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Influence of organic and inorganic markers in the source apportionment of airborne PM₁₀ in Zaragoza (Spain) by two receptor models.

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Abstract

Improving knowledge on the apportionment of airborne particulate matter will be useful to handle and fulfill the legislation regarding this pollutant. The main aim of this work was to assess the influence of markers in the source apportionment of airborne PM₁₀, in particular, whether the use of particle PAH and ions provided similar results to the ones obtained by using not only the mentioned markers but also gas phase PAH and trace elements. In order to reach this aim, two receptor models: UNMIX and positive matrix factorization were applied to two sets of data in Zaragoza city from airborne PM₁₀: a previously reported campaign: 2003-2004 (Callén et al., 2009), where polycyclic aromatic hydrocarbons (PAH) associated to the gas and particle phases, ions and trace elements were used as markers and a long sampling campaign: 2001-2009, where only PAH in the particle phase and ions were analyzed.

For both campaigns, PMF was able to explain a higher number of sources than the UNMIX model. Independently of the sampling campaign and the receptor model used, soil resuspension was the main PM₁₀ source, especially in the warm period (21st March-21st September), where most of the PM₁₀ exceedances were produced. Despite some of the markers of anthropogenic sources were different for both campaigns, common sources associated to different combustion sources (coal, light-oil, heavier-oil, biomass, traffic) were found and PAH in particle phase and ions seemed to be good markers for the airborne PM₁₀ apportionment.

Keywords: PM₁₀; PAH; ions; receptor model; UNMIX; PMF; air pollution; source apportionment

Introduction

Air monitoring is a complex task involving not only direct measurement but also quality assurance to confirm the adequacy of the methods used to quantify air pollutants. These measurements can be transformed into important tools to preserve and to improve air quality by upgrading the current legislation regarding air pollutants. Meteorological factors are also important in order to interpret air

monitoring results because they primarily help to quantify atmospheric characteristics, like pollutant transport and diffusion. The main concern of preserving air quality is related to health and environmental problems, being particulate matter one of these pollutants with proven negative impact on human health (Samoli et al. 2005). At European level, Directive 2008/50/EC on ambient air quality and cleaner air for Europe requires Member States to limit the exposure of citizens to the airborne particles known as PM₁₀. The legislation sets limit values for exposure, which had to be met by 2005 covering both an annual concentration value (40 µg/m³), and a daily concentration value (50 µg/m³) that must not be exceeded more than 35 times in any calendar year. Despite the commitment of the European countries to comply with EU air quality limit values for airborne particles PM₁₀, some Member States located at the Mediterranean Sea like Italy, Spain, Portugal, Cyprus have so far failed to effectively tackle excess PM₁₀ emissions due to important contribution of North-African intrusions, which increase remarkably the PM₁₀ natural concentrations. Therefore, it is necessary a deep characterization of the main PM₁₀ pollution sources to handle these exceedances.

With this aim, receptor models based on multivariate statistical methods are widely applied to identify and to quantify air pollutants at a receptor location. Two of the models developed by the United States Environmental Protection Agency (U.S.EPA) are the UNMIX (Henry 2000; Henry 2003) and the Positive Matrix Factorization (PMF) (Paatero and Tapper 1994; Paatero 1997) methods for use in air quality management. These receptor models have been widely used to apportion particulate matter sources by characterizing the inorganic component of the particulate matter (Ramadan et al. 2000; Qin et al. 2002; Song et al. 2006; Viana et al. 2008; Oanh et al. 2009; Vedal et al. 2009; Mooibroek et al. 2011; Sahu et al. 2011; Yubero et al. 2011; Pant and Harrison, 2012) although their application to organic compounds like polycyclic aromatic hydrocarbons is more limited and recent (Lee et al. 2004; Park and Kim 2005; Shrivastava et al. 2007; Callén et al. 2009; Dutton et al. 2010; Okuda et al. 2010; Wingfors et al., 2011) due to the more complex nature of PAH and the low concentrations at which these pollutants are found in the atmosphere (EU, 2001; Ravindra et al., 2008) in comparison to other classical pollutants like SO₂, NO₂.

