

# RECEPTOR MODELING FOR SOURCE APPORTIONMENT OF PARTICLE BOUNDED POLYCYCLIC AROMATIC HYDROCARBONS AT AN URBAN LOCATION IN SPAIN

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## **Abstract:**

Polycyclic Aromatic Hydrocarbons (PAH) are a group of organic pollutants, which are mainly formed from both natural and anthropogenic sources. PAH are an environmental concern because their carcinogenic, mutagenic and immuno-toxic properties and for this reason, EPA (Environmental Protection Agency of United States) has included 16 PAH on its list of priority pollutants.

In this paper, the PAH associated to the airborne particulate matter less or equal than 2.5  $\mu\text{m}$  (PM<sub>2.5</sub>) were studied by using two receptor models based on multivariate statistical tools (UNMIX and PMF) in the city of Zaragoza, Spain. A high volume air sampler with a PM<sub>2.5</sub> cut off was used to collect samples from June 2011-May 2012. PAH on the particle phase were extracted by Soxhlet and 19 PAH were analyzed by gas-chromatography with mass spectrometry mass spectrometry detection (GC-MS-MS). Chrysene, benzo(b)fluoranthene, fluoranthene, pyrene and benzo(e)pyrene represented the 47% of the average total PAH.

Good correlations were obtained between the experimental and the modeled PAH by both models and a comparison of the different quantified factors was carried out. Despite no episodes of benzo(a)pyrene (BaP) equal or higher than 1.0  $\text{ng}/\text{m}^3$  were obtained (Directive 2004/107/EC), the concentration of PM<sub>2.5</sub> exceeded the limit value of 25  $\mu\text{g}/\text{m}^3$  (Directive 2008/50/EC) in several occasions. These episodes were interpreted according to both models in order to check the impact of different anthropogenic sources, especially the traffic emissions factor.

**Key words:** PAH, PM<sub>2.5</sub>, UNMIX, PMF, BaP

## **INTRODUCTION**

Polycyclic aromatic hydrocarbons are organic pollutants only constituted by carbon and hydrogen arranged in two or more fused aromatic rings. PAH originate from both natural and anthropogenic sources and they are formed by incomplete combustion of organic matter (Harvey 1997). They are released to the atmosphere in gas phase and/or associated to the particulate matter so that they can overcome long-range transport affecting not only the site where these pollutants are generated. The concern of PAH is related to their carcinogenic and mutagenic properties (Sanderson, E.G. et al., 2004; Luch, A. 2005; Wang, G. et al., 2007) and they have been listed as priority pollutants by the United States Environmental Protection Agency. In this way, it is priority to discern the sources producing these pollutants.

Receptor models based on statistical approaches are widely used to identify and apportion PAH sources in different environments (air, soil, sediments)(Larsen III, R.K. and J.E. Baker, 2003;Hopke, P.K. et al., 2006; Zuo, Q. et al., 2007; Callén, M.S. et al., 2012). Among these, positive matrix factorization (PMF)(Paatero, P. 1997) and UNMIX (Henry, R.C. 1997) are some of the most used multivariate models. These models provide important knowledge for effective pollution control and abatement. In this work, two receptor models based on positive matrix factorization (PMF) and UNMIX have been used in order to know quantitatively the PAH pollution sources associated to the airborne particle PM<sub>2.5</sub> in Zaragoza.

## **Experimental**

The study was performed in Rio Ebro Campus (length= 41.68, latitude= -0.89), University of Zaragoza as previously described (Callén, M.S. et al., 2008a, 2009). 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 =11420 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).

A MCV high-volume air sampler (30  $\text{m}^3/\text{h}^{-1}$ ), provided with a PM<sub>2.5</sub> cut off inlet at 2.5  $\mu\text{m}$  and located at the top of the roof (approximately 6m from the ground), was used to collect particulate phase PAH over quartz fibre filters QF1-150 (150 mm diameter) provided by MCV, S.A. A total of 61 samples (each sample corresponding to 24 h of continuous sampling, two samples per month and two continuous weeks, from Monday to Saturday, for each season) were collected from June 27<sup>th</sup>, 2011 to May 19<sup>th</sup>, 2012. Briefly, filters were cleaned-up by Soxhlet with dichloromethane (DCM) previous to the sampling. PM<sub>2.5</sub> 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.

