Nature and Sources of Particle Associated Polycyclic Aromatic Hydrocarbons (PAH) in the Atmospheric Environment of an Urban Area

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Abstract

The total PAH associated to the airborne particulate matter (PM₁₀) was apportioned by one receptor model based on positive matrix factorization (PMF) in an urban environment (Zaragoza city, Spain) during February 2010-January 2011. Four sources associated with coal combustion, gasoline, vehicular and stationary emissions were identified, allowing a good modelling of the total PAH ($R^2=0.99$). A seasonal behaviour of the four factors was obtained with higher concentrations in the cold season. The NE direction was one of the predominant directions showing the negative impact of industrial parks, a paper factory and a highway located in that direction. Samples were classified according to hierarchical cluster analysis obtaining that, episodes with the most negative impact on human health (the highest lifetime cancer risk concentrations), were produced by a higher contribution of stationary and vehicular emissions in winter season favoured by high relative humidity, low temperature and low wind speed.

Keywords: PM₁₀; PAH; receptor model; PMF; source apportionment.

Episodes with the most negative impact on human health regarding PAH were produced by a higher contribution of stationary and vehicular emissions in winter season.

1. INTRODUCTION

The study of the air quality in cities is quite interesting from an environmental point of view, especially due to the negative potential impact that anthropogenic activities can have on human health. Polycyclic aromatic hydrocarbons (PAH) are a group of organic compounds containing only carbon and hydrogen and constituted by two or more aromatic rings fused together. They have been regarded as persistent organic pollutants (POPs) and they are mainly formed by incomplete combustion processes of organic materials such as biomass combustion, vehicular emissions, industrial processes, etc (Katsoyiannis et al., 2011; Manoli et al., 2004; Ravindra et al., 2008; Simoneit, 2002). Their main concern is related to their potential exposure and adverse health effects on humans (Boström et al. 2002; Gammon and Santella, 2008; Luch et al., 2005; Okona-Mensah et al., 2005; Rybicki et al., 2006) so that some of them have been identified as carcinogenic, mutagenic and teratogenic. The US-EPA (2001) has classified seven PAH (benzo[a]pyrene (BaP), benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene,

and indeno[1,2,3-cd]pyrene) as Group B2, probable human carcinogens. These seven PAH have also been classified by the International Agency for Research on Cancer (IARC, 2010) where benz[a]anthracene and BaP are considered as Group 2A, probable human carcinogens and the other PAH as possible human carcinogens (Group 2B). The UK air quality standard for BaP is 0.25 ng/m^3 according to the Expert Panel on Air Quality (EPAQS, 1999). This concentration was adopted as a provisional national air quality strategy objective for England, Wales and Scotland to be achieved by 31 December 2010. In Europe, the Directive 2004/107/EC establishes a target value of BaP= 1.0 ng/m^3 for the total content in the PM₁₀ fraction averaged over a calendar year to be achieved by 31 December 2012. Although the knowledge of the pollutant concentrations constitutes one of the first steps in the air quality, the scope for making further reductions in polluting emissions is aimed to avoid the risk to human health protecting the environment as a whole. This is the reason why it is important to discern the main pollution sources affecting air quality. In this way, receptor models have been widely used (Bzdusek et al., 2004; Kim et al., 2003; Park et al., 2011; Xie et al., 2010; Zhang et al., 2012) as tools that assess contributions from various sources based on observations at sampling sites.

In this work, the total PAH concentrations bound to the PM₁₀ were modelled by a PMF model by first time in a Spanish city. The conditional probability function and cluster analysis allowed distinguishing the main directions contributing to total PAH for each identified source and classifying PAH samples, which were interpreted as a function of the meteorological conditions and the risk for human health. The aim was to provide a better knowledge on the PAH pollution sources in order to improve air quality policies, which could further reduce harmful effects on human health.

2. MATERIALS AND METHODS

2.1 Sampling description

The study was performed in Rio Ebro Campus (length= 41.68, latitude= -0.89), University of Zaragoza. It belongs to Rey Fernando quarter, a residential area located at the North of Zaragoza

city (Spain) (Figure 1). The sampling location was a sub-urban area mainly influenced by vehicle traffic due to the proximity of the AP-2 highway (~50 m) joining Zaragoza with Barcelona (daily average intensity in 2011 =11 420 vehicles, 11.2% of heavy-duty vehicles), heating oil and natural gas combustion for domestic heating, agricultural burning, wood combustion (small villages) and industrial emissions (industrial parks located in the surroundings of the city, paper fabrics and power stations). The sampling site has been previously described in detail (Callén et al., 2008a, 2009) although during this campaign, it is worthy pointing out that the site was influenced by construction activities carried out in order to increase the number of lines in the AP-2 highway.

