF, BghiP and IcdP (HMWPAHs) were present at the
198 highest concentrations (see Table 1), whereas Nap, Acp and Ant (LMWPAHs) were
199 present at the lowest. Acy and Flr were not detected in any samples. Also, the
200 average concentration of BaP was 0.029 ng/m^3 (range 0.002-0.110 ng/m^3), which
201 accounted for 4.8% of the average ∑PAHs in ambient air.

202 In indoor air, the average PM_{10}-bound ΣPAHs was 0.186 ng/m^3 for the study period
203 (range 0.032-0.49 ng/m^3), which was ~3 times lower than that found in ambient air.
204 However, similar to ambient air, the ΣHAPs of indoor air were not constant during the
205 study period. The highest values were observed in autumn 2017 (0.325 ng/m^3),
206 followed by spring 2017 (May, June 0.239 ng/m^3) and winter 2018 (0.226 ng/m^3),
207 spring 2018 (April, 0.117 ng/m^3) and finally summer 2017 (0.061 ng/m^3). Similar to
208 ambient air, the lowest concentrations of PM_{10}-bound PAHs were detected during
209 summer, while the highest were detected during autumn. The total PAHs for the
210 study period was 2.230 ng/m^3. Like ambient air, HWMPAHs (1.650 ng/ m^3; 74% of
211 the total) contributed the most to the total PAHs, followed by MMWPAHs (0.446 ng/

212 m^3; 20%) and LMWPAHs (0.134 ng/ m^3; 6%). However, the level of contribution of
213 each group was not constant throughout the year and, as shown in Figure 2, the
214 HMWPAHs represented the largest contribution in spring (May 2017 and April 2018),
215 summer (July-August 2017) and late autumn (November-December 2017). Lower
216 concentrations of HMWPAHs were observed during June, September and January
217 2018, indicating an irregular pattern, in contrast to the clear pattern observed for
218 ambient air. Generally speaking, LMWPAHs concentrations were higher during the
219 months in which the concentrations of HMWPAHs were lower.

220 As in ambient air, the PAHs BbjF, BghiP and IcdP were present at the highest
221 concentrations in indoor air, and Nap, Acp, BaA and DahA were detected at lower
222 concentrations. Acy and Flr were not detected in any of the samples. The average
223 concentration of BaP in indoor air was 0.016 ng/m^3 (range: 0.002-0.05 ng/m^3),
224 representing 8.4% of the average ∑PAHs found in indoor air.

225 A comparison of the average levels of individual PAHs between ambient and indoor
226 air were highly correlated with month (r = 0.9481, goodness of fit of 90%) and season
227 (r = 0.8647 to 0.9795, goodness of fit 82% to 95%), which reveals that both locations
228 had the same qualitative profile during the study period (see Figure 3 and S2,
229 respectively). Even, there were no statistically significant differences in the average
230 monthly level of each PAH between ambient and indoor air ($p>0.05$, Kruskall-Wallis
231 test). Nevertheless, statistically significant differences in the average level of
232 individual PAH was observed between ambient and indoor air during summer 2017
233 and winter 2018. A significant difference in the concentration of total PAHs
234 (accumulated exposure) between ambient and indoor air was also observed.

According to some authors[20], meteorological variables can influence the extent to which PAHs are present. The meteorological parameters analyzed in this study, taken together, were slightly to moderately correlated with the monthly concentrations of ΣPAHs (r = 0.761 for ambient air and r = 0.622 for indoor air, relative humidity was identified as the main meteorological parameter accounting for the positive correlation (Figure S3). However, temperature was highly, although negatively, correlated with the concentration of PAHs, especially during the months of May to December 2017 (r = -0.955 and -0.866 for outdoor and indoor air, respectively; Figure S3).

Barrado et al.[21] studied the levels of PM_{10}-PAH in a semi-urban area of Madrid from January 2008 to February 2009. These authors showed that PAH levels were higher in autumn and winter compared to spring or summer, consistent with the findings reported here. However, they also reported generally higher mean values for individual PAHs than those found here. Although the mean values of Nap, Ace, BbjF and BkF were similar between the two studies, those of Phe, Ant, Flt, Pyr, BaA, Chr and BaP were 3-8 times higher in the study by Barrado et al. Moreover, in the present study, Flr was not detected.