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) (Callén, M.S. et al., 2008b). Briefly, 1/2 of the filter was extracted by Soxhlet with dichloromethane after the addition of a surrogate standard solution (An-d<sub>10</sub>+BaP-d<sub>12</sub>+BghiP-d<sub>12</sub>). After concentration by rotary evaporator, samples were cleaned-up through a silica gel cartridge with dichloromethane and concentrated in a pure N<sub>2</sub> 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 were 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<sup>2</sup>>0.99.

#### UNMIX and PMF model

The UNMIX 6.0 and the PMF 3.0 models available at EPA site (<http://www.epa.gov/heasd/products/unmix/unmix.html>; <http://www.epa.gov/heasd/products/pmf/pmf.html>) were used to develop the PAH source profiles.

61 samples with 16 variables were used as input to the UNMIX model. Values equal to one half the analytic detection limits were used in source apportionment modeling for species with concentrations below the detection limit. All monitoring data were included in the model. The fitting species were chosen using the select initial species function and the suggesting more species function. Species having a signal/noise ratio greater than 2 and a minimum R<sup>2</sup> of 0.8 were used to discern the sources. Good edge species obtained by plotting the total PAH versus species concentration were also chosen to find minimum possible solution (Henry, R.C. 2003; Hu, S.H. et al., 2006). Numerous attempts were made in order to resolve the number of sources using various sets of fitting species. Additional species were included to test the stability of the solution and determine if this measure could enhance the number and resolution of sources. Specific variances (SV>0.5) allowed rejecting one variable: MePhe9. The model was set to consider total PAH as the total mass. The optimal solution showed a correlation coefficient (R<sup>2</sup>) of 0.93 with a minimum signal to noise ratio of 3.23, obtaining as “optimal solution” three sources by including 16 species. The uncertainties were calculated by Unmix using a bootstrap procedure re-sampling the data 100 times. A total of three sources were obtained: natural gas (mainly associated with MePhe24, Phe, Flt, Py, Chry), coal combustion (Flt, Py, Phe, An) and vehicular+stationary emissions (BbF, BkF, BeP, BaP, IcdP+DahA, BghiP, Cor) contributing 12%, 13% and 75% to total PAH (see Table 1 for source profiles). A good correlation with R<sup>2</sup>= 0.98 was obtained for the total PAH with a slope=0.96 and the ordinate at the origin=0.24.

For the PMF model, a set of 61 samples and 19 species was used as input of the model. The following species were considered as bad species: MePhe9, MePhe24 and DiMePhe. Phe, An and total PAH were identified as weak species and the 13 remaining species as strong variables. An extra modelling uncertainty of 5% was used to obtain model output. The model was run with different number of factors ranging from 3 to 6 obtaining the optimum solution with 4 factors. The values of Q (Robust) and Q (True) were equal to 591.5 for all the 30 runs and the minimum Q (Robust) estimated in 4<sup>th</sup> run was 0.97 times the Q (Theoretical)(610)=(samples\*good species)+((samples\*weak species)/3)-(samples\*factors estimated)).

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, A.V. et al., 1998). There were no missing data. Sample specific uncertainties were provided according to  $S_{ij} = DL/3 + c * x_{ij}$ , where  $s_{ij}$ = uncertainty, DL =detection limit, c =constant (0.1 if  $x_{ij} > 3 * DL$ , 0.2 if  $x_{ij} < 3 * DL$ ) and  $x_{ij}$ =variable (based on Chueinta, W. et al., 2000). The scaled residuals for all variables were normally distributed and only four data exceeded the model output threshold. The source profiles developed by PMF model are shown in Table 1. The four identified factors contributed to the total PAH with the following percentages: 25%, 24%, 29% and 21% corresponding to coal combustion (Flt, Py, Phe), vehicular emissions (IcdP, BghiP, Cor, BbF, BkF, BjF, BeP), stationary emissions

(BaP, BaA, BkF, BbF) including natural gas, oil combustion and heavy-oil combustion and a fourth factor, which was not well defined (MePhe1, An, Phe)(Liu, Y. et al., 2009) corresponding to volatile PAH. This factor is suggested to be indicative of volatilization or spill of petroleum-related products and it could be believed to be the petrogenic source of PAH.

