

Source Apportionment of PM₁₀-Bound Polycyclic Aromatic Hydrocarbons by Positive Matrix Factorization in Córdoba City, Argentina

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Abstract The composition and concentration of polycyclic aromatic hydrocarbons (PAHs) adsorbed on particles smaller than 10 microns (PM₁₀) were analyzed in an urban area during a 2-year period from August 2011 to August 2013. Diagnostic ratios (DR) and positive matrix factorization (PMF) were employed to assess emission sources. To discount weather influence, a multiple linear regression model was generated and also a photodecomposition index was calculated for each sample. Despite the fact that mean PM₁₀ levels showed a similar pattern all around the year, majority of PAHs showed higher concentrations during the cold than the warm period, indicating a strong seasonal variation. A 38% of PAHs variation could be explained by meteorological variables, with wind speed, wind direction, and dew point being the significant regressor variables in the model. The source apportionment of PAHs was performed using PMF although they are photosensitive compounds. The sampling period was separated in warm and cold seasons according to a photodecomposition index and cold period was used. Also, DR were calculated. DR as well as PMF analysis suggested that both gasoline and diesel vehicular emissions are the main PAHs emission sources in this urban area.

Polycyclic aromatic hydrocarbons (PAHs) are persistent and ubiquitous pollutants that exist in the atmosphere in the vapor as well as in the particulate phase. Low molecular weight PAHs are usually distributed in the gas phase, whereas high molecular weight PAHs are distributed in the particulate phase. These compounds have been classified as priority pollutants because of the toxicity as well as carcinogenic, mutagenic, and teratogenic effects (IARC 2010). Indeed, they are the main responsible for the toxicity of particles since most carcinogenic PAHs are associated with airborne particles rather than in the gas phase (Ravindra et al. 2008; Srogi 2007).

The presence and sources of PAHs have been extensively studied worldwide (Lee et al. 2011; Liu et al. 2015; Nizzetto et al. 2008; Tan et al. 2011). It is already accepted that the main emission source of PAHs is the incomplete combustion of biofuel (Zhang and Tao 2009) and indoor fire wood (Shen et al. 2013). Although in some cities burning biomass for heating is one of the major sources of emission (Abdel-Shafy and Mansour 2015), this is not the case for Córdoba city, where most houses are connected to an extensive network of natural gas for domestic heating or cooking. Other emission sources include coal and wood combustion, vehicle exhaust, straw and waste burning, cigarette smoking, and industrial production, such as metal, coke, and iron production (He et al. 2014). Among these sources, vehicle exhaust and certain industrial processes are the main contributors (Mantis et al. 2005; Hien et al. 2007). Vehicle exhaust was even reported to be the most predominant PAHs source, especially in regions where coal and coke were replaced by gas or oil (Guo et al. 2003; Hong et al. 2007; Lee and Kim 2007).

Besides emission sources, the concentration of PAHs in the atmosphere is largely affected by meteorological

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variables, such as temperature, rainfall, solar intensity (Tan et al. 2006; Zhou et al. 2005), and wind speed (He et al. 2014). As PAHs are adsorbed to particles, other variables that influence their composition and concentration are rainfall (Guo et al. 2003; Zhou et al. 2005), visibility, and wind speed (He et al. 2014), among others. Li et al. (2006) and Sikalos et al. (2002) reported that wind speed was one of the variables that most influenced HAPs levels in the atmosphere. During calm and atmospheric stability, the dispersion of pollutants is minor; therefore, they accumulate increasing their concentration. Temperature is negative related to PAHs concentration, because in warm periods the photodegradation is bigger (Caricchia et al. 1999). Also, higher temperatures imply that PAHs adsorbed to particles become PAHs in gaseous phase (Zhao et al. 2011), and therefore when temperatures are lower, the condensation of these compounds on the particles is higher (Hong et al. 2007). Thus, higher concentrations of PAHs are frequently found during the cold respect to the warm periods in many urban areas (Hu et al. 2012; Tang et al. 2005; Zhou et al. 2005). Similarly, high concentrations of particle-bound PAHs were already found during wintertime in Cordoba city (Amarillo et al. 2014). However, the influence of meteorological conditions and emission sources that could explain the temporal variation in PAH's composition is not fully understood yet.

Receptor models include many tools ranging from simple mathematical calculations and basic physical assumptions to complex models that require pre- and post-data processing and several interfaces (Belis et al. 2013). Diagnostic ratios (DR) are one of the simplest expressions to assess the contribution of different sources to PAHs atmospheric concentrations (Hanedar et al. 2011; Tobiszewski and Namieśnik 2012), whereas positive matrix factorization (PMF) is a more complex technique that has been extensively used because it allows source apportionment studies even when there is no data on local source profile inventories (Hanedar et al. 2014; Reff et al. 2007).