This remarkable decrease in particle-bound PAHs could be in line with a decrease in the emission of particles, as described in the latest emission inventory report of the city of Madrid[22]. According to the inventory report, the average concentration of BaP (extracted from PM_{10}) was 0.18 ng/m^3 at an urban location with traffic emission sources during 2017; the highest value was recorded in winter (~0.55 ng/m^3) and the lowest during warm season (< 0.05 ng/m^3). In addition, average BaP levels have remained constant over the last several years: concentrations of 0.14, 0.15 and 0.17 ng/m^3 were reported for 2014, 2015 and 2016, respectively. Here, the average BaP

concentration measured was 0.029 ng/m^3, a value more representative of urban background stations with no significant traffic emissions.

In another study conducted in the city of Madrid, Mirante et al.[23] evaluated $PM_{2.5-10}$ PAH levels at a roadside location in the city center. These authors reported average ΣPAHs of 0.501 and 0.11 ng/m^3 in June 2009 and February 2010, respectively. In the present study, average ΣPAHs were 0.147 and 0.77 ng/m^3 in June 2017 and February 2018, respectively. Curiosly, in the study by Mirante et al., the average ΣPAHs in June was higher than in February; however, this is quite an unusual situation. Large differences in the concentration of individual PAHs were observed between that and the present study: the values reported by Mirante et al., for Pyr, BaA, Chr, BaP, IcdP and DahA in June were 2-9 times higher, while BaA, BaP, BbjF and BkF in February were 2-5 times higher. In addition, Flr, Nap, Phen and Ant were not detected during these months in the present study.

Overall, the averages of both BaP and ΣPAH determined in the present study may be representative of an urban background environment, as the levels fall within the range of those reported by other Spanish and European urban cities (see Table S3).

Source identification and apportionment

The analysis of PAH diagnostic ratios (DRs) identified pyrogenic processes linked to petroleum combustion processes at high temperatures and vehicular diesel emissions as the major emission sources at both locations (Table 2 and Figure S4). The lower presence of Ant compared to Phe also supports pyrogenic processes as a potential source of PAHs in ambient air[24]. In agreement with the DRs analysis, the results of the PAH binary ratios analysis also confirmed that pyrogenic processes

linked to both petroleum and fossil fuel combustion were the major emission sources of PAHs in both outdoor and indoor air (Figure S5).

However, changes in DR values during the atmospheric transport of PAHs may complicate the conclusions drawn about emission sources of PM_{10}-bound PAHs recognized by DRs and binary ratio models[25]. Therefore, statistical analyses were conducted to corroborate the above conclusions. The PCA results obtained for outdoor and indoor environments are reported in Table 3. In addition, PCA-MLR was applied on the factor loadings obtained from the PCA in order to quantify the contribution of the different emission sources[26]. In general, the results of the PCA and PCA-MLR (Figure S6) were in agreement with the DRs and binary ratios analyses. The main components in ambient air accounted for 94.22% of the total variance, in which emissions from diesel and vehicular processes accounted for 27.14%, while combustion processes accounted for 29.54%. Taken together, these sources accounted for 56.68% of the total variance for the period under investigation. Evidence of vehicular emission can also be assessed by the presence of certain HMWPAHs[27]. In the present study, the HMWPAHs BbjF, BghiP, IcdP and BkF were present, further supporting vehicular emission as a major source. The results of the PCA and PCA-MLR for indoor air were similar to those for ambient air. The main components accounted for 85.86% of the total variance, with 22.91% explained by emissions from diesel and vehicular processes, and 24.81% explained by combustion processes. Taken together, these sources accounted for 47.72% of the total variance for the period under investigation.