In this paper, the airborne PM₁₀ of an urban area located in a Mediterranean country (Zaragoza, Spain) was apportioned by two receptor models (UNMIX and PMF). This work was focused to provide a better understanding of the sources affecting the PM₁₀ and to assess the influence of organic and inorganic markers on the PM₁₀ apportionment by comparing two sampling campaigns: a) The 2001-2009 campaign

in which the PM₁₀ was characterized regarding polycyclic aromatic hydrocarbons (PAH) contained in the particle phase and water-soluble ions. b) The 2003-2004 campaign in which the PM₁₀ composition was apportioned concerning PAH in gas+particle phases, trace elements and water soluble ions as mentioned in a previous article (Callén et al. 2009).

Experimental

Study area and sampling description

The study was performed in Rio Ebro Campus located in a medium-size city, Zaragoza in the North-East of Spain (41°39'49.38"N; 0°53'16.68"W). The sampling site is close to a heavy traffic motorway (approximately 50 m), several industrial parks, four paper factories and two waste water treatment plants located (Callén et al. 2008a) in the surroundings of the city (Figure 1). In addition to these local pollution sources, domestic heating systems, agricultural burning, wood combustion and the influence of thermal power stations could also contribute to PAH emissions.

Regarding the climate, Zaragoza is located in a wide basin surrounded by mountains and affected by a typical cold and dry wind called Cierzo blowing from the NW. Zaragoza is often characterized by a "continental" climate with warm, dry summers reaching up to 40°C and cold winters (usually 0 to 10°C) showing high thermal contrasts. The rainfall is scarce and centres in spring.

Samples were collected by using a Graseby Andersen high-volume air sampler (1.13 m³/min) provided with a PM₁₀ cut off inlet to collect particulate phase on a Teflon-coated, fibre-glass filter (0.6 µm pore size; 20.5 cm × 25.5 cm) (Callén et al. 2008a, 2008b). Samples of 24 hours were collected during four sampling periods: every two weeks from July 12, 2001 to July 26, 2002, every week from April 7, 2003 to July 5, 2004, during consecutive days from May 23 to June 6, 2008 and from January 13 to 27, 2009 collecting a total of 112 samples covering the seasonal variations over several years. The meteorological conditions were provided by the AULA-DEI (CSIC). The PM₁₀ was determined by gravimetric method after conditioning the filter according to EN12341:1998. More details regarding the sampling site and procedure were given in previous articles (López et al. 2005; Callén et al. 2008b).

Analyses of water soluble ions

Sample extraction

One-eighth of the filter was cut in small pieces and extracted by ultrasonic bath for 30 minutes in 15 mL of Milli-Q water. The extract was filtered through a cellulose acetate membrane filter (0.22 µm pore size

and 30 mm filter diameter) and rinsed up to a final volume of 15 ml for further ion analysis (Callén et al. 2012).

Analytical technique

Analyses of anions (Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-}) and cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) were carried out by a Dionex ICS2000 ion chromatography system and a conductivity detector with Chromeleon version 6.60SP2 software (Callén et al. 2009). The anion and cation methods used the AS17 analytical column (2 mm x 250 mm) and the CS17 analytical column (3 mm x 250 mm), respectively. An eluent suppressor working at 19 mA (anions) and 62 mA (cations) was placed before the detector in order to prevent saturation by the background signal. The sulphate concentration of marine origin, mSO_4^{2-} was determined indirectly by considering the Na^+ soluble concentration according to the ratio: $\text{mSO}_4^{2-}/\text{Na}^+ = 0.25$ in weight (Duce et al. 1983). The non-sea-salt-sulphate, nmSO_4^{2-} , generally of anthropogenic origin, was obtained by subtracting the mSO_4^{2-} concentration from the total SO_4^{2-} concentration value. The ions quantification was carried out by using standards mixtures from respective ions at different concentrations.