Several studies conducted in Argentina determined the concentration of airborne particles in some populated cities (Carreras et al. 2008, 2013; López et al. 2011; Rehwagen et al. 2005). A characterization and source identification study of particle matter have been carried out previously in the city of Cordoba considering their inorganic composition (López et al. 2011). However, little attention had been paid to PAHs despite the fact that the genotoxicity of particles is largely due to the presence of these compounds (Amarillo and Carreras 2012; Carreras et al. 2013). In the present study, we described the temporal variation in particle phase PAHs concentration and composition in relation to meteorological variables and emission sources.

Materials and Methods

Study Area

Cordoba city is the second largest city in Argentina located in the center of the country (31°24'S, 64°11'W) with a population of 1.3 million people. Its topography is concave which reduces air circulation and causes frequent thermal inversions during the cold periods (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.

Automobiles are the main air pollution source in Cordoba city with a strong contribution of primary pollutants, such as CO, NO_x, and PM₁₀. There also is contribution of air pollutants from metallurgic and mechanical industries. 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 European Union limit values for air quality (López et al. 2011). In addition, an increase in airborne particle concentration have been related to higher morbidity due to respiratory diseases (Amarillo and Carreras 2012; Carreras et al. 2008).

Sampling

Daily samples were taken from August 2011 to August 2013, obtaining a total of 314 samples. Total suspended particles (TSP) were collected with a medium-volume sampler (Handi-Vol Energética, Brazil) located 7 m high on the roof of the Chemistry Department at the FCEFYN, Cordoba University, working at a flow rate of 0.2 m³/min. TSP were collected on glass fiber filters which were dehumidified and weighted before sampling. After sampling, filters were wrapped in aluminum foil conditioned in a desiccator for 24 h to remove moisture and stored refrigerated (−18 °C) until the analysis. Particle mass was determined gravimetrically, considering filter weights before and after the exposition and their concentration (μg/m³) was obtained referring the mass to the filtered air volume. PM₁₀ was estimated by using a conversion factor (PM₁₀ = 0.62 × TSP) (Gómez et al. 2003).

PAHs Determination

The organic fraction was extracted with dichloromethane (DCM, HPLC grade, Chromanorm). The filters were immersed in 40 mL DCM with ultrasound for two 30-min periods using a cooling device fitted over the flask's mouth to avoid sample loss. The extracts were concentrated with a

rotary evaporator, at 40 °C, evaporated under a soft nitrogen flow, filtered with Teflon filters (0.22 µm) and brought up to 1 mL using acetonitrile. PAHs extracted from particles were analyzed by high-performance liquid chromatography (HPLC—Perkin Elmer series 200, USA) using fluorescence detector, and a reverse phase C-18 column (Luna 5u C18 100A). A gradient elution program was used for 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 L/min. Detection wavelengths were the same as used in previous work (Amarillo et al. 2014).

Six-point calibration curves from 1 to 100 µg/L ($r^2 > 0.95$, $p < 0.001$) were prepared from the 16 EPA target PAHs standard solution (EPA 610 PAHs Mixture) purchased from Supelco (Argentina). It contained Naphthalene (Naph), Acenaphthylene (Acl), Acenaphthene (Ace), Fluorene (Fluo), Phenanthrene (Phe), Anthracene (Anth), Fluoranthene (Flt), Pyrene (Pyr), Benzo[a]anthracene (BaA), Chrysene (Chry), 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 and Ind could not be determined, because the first has no fluorescence and Ind elutes between DBahA and BghiP, which obstruct its identification. PAH detection limits were found to be between 5 and 43 pg/m³. For statistical analysis, mean and standard deviation of PM₁₀ bound-PAH were calculated for the warm (spring and summer) and cold (fall and winter) periods.

Meteorological Data

Meteorological data were obtained from the National Weather Service for the entire sampling period. We calculated daily averages for temperature (T) (°C), dew point (DP) (°C), relative humidity (RH) (%), atmospheric pressure (P) (hPa), wind speed (WS) (km/h) and visibility (V) (km), and registered daily accumulated rainfall (R) (mm). We also calculated daily mode values for wind direction (WD) (°).

Statistical Analysis

To analyze the relationship between total PAHs concentration and meteorological variables, we calculated Spearman correlation coefficients, whereas Kruskal–Wallis analysis with Mann–Whitney U test ($p < 0.05$) was performed to evaluate the influence of the categorical variables WD and R on PAHs concentration. WD was categorized as north, south, east, and west. R was categorized in three ranges: 0–1, 1–10, and >10 mm.