A more detailed analysis of the emission sources in ambient air indicated that, in warmer months (>15 ºC), diesel and vehicular emissions explained 28.23% of the total variance, while combustion processes explained 44.13%, which, together,

accounted for 72.36% of the total variance. During colder months (<15 ºC), diesel and vehicular emission and combustion processes accounted for 22.36% and 35.73% of the total variance, respectively. In addition, a new source, biomass burning plus coal and wood combustion, was identified, which accounted for 10.94% of the total variance. All together, these sources accounted for 69% of the total variance.

Contribution of indoor and outdoor emission sources to the indoor PAH concentration

Indoor-to-outdoor (I/O) concentration ratios were calculated to investigate the influence of the indoor and outdoor emission sources on PAH levels indoors. However, this ratio is not intended to assess the contribution of indoor emission sources alone to indoor levels. For that aim, the I/O ratio of chrysene, a tracer compound, was calculated as a way to estimate an infiltration factor (F_{inf}) for particle-bound PAHs, as successfully used in other studies (see e.g.[28], particularly given that other factors such as exfiltration, deposition, air exchange rate, particle penetration and particle deposition were not investigated in the present study.

Based on the I/O concentration ratios (see Figure S7), outdoor emission sources greatly contributed to indoor PAHs levels (I/O ratio <1 in 65.83% of the cases). According to the I/O ratios of the three PAH groups, HMWPAHs, MMWPAHs and LMWPAHs originating from outdoor sources contributed 68%, 71% and ~30%, respectively, to the indoor levels of these groups.

Similarly, chrysene I/O ratios, calculated over the monitored period, were less than (in 75% of the cases; range: 0.06-0.50) or equal to 1 (in 25% of the cases), indicating that the presence of indoor chrysene originated from mainly outdoor sources[29]. In other words, these results corroborate a positive contribution of outdoor emission

sources to indoor PAHs levels. According to the chrysene I/O ratios, and assuming that the chrysene infiltration factor acts as a proxy for other particle-bound PAHs, the HMWPAHs, MMWPAHs and LMWPAHs originating from outdoor sources contributed 72%, 80% and ~60%, respectively, to the indoor levels of the three PAH groups. The most notable difference between the two I/O ratio analyses was in the contribution of outdoor LMWPAHs to indoor air (by a factor of 2).

In terms of individual PAHs (Figure S8), the I/O ratio analysis showed that indoor sources predominantly accounted for the levels of Nap, Ant and DahA. The Indoor-air sampling point was located central in a corridor (fisrt floor) of an International Vaccination Center. Several medical consultation offices open to the corridor. These offices are equipped with electronic devices and the base covered with parquet floor. The sampling point was far from the center's kitchen facility.

Mullins et al. (2013) identified printers, photocopiers and computers as possible emission sources of indoor PAHs. Even, PAHs may be emitted by printed paper (Wolkoff et at., 1993). In the same line, Destaillats et al. (2008) reported that the amount of dust released during computers operation could amount 4.0 - 6.3 mg dust per day, and in particular naphthalene and anthracene were found in non-smoking offices between 0.06-0.52 µg/g and between 0.16-0.94 µ/g, respectively.

This contrasts with the chrysene I/O ratio analysis which indicated that outdoor sources predominantly accounted for the levels observed for these same compounds (Figure S9). Outdoor sources accounted for more than 50% of the level of the rest of the compounds, with no clear differences between carcinogenic and non-carcinogenic PAHs.

A high contribution of outdoor emissions to indoor PAHs levels was detected during the cold season (November to February 2018), while the lowest contribution was in spring (May-June 2017 or March-April 2018) (Figure S10). During cold periods, several factors favor the presence of PAHs in outdoor air and, consequently, their movement to indoor air. First, the temperature outdoor is lower than indoor, which increases the condensation of PAHs onto atmospheric particulate matter[30]. Second, the combustion of fossil fuels and/or biomass burning from household heating systems increases the level of outdoor PAHs[31]. Another reason could be the shrinking boundary layer in the wintertime, and so if the boundary layer is smaller, then pollutants are concentrated. Finally, meteorological conditions prevent PAHs in outdoor air from chemically decomposing through photochemical reactions[30].