Table 1. Factor profiles for the PMF and UNMIX models (concentration of species in ng m<sup>-3</sup>)

	PMF model				UNMIX model		
	Coal comb.	Vehicular emissions	Stationary emissions	Volatile PAH	Natural gas	Coal comb.	Vehic+station. emissions
Phe	0.027	0.007	0.002	0.018	0.016	0.012	0.682
An	0.001	0.002	0.002	0.004	-0.001	0.004	-0.071
1 MePhe	0.010	0.001	0.000	0.039			
2+2/4 MePhe					0.026	0.008	1.510
Flt	0.137	0.051	0.000	0.015	0.046	0.041	0.556
Py	0.155	0.032	0.004	0.003	0.043	0.042	0.508
BaA	0.034	0.002	0.083	0.008	0.012	0.015	0.414
Chry	0.058	0.023	0.113	0.037	0.041	0.028	0.744
BbF	0.020	0.085	0.077	0.023	0.012	0.013	0.484
BkF	0.002	0.018	0.031	0.006	0.000	0.005	-0.038
BjF	0.011	0.054	0.044	0.014	0.009	0.009	0.507
BeP	0.015	0.058	0.061	0.023	0.009	0.011	0.387
BaP	0.007	0.021	0.076	0.009	-0.002	0.007	-0.143
IcdP+DahA	0.000	0.037	0.034	0.015	-0.002	0.011	-0.112
BghiP	0.008	0.071	0.063	0.024	0.009	0.020	0.216
Cor	0.011	0.034	0.027	0.009	0.005	0.010	0.280
Total PAH	0.525	0.511	0.616	0.452	0.297	0.258	1.500
%							
Total PAH	25.0	24.3	29.3	21.5	14.5	12.6	73.0

#### Comparative evaluation of PMF and UNMIX models.

Table 2 shows the results obtained for the regression diagnosis for each individual and total PAH by the PMF and the UNMIX models respectively. Good correlations between the modelled and the experimental variables were obtained indicating the adequacy of the model. R<sup>2</sup> close to 1 was obtained for most of the species (the lowest R<sup>2</sup>=0.76 for Phe and the highest R<sup>2</sup>=1.00 for MePhe1) with the maximum error for Phe (-23.6% PMF model) and BaA (12.2% UNMIX model) with slopes close to 1 and intercepts close to zero. In general, PMF underestimated most of the species whereas UNMIX model overestimated them.

Table 2. Regression diagnosis for each individual and total PAH obtained by the PMF and UNMIX models.

	PMF model				UNMIX model			
	Intercept	Slope	R <sup>2</sup>	Error	Intercept	Slope	R <sup>2</sup>	Error
Phe	0.01	0.64	0.76	-23.56	0.96	0.01	0.87	-3.38
An	0.00	0.66	0.77	-11.63	0.95	0	0.87	3.11
1 MePhe	0.00	0.98	1.00	-0.65				
2+2/4 MePhe					1.00	0	0.94	-0.18
Flt	0.01	0.91	0.98	-3.22	1.05	-0.02	0.95	4.78
Py	0.00	0.96	0.98	-2.79	1.04	-0.01	0.93	3.39
BaA	0.01	0.92	0.99	-3.84	1.00	-0.02	0.96	12.18
Chry	0.02	0.89	0.94	-1.58	0.97	-0.02	0.94	11.53
BbF	0.02	0.87	0.96	-3.81	0.99	0	0.99	2.28
BkF	0.00	0.91	0.96	-8.86	1.02	0	0.97	3.36
BjF	0.00	0.96	0.98	-2.72	1.00	0	0.98	-0.22
BeP	0.01	0.92	0.98	-2.29	1.00	0	0.99	-0.50
BaP	0.00	0.95	0.93	-6.71	1.02	-0.01	0.96	6.32
IcdP+DahA	0.00	0.94	0.99	-2.04	0.99	0	0.98	2.60
BghiP	-0.01	1.07	0.99	0.65	0.98	0.01	0.96	-3.20
Cor	0.00	1.02	0.96	-3.76	0.98	0	0.95	-2.71
Total PAH	-0.08	1.02	0.98	-1.52	0.97	0.15	0.98	-3.82

The source profiles obtained from UNMIX model and PMF model were also compared by plotting scatter plots between the profiles. The common factors associated with coal (R<sup>2</sup>=0.78) and vehicular+stationary emissions (R<sup>2</sup>=0.99) showed a good match for both models although the factor associated with volatile PAH and natural gas only presented a low correlation (R<sup>2</sup>=0.28) indicating its different nature. In general and as reported in

several studies (Callén, M.S. et al. 2009), both models provided a feasible solution although the UNMIX model derived less factors compared to PMF model, as reported in several studies. In fact, some of the weaknesses of UNMIX are its difficulty to identify ubiquitous sources, very infrequent sources and relatively small sources (contributing less than about 10% to the total mass). The strength of the PMF in contrast to UNMIX is that PMF uses the uncertainties to weight data, does not require source contributions to occasionally fall to zero and is better able to identify small sources (EPA Technical Report 910-R-03-004). Typically, UNMIX resolves fewer factors than PMF and the nature of the resolved factors is much more dependent on the precise choice of input species than in the case for PMF (Maykut, N.N. et al, 2003)

Although no exceedances of BaP ( $\text{BaP}=1.0 \text{ ng m}^{-3}$ ) were obtained during the sampling campaign according to Directive 2004/107/EC, a study was also performed regarding the samples exceeding the lower ( $12 \text{ } \mu\text{g m}^{-3}$ ), the upper assessment threshold of PM<sub>2.5</sub> ( $17 \text{ } \mu\text{g m}^{-3}$ ) and the limit value of PM<sub>2.5</sub> ( $25 \text{ } \mu\text{g m}^{-3}$ ) for a calendar year according to the Directive 2008/50/EC. 54%, 21% and 5% of the samples, respectively exceeded these values. For the upper assessment threshold, most of these episodes were produced during the warm period (summer and spring) 66% whereas only 3 episodes of exceedances of the limit value of PM<sub>2.5</sub> were obtained and 67% occurred in cold season for the lower assessment threshold. In order to compare these exceedances of PM<sub>2.5</sub> for both models, two of the factors obtained by the PMF model were added in order to compare with the UNMIX model. The vehicular+stationary emissions factor showed a higher contribution for all these episodes. A remarkable decrease in the coal combustion and volatile factor (natural gas for the PMF model) was obtained during the PM<sub>2.5</sub> exceedances by increasing the vehic+station factor.

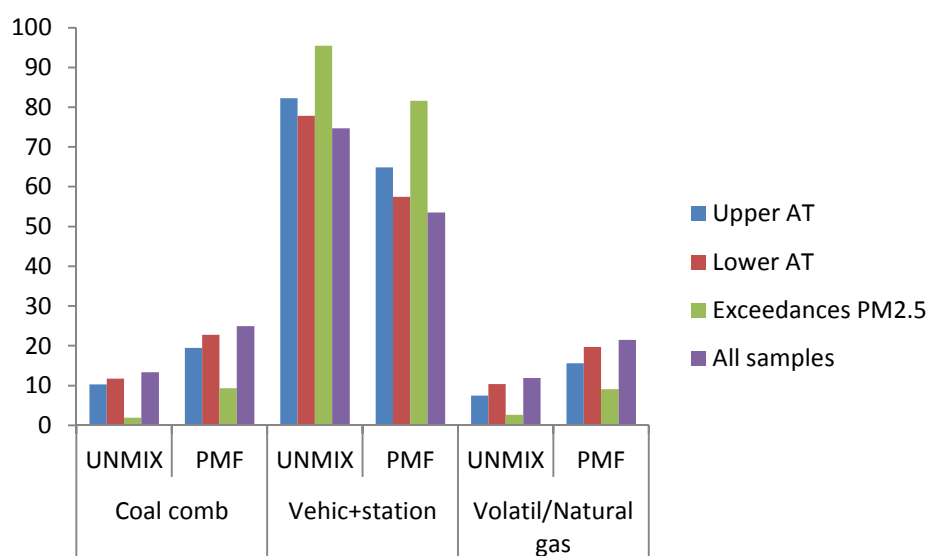


Figure 1. Comparison of factors apportioned (%) by the UNMIX and PMF models for the average all samples, exceedances of the PM<sub>2.5</sub>, lower and upper assessment threshold of PM<sub>2.5</sub> (AT= assessment threshold).

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