2.2. Sampling campaign

A Graseby Andersen high-volume air sampler ($1.13 \text{ m}^3/\text{min}$), provided with a PM₁₀ cut off inlet at 10 μm and located 3.5 m from the ground, was used to collect particulate phase PAH over quartz fibre filters QF1-150 (20x25 cm) provided by MCV, S.A. Seven samples per month (each sample corresponding to one day of a continuous week, time of sampling=24 hours) were collected from February 1st, 2010 to January 16th, 2011, obtaining a total of 84 samples. Briefly, filters were cleaned-up by Soxhlet with dichloromethane (DCM) previous to the sampling. PM₁₀ mass concentration was determined gravimetrically by weighting the filters, before and after sampling in a microbalance (accuracy 10 μg), once the filters were conditioned in desiccators. More details regarding the sampling method were given in previous articles (Callén et al., 2008a; López et al., 2005).

2.3 PAH analysis

The following PAH (phenanthrene (Phe), anthracene (An), 2+2/4-methylphenanthrene (2+2/4MePhe), 9-methylphenanthrene (9MePhe), 1-methylphenanthrene (1MePhe), 2,5-/2,7-/4,5-dimethylphenanthrene (DiMePhe), fluoranthene (Flt), pyrene (Py), benz[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF), benzo[j]fluoranthene (BjF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP),

dibenz[a,h]anthracene (DahA), benzo[ghi]perylene (BghiP) and coronene (Cor) were quantified according to previous publications using gas chromatography mass spectrometry mass spectrometry (GC-MS-MS) (Table 1S, Supplementary Information)(Callén et al., 2008b). Briefly, ¼ of the filter was extracted by Soxhlet with dichloromethane after the addition of a surrogate standard solution (An-d₁₀+BaP-d₁₂+BghiP-d₁₂). After concentration by rotary evaporator, samples were cleaned-up through a silica gel column with dichloromethane and concentrated in a pure N₂ stream. The solvent was exchanged to n-hexane and p-terphenyl native was added as recovery standard. Each compound was quantified by GC-MS-MS operating at electron impact energy of 70 eV and using the multiple reaction monitoring (MRM) mode. A Varian Select PAH capillary column (30 m x 0.25 mm internal diameter x 0.25 µm film thickness) was used to quantify PAH and 1 µL of sample was injected in splitless mode. The GC conditions were: 1.5 ml/min Helium flow; temperature-time programme: 70°C, 1 min, increasing 10°/min till 325°C and isotherm for 18.5 minutes. The injector temperature was set to 280°C, the transfer line to 300°C, the ion trap to 220°C and the manifold to 60°C. The identification and quantification of PAH was done according to retention times and the internal standard method relative to the closest eluting PAH surrogate. Calibration curves were prepared with PAH concentrations between 20-1000 ppb in n-hexane. The concentrations of the surrogate and recovery standard were the same and identical as those of the sample extracts. The correlation coefficients of the calibration curve for the different PAH were $R^2 > 0.99$.

2.4. Quality assurance

Repeatability was evaluated by performing four analyses of a standard PAH solution containing the above mentioned PAH and the surrogate and the recovery standards (250 ppb) the same day in the same conditions. Reproducibility was also evaluated by performing analysis of that standard on six different days. In both cases, relative standard deviations (RSD) of the relative response factors were below the 10% for all PAH. The accuracy of the method was determined by analysing the Standard Reference Material (SRM1649a, Urban Dust) from the National Institute of Standards and Technology (NIST) (40 mg, n=4) obtaining errors below the 25% (with the exception of An, 28%).

Both field and laboratory blank samples were prepared and analyzed and all data were corrected with reference to a blank. The method detection (DL) and quantification limits (QL) were calculated as the concentrations equivalent to three and ten times the noise of the quantifier ion for a blank sample (sample air volume=1600 m³) (QL ranged from 0.01 ng/m³ (DiMePhe) to 0.08 ng/m³ (Phe). Recovery efficiencies of surrogate deuterated PAH between 75-108% were achieved and no corrections were applied to PAH samples.

2.5 PMF model

The EPA positive matrix factorization (PMF) model (3.0 software program) was applied to all samples in order to apportion the main PAH pollution sources. Rather than considering the theoretical approach of this model, which has already been described in detail in different publications (Chueinta et al., 2000; Paatero and Tapper, 1994; Paatero, 1997), this paper was focused on the model considerations. As with other receptor models based on statistical factor analysis, numerous procedural decisions have to be made when running this model because results may be sensitive to these decisions. In particular, analysis is limited by the accuracy, precision and range of species measured at the receptor site. However, one of the main advantages of the PMF model with regard to other receptor models is the use of the uncertainty matrix so that concentrations below the detection limit can be underweighted. Concentrations below the detection limit were substituted by half the detection limit and their overall uncertainties were set at five-sixths of the detection limit values (Polissar et al., 1998). There were no missing data. Sample specific uncertainties were provided according to $S_{ij} = DL/3 + c \cdot x_{ij}$, where s_{ij} = uncertainty, DL = detection limit, c = constant (0.1 if $x_{ij} > 3 \cdot DL$, 0.2 if $x_{ij} < 3 \cdot DL$) and x_{ij} = variable (Chueinta et al., 2000).