Incremental cancer risk to humans by inhalation exposure to PM_{10}-bound PAHs

The average monthly/annual concentration of BaP at both sites did not exceed the threshold value of 1 ng/m^3 established by European legislation[32], which is used as a marker for the carcinogenic risk of PAHs in ambient air.

As carcinogenic risk cannot be assessed solely on the basis of BaP concentrations, annual BaPeq concentrations were measured for PAH mixtures derived from outdoor, indoor and indoor-generated individual PAH concentrations. Estimated average BaPeq concentrations were 0.072, 0.035 and 0.027 ng/m^3, respectively, for the different mixture samples. According to the WHO guidelines for Europe, a lung cancer risk of 8.7 x 10^{-5} is estimated if air polluted with 1 ng/m^3 BaP is inhaled over a lifetime of 70 years[16]. Based on the results presented here, 6.2 x 10^{-6}, 3.1 x 10^{-6} and 2.3 x 10^{-6} cases of lung cancer is estimated, attributable to annual exposure to outdoor, indoor and indoor-generated PM_{10}-bound PAHs for 24 hours, respectively.

The lung cancer risk estimated in this study is more than ten times lower than the carcinogenic risk reported by the WHO. The estimated carcinogenic risk also falls within the range of acceptable risk targeted by the EPA (10^{-4} to 10^{-6})[33].

Another approach considers the incremental lung cancer risk (ILCR) associated with lifetime PAHs exposure. Average ILCR values derived from the mean inhalation exposure to outdoor, indoor and indoor-generated concentrations of PAH mixtures by population are shown in Table S4. Under most regulatory programs, ILCRs between 10^{-6} and 10^{-4} indicate potential risk, with 10^{-6} or less denoting virtually no risk and greater than 10^{-4} a potentially high risk[34]. In the present study, the ILCRs for all population groups were lower than the baseline value of acceptable risk, indicating an acceptable carcinogenic risk.

Conclusions

In the present study, the concentrations of PAHs bound to PM_{10} atmospheric particles were measured at an outdoor and an indoor location in an urban background area in the city of Madrid for one year (May 2017 to April 2018). The average concentration of ΣPAHs was 0.577 ng/m^3 in ambient air and 0.186 ng/m^3 in indoor air. The average concentrations of individual PAHs in ambient and indoor air showed a strong correlation. In fact, the concentrations present in indoor air were strongly influenced by emission sources originating from the ambient air. The average PAH level at each location was not constant throughout the year, and the results highlighted a strong increase (by a factor of 4) in outdoor PAH levels in the winter compared to summer. Among the meteorological factors analyzed, relative humidity was positively correlated with the concentration of PM_{10}-bound PAHs, while temperature was negatively correlated with it. Another important factor influencing

PAHs concentrations was the differential contribution of emission sources at different times of the year. In general, the measured PM_{10}-bound PAHs originated mainly from combustion processes at high temperatures and vehicular emissions; however, in winter, biomass burning was identified as an additional source. Taken together, the major findings of this study corroborate the study area as an urban background similar to other cities in Spain and without any influence of a particular emission source. Furthermore, they indicated that the levels of PM_{10}-bound PAHs present in these locations are unlikely to impact human health: average BaP levels were 0.029 ng/m^3 and 0.016 ng/m^3 in ambient and indoor air, respectively, which are well under the EU limit (1 ng/m^3) to protect human health, and, according to WHO guidelines, the estimated ΣPAHs poses a low potential risk of incremental lung cancer incidence.

It is remarkable note that, PAH levels in the ambient air of the Madrid City have declined over the last 10 years.

Contributions

David Galán conducted the validation process of analytical method, performed the statistical analyses of the data set.

David Galán and Jesús Pablo García designed the experiment, sampling plan, evaluated the results, wrote and discussed the manuscript.

Regina Muñoz and June Mérida conducted the analytical experiments and, in collaboration with Saúl García, carried out the sampling process.

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430 **Conflict of interest**

431 The authors declare that there are no conflicts of interest.

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