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[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenzo[a,h]anthracene (DahA), benzo[ghi]perylene (BghiP) and coronene (Cor) were quantified by gas chromatography mass-spectrometry mass-spectrometry detection (GC-MS-MS) according to a previous publication (Callén et al. 2008b). Briefly, samples were extracted by Soxhlet for 24 hours with dichloromethane (DCM) after the addition of a surrogate deuterated solution (An-d₁₀, BaP-d₁₂, BghiP-d₁₂) to account for any losses of analytes during sample treatment. Samples were eluted through a silica gel column with DCM to finally exchange the solvent to hexane. P-terphenyl native was added as internal standard previous to GC-MS-MS quantification as it is absent in air samples and shows a physical and chemical behavior similar to PAH in pretreatment and chromatographic separation. For quantitative determinations a set of standard mixtures of PAH were spiked with the same surrogate deuterated solution used for samples and average response factors were calculated for all analytes with respect to the closest deuterated standard eluted in the chromatogram.

Quality control and quality assurance

Field blank determinations were used for background correction on the sampled filters and the detection and quantification limits were determined according to three and ten times the blank standard deviation (ions: the lowest detection limit for SO_4^{2-} : 0.074 mg L^{-1} , the highest detection limit for Na^+ : 0.530 mg L^{-1} ; PAH: the lowest detection limit for BaA and Chry: 6 pg m^{-3} the highest detection limit for Phe: 110 pg m^{-3}). Analyses of standard reference materials, SRM1944 and SRM1649a provided by the National Institute of Standards and Technology (NIST), were carried out in order to check the analytical accuracy and precision of ions and PAH quantification. Measured values were satisfactorily comparable to certified values with deviations lower than 20% for PAH (with the exception of Chry, probably due to the interference of triphenylene (40%)) and lower than 16% for ions.

Models

Table 1 shows a summary of the mean concentrations of the different chemical species analysed, the standard deviation, and the minimum and maximum concentrations along the sampling as well as the meteorological conditions used as input data for the two models. Each model has its advantages and disadvantages but basically, both models are based on the mass balance principles although they use two different mathematical approaches to provide a solution. UNMIX determines the edges in the dataset, whose number and direction depend on the number of species chosen for the model. UNMIX incorporates the algorithm "NUMFACT" that estimates the number of factors in the data using principal component analysis on randomly sampled subsets of the original data (Henry, 2003). PMF derives a solution that minimizes an object function, Q, which is determined based on the uncertainties associated with individual measured data subject to non-negative constraints (Polissar et al., 2001), frequently resulting in a more physically interpretable result. These features make that PMF model has been widely used for source apportionment of airborne particulate matter and total PAH in the last years (Moon et al., 2008; Viana et al., 2008; Callén et al., 2009; Okuda et al., 2010; Ma et al., 2010; Sofowote et al., 2011; Vestenius et al., 2011; Wingfors et al., 2011).

In this work, the same version of the models (UNMIX 6.0 and PMF 1.1 available at United States Environmental Protection Agency (US-EPA) and the same considerations than in the previously reported article (Callén et al. 2009) were taken into account in order to compare results.

Input data for the UNMIX model:

In 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^2 of 0.8 were used to discern the sources. Good edge species obtained by plotting the PM10 mass versus species concentration were also chosen to find minimum possible solution (Henry, 2003; Hu 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 three variables: Cl^- , Na^+ and Phe. In general, model inputs of four and five sources were obtained. Models identifying five sources were discarded due to negative factors obtaining as “optimal solution” four sources by including 17 species (PM10, $nmSO_4^{2-}$, K^+ , Ca^{2+} , 2+2/4MePhe, 9MePhe, 1MePhe, DiMePhe, Flt, Py, Chry, BbjkF, BeP, BaP, IcdP+DahA, BghiP, Cor) with the highest correlation between predicted and measured concentrations of PM10. The model was set to consider PM10 as the total mass. The optimal solution showed a correlation coefficient (R^2) of 0.87 with a minimum signal to noise ratio of 3.94, fulfilling the requirements of the model. The uncertainties were calculated by Unmix using a bootstrap procedure re-sampling the data 100 times.

