



Exposure to polycyclic aromatic hydrocarbons in urban environments: Health risk assessment by age groups



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ABSTRACT

A detailed investigation was conducted into the concentration of polycyclic aromatic hydrocarbons (PAHs) associated with PM₁₀ particles collected during 2012 in an urban area in Córdoba, Argentina. Their composition was studied and the lifetime lung cancer risk resulting from exposure to total and individual PAHs was estimated. Samples of PM₁₀ were collected daily on fiber glass filters with PAHs being extracted with methylene chloride and analyzed by HPLC. Mean PAH concentrations were higher during autumn and winter. In contrast, during warm months, high ambient temperature and wind speed contributed to a decrease in the PAH ambient concentrations. The PAH levels found in the present study were within the range of those reported in other polluted urban areas. However risk factors calculated for exposure to individual and cumulative PAHs exceeded the carcinogenic benchmark level of 1×10^{-6} early in childhood, implying that these PAH concentrations represent a serious risk to public health.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants containing at least two condensed rings, with physicochemical properties that make them highly mobile in the environment, thus allowing their distribution across air, soil and water bodies. The main concern with PAHs is that they produce adverse effects on health, with some being well-known carcinogens, mutagens and teratogens (EPA, 2011). Indeed, many PAHs have been classified as priority pollutants by both the U.S. Environmental Protection Agency and the European Environment Agency.

The presence of PAHs in the environment is primarily due to emissions from incomplete combustion of carbon containing fuels from natural, industrial, commercial, vehicular and residential sources. It has been estimated that stationary sources contribute to approximately 90% of total PAH emission (Caricchia et al., 1999). However, in urban environments the concentrations of atmospheric PAHs are mainly due to vehicular traffic and the poor dispersion of pollutants. These compounds can exist in the atmosphere in both the vapor and particulate phases; low molecular weight PAHs tend to be more concentrated in the vapor phase,

while those with higher molecular weights are often associated more with particulates.

Regarding toxicity, most carcinogenic PAHs are associated with airborne particles rather than the gas phase (Cautreels and Van Cawenberghe, 1978; Lyall et al., 1988). Indeed, a significant correlation was found between the amounts of dust in the air and PAH concentrations in the particulate phase (Kuo et al., 2012). For this reason, PAHs have been the most widely investigated organic compounds in studies exploring the mutagenic and potentially carcinogenic activities of ambient particulate matter (Arey, 1998; IARC, 1998).

Risk estimation for PAH exposure is complex for several reasons. First, there are few reported human epidemiological studies of individual PAHs. On the second place, individual PAHs are likely to induce cancer through different mechanisms, with some evidence indicating that mixtures of PAHs may be even more carcinogenic to humans than individual PAHs (Van Houdt et al., 1987). Thirdly, as only 30–40% of particles organic compounds have been identified, the effects of the complex mixture give more realistic results of carcinogenicity than any test of their individual components due to the occurrence of synergisms or antagonisms (Alink et al., 1983; Van Houdt et al., 1987). On the other hand, as benzo[a]pyrene (BaP) is the most studied PAH, other PAHs have been ranked according to their cancer potency relative to BaP by using toxic equivalence factors (TEFs). Therefore, the application of these TEFs combined with the WHO quantitative risk assessment methodology can be used to

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estimate the excess lifetime risk of lung cancer due to PAH exposure (Morello-Frosch et al., 2000; WHO, 2001).

Several studies have been conducted in Argentina to determine the concentration of airborne particles in its most populated cities, including Buenos Aires and Cordoba (Carreras et al., 2008, 2013; López et al., 2011; Rehwagen et al., 2005). However, little attention has been paid to the levels of PAHs associated to particles distributed in the urban atmosphere, despite the fact that their concentration in the atmosphere is a serious environmental problem, particularly in Cordoba city (Amarillo and Carreras, 2012; Carreras et al., 2013; Wannaz et al., 2010). Thus, in the present study it was conducted a detailed investigation concerning the concentration of PAHs (most of them included in the U.S. EPA Priority List, ASTDR, 2005) associated to atmospheric particulate matter collected during different seasons, and the health risk related with people living in urban areas of Cordoba city.