Multiple Linear Regression Model

A multiple linear regression model was run to explain the concentration of PAHs using meteorological variables as predictors, employing the maximum likelihood estimation (REML) method (Di Rienzo et al. 2011). Total PAHs were transformed to natural logarithm and year, season, month, and day of the week were considered as crossed random factors. The variables entering the model were chosen with a step-wise method. The lack of independence between samples was resolved by using order 1 autoregressive correlation. AIC criteria were used to select the most parsimonious model using Software InfoStat version 2013 (Di Rienzo et al. 2011).

Source Apportionment

The diagnostic ratio (DR) method for PAH source identification requires the comparison of pairs of frequently found PAHs emissions (Ravindra et al. 2008). These ratios indicate the prevalence of gasoline or diesel engines as well as the relative contribution of traffic, domestic heating, wood combustion, and other sources. Their values vary according to the gas-particle partitioning of PAHs in the atmosphere (Tasdemir and Esen 2007). Therefore, DR is highly affected by ambient air temperature (Esen et al. 2008). Consequently, to avoid underestimations of PAHs levels in the particulate phase, we analyzed the PAHs photodecomposition rate in our samples through calculating the relative BaP concentration [$\text{BaP}/(\text{BaP} + \text{BbF})$] (Park et al. 2011). Then, we compared mean values of these photodecomposition indexes comparing samples from winter and summer. Because we found a significantly higher photodecomposition rate during summertime, only samples from the cold period were used for the calculation of DR.

PMF is a multivariate tool developed by Paatero and Tapper (1994) that decomposes a matrix of data sample into two sub-matrices, the factor profiles and factor contributions. It is used to resolve dominant positive factors on the basis of observations, without detailed previous knowledge of the sources and sources profiles. We used the EPA PMF 5.0 software.

All receptor models, either DR or PMF, has the following assumptions: (1) sources profiles do not change significantly over time or do so in a reproducible manner representing a quasi-stationary system; (2) receptor species do not react chemically or undergo phase partitioning throughout transport from source to receptor (Belis et al. 2013). Therefore, PMF analysis was performed only with samples collected during the cold season (autumn and winter) because we already proved a higher photolysis rate during the warm period.

Before PMF analysis data needs to be prepared. Two spreadsheets were made: one with concentration data of each PAH ordered by date and the other with uncertainty data associated with the same order. Outliers were eliminated by identifying them in the time series graphs.

The analytical uncertainty associated with each PAH determination was calculated according to Miller et al. (2002) as

$$u_{sj} = \sqrt{(0.5 * MDL_{sj})^2 + (0.1 * x_{sj})^2} \quad (1)$$

where u_{sj} is the uncertainty, MDL_{sj} is the method detection limit and x_{sj} is the PAH concentration, all referring to j th species in the s th sample. The MDL was calculated for each PAH according to Miller et al. (2002) as

$$MDL = Y_B + 3S_B \quad (2)$$

where Y_B is the average signal of blanks and $3S_B$ is three times the standard deviation of blank samples. When the measured values were below the MDL for species j , they were replaced by half the MDL value and their associated uncertainties were set at 5/6 of the MDL values (Wu et al. 2007). PMF analysis weights the relative importance of PAHs according to their associated uncertainties while makes a multivariate order and estimates emission sources.

The variables included in PMF analysis were selected considering their signal to noise ratio (S/N). If S/N was less than 0.2, the variable was excluded from the analysis. If S/N was greater than 0.2 but less than 2, it was categorized as weak and down-weighted, and if S/N was greater than 2, it was categorized as strong (Paatero and Hopke 2003).

The most critical step in PMF analysis is to determine how many factors explain data variability, because there is no mathematical criteria to predict the optimal number of factors (Paatero 2000) and a priori knowledge of the modeled receptor sites is required (Belis et al. 2013). Hence, for the determination of the number of factors, our main consideration was to obtain a good fitting of the model to the original data. Besides, the number of factors was chosen to avoid redundancies among them, and this was proved by analyzing scatter plots of each factor versus the others.

Relationship of the Factors with Temporal and Meteorological Variables

To complete the analysis of source apportionment, after describing the influence of meteorological variables on total PAHs, we analysed the annual variation of factors (groups of PAHs that variate together a long time) using the nonparametric Kruskal–Wallis analysis of variance with Mann–Whitney U test. For meteorological variables, we did a simple Spearman correlation between factors and

the continuous variables: T , DP , RH , P , WV , V , and R , and Kruskal–Wallis for comparing factors according WD .