Input data for the PMF model

The PMF model used additionally the uncertainties matrix which was calculated by considering the detection limit for each variable and the error after comparing results with certified values from SRM. The PMF was run in robust mode and different runs were performed in order to obtain the optimal solution by modifying the species category: strong, weak according to signal/noise ratios and the factors chosen (3 and 10 factors). The election of variables and the optimal number of factors was conditioned by the signal to noise ratio (S/N), the convergence of results between the Q robust and Q true, the distribution of residuals for individual compounds and the scatterplots of predicted mass versus the actual mass. An optimal solution with 8 factors was obtained by including a weak (Phe) and 22 strong variables (PM10, Cl^- , NO_3^- , $nmSO_4^{2-}$, Na^+ , K^+ , Ca^{2+} , 2+2/4MePhe, 9MePhe, 1MePhe, DiMePhe, An, Flt, Py, BaA, Chry, BbjkF, BeP, BaP, IcdP+DahA, BghiP, Cor). All samples were included in the model and 7% of the extra modelling uncertainty was considered. The theoretical Q value was 1392, the robust Q was 1481.34 and the true Q was 1486.50. The PMF was run with 8 factors, 50 random starting points and with random

seed equal to rand as well as with different random seed values. Across the 6 runs with different initial seeds the Q value had a coefficient of variation (CV) less than 0.0005% for the eight-factor solution with minimum variations in the factor profiles suggesting a stable solution. The statistical uncertainties in the modelled solution were estimated by a bootstrapping technique running a total of 200 bootstrap, with a minimum R-value for base-boot factor mapping of 0.6, finding that all runs converged. Residuals were also checked to be between -3 and 3 for all species for at least 84% of the observations.

Conditional probability function.

More information regarding the source contribution from a given wind direction was obtained by the conditional probability function (CPF) (Kim and Hopke 2004).

$$CPF_{\Delta\theta} = \frac{m_{\Delta\theta}}{n_{\Delta\theta}} \quad (1)$$

The CPF is defined with the above equation where $m_{\Delta\theta}$ is the number of occurrence from wind sector $\Delta\theta$ that exceeded the threshold criterion (75th percentile), and $n_{\Delta\theta}$ is the total number of data from the same wind sector. In this study, 12 sectors were used ($\Delta\theta=30^\circ$).

Results and discussion

Comparison between UNMIX and PMF models for the 2001-2009 sampling

UNMIX identified four sources: heavier-oil combustion traced by IcdP+DahA, BghiP and Cor (representing 6.2% (2.05 $\mu\text{g}/\text{m}^3$) of the experimental PM10) (Lee et al. 2004), coal combustion traced by 2+2/4MePhe, 1MePhe, DiMePhe, Flt, Py, Chry (13.1%; 4.3 $\mu\text{g}/\text{m}^3$), industrial emissions related to light-oil combustion traced by BbjkF, Chry, BeP and BaP (2.5%; 0.83 $\mu\text{g}/\text{m}^3$) (Bari et al. 2009) and soil resuspension traced by nmSO_4^{2-} and Ca^{2+} (63.5%; 20.9 $\mu\text{g}/\text{m}^3$).

PMF allowed distinguishing eight factors: marine factor (Na^+ and Cl^-) (6.9%; 2.2 $\mu\text{g}/\text{m}^3$), heavier-oil combustion (0.4%; 0.12 $\mu\text{g}/\text{m}^3$), light-oil combustion (5.4%; 1.77 $\mu\text{g}/\text{m}^3$), coal combustion (0.8%; 0.25 $\mu\text{g}/\text{m}^3$), soil resuspension (57.0%; 18.5 $\mu\text{g}/\text{m}^3$), traffic emissions (BbjkF, IcdP+DahA, Phe, 9MePhe) (Bari et al. 2009) (18.5%; 6.1 $\mu\text{g}/\text{m}^3$), biomass combustion (NO_3^- , K^+ and nmSO_4^{2-}) (Jeong et al. 2008) (3.2%; 1.07 $\mu\text{g}/\text{m}^3$) and natural gas combustion (BaA, Chry, IcdP+DahA) (Bourotte et al. 2005; Khalili et al. 1995) (2.9%; 0.94 $\mu\text{g}/\text{m}^3$).

Four common sources were identified by the two models: resuspension, light-oil combustion, coal combustion and heavier-oil combustion. For both models, the soil resuspension factor was the main source contributing to the PM10 followed by the coal combustion factor in the UNMIX model and by the

traffic emissions factor in the PMF model. Figure 2 shows the percentage of species apportioned to each PM10 source identified by the UNMIX and the PMF models.

Both models provided good results to reproduce experimental PM10 concentrations (Figure 1S, Supplementary Information) with similar slopes and the highest correlation coefficient for the PMF model (UNMIX ($R^2=0.85$, slope=1.00, intercept=4798 ng/m³), PMF ($R^2=0.93$, slope=1.00, intercept=1622 ng/m³). Both models underestimated the PM10 but PMF was able to explain 94% of the experimental PM10 (31.05 $\mu\text{g m}^{-3}$) whereas UNMIX explained the 85% (28.06 $\mu\text{g m}^{-3}$) (Table 1S, Supplementary Information). The correlation coefficients for the different species were quite good for both models, although the PMF showed two exceptions: Phe ($R^2=0.32$), which was considered as a weak variable and Na⁺ ($R^2=0.36$).

The temporal contribution of each source and the conditional probability function (CPF) according to the season: cold (winter and autumn) and warm (summer and spring) are showed in Figure 3 for both receptor models. The soil resuspension factor presented higher concentrations during the warm season with a seasonal trend statistically significant at 99% level with the PMF model indicating a typical profile of Mediterranean countries, which are affected by a combination of local soil and episodes of North-African intrusions favoured by arid weather, high temperature, scarce rain and stable atmospheric pressure. These results corroborated results previously reported by other authors (Bogo et al. 2003; Artiñano et al. 2009), suggesting that the higher values of particulate matter found in summer with respect to winter are in agreement with the abundance of resuspended material during the warm season due to the effect of meteorological conditions. In fact, a positive correlation coefficient was found between the soil resuspension factor obtained by the PMF model and the average temperature for each sampling date ($R^2=0.62$). The CPF indicated that the soil resuspension factor was highly affected by the SW winds, indicating more atmospheric transport from that direction (Figure 3). By considering the markers used to identify this source, Ca is a marker for cement dust (Kim et al. 2004) and the SW direction was mainly influenced by quarries and an important cement plant. Moreover, different mountains of limestone and dolomite are located along the SW and SE directions. Therefore, construction activities, unpaved road, soil resuspension produced by traffic and long-range transport from African dust during the warm season could favour this factor. In addition, the ageing of anthropogenic SO₂ emissions from combustion processes, enhanced by atmospheric photochemical activity, also could contribute to this factor showing a double origin: natural and anthropogenic. A total of five dates, three of them produced during summer

season and corresponding to PM10 exceedances associated with North-African intrusions and regional episodes, were remarked on Figure 3.