2. Material and methods

2.1. Study area

Cordoba is the second largest city in Argentina, located at the center of the country (31° 24' S, 64° 11' W) at an altitude of approximately 400 m above sea level. It has a population of 1.3 million and an irregular topography. Its general structure is funnel-shaped, with an increasing positive slope from the center towards the surrounding area. This somewhat concave formation reduces the air circulation and causes frequent thermal inversions both in autumn and winter (Olcese and Toselli, 2002). The climate is sub-humid, with an average annual rainfall of 790 mm, concentrated mainly in summer. The mean annual temperature is 17.4 °C and the prevailing winds come from the NE, S and SE.

The main sources of air pollution in Cordoba city are automobile sources, with a strong relationship with primary pollutants (CO, NO_x and PM₁₀). The city also has an important industrial development of mainly metallurgic and mechanical industries (Amarillo and Carreras, 2012). Previous studies have found that in Cordoba urban area, the average PM₁₀ and PM_{2.5} values are almost 2.5 and 2.8 times higher respectively than the corresponding EU limit values for air quality (24-h limit value of 40 mg m⁻³ for PM₁₀ and 25 mg m⁻³ for PM_{2.5}, López et al., 2011). Indeed, previous studies had shown that increases in its airborne particulate pollution were related to a higher morbidity due to respiratory diseases (Carreras et al., 2008).

2.2. Sampling

Sampling was carried out for 24 h every day with no rain from January to December 2012. A total of 314 samples were obtained. A medium volume sampler for total suspended particles (TSP, Energética, Brazil) was located 7 m high on the roof of the Chemistry Department at the FCEFYN, Cordoba University. It was operated at a flow rate of 0.2 m³ min⁻¹ to obtain a total sample volume of greater than 300 m³ over the 24 h period. The TSP data was transformed in PM₁₀ using the conversion factor (PM₁₀ = 0.83 × TSP) suggested by the 1999 Council Directive of European Commission (Council Directive EC, 1999). Before sampling, glass fiber filters were baked at 200 °C for at least 24 h, to volatilize any organic contaminants. After sampling, the filters were wrapped in aluminum foil to avoid photo degradation. All freshly exposed filters were conditioned in a desiccator for 24 h to remove moisture. Exposed filters were then folded and rewrapped in aluminum foil, stored in sealed plastic bags and kept refrigerated (-18 °C) until the day of analysis (<1 month). Meteorology data was also collected including temperature (°C), relative humidity (%), wind speed (km h⁻¹), rainfall (mm) and atmospheric pressure (mmHg) (Table 1). The concentration of particles (μg m⁻³) was determined by differences in the filter weights before and after the 24 h exposures divided by the filtered air volume.

Table 1
Seasonal meteorological conditions during the sampling period.

	Autumn		Winter		Spring		Summer	
	Mean	SE	Mean	SE	Mean	SE	Mean	SE
PM ₁₀ (μg m ⁻³)	93.19	8.11	147.90	14.68	124.71	10.52	141.70	12.39
Temperature (°C)	15.30	0.59	13.45	0.62	19.98	0.62	24.36	0.38
Relative humidity (%)	63.80	1.81	57.37	2.20	56.93	1.28	59.56	1.84
Atm. pressure (hPa)	960.8	0.47	960.0	0.88	956.5	0.81	956.6	0.52
Wind speed (km h ⁻¹)	12.77	0.52	12.96	0.70	15.49	0.65	14.15	0.62
Rainfall (mm)	3.80	3.10	6.33	6.33	6.41	3.80	11.94	4.92

Table 2

Fluorescence excitation and emission wavelengths and composition of the mobile phase used in the present study.

Time(min)	Fluorescence excitation λ _{exc} (nm)	Fluorescence emission λ _{em} (nm)	Mobile Phase % (Water: ACN)
0	290	430	40:60
3.2	260	352	20:80
6.2	250	390	10:90
7.1	270	440	10:90
7.8	250	390	0:100
11.5	290	430	0:100

2.3. Organic matter extraction

The solvent-extracted organic matter (SEOM) was obtained immersing the filters in 30 mL methylene chloride (MC) (HPLC grade, Chromanorm) with ultrasound for two 30 min periods, to ensure that all compounds of interest had been extracted. In order to avoid MC evaporation (likely to take place during extraction, as it has a relatively low boiling point) and the subsequent possibility of losing the compounds of interest in the process, a cooling device was fitted over the flask's mouth containing both the sample and MC. The extracts were concentrated with a rotavapor, at 30 °C, and then evaporated under a soft nitrogen flow. The concentrates were filtered with syringe Teflon filters (0.22 μm) and brought up to 1 mL using acetonitrile.

2.4. Instrumental analysis

PAHs extracts were analyzed by High-Performance Liquid Chromatography (HPLC- Perkin Elmer series 200) using fluorescence detectors. Separation was performed by means of a reverse phase C-18 column (Luna 5u C18 100A). A gradient elution program was utilized using mobile phases of acetonitrile and distilled deionized water. The column temperature was 30 °C, and the flow rate of the mobile phase was 1.8 mL min⁻¹. The changes in the composition of the mobile phase and detection wavelengths are shown in Table 2.

The system was calibrated for the 16 EPA target PAHs with a standard solutions (EPA 610 PAHs Mixture) purchased from Supelco (Argentina). The solution contained Naphthalene (NAP), Acenaphthylene (ACL), Acenaphthene (AC), Fluorene (FL), Phenanthrene (PHE), Anthracene (ANT), Fluoranthene (FLU), Pyrene (PYR), Benzo[a]anthracene (BaA), Chrysene (CHR), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benzo[a]pyrene (BaP), Dibenzo[a,h]anthracene (DBaA), Benzo[g,h,i]perylene (BghiP), and Indeno[1,2,3-c,d]pyrene (IND). ACL was not measured because it has no fluorescence, while IND was not measured because it elutes between DBaA and BghiP, therefore its identification is difficult. Six-point calibration curves were obtained for all PAHs, ranging from 1 to 100 μg L⁻¹ (R² > 0.95, p < 0.001). PAH detection limits were found to be between 5 and 43 pg m⁻³.

2.5. Risk assessment

As was stated above, assessing the toxicity of the individual PAHs in a mixture of PAHs is complex. Although several approaches have been developed, such as the use of TEFs based on BaP, the use of these factors does not take into account individual differences mainly due to age, which could therefore result in an over estimation of the risks. According to EPA (EPA, 1998), human health risk depends on the intake of every single contaminant inhaled by the receptor, the extent of exposure, as well as on their toxic effects. The chemical-specific risks were calculated considering the Life Averaged Daily Dose and the Slope Factor using the linear Equation (1), where LADD is the Life Averaged Daily Dose, (mg (kg day)⁻¹) and SF is the slope factor ((kg day⁻¹) mg⁻¹). The LADD is the chronic daily intake of carcinogenic substances and can be calculated from the compound concentration (CA, mg m⁻³) and intake factor (IF, m⁻³ kg⁻¹ day⁻¹, Equation 2). The intake factor was calculated from age-specific physiological and exposure parameters (Equation 3). On the other hand, the slope factor is an estimate of the upper-bound probability of the individual developing a cancer as a result of the lifetime exposure to certain level of potential

Table 3

Cancer potency factor expressed as inhalation unit risk ($\text{m}^3 \mu\text{g}^{-1}$) for PAHs (OEHHA, 2002; EPA, 2003).