Results and Discussion

Particles and PAHs Levels

PM_{10} concentration for the study period ranged from 0.033 to 1022.484 $\mu\text{g}/\text{m}^3$ with no significant seasonal variation between the warm and cold periods (Table 1). The level of particles increased over the last years in the city of Córdoba, doubling the values measured in the 1996–1997 period (Sbarato et al. 2000) and being 1.3 times higher than the values measured in the 2009–2010 period (López et al. 2011), even surpassing the levels measured in other Latin American cities, such as Santiago de Chile (Toro et al. 2014), San Pablo (Bourotte et al. 2005), and México City (Amador-Muñoz et al. 2013). The overall average PM_{10} concentration for the entire period did not exceed the standard of 150 $\mu\text{g}/\text{m}^3$ (EPA 2013); however, 13.9% of PM_{10} samples had values higher than 150 $\mu\text{g}/\text{m}^3$, indicating that the condition of not exceeding this limit more than once a year was not met.

Total PAHs concentration (TPAHs) adsorbed on particles ranged from 0.13 to 37.70 ng/m^3 with an average value of $4.5 \pm 4.3 \text{ ng}/\text{m}^3$ for the whole sampling period. These values were higher than those reported for PAHs in particulate phase in other urban areas, such as Baltimore (1.59 ng/m^3) in USA (Dachs et al. 2002), Naples in Italy (2.19 ng/m^3) (Di Vaio et al. 2016), or Kuala Lumpur in Malaysia ($2.03 \pm 0.57 \text{ ng}/\text{m}^3$) (Jamhari et al. 2014)—similar to values obtained in La Plata, Argentina (4.74 ng/m^3) (Rehwagen et al. 2005), Flanders in Belgium (5.5 ng/m^3) (Brits et al. 2004) and smaller than values observed in Lhasa (15 ng/m^3) (Liu et al. 2013) and Guangzhou in China (23.7 ng/m^3) (Li et al. 2006).

Most individual PAHs had strong seasonal variations with the exception of Naph, BkF, and BbF. For instance, mean BaP concentration for the whole period was $0.17 \pm 0.27 \text{ ng}/\text{m}^3$ and showed significant differences between the cold and warm seasons. These values were smaller than the range observed in European urban sites for BaP (0.4–2 ng/m^3) (Hailwood et al. 2001). TPAHs concentration was higher during the cold than the warm period (5.27 ± 5.32 vs. $3.74 \pm 2.89 \text{ ng}/\text{m}^3$) and was comparable to the values reported for an industrial site in Argentina (5.74 ng/m^3) (Rehwagen et al. 2005). Higher values of PAHs during the winter season also have been reported in many other urban areas, with winter values that exceeded summer values by a factor of 1.5–10 (Amodio et al. 2009; Sharma et al. 2007; Zhu et al. 2009).

Table 1 Seasonal average concentration and standard deviation (SD) of PM₁₀, individual and total polycyclic aromatic hydrocarbons (PAHs) (ng/m³) measured in Cordoba City during 2011–2013

	Whole period		Cold season		Warm season	
	Mean	SD	Mean	SD	Mean	SD
PM ₁₀	98.423	72.315	96.453	74.098	100.361	70.617
Naphtalene	1.913	2.342	2.079	2.312	1.755	2.363
Acenaphtene	0.101	0.201	0.127*	0.270	0.075*	0.083
Fluorene	0.361	0.542	0.508*	0.609	0.213*	0.418
Phenanthrene	0.285	0.361	0.331*	0.384	0.241*	0.331
Anthracene	0.007	0.010	0.010*	0.012	0.004*	0.005
Fluoranthene	0.208	0.34	0.309*	0.445	0.107*	0.117
Pyrene	0.120	0.207	0.190*	0.268	0.051*	0.066
Benz[a]anthracene	0.191	0.253	0.263*	0.324	0.119*	0.118
Chrysene	0.162	0.305	0.247*	0.398	0.079*	0.125
Benzo[b]fluoranthene	0.390	0.630	0.437	0.782	0.343	0.426
Benzo[k]fluoranthene	0.260	0.491	0.127	0.151	0.388	0.648
Benzo[a]pyrene	0.165	0.266	0.240*	0.343	0.092*	0.121
Dibenzo[a,h]anthracene	0.048	0.068	0.071*	0.082	0.024*	0.036
Benzo[ghi]perylene	0.371	0.402	0.463*	0.506	0.280*	0.230
Total PAH	4.500	4.341	5.266*	5.321	3.741*	2.892

* Significant differences between seasons ($p < 0.05$)

Meteorological Variables

Average meteorological conditions for the whole study period are shown in Table 2 and Fig. 1. Temperature, dew point, and rainfall followed the regular pattern for the city of Córdoba, which usually has humid summers and dry winters. These prevailing climatic conditions, together with the concave formation where the city is located, reduce the air circulation and causes frequent thermal inversions in autumn and winter (Amarillo et al. 2014).

Multiple Linear Regression Model

We adjusted a multiple linear regression model (Eq. 3), employing the natural logarithm of TPAHs as dependent

variable and meteorological parameters that already showed a significant relationship with the outcome, as linear predictors. With this model, it was possible to explain a 38% of TPAHs variability, according to a R^2 value equal to 0.38 ($p < 0.05$)

$$\text{LnTHAPs} = 1.96 + 0.02\text{WD}_N + 0.17\text{WD}_W - 0.17\text{WD}_S - 0.02\text{DP} - 0.02\text{WS} \quad (3)$$

where LnTPAHs is the natural logarithm of total PAHs, WD_N , WD_W , WD_S are Wind Direction from North, West, and South, respectively ($^\circ$); DP is dew point ($^\circ\text{C}$) and WS is Wind Speed (km/h).

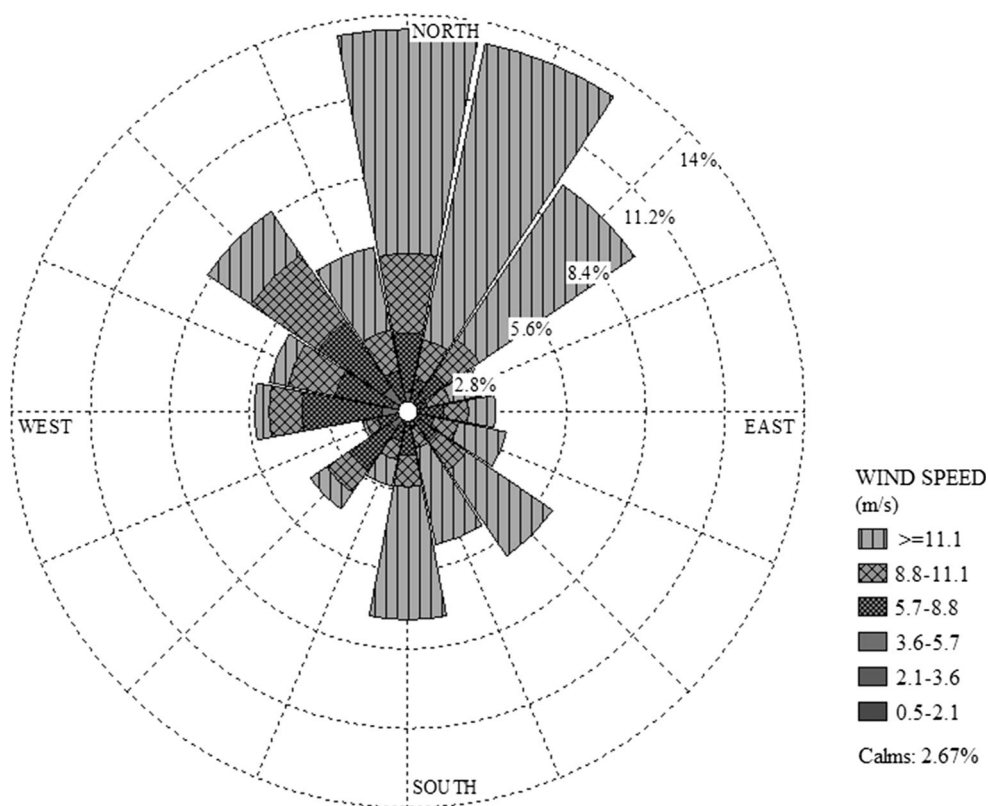
TPAHs were inversely associated with wind speed in agreement with Li et al. (2006)_ENREF_28_ENREF_28

Table 2 Meteorological conditions during the sampling period in Córdoba City (2011–2013)

Variables	Whole period				Cold season				Warm season			
	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max
T ($^\circ\text{C}$)	19.06	6.22	3.38	34.34	15.02	4.78	3.38	24.24	23.57	4.22	10.6	34.34
DP ($^\circ\text{C}$)	11.31	6.08	-5.78	24.46	7.63	5.67	-5.78	19.04	14.91	3.92	1.06	24.46
P (hPa)	965	5	949	983	967	5	953	981	964	5	950	983
RH (%)	60.21	11.78	31.46	94.96	61.43	12.91	31.46	90.46	58.85	10.23	33.30	94.96
WS (km/h)	8.66	4.52	0	27.29	7.27	4.33	0	27.29	10.22	4.21	0.17	22.54
V (km)	9.66	0.79	3.08	13.75	9.64	0.80	4.47	10.42	9.69	0.79	3.08	13.75
R (mm)	1393.1				193.4				1199.7			

T temperature, DP dew point, P atmospheric pressure, RH relative humidity, WS wind speed, V visibility, R accumulated rainfall

Fig. 1 Wind rose for the whole sampling period in Córdoba city (winter 2011 to winter 2013)



and Sikalos et al. (2002)_ENREF_44, who described that wind speed was one of the variables that influenced the most PAHs concentration attributing the increasing PAHs concentration in the atmosphere to the limited pollutant dispersion during calm and stable atmospheric conditions. Wind direction was the meteorological variable with the highest influence on TPAHs concentration. Higher values were observed when winds came from the west side, where it is located a main avenue with intense medium and heavy traffic during all day. Figure 2 shows the concentration of PAHs according to WD. We also observed a negative relationship with dew point, probably related to the high photodegradation rate that takes place during the warm period (Tham et al. 2008) and the fact that particle bound PAHs are easily transferred to the gaseous phase with high temperatures (Zhao et al. 2011).

Source Apportionment

Regarding the source apportionment methodology, some authors still use DR to assess pollutant emission sources (Park et al. 2011; Tobiszewski and Namieśnik 2012), although this methodology should be used with caution, because their results can be rather confusing (Ravindra et al. 2006). Ratios can be altered due to the reactivity of some PAH species with other atmospheric species (Robinson et al. 2006) or the PAHs photolysis may occur

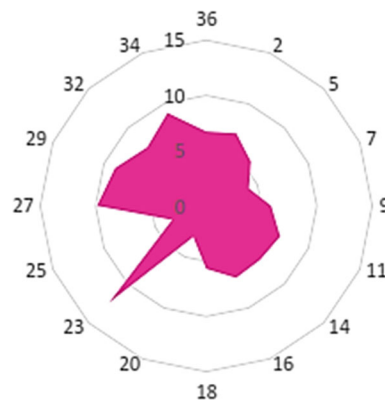


Fig. 2 Average concentration of total polycyclic aromatic hydrocarbons (TPAHs) (ng/m^3) according to wind direction (decade degrees)

during the sampling procedure (Tsapakis and Stephanou 2003). Nevertheless, DR can be useful for exploratory analysis in sampling areas with unknown emission sources. With this purpose, we calculated several different diagnostic ratios using only data from the cold period to avoid differences due to PAHs photodegradation (Table 3).

Most ratios indicated that PAHs came from vehicular emissions, either diesel or gasoline, whereas the $[\text{Flt}/(\text{Flt} + \text{Pyr})]$ ratio indicated a biomass burning origin. However, there was only a slight difference between the values of this last ratio for coal combustion and biomass

Table 3 Comparison between average diagnostic ratios (DR) calculated from the concentration of PAHs measured during the cold season in Cordoba City and reference values mentioned in the bibliography

DR	Reference value	Indicator source	Mean DR in this study	Probable sources	References
BaP/ (BaP + Chry)	0.5	Diesel	0.50	Diesel	Guo et al. (2003), Khalili et al. (1995)
	0.73	Gasoline			
BaP/BghiP	<0.6	Non traffic emissions	2.95	Traffic emissions	Katsoyiannis et al. (2007)
	>0.6	Traffic emissions			
BbF/BkF	>0.5	Diesel	3.96	Diesel	Fang et al. (2004), Park et al. (2002), Ravindra et al. (2006)
Fluo/ (Fluo + Pyr)	>0.5	Diesel	0.65	Diesel	Fang et al. (2004), Ravindra et al. (2006)
	<0.5	gasoline			
Flt/(Flt + Pyr)	<0.4	Petrogenic	0.60	Grass, wood, coal combustion	Roberto et al. (2009)
	0.4–0.5	Fossil fuel combustion			
	>0.5	Grass, wood, coal combustion			
BaA/ (BaA + Chry)	0.2–0.35	Coal combustion	0.58	Vehicular emissions, combustion	Akyüz and Çabuk (2010), Yunker et al. (2002)
	>0.35	Vehicular emissions, combustion			
	<0.2	Petrogenic			

burning (0.5 vs. 0.6), suggesting this was not a conclusive result.

Regarding the PMF analysis, the best fit for the model was obtained with two factors (Fig. 3). The most important factor in terms of mass contribution was factor 1 (63.7%); the compounds that contributed the most to this factor were BghiP (22.35%), BbF (14.73%), Fluo (10.37%), and BaA (10%). This factor was attributed to vehicle emissions, because BghiP specifically is a tracer of gasoline engine vehicles (Kulkarni and Venkataraman 2000). Besides, high molecular weight PAHs are the dominant emissions of light-duty gasoline vehicles (Fujita et al. 2007). Indeed, a high factor loading for BghiP suggests gasoline-powered vehicles (Teixeira et al. 2012), whereas Guo et al. (2003) also include BaA, BaP, BbF, and BghiP as source markers for gasoline emission.

The second factor in term of mass contribution was factor 2 (36.3%), with a high loading of Naph (67.66%) and a small contribution of Phe (10.13%). Naph is a characteristic marker of volatilization from creosote or coal tar, while high loadings of Phe were attributed to either coal combustion or unburned petroleum from vehicles (Suman et al. 2016). If that was the case, the temperature would be strongly correlated with this factor, because it affects the gas-particle conversion rate. However, we did not find any relationship between the contribution of this factor and temperature (results not shown). Therefore, we could not attribute the levels of Phe to unburned coal and concluded that the main emission source of the organic

compounds associated with factor 2 is the incomplete combustion of fossil fuels from vehicles. Indeed, Naph and Phe have already been mentioned as the most abundant PAHs in diesel emissions (He et al. 2010). Moreover, previous studies found that diesel emissions have a high factor loading for Flt, Phe, Ant, and Pyr (Fang et al. 2004; Omar et al. 2002; Ravindra et al. 2006), and the major source of light weight PAHs are trucks powered by diesel.

We observed a fairly good correlation between the measured and modeled individual PAHs ($r^2 > 0.7$), which suggested a good model performance; the best estimations were found for BbF ($r^2 = 0.95$), Chry ($R^2 = 0.91$), and BaA ($r^2 = 0.90$).

To complete our understanding of source apportionment, we described the relationship of the factors with meteorological variables. Factor 1 showed a positive relation with P and a negative one with WS and V . Factor 2 was positive related to T and DP (Table 4). When comparing factors according WD , no differences were found, although total PAHs do relate with WD as described in “Multiple Linear Regression Model” section. The interpretation of these results can be explained considering that diesel vehicles emit more gas-phase PAHs and fewer particulate-phase PAHs than gasoline-powered vehicles (Zielinska et al. 2004). PAHs emitted by gasoline are heavy and are mostly in particulate phase and when the wind is stronger the atmosphere is cleared of particles and consequently those PAHs decrease their concentration. PAHs emitted by diesel vehicles are light and their presence in

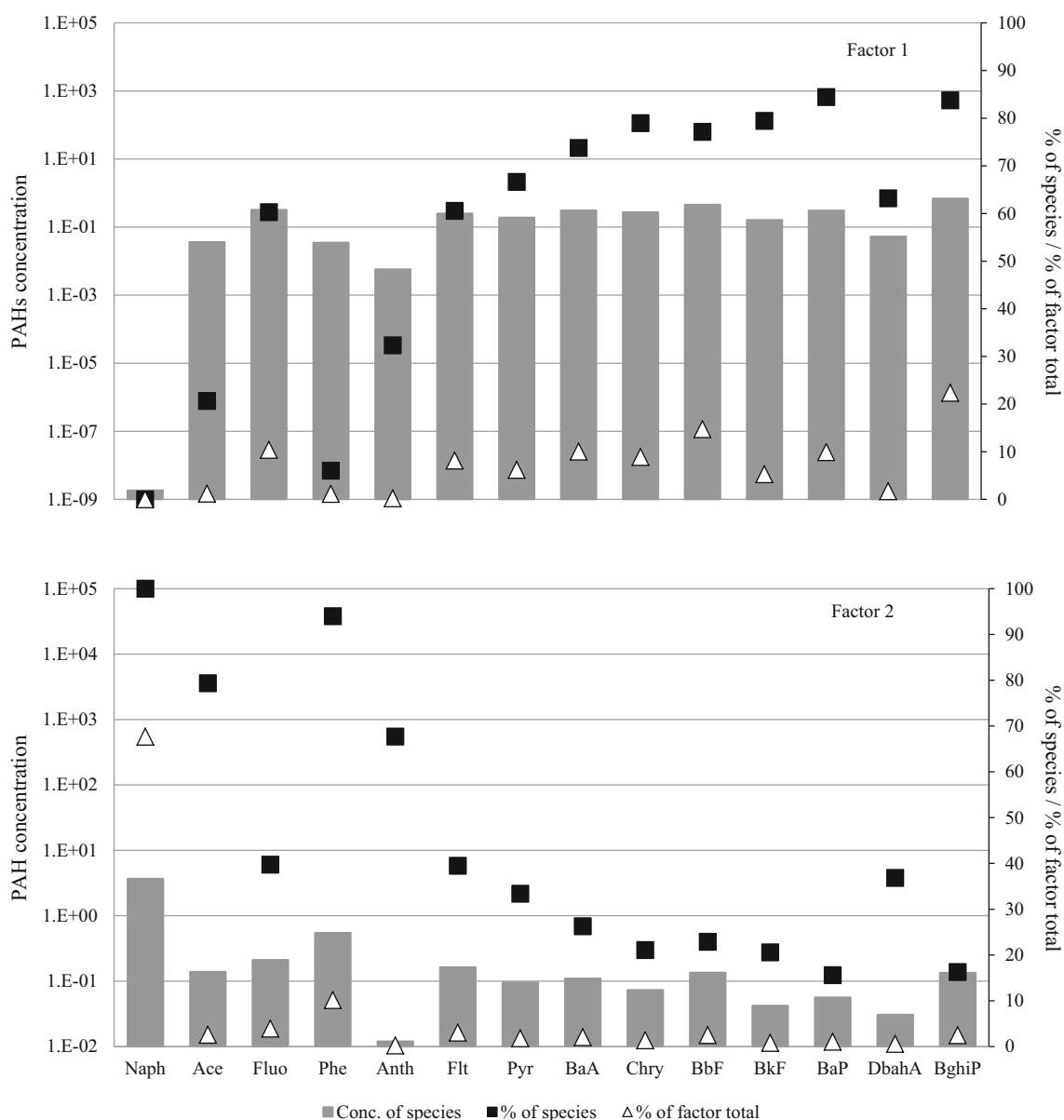


Fig. 3 Factor profiles of PM₁₀-bound polycyclic aromatic hydrocarbons resolved from positive matrix factorization in the cold season. Element concentration (*bars*), percentage of each element distributed between factors (*squares*) and percentage of each element in each factor (*triangles*)

the particles is conditioned to the temperature, because they alternate between gas and particulate phases. When temperatures are low in winter, volatile and semi-volatile PAHs condensate into preexisting particles (Ho et al. 2009).

Conclusions

Although the inorganic characterization of PM₁₀ in the city of Cordoba have already been studied, there was almost no information regarding the organic compounds associated with this type of particles. This is an important issue from

the human health point of view, because most PAHs found in urban atmospheres are classified as genotoxic. To our knowledge, this is the first study in Argentina to assess PAHs emission sources in urban environments.

Variations in total PAHs concentration could be explained in 38% by meteorological conditions, particularly wind speed, wind direction, and dew point temperature. Those variables influenced in different ways the PAHs composition in accordance with molecular weight, particularly the two factors or sources of PAHs. The emission rates of those sources would not explain the variation on PAHs composition, because PM₁₀ concentration had no seasonal differences. Furthermore, these meteorological

Table 4 Spearman correlation coefficients between positive matrix factorization (PMF) factors obtained for polycyclic aromatic hydrocarbons (PAHs) and meteorological variables

Meteorological variable	Factor 1	Factor 2
<i>T</i> (°C)		-0.166*
DP (°C)		-0.199**
RH (%)		
<i>P</i> (hPa)	0.226**	
WS (km/h)	-0.271**	
<i>V</i> (km)	-0.16*	
<i>R</i> (mm)		

Only significant coefficients are shown: * $p < 0.05$; ** $p < 0.01$

variables can be used to estimate PAHs values when there are no real measurements available.

Although the use of receptor models to estimate PAH emission sources have some limitations because of different photodecomposition rates, it was still possible to estimate their emission sources avoiding data from the warm period. Our results provide evidence that light and heavy traffic are the main PAHs emission sources in the urban area. Therefore, to reduce the levels of organic pollutants effective control, measures should be applied to reduce mobile sources in the city.

Another limitation of our research is that we used estimated PM₁₀ values. PAHs bound to particles could be under- or overestimated. We only measured particulate phase PAHs; therefore, the concentration of these compounds in the atmosphere could be higher due to the presence of gas phase PAHs, particularly during the warm period. However, we do not expect too much change during the cold period. Hence, results of the source apportionment analysis are still valid.

Despite the limitations, the present study provides important information regarding the variables affecting PAH composition and concentration in an urban environment with strong climatic and seasonal differences contributing to the air quality management.

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