The other three common factors obtained by both models and the other four additional factors identified by the PMF model, presented higher concentrations during the cold season with a seasonal behaviour statistically significant at 99% level favoured by meteorological conditions such as low ambient temperature, low mixing layer and low photochemical degradation and also favoured by the consume of fossil fuels used for domestic heating. This was reflected in most of the highlighted dates of Figure 3 coinciding with high PAH concentrations and indicating the most negative impact of anthropogenic pollution sources during the cold season. These factors showed the NE and N directions as prevailing directions (Figure 3). Whereas in the case of the marine factor, its origin was mostly natural due to the influence of the Mediterranean and Cantabrian Seas and to different salt mines located in Monzón (NE), Huesca province (N) and Remolinos (NW), in the case of the other factors, the influence of anthropogenic sources was reflected with special relevance of the paper industry emissions, the industrial parks, the highway, the roads, the airport and the different power stations located in the N, S and SE directions, one of them with 1050 MW placed in Teruel and using coal as fuel. In the case of the natural gas factor, its contribution was due not only to industrial emissions but also to domestic heating systems because natural gas is the main fuel used for this purpose in Zaragoza.

Comparison of receptor models between 2001-2009 and 2003-2004 sampling campaigns

Before the comparison, a brief summary was reported in order to remind the reader on the PM10 apportionment for the 2003-2004 campaign (Callén et al. 2009): 1) The UNMIX model discerned a total of five sources: industry+traffic (traced by Cu, Cr, Pb, Mn, Fe and Zn; 9%), evaporative emissions (1MePhe, DiMePhe, 2+2/4MePhe, 9MePhe; <1%), heavy-duty vehicles (IcdP+DahA, BghiP, Cor; 15%) named as heavier-oil combustion in this paper, marine (Na^+ , Mg^{2+} , Cl; 10%) and crustal 1 (Ca^{2+} , nmSO_4^{2-} , Mg^{2+} ; 65%) named as soil resuspension in this paper. 2) A total of eight sources were distinguished by the PMF model: traffic (Ba), industry+traffic (2%), heavy-duty vehicles (7%), biomass combustion (NO_3^- , NH_4^+ , K^+ ; 6%), evaporative emissions (18%), fossil fuel combustion (6%), marine (7%), crustal 1 (39%) and crustal 2 (Sr and Al; 1%).

It is worthy explaining that the main differences between the two campaigns were: 1) a higher number of samples was considered in this work (2001-2009 campaign)(n=112 samples) versus the previously reported (2003-2004 campaign)(n=50 samples). 2) PAH and ions in the particle phase were analysed in

this sampling campaign whereas in the previous one, PAH in both (gas and particle) phases were considered as well as ions and trace elements in particle phase. By considering a different number of samples and different markers could affect not only the source contributions due to the weight of the different pollution sources for both sets of data but also the identification of individual or blending of sources. Therefore, rather than the comparability in the contribution of the pollution sources, this section was focused on the similarity of identified sources by using organic and inorganic markers.

For both models and campaigns, partial natural sources related to soil resuspension were the main factor contributing to the PM₁₀ (Table 2). It is worth saying that the PMF model showed a slight advantage for the 2003-2004 campaign so that the introduction of trace metals allowed distinguishing two crustal sources: one associated with soil resuspension and African intrusions and the other one related to clay minerals, which are very frequent in Aragón. Good correlations were obtained for the soil resuspension factor among the different models and set of samples, with the highest correlation between the UNMIX 2001-2009 and the 2001-2009 PMF models ($R^2=0.93$) (Figure 2Se), Supplementary information). Concerning the other natural source: the marine component, similar mean concentrations were obtained by the different models and sets of data, and the best correlation ($R^2=0.90$) (Figure 2Sh), Supplementary information) was obtained between the 2001-2009 PMF and the 2003-2004 UNMIX models.