PAH	IUR $\text{m}^3 \mu\text{g}^{-1}$
Naphtalene	3.4×10^{-5}
Acenaphthene	1.1×10^{-6}
Fluorene	1.1×10^{-6}
Phenanthrene	1.1×10^{-6}
Anthracene	1.1×10^{-5}
Fluoranthene	1.1×10^{-6}
Pyrene	1.1×10^{-6}
Benz (a)anthracene	1.1×10^{-4}
Chrysene	1.1×10^{-5}
Benzo (b) fluoranthene	1.1×10^{-4}
Benzo (k) fluoranthene	1.1×10^{-4}
Benzo (a) pyrene	1.1×10^{-3}
Dibenz (ah) anthracene	1.2×10^{-3}
Benzo (ghi) perylene	1.1×10^{-5}

carcinogen (Bartoš et al., 2009). It was calculated considering the inhalation unit risks (IUR), derived from cancer potency factors for inhalation exposure (EPA, 1998), and physiological parameters (3). The IUR values used in this risk assessment are presented in Table 3 and expressed as $\text{m}^3 \mu\text{g}^{-1}$.

$$\text{Risk} = [\text{LADD}] \times \text{SF} \quad (1)$$

$$\text{Risk} = [\text{CA} \times \text{IF}] \times \text{SF} \quad (2)$$

$$\text{Risk} = \left[\text{CA} \times \left(\frac{\text{IR}_a \times \text{EF} \times \text{ED} \times \text{ET}}{\text{BW} \times \text{AT}} \right) \right] \times \left(\frac{\text{IUR} \times \text{BW} \times 1000}{\text{IR}_b} \right) \quad (3)$$

Body weight (BW) is the default weight of the receptor body (kg); 1000: the conversion factor ($\mu\text{g} \text{mg}^{-1}$); IR is the breathing rate, IR_a is IR expressed as $\text{m}^3 \text{h}^{-1}$ and IR_b is IR expressed as $\text{m}^3 \text{day}^{-1}$; exposure frequency (EF) is the number of exposures per year; exposure duration (ED) is the duration of exposure in years; exposure time (ET) is the number of hours per exposure and averaging time (AT) is the average exposure extent over a lifetime (28489.5 days of carcinogenic exposure).

To assess age differences the exposure factors provided by EPA (2011) were used and calculated the parameters shown in Table 4 which were then employed for risk assessment.

The carcinogenic benchmark level used represents an exposure that poses an upper-bound lifetime excess cancer risk of 1×10^{-6} (EPA, 2003). Therefore exposure for which the risk factor exceeded 1×10^{-6} (i.e. one occurrence over 1 million people) was then scored as significant.

2.6. Statistical analysis

Descriptive statistics were calculated for the PAHs and meteorological parameters. In addition, a correlation analysis was performed between these variables. All statistical analyses were carried out using IBM SPSS 19.0 (IBM Corp., Armonk, NY, USA) and significance was taken as $p < 0.05$.

3. Results and discussion

Table 5 presents the mean, maximum and minimum concentrations of individual and total PAHs as well as their variation coefficients. Several blank samples were analyzed and their mean PAH concentrations were subtracted from all other samples. The recoveries of PAHs from particulates ranged from 70% (Phe) to 99%

Table 4

Parameters employed for risk exposure assessment.

Age groups (years old)	$\text{IR}_a(\text{m}^3/\text{h})$	$\text{IR}_b(\text{m}^3/\text{day})$	ED(years old)	ET(hours/day)	BW(kg)
<1	0.23	5.4	0.5	1.29	7.7
1 – 6	0.39	9.44	3.5	1.44	16.2
7 – 11	0.50	12	8.5	2.20	31.8
12 – < 16	0.63	15.2	13.5	1.67	56.8
17 – 21	0.68	16.3	18.5	1.70	71.6
22 – 61	0.66	15.8	41.0	4.68	80
62 – 71	0.59	14.2	66.0	4.83	80
72 – 81	0.54	12.9	76.0	4.97	80

Table 5

Mean, standard error (SE), coefficient of variation (CV), minimum (Min) and maximum (Max) values of individual and total PAHs collected in, Cordoba, Argentina, 2012

PAHs	Mean (ng m^{-3})	SE (ng m^{-3})	CV	Min (ng m^{-3})	Max (ng m^{-3})	Detections(%)
Nap	4.708	0.277	1.208	nd	27.43	94
Ace	0.215	0.017	0.897	nd	2.590	98
Fl	0.466	0.056	0.589	nd	6.152	76
Phe	0.725	0.038	1.338	nd	2.679	96
Ant	0.017	0.001	1.031	nd	0.123	93
Flu	0.364	0.034	0.756	0.031	4.094	100
Pyr	0.206	0.021	0.695	nd	2.278	95
BaA	0.296	0.029	0.735	nd	3.187	99
Cry	0.263	0.030	0.618	nd	3.145	99
BbF	0.508	0.036	0.994	nd	2.884	95
BkF	0.294	0.046	0.451	nd	4.857	97
BaP	0.221	0.019	0.817	nd	1.428	94
DBahA	0.088	0.009	0.731	nd	0.619	93
BghiP	0.669	0.051	0.926	0.049	5.009	100
Σ PAHs	9.040	0.419	1.532	0.693	32.73	

nd: not detected (values under the limit of detection).

(DBahA), while the coefficients of variation ranged from 0.5% (BkFl) to 1.3% (Phe). The levels reported were a good estimation of the environmental levels, except for the most volatile PAHs such as Nap, Ace and Fl, which existed predominantly in the vapor phase thus their particulate concentrations showed large standard deviations. The total PAH values were similar to those measured in other urban areas such as Baltimore ($0.33\text{--}6.52 \text{ ng m}^{-3}$) and New Brunswick ($0.38\text{--}11.6 \text{ ng m}^{-3}$) in USA (Dachs et al., 2002; Gigliotti et al., 2000). Also, on comparing the values measured in the present study with measurements obtained in urban and industrial areas in another region of Argentina, it could be seen that total PAHs values were similar to the ones informed for the industrial site (Rehwagen et al., 2005), which could be due to both, differences in the number of local sources (mainly traffic) as well as climate differences. These results clearly demonstrate the need to further analyze other conditions when comparing different geographical areas.

Profiles of the mean particle-associated individual and total PAH concentrations over the different seasons are shown in Table 6. The concentrations of total PAHs found in fall and winter were much higher than in spring and summer, which suggests that there was a considerable influence of low temperature on PAH condensation in addition to the effect of other meteorological conditions such as inversion conditions and low wind speeds. During the calm and

Table 6

Mean particle-associated individual and total PAH concentrations collected over the different seasons in Cordoba, Argentina, 2012.

PAHs	Autumn		Winter		Spring		Summer	
	Mean	SE	Mean	SE	Mean	SE	Mean	SE
ng m^{-3}								
Nap	5.759	0.389	4.985	0.586	5.302	0.375	2.981	0.698
Ace	0.248	0.027	0.308	0.070	0.261	0.014	0.078	0.016
Fl	0.789	0.156	0.773	0.143	0.217	0.050	0.190	0.045
Phe	0.836	0.058	0.878	0.095	0.998	0.053	0.264	0.062
Ant	0.026	0.002	0.027	0.004	0.014	0.001	0.005	0.001
Flu	0.536	0.062	0.681	0.135	0.205	0.013	0.138	0.013
Pyr	0.314	0.042	0.394	0.081	0.093	0.011	0.086	0.008
BaA	0.451	0.076	0.513	0.077	0.139	0.026	0.152	0.015
Cry	0.416	0.076	0.516	0.093	0.106	0.023	0.096	0.010
BbF	0.550	0.057	0.778	0.116	0.234	0.037	0.543	0.068
BkF	0.167	0.018	0.182	0.027	0.067	0.011	0.699	0.149
BaP	0.321	0.040	0.357	0.061	0.083	0.023	0.166	0.020
DBahA	0.177	0.023	0.106	0.015	0.041	0.007	0.035	0.008
BghiP	1.141	0.137	0.827	0.120	0.274	0.038	0.483	0.040
Σ PAHs	11.73	0.699	11.33	1.238	8.035	0.452	5.916	0.755

stable atmospheric conditions in wintertime, the pollutant dispersion resulted in less accumulation and more gas-to-particle conversion of PAHs, which in turn led to higher concentration of PAHs. In agreement, Li et al. (2006) and Sikalos et al. (2002) reported that wind speed was one of the most important influencing factors on PAHs levels in air. In contrast, during the summer season it was observed the lowest PAH concentrations suggesting also the influence of temperature and wind speed in the atmospheric dispersion of pollutants, along with the photochemical degradation of PAHs by highly reactive radicals such as OH and NO₃, which are more active when warm temperatures and high sunlight conditions are present (Liu et al., 2007). The average levels of total PAHs corresponding to fall and winter were higher than the values reported in other smaller cities in Argentina (5.74 ng m⁻³) and Germany (4.39 ng m⁻³, Rehwagen et al., 2005). However, the values presented here were similar to those reported in urban areas in Italy (8.41 ng m⁻³, Amodio et al., 2009) and lower than those reported in Indian urban areas (145.5 ng m⁻³, Sharma et al., 2007). A higher PAH concentration occurring in winter has been reported in many other urban atmospheres. Indeed several other studies from Europe and USA have reported that PAH levels in winter are generally higher by a factor of 1.5–10 than those in summer (Amodio et al., 2009; Lee et al., 2006; Sharma et al., 2007; Zhu et al., 2009).

The most abundant PAH was Nap, with concentrations 5 times higher than the other compounds in every season. However, these values were below those measured in other places, such as Hong Kong where mean Nap concentration was 993 ng m⁻³ (Ho and Lee, 2002). The second highest PAH concentration were Phe and BghiP, whose levels ranged from (0.8–0.26) ng m⁻³ and (1.14–0.48) ng m⁻³, respectively. Nevertheless, these values were considerably lower than the ones reported in India (Sharma et al., 2007), where mean values of Phe and BghiP were found around 150 ng m⁻³ and 60 ng m⁻³, respectively. The daily levels of BaP, the most investigated PAH and often used as an indicator of carcinogenic risk, were in the range (0.00–1.3) ng m⁻³, which are relatively high compared to those found in other Latin American urban areas, such as Sao Paulo, Brazil (0.13–0.28 ng m⁻³; Vasconcellos et al., 2003), but similar to previous values reported for La Plata, Argentina (0.381 ng m⁻³; Rehwagen et al., 2005) Los Angeles, USA (0.21 ng m⁻³; Venkataraman et al., 1994) and several Asiatic urban areas (Suvarapu et al., 2012). These values can be regarded as total concentrations, since in the atmosphere almost 90% of total BaP is found in the particulate phase (Kim et al., 2013).

To assess the influence of meteorological conditions on PAH concentrations a multiple linear regression analysis for each PAH as the dependent variable was made, and temperature, humidity, atmospheric pressure, wind speed and precipitation as independent factors. Temperature was found to be the most significant negative predictor for Ace, Fl, Flu, Pyr and BaA, with their β coefficients (-0.501, -0.558, -0.430, -0.0461 and -0.370, respectively) decreasing with increasing molecular weight, thereby revealing a strong influence of temperature on the most volatile compounds. Humidity was a significant negative predictor for Nap and Ace, shown by their levels decreasing by 0.316 and 0.395 ng m⁻³ respectively, for a one unit increase in humidity. Wind speed was a negative predictor for all PAHs, although its influence was significant only for BaA and BghiP, with a 0.322 and 0.420 ng m⁻³ decrease in their concentrations respectively, for a one unit increase in wind speed.

Regarding the contribution of light and heavy PAHs, a higher proportion of 2- and 3- ring PAHs to the total PAHs during fall and winter was observed, while the proportion of heavier PAHs increased during spring and summer (Fig. 1). The observed trend was probably a consequence of meteorological conditions, since low molecular weight PAHs are more volatile and therefore more

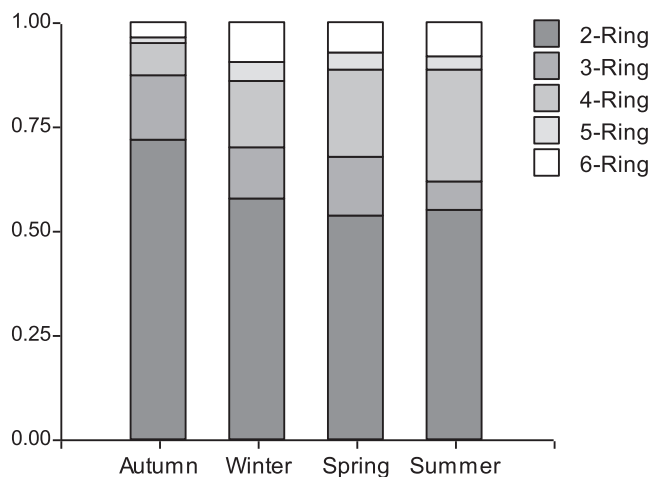


Fig. 1. Contribution of light and heavy PAHs over different seasons in Cordoba, Argentina.

affected by ambient temperature. In contrast, the heavier PAHs show high partitioning into the particle-phase and are less affected by temperature (Omar et al., 2006). The results presented are in agreement with those reported by Salam et al. (2011) and Jamhari et al. (2014) who observed that during high ambient temperature periods, the lower ring-number molecules are present in the gas phase.

As the concentrations of several PAHs were relatively high, a seasonal health risk was now calculated as the average of the partial risks of the individual pollutants, for a person in the 61–71 age-group (Fig. 2). As expected, the highest risk was observed during the cold seasons, with values in fall and winter being almost double those of spring and summer (1.23×10^{-4} and 1.17×10^{-4} vs 5.13×10^{-5} and 6.69×10^{-5} , respectively). Other studies made in the Western Balkans also found that PAH related human health risks increased between the summer and winter seasons, although the values reported were several orders of magnitude lower than those of the present study (Bartoš et al., 2009).

Regarding the individual toxicity of the target PAHs, the compounds that contributed most to the total estimated risk were BaP, Nap and DBahA when ambient temperature was low, while BaP, Nap and BkF were the compounds that contributed the most during

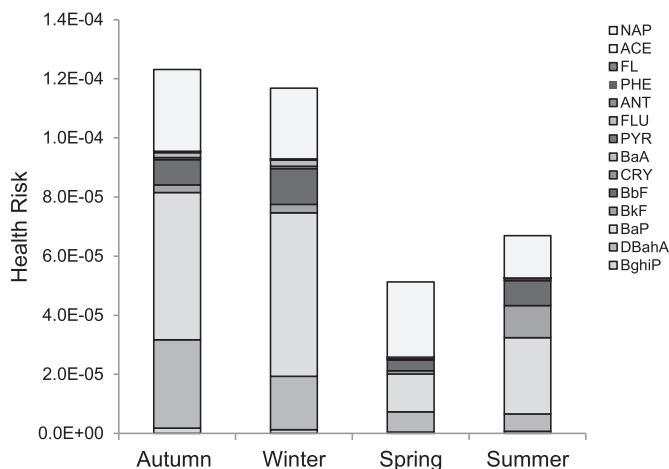


Fig. 2. Average estimated lifetime lung cancer risk per person exposed, by period and PAH.

the warmer months. These results are related to both the high levels of Nap in the atmosphere and to the very high potency factors of BaP or DBaA (WHO, 2001), despite the fact that their levels in the atmosphere were relatively low. This is not surprising considering that most of the 5- and 6-ring PAHs have revealed the highest cancer potencies (Omar et al., 2006; Cincinelli et al., 2007). Similarly, Chiang et al. (2003) reported that even though the concentrations of 3- and 4-ring PAHs are high, the health risks are mostly associated with particulate phase 5- and 6-ring PAHs. The risks informed in the present study can be considered to be the total PAH exposure risk of the population, since other studies have demonstrated that almost all the cumulative risk can be assigned to particle-associated compounds with only a minor percentage being due to gas-phase PAH (Kim et al., 2013).

The cumulative cancer risk associated to each age category (Table 7) was also calculated and it was found that the upper-bound lifetime excess cancer risk of 1×10^{-6} established by EPA (2003) was exceeded as early as in the 1–6 year-old category, implying that there is a risk that one 6 year-old child per million would have cancer due to exposure to PAHs. This risk is increased by one order of magnitude in adults older than 21 years of age, and after this the risk rises with age due to the increased exposure time. Summing up, the results presented here are extremely worrisome especially when considering that as early as 6 year of age a child living in the city of Cordoba already has a significant cancer risk, which is also thought to increase due to exposure to other carcinogenic compounds all throughout life. The International Agency for Research on Cancer (IARC) recently concluded that exposure to outdoor air pollution and to particulate matter in outdoor air are carcinogenic to humans and cause lung cancer (IARC, in press; Loomis et al., 2013). However, the evidence provided is still inconclusive regarding which specific components of the air pollution mixture are driving the increased risk (Hamra et al., 2014). The results provided here are strong evidence of the carcinogenic potential of individual components in the air pollution mixture and could be useful to understand the contribution of organic compounds to cancer risk.

4. Conclusions

The main objectives of the present investigation were to analyze the composition and seasonal variations of particulate-phase PAHs in the urban area of Cordoba city as well as to estimate the resulting health risks. It was found that during wintertime, the magnitudes of particle-bound PAHs were high enough to pose a threat to human health. Their levels in the environment may partly be explained by atmospheric conditions, but they could also be further influenced by photo degradation, chemical oxidation and the physicochemical characteristics of the atmosphere. As there are evidently other factors affecting PAH concentrations; further studies are needed to improve the understanding of the physical–chemical processes that govern the composition of ambient PAH levels.

Table 7

Mean cumulative cancer risk associated with each age category.

Age category	Mean	SE
<1	1.8×10^{-7}	1.0×10^{-8}
1–6	1.4×10^{-6}	8.1×10^{-8}
7–11	5.2×10^{-6}	2.9×10^{-7}
12–16	6.2×10^{-6}	3.5×10^{-7}
17–21	8.6×10^{-6}	4.9×10^{-7}
22–61	5.3×10^{-5}	3.0×10^{-6}
62–71	8.7×10^{-5}	4.9×10^{-6}
72–81	1.0×10^{-4}	5.8×10^{-6}

The results presented here might have incurred some imprecisions due to the application of the EPA unit risk values being based on 95% upper confidence limits of cancer slopes. In addition, health risks may have been underestimated because inhalation was the only kind of exposure considered in this study, while ingestion exposure via food or water consumption may be significant exposure scenarios for other carcinogenic compounds. Moreover, any chemical interactions or synergic effects were considered, which could be other sources of potential errors. Another limitation of the study is the fact that due to the sampling technique employed, we may have collected some gaseous PAHs adsorbed to particles and lost some others due to the removal of particles from the filter during sampling. However, these minor differences may not have contributed significantly to general PAH trends.

Nevertheless, despite these weaknesses, to our knowledge this is the first comprehensive study that discriminates the human health risk posed by PAHs among different age groups. The results provide strong evidence that PAHs levels in Cordoba urban area are actually a threat for human health, early in childhood which is expected to increase over the lifespan. In addition, these findings could be useful for better quantifying the cancer risk associated with air pollution.

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