A critical step in PMF analysis is determining the correct number of factors. The optimal number of factors (p) was achieved based on: the closeness of Q_{Robust} to $Q_{Theoretical}$ ($Q_{Theoretical} = n \cdot m - p \cdot (n + m)$ where n = number of samples, m = number of variables and p = number of factors); the maximum individual column mean of the scaled residual matrix (IM); the maximum individual column

standard deviation of the scaled residual matrix (IS); the majority of scaled residuals between -3 and 3; the absence or a reduced number of non-explained species (non-explained variation: $NEV \leq 0.25$) and the physical significance of the solution found (Chueinta et al., 2000; Juntto and Paatero, 1994; Lee et al., 1999; US-EPA, 2008).

The data set used was an 84x17 matrix (sample number, number of compounds) and the model was run in the default robust mode to decrease the influence of extreme values on the PMF solution. Only one variable, the total PAH was down-weighted as a weak variable and the data were fitted using 17 strong variables (Phe, An, 2+2/4MePhe, 9MePhe, 1MePhe, Flt, Py, BaA, Chry, BbF, BkF, BjF, BeP, BaP, IcdP+DahaA, BghiP, Cor). Solutions between three and seven factors were considered and the optimal solution extracted four factors by running the data with 20 initial random starting points and 10% extra modelling uncertainty. The Q theoretical was 1024, the Q robust 1243.9 and the Q true 1249.1. To ensure that the appropriate number of factors was chosen, the scaled residuals were also examined. A reasonable solution should have scaled residuals distributed mostly between -3 and +3, obtaining 88% of the scaled residuals estimated by PMF distributed in that way. Fpeak model was run with strength of fpeak of 0.1 although no variations were found. A bootstrap model run was also carried out by running 100 bootstraps with a minimum correlation value of 0.6. The percentage of bootstrapped factors assigned (mapped) to their corresponding base factors is indicative of the uniqueness of a given factor profile. When a high amount of a given bootstrapped factor is spread over more than one base factor, it may suggest that the factor profile solutions are not unique and the number of factors may have to be reduced (Sofowote et al., 2011) (Table 2S, Supplementary Information).

2.6. Conditional probability function

The conditional probability function (CPF), which is the conditional probability that a given factor contribution from a given wind direction will exceed a predetermined threshold criterion, was used. Local meteorological data (wind speed and direction) and source contributions from the PMF analysis were combined to identify the likely directions of the PAH sources.

The formula of the CPF is:

$$CPF_{\Delta\theta} = \frac{m_{\Delta\theta}}{n_{\Delta\theta}}$$

where $m_{\Delta\theta}$ is the number of occurrences from wind sector $\Delta\theta$ where the source contributions are in the upper 25th percentile, and $n_{\Delta\theta}$ is the total number of occurrence from this wind sector. A total of 12 sectors were considered in this study ($\Delta\theta = 30^\circ$).

2.7 Statistical tools

Statistical analysis, including ANOVA and t-test were performed using Software SPSS 16.0. A one-way ANOVA procedure was performed to test the significant differences of the dataset and PMF contribution factors. SPSS was also used to classify samples according to hierarchical cluster analysis using Ward method to data from the contributions of the PMF model.

2.8 BaP-eq and lifetime lung cancer risk

The BaP equivalent concentration (BaP-eq), which considers not only the carcinogenic character of BaP but also other PAH, was calculated by summing the products of each PAH concentration and their respective toxic equivalent factor (TEF). In this case, the TEF calculated by Larsen and Larsen (1998) were used.

The lifetime lung cancer risk was calculated with the formula:

$$\text{Lifetime lung cancer risk} = \text{BaP-eq (ng/m}^3\text{)} \times \text{UR}$$

where UR is the inhalation unit risk of exposure to BaP (the calculated, theoretical upper limit possibility of contracting cancer when exposed to BaP at a concentration of one nanogram per cubic meter of air for a 70 year lifetime) (OEHHA 1993, 2005). In this work, the $\text{UR} = 8.7 \times 10^{-5}$ per ng/m^3 was taken according to the World Health Organization (WHO), based on an epidemiology study on coke-oven workers in Pennsylvania (WHO 2000).