Regarding the anthropogenic sources for both sets of samples, the heavier-oil combustion factor, called as heavy-duty vehicles in the 2003-2004 campaign was the anthropogenic pollution source showing the highest correlation between the two sampling campaigns for the UNMIX model ($R^2=0.92$) and between the two models for the 2001-2009 campaign ($R^2=0.96$) (Figure 2Sj) 2Sk), Supplementary information). This factor associated with the higher molecular weight PAH, IcdP+DahA, BghiP and Cor and mainly collected in the particle phase seemed not to be affected neither by the receptor model nor by the sampling campaign.

One of the advantages of collecting PAH in the gas and the particle phases was that, an additional anthropogenic pollution source was estimated for the 2003-2004 campaign. This source was the evaporative emissions associated with Phe and \sum MePhe and mainly captured in the gas phase. In the 2001-2009 campaign, this source could be partially included in the coal combustion factor where the contribution of different MePhe was considerable. However and because PAH in the gas phase were not collected, the contribution of this factor was not representative for the 2001-2009 campaign. Therefore, a possible limitation of sampling PAH, only in the particle phase, is that it could lead to PAH

underestimation, especially the most volatile PAH, not being discerned the evaporative emissions as an individual source for the 2001-2009 campaign due to the lower impact of this source and/or blending of pollution sources.

One of the most important differences between the two sampling sets was related to the industry+traffic and the fossil fuel factors. The industry+traffic source was associated with trace metals for the 2003-2004 campaign whereas for the 2001-2009, both models identified a light-oil combustion factor mainly associated with specific PAH. The lowest correlations obtained among these factors for the different campaigns confirmed the non-comparability of sources due to the use of different markers and not including gas phase PAH in the 2001-2009 campaign. Nevertheless, a good agreement was obtained by regressing the different models for the same campaigns (Figure 2Sq, Supplementary information)($R^2=0.91$). With regard to the fossil fuel combustion factor and by checking the different chemical compounds involved on this source, it seemed to be that the natural gas source was included in this factor in the 2003-2004 PMF model, whereas in the 2001-2009 PMF model, the coal combustion factor and the natural gas were considered separately. Nevertheless, a very low correlation was found when the coal+gas natural source was plotted against the fossil fuel combustion factor for the different campaigns indicating consequent differences and non-comparability between the chemical profiles for these sources. This lack of comparability could be attributed to the different number of samples considered for both campaigns, which could have different impact on the source contribution. The main advantage of the PMF model for the 2001-2009 campaign was the remarkable influence of traffic in the sampling point reflected by the traffic emissions factor (organic markers), whereas in the 2003-2004 campaign, the model could discern two components related to traffic: tyre and industry+traffic favoured by the introduction in the model of inorganic tracers, which allowed a higher specificity in the source apportionment. In any case, the PMF model allowed discerning a higher number of anthropogenic pollution sources than the UNMIX model independently of the campaign so that this last model could be used as a first estimation of pollution sources in the PM10 apportionment. This higher capacity of resolving sources for the PMF model could be also explained by how the PMF and UNMIX analyses were conducted because most of the chemical constituents were included for the PMF model while some of them were excluded in the UNMIX modelling.

Finally, an inter-comparison was also performed between the different models and campaigns with regard to the total PM10 modelled (Figure 3S, Supplementary information). It was observed that good

correlations ($R^2=0.82-0.85$) were obtained, confirming a satisfactory characterization of the sources affecting to the PM₁₀ of Zaragoza despite the use of different markers.

Conclusions

The particulate matter of Zaragoza city was apportioned by two multivariate receptor models: UNMIX and PMF during two sampling periods (2001-2009 and 2003-2004, previously reported) in order to improve knowledge regarding receptor models and to compare the influence of organic and inorganic markers on the PM₁₀ pollution sources.

The similarities between both sampling campaigns were: 1) both models were able to identify the main pollution sources contributing to the PM₁₀ in accordance to the sampling location. 2) Partial natural sources associated with soil resuspension contributed majority to the PM₁₀ with high concentrations during the warm season independently of the model and campaign. 3) The PMF model proved to be more specific in the source identification discerning a higher number of identified sources than the UNMIX model. 4) Despite different organic and inorganic markers were used for both campaigns, similar anthropogenic pollution sources related to combustion were identified including coal, industry, traffic.

The main differences between both campaigns were: 1) evaporative emissions were not identified during the 2001-2009 campaign due to only PAH in the particle phase were collected. This was a possible limitation of sampling PAH only in the particle phase. 2) The use of trace metals as markers allowed distinguishing another crustal component not identified during the 2001-2009 campaign. 3) The industry and traffic factors were associated to inorganic markers in the 2003-2004 campaign and the PMF model discerned an additional component related to traffic (brake abrasion factor) whereas in the 2001-2009 sampling, the main markers for sources related to light-oil combustion and traffic emissions were organic markers, in particular PAH. However, it was confirmed that PAH in the particle phase and ions were good organic and inorganic markers, respectively to apportion most of the anthropogenic pollution sources in the airborne PM₁₀ of Zaragoza.

Concerning the two models, UNMIX and PMF, the UNMIX model could be used as a first approximation to identify the main pollution sources of the PM₁₀ whereas the PMF model seemed to be more adequate, specific and successful in order to discern a higher number of sources in the apportionment of airborne PM₁₀ in Zaragoza city. It was probably due to one of the strengths of this model, which weights species concentrations by their analytical precisions, corroborating the better adequacy of the PMF model versus the UNMIX model, as reported previously in the short campaign. The differences in how the PMF and

UNMIX analyses were conducted could also explain the different number of sources identified by each model because the number of chemical constituents introduced by the PMF was higher than the ones introduced by the UNMIX modelling.

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Appendix A. Supplementary data

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

References

- Artiñano B, Salvador P, Pujadas M (2009) Study of atmospheric pollution by particulated matter in Madrid (I): source apportionment. *Física de la Tierra* 21:41-49.
- Bari MA, Baumbach G, Kuch B, Scheffknecht G (2009) Wood smoke as a source of particle-phase organic compounds in residential areas. *Atmos Environ* 43:4722–4732.
- Bogo H, Otero M, Castro P, Ozafrán M J, Kreiner A, Calvo EJ, Martín Negri R (2003) Study of atmospheric particulate matter in Buenos Aires city. *Atmos Environ* 37:1135-1147.
- Bourotte C, Forti MC, Taniguchi S, Bicego MC, Lotufo PA (2005) A wintertime study of PAHs in fine and coarse aerosols in Sao Paulo city, Brazil. *Atmos Environ* 39:3799–3811.
- Callén MS, de la Cruz MT, López JM, Navarro MV, Mastral AM (2009) Comparison of receptor models for source apportionment of the PM10 in Zaragoza (Spain). *Chemosphere* 76:1120-1129.
- Callén MS, de la Cruz M T, López JM, Murillo R, Navarro MV, Mastral AM (2008a) Long-range atmospheric transport and local pollution sources on PAH concentrations in a South European urban area. Fulfilling of the European Directive. *Water Air Soil Poll* 190:1-4.
- Callén MS, de la Cruz MT, López JM, Murillo R, Navarro MV, Mastral AM (2008b) Some inferences on the mechanism of atmospheric gas/particle partitioning of polycyclic aromatic hydrocarbons (PAH) at Zaragoza (Spain). *Chemosphere* 73:1357-1365.
- Directive 2008/50/EC of the European parliament and of the council of 21 May 2008 on ambient air quality and cleaner air for Europe.
- Duce RA, Arimoto BJ, Ray BJ, Unni CK, Harder PJ (1983) Atmospheric trace elements at Enewetak Atoll: 1, Concentrations, sources and temporal variability. *J Geophys Res* 88:5321-5342.
- Dutton SJ, Vedal S, Piedrahita R, Milford JB, Miller SL, Hannigan MP (2010) