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# 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 $PM_{10}$ particles collected during 2012 in an urban area in Cordoba, Argentina. Their composition was studied and the lifetime lung cancer risk resulting from exposure to total and individual PAHs was estimated. Samples of $PM_{10}$ 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 $1 \times 10^{-6}$ early in childhood, implying that these PAH concentrations represent a serious risk to public health.

## 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 $PM_{10}$). 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 $PM_{10}$ 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 $PM_{10}$ 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 $m^3$ $min^{-1}$ to obtain a total sample volume of greater than 300 $m^3$ over the 24 h period. The TSP data was transformed in $PM_{10}$ using the conversion factor ($PM_{10} = 0.83 \times TSP$) 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 2**

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

| Time(min) | Fluorescence excitation $\lambda_{exc}$(nm) | Fluorescence emission $\lambda_{emi}$(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 (DBahA), 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 DBahA and BghiP, therefore its identification is difficult. Six-point calibration curves were obtained for all PAHs, ranging from 1 to 100 μg $L^{-1}$ ($R^2 > 0.95$, $p < 0.001$). 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 1**

Seasonal meteorological conditions during the sampling period.

| | Autumn | | Winter | | Spring | | Summer | |
|---|---|---|---|---|---|---|---|---|
| | Mean | SE | Mean | SE | Mean | SE | Mean | SE |
| $PM_{10}$ (ug $m^{-3}$) | 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 |