3. RESULTS AND DISCUSSION

3.1. PM10 temporal variations

A brief summary of the temporal variations of PM₁₀ is included in Table 1 for the campaign performed in Zaragoza. The mean PM₁₀ concentration was $34.4 \pm 29.0 \mu\text{g}/\text{m}^3$ and although the annual limit value of PM₁₀ according to Directive 2008/50/EC ($40 \mu\text{g}/\text{m}^3$) was not exceeded (Table 1), 20% of the samples exceeded the daily limit value ($50 \mu\text{g}/\text{m}^3$) and 31% exceeded the annual limit value when it is only permitted 35 times per year.

Similar concentrations of PM₁₀ were reported in other Spanish cities like Madrid ($35\text{--}45 \mu\text{g}/\text{m}^3$) (Artiñano et al. 2003) and different European capitals like Sofia ($29.7 \mu\text{g}/\text{m}^3$) and Praga ($36.9 \mu\text{g}/\text{m}^3$) (Farmer et al., 2003). A range of PM₁₀ between $10\text{--}48 \mu\text{g}/\text{m}^3$ was found in Rome (Cattani et al., 2003), $10\text{--}41.5 \mu\text{g}/\text{m}^3$ in Birmingham (Harrison et al., 2003) and $12\text{--}21 \mu\text{g}/\text{m}^3$ in different stations in A Coruña during 2007 (Sanjurjo-Sánchez, 2011). Higher PM₁₀ concentrations were reported by different authors in other European cities like Athens ($90 \mu\text{g}/\text{m}^3$) (Valavanidis et al., 2006), ($77 \mu\text{g}/\text{m}^3$) (Chaloulakou et al., 2003), Thessaloniki ($78\text{--}89 \mu\text{g}/\text{m}^3$) (Voutsas et al., 2002) and Belgrade ($77 \mu\text{g}/\text{m}^3$) (Rajsic et al., 2004).

When samples were divided into two seasons: cold season (winter and autumn months) and warm season (spring and summer months), it was observed that mean PM₁₀ concentrations in the warm season ($38.2 \pm 37.4 \mu\text{g}/\text{m}^3$) were slightly higher than in the cold season ($30.6 \pm 16.5 \mu\text{g}/\text{m}^3$) with no seasonal variations statistically significant. This trend was already reported in Zaragoza in this sampling site (López et al., 2005) and in other Spanish cities as well as rural and industrial areas (Artiñano et al., 2001; Rodríguez et al., 2002; Sanjurjo-Sánchez, 2011) showing the special characteristics of the Mediterranean region: the high impact of mineral matter (African intrusions) (Artiñano et al., 2001), higher solar radiation as well as meteorological conditions that favour the pollutant accumulation: low rainfall and scarce renovation of the air masses.

3. 2. PAH concentrations in the sampling campaign

The mean total PAH concentration for the whole sampling period was $1.78 \pm 1.86 \text{ ng}/\text{m}^3$, whereas the total PAH concentration during the cold season ($2.84 \pm 2.09 \text{ ng}/\text{m}^3$) was four times higher than that found during the warm season ($0.72 \pm 0.60 \text{ ng}/\text{m}^3$) (Table 1). A seasonal behaviour of PAH

statistically significant at 99% level was found with higher concentrations in the cold period and lower concentrations during the warm season. This seasonal behaviour has already been reported by different authors (Chen et al., 2009; Holoubek et al., 2007; Lammel et al., 2010) due to the influence of the meteorological conditions: low temperature, low solar radiation, low photochemical degradation and increased emissions by anthropogenic sources, like domestic heating, in the cold period.

The dominant PAH were Phe, BaA, Chry, Flt, Py, BbF and BghiP with a percentage value of 65% (46-79%). These PAH are associated with fossil fuel, coal and biomass combustion sources including vehicular emissions (Ravindra et al., 2008) although the origin of the possible pollution sources will be faced in more detail in the next section. One of the most interesting PAH to study due to its carcinogenic and mutagenic character is the BaP. The mean BaP concentration was $0.09 \pm 0.11 \text{ ng/m}^3$ and although the guideline value of BaP = 1.0 ng/m^3 according to Directive 2004/107/EC was not exceeded during this campaign, the UK Air Quality guideline value of 0.25 ng/m^3 was exceeded in 11% of the samples, all of them in winter season. BaP is considered one of the most carcinogenic PAH, nevertheless this PAH can underestimate the carcinogenic character of the particulate matter (Wickramasinghe et al., 2012). This is the reason why the BaP-eq was calculated for each individual sample by taking into account the TEF (Larsen and Larsen, 1998) of different PAH. As happened with the BaP, the mean BaP-eq concentrations were higher during the cold season ($0.29 \pm 0.23 \text{ ng/m}^3$), involving a higher potential risk for human health.

3.3. PAH source apportionment by PMF

A total of four factors associated to the particle total PAH were apportioned by the PMF model. The model performance was quite good with an $R^2 = 0.99$, slope=1 (Figure 1S, Supplementary information) and the standard error of the estimates for each individual PAH was less than 20% (exception An=26%) (Table 3S, Supplementary information).

Figure 2 shows the contribution of each factor and the source profiles for the PMF resolved factors.

The first factor mainly characterized by 2+2/4 MePhe, Phe, Flt and Py contributed 24% to the total PAH. The presence of Flt, Phe and An can be attributed to both coal combustion and vehicular exhaust emissions (Abrantes et al., 2004; Ho et al., 2002). Coal is one of the main fuels used in Aragón for power generation representing 25% of the generated energy in 2008 so this factor was considered as coal combustion emissions. As shown in the time series plot (Figure 3), the highest source contributions were on the 13/12/2010 and the 01/02/2010 but also the 09/06/2010 indicating that although the contribution of the heating systems in the winter season could be reflected, industrial parks using this fuel and coal power stations located in Teruel province were mainly responsible of this factor along the year. The conditional probability function (Figure 3) indicated the higher contribution of this factor during the cold period in the NE direction whereas during the warm seasons, the transport from the S and SE directions, where several coal power stations are installed, influenced on the PAH concentrations.

The second factor exhibited the highest source contribution, 32% of the total PAH and it was mainly associated with BkF, BbF, BjF, IcdP+DahA and BghiP. The factor accounted for 83% and 61% of the total BkF and IcdP+DahA, respectively. BbF and BkF are typical markers of diesel emissions (Harrison et al., 1996; Lee et al., 2004). IcdP was associated with diesel and also gasoline emissions (Boström et al., 2002; Ravindra et al., 2008; Riddle et al., 2007). Diesel exhaust is known to contain more particulate matter than gasoline exhaust, and heavier PAH, such as DahA, BghiP and IcdP are associated with these particles (Cristale et al., 2012; Manoli et al., 2004; Ravindra et al., 2008; Umbuzeiro et al., 2008). Different authors also attributed the high contribution of high molecular weight to both maritime and airport traffic emissions (Contini et al., 2011; Lee et al., 2004; Moldanová et al., 2009). The CPF (Figure 3) plot for this factor points that high source contribution was more likely related to an easterly wind direction in the cold period suggesting an impact from the highways and an industrial park known as “Ciudad del Transporte” (Figure 1) where most of the heavy-duty vehicles are parked. This industrial park is located at 6 km from the North of Zaragoza, close to the A-23 and A-2 highways and it is composed by more than 20

factories related with the transport and logistics. During the warm seasons, it pointed to the S-W showing the influence of the airport and the central train/bus station so this factor was considered as vehicular emissions.

The third factor accounted for 20% of the total PAH and it was characterized by a majority of 9MePhe (93%), 1MePhe (42%), Phe (37%), BghiP (33%) and IcdP+DahA (29%) (Figure 2). BghiP appears to be the main tracer for gasoline emissions (Li et al., 2003; Wang et al., 2009). IcdP and Py are also PAH indicators of gasoline engine combustion so this factor was named as gasoline emissions. The CPF (Figure 3) indicated the location of different highways in the cold period as well as the location of two petrol stations located in the S direction of the sampling point (0.22 km and 0.34 km to the sampling point), which could also corroborate the contribution of this fuel.

Finally, the fourth factor was characterized by a majority of Cor (71%), BaA (62%) and BaP (52%) explaining 24% of the total PAH. The origin of this factor is not very clear but BaA and Chry are natural gas markers and this is one of the main fuels used in Zaragoza for domestic heating whereas BeP and BaP are the fingerprints of light oil burning (Bari et al., 2009), which is also mainly used for domestic heating and industrial processes. BaP can be a good tracer for wood combustion (Kulkarni and Venkataraman, 2000). The presence of several paper fabrics (one of them in NE direction, at 5.4 km to the sampling point), different industries located in Aragón using light-oil, natural gas and biomass as main fuels and the use of light-oil and natural gas for domestic heating systems could corroborate this factor considered as stationary emissions.

For all the factors, seasonal variations statistically significant at 99% level (t-test for independent samples) were found between the cold (winter and autumn) and the warm (summer and spring) periods, always with higher values during the cold season justifying the higher influence of anthropogenic activities in addition to the meteorological conditions, which would favour the PAH accumulation in the particle phase. Vehicular and gasoline emissions kept a similar percentage for the cold and warm periods whereas stationary emissions (Figure 2) increased from 14 to 27% during the cold season because of the increase of natural gas use as domestic heating fuel.

3.4. Cluster analysis and lifetime lung cancer risk

Hierarchical cluster analysis was applied to the contribution of the different factors obtained by the PMF model obtaining a dendrogram with the Ward method (Figure 2S, Supplementary Information) and the Euclidean distance square that allowed classifying samples by cases. The results obtained by the dendrogram were studied and interpreted by taking into account not only the PMF factors but also the meteorological conditions, the PM10 and the BaP-eq concentrations. In fact, one of the main concerns of PAH study is related to the carcinogenic character of PAH.

A total of eight different clusters were obtained (Table 2) although these could be classified into two major clusters: A (cluster 1+2+3+4) and B (Cluster 5+6+7+8) (Figure 4) corresponding to 80% and 20% of the samples. Trying to discern the main difference between both clusters, an independent t-test was carried out and the variables statistically significant at 95% between these two major clusters were: the vehicular, the gasoline and the stationary emissions, the BaP, BaP-eq, the total PAH and most of the meteorological variables: T, wind direction, relative humidity, solar radiation and wind speed. The characteristics of the meteorological conditions for the first cluster A, associated with low total PAH concentrations and lower contributions of PMF factors, were high temperature (Table 2) (15.7°C versus 5.6°C), high solar radiation (222 W/m² versus 98 W/m²) and lower relative humidity (61% versus 81%) with higher wind speed (3.8 m/s versus 1.7 m/s), typical conditions of the warm period favouring the pollutant dispersion and possible photo-degradation. In fact, 63% of the samples corresponded to the warm season whereas only 15% of the samples took place in winter season. On the contrary, the second main cluster B (20% of the samples), with higher total PAH concentrations and higher contributions of the PMF factors, showed typical meteorological conditions of the cold period; 76% of the samples corresponded to winter season and 24% to autumn season. The first main cluster: A (80% of the samples), associated with most of the samples, could be divided into two main subgroups representing 71% (cluster 1+cluster 2=60 samples) and 8% (cluster 3+cluster 4= 7 samples) of the total samples. The variables statistically significant at 95% between both subgroups were the coal combustion, the BaP, the BaP-eq, the total

PAH and the temperature and solar radiation. Again the cluster with lower number of samples (8%) showed the highest concentrations of coal combustion, BaP, BaP-eq and total PAH with lower temperature (8°C versus 17°C) and solar radiation (169 versus 227 W/m²).

The second main cluster: B representing 20% of the total of the samples was also studied by an independent t-test. This cluster was characterized by cluster 5 (3.7%) and cluster 6+7+8 (17%). In this case, although no variations statistically significant at 95% level were found for the meteorological conditions, it was observed that the vehicular and the stationary emissions showed significant variations with higher contributions of these factors for the lower number of samples (3.7%) reflecting the impact of these anthropogenic pollution sources.

The contribution of each PMF factor for each one of the eight clusters obtained by the dendrogram was represented in Figure 4. It was also plotted the estimated lifetime lung cancer risk from PAH in the atmosphere. Regarding the factors contributing to this carcinogenic character, it was observed that stationary emissions followed by vehicular emissions contributed majority to the total PAH. Cluster 5 showed the highest lifetime lung cancer risks with an average value of 7.0×10^{-5} (7 additional cases per 100 000 people exposed), which was higher than the target excess individual lifetime risk, which is 10^{-6} (US-EPA, 2012). All these episodes were produced in winter season (02/02/2010, 03/02/2010, 14/01/2011) and were characterized by low temperature (3°C), high relative humidity (85%), low solar radiation (13 W/m²) and low wind speed (1.3 m/s). For the 03/02/2010 there was some rain and for the 14/01/2011, there was foggy weather, scenarios that could favour the pollutant accumulation and the deposition of pollutants to the particulate matter, respectively. The important role of climate has also been remarked by different authors (Cachada et al., 2012; Desaulles et al., 2008), indicating that the lower temperatures and the higher levels of precipitation may enhance wet deposition process and condensation.

These results indicate that the total lifetime cancer risk of PAH in Zaragoza may represent some concern, especially vehicular and stationary emissions, in particular during the cold season favoured

by stagnant meteorological conditions. This impact could be even more negative over the most sensitive population: elderly people and children.

4. CONCLUSIONS

The PMF receptor model successfully allowed the identification and quantification of four sources with similar contribution: coal combustion, vehicular emissions, gasoline emissions and stationary emissions, associated to the total PAH bound to PM₁₀ of Zaragoza.

The CPF showed that the NE direction was one of the prevailing directions providing high total PAH concentrations, especially during the cold season, due to the influence of anthropogenic activities related with industrial parks, highways and a paper fabric located in that direction. Hierarchical cluster analysis showed that samples were classified into two major clusters whose main differences were related to meteorological conditions and factor contributions. Episodes involving higher risk for human health according to the lifetime cancer risk were favoured by typical meteorological conditions of the winter season and higher contributions of the stationary and vehicular emission factors. This corroborated the impact, not only of the anthropogenic pollution sources but also the meteorological conditions, specially those winter days with very low temperature, fog, no wind and high relative humidity that can be more dangerous for human health.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at:

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Table 1. Mean and standard deviations of the PM10 ($\mu\text{g}/\text{m}^3$), individual PAH (ng/m^3), total PAH (ng/m^3), BaP-eq (ng/m^3), meteorological conditions for the whole sampling campaign, the cold and the warm seasons (N= number of samples). The toxic equivalent factors (TEF) provided by Larsen and Larsen are also included.

	Whole period		Cold season		Warm season		TEF (Larsen&Larsen)
	Average	SD	Average	SD	Average	SD	
PM10	34.4	29.0	38.2	37.4	30.6	16.5	
Phe	0.10	0.12	0.15	0.15	0.04	0.04	0.0005
An	0.01	0.01	0.01	0.01	0.01	0.00	0.0005
2+2/4MePhe	0.02	0.02	0.03	0.03	0.01	0.01	
9MePhe	0.03	0.04	0.05	0.06	0.01	0.01	
1MePhe	0.04	0.05	0.06	0.05	0.01	0.01	
DiMePhe	0.04	0.06	0.05	0.04	0.03	0.07	
Flt	0.19	0.21	0.31	0.24	0.08	0.07	0.05
Py	0.20	0.19	0.29	0.21	0.10	0.09	0.001
BaA	0.10	0.13	0.16	0.16	0.03	0.05	0.005
Chry	0.25	0.29	0.40	0.34	0.10	0.10	0.03
BbF	0.15	0.15	0.23	0.17	0.06	0.06	0.1
Bkf	0.05	0.06	0.08	0.06	0.02	0.02	0.05
BjF	0.09	0.10	0.15	0.11	0.03	0.04	0.05
BeP	0.12	0.11	0.18	0.13	0.05	0.04	0.002
BaP	0.09	0.11	0.15	0.12	0.03	0.04	1
IcdP+DahA	0.08	0.11	0.14	0.13	0.02	0.02	0.6
BghiP	0.15	0.18	0.25	0.20	0.06	0.05	0.02
Cor	0.09	0.12	0.15	0.14	0.03	0.03	
Total PAH	1.78	1.86	2.84	2.09	0.72	0.60	
BaP-eq	0.18	0.21	0.29	0.23	0.06	0.06	
Wind direction (°)	216	74	212	82	220	66	
Rainfall (mm)	0.05	0.17	0.04	0.14	0.06	0.19	
Temperature (°C)	13.7	7.9	8.3	5.6	19.1	6.0	
Relative humidity (%)	65	14	71	14	59	10	
Solar radiation (W/m ²)	196	97	129	61	264	77	
Wind speed (m/s)	3.4	2.5	3.4	2.4	3.4	2.7	
N	84		42		42		

TEF IcdP=0.1, TEF DahA=1.1

able 2 Mean concentrations and standard deviations (SD) of the four factors obtained by the PMF model, BaP-eq, PM10, total PAH and meteorological conditions for each cluster obtained by hierarchical cluster analysis (N= number of samples in each cluster).

Coal combustion (ng/m ³)											Vehicular emissions (ng/m ³)									
Cluster	A	B	1	2	3	4	5	6	7	8	A	B	1	2	3	4	5	6	7	8
N	67	17	47	12	4	4	3	4	3	7	67	17	47	12	4	4	3	4	3	7
Mean	0.32	0.65	0.16	0.33	1.20	1.38	1.31	1.32	0.13	0.22	0.32	1.54	0.17	0.68	0.27	1.08	2.50	1.06	1.63	1.37
SD	0.45	0.69	0.16	0.23	0.48	0.86	0.46	0.71	0.19	0.26	0.35	0.61	0.18	0.27	0.21	0.46	0.67	0.47	0.20	0.22
Gasoline emissions (ng/m ³)											Stationary emissions (ng/m ³)									
Cluster	A	B	1	2	3	4	5	6	7	8	A	B	1	2	3	4	5	6	7	8
N	67	17	47	12	4	4	3	4	3	7	67	17	47	12	4	4	3	4	3	7
Mean	0.18	1.02	0.13	0.36	0.30	0.14	0.95	1.80	1.34	0.48	0.16	1.47	0.09	0.37	0.04	0.44	2.70	1.07	1.87	0.99
SD	0.15	0.66	0.08	0.22	0.24	0.03	0.67	0.40	0.30	0.34	0.21	0.76	0.12	0.21	0.10	0.50	0.77	0.27	0.35	0.27
BaP-eq (ng/m ³)											Total PAH (ng/m ³)									
Cluster	A	B	1	2	3	4	5	6	7	8	A	B	1	2	3	4	5	6	7	8
N	67	17	47	12	4	4	3	4	3	7	67	17	47	12	4	4	3	4	3	7
Mean	0.09	0.51	0.05	0.18	0.12	0.29	0.80	0.48	0.64	0.36	1.04	4.69	0.59	1.79	1.88	3.22	7.30	5.14	5.37	3.03
SD	0.09	0.20	0.04	0.05	0.03	0.14	0.19	0.11	0.11	0.10	0.89	1.85	0.34	0.34	0.40	1.56	1.83	1.18	0.61	0.45
PM10 (µg/m ³)											BaP (ng/m ³)									
Cluster	A	B	1	2	3	4	5	6	7	8	A	B	1	2	3	4	5	6	7	8
N	67	17	47	12	4	4	3	4	3	7	67	17	47	12	4	4	3	4	3	7
Mean	34.7	33.1	30.1	36.9	75.3	42.2	46.9	15.5	29.4	38.7	0.05	0.26	0.02	0.09	0.05	0.14	0.45	0.24	0.30	0.18
SD	31.5	16.4	16.8	15.9	114.5	28.6	10.4	13.0	21.6	9.7	0.04	0.11	0.02	0.03	0.01	0.08	0.11	0.06	0.03	0.06
Wind direction (°)											T (°C)									
Cluster	A	B	1	2	3	4	5	6	7	8	A	B	1	2	3	4	5	6	7	8
N	67	17	47	12	4	4	3	4	3	7	67	17	47	12	4	4	3	4	3	7
Mean	231	158	234	198	239	284	107	217	141	154	15.7	5.6	18.1	11.4	10.6	5.4	3.2	3.1	5.8	8.1
SD	69	64	64	83	94	27	34	76	9	62	7.4	3.5	6.6	4.7	9.6	4.2	1.5	0.7	2.3	3.9
Rainfall (mm)											Relative humidity (%)									
Cluster	A	B	1	2	3	4	5	6	7	8	A	B	1	2	3	4	5	6	7	8
N	67	17	47	12	4	4	3	4	3	7	67	17	47	12	4	4	3	4	3	7
Mean	0.06	0.01	0.06	0.04	0.07	0.00	0.01	0.00	0.00	0.01	61	81	60	65	58	68	85	74	81	82
SD	0.19	0.01	0.21	0.08	0.13	0.01	0.01	0.01	0.00	0.02	11	12	10	12	17	4	12	14	5	15
Solar radiation (W/m ²)											Wind Speed (m/s)									
Cluster	A	B	1	2	3	4	5	6	7	8	A	B	1	2	3	4	5	6	7	8
N	67	17	47	12	4	4	3	4	3	7	67	17	47	12	4	4	3	4	3	7
Mean	222	98	247	163	169	150	106	78	100	105	3.8	1.7	3.8	3.2	5.4	5.1	1.3	2.6	1.4	1.5
SD	88	64	84	74	57	50	58	28	3	94	2.6	1.0	2.6	2.3	4.3	1.0	0.2	1.9	0.5	0.5

Figure 1. Location of the sampling point at Zaragoza (Spain). The main highway: A-2 and some roads: Z-30, Z-40 as well as different industrial parks are remarked. I.P.= Industrial parks, WWT= water treatment plant

a)

Cold season

b)

Warm season

c)

d)

Figure 2. PMF receptor model applied to total PAH samples in Zaragoza, a) contribution of sources (ng/m³ and percentage) for the whole sampling campaign, b) for the cold season, c) for the warm season and d) source profiles for the PMF four factors.

The solid bars represent the amount of each species apportioned to the factor and the dots line represent the total of each PAH obtained experimentally.

Coal combustion

Vehicular emissions

Gasoline emissions

Stationary emissions

Figure 3. Time-resolved source contributions (ng/m^3) for the four factors apportioned by the PMF model (right) and the conditional probability function for each factor (left): dot lines in blue colour for the cold season; dot lines in red colour for the warm season.

Figure 4. Plot of the average contribution (ng/m^3) of each factor resolved by the PMF model to the different clusters obtained by the cluster analysis. The dots line represents the average lifetime cancer risk for each cluster and it is represented on the right vertical axes based on a $\text{UR}_{\text{BaP}} = 8.7 \times 10^{-5} \text{ ng}/\text{m}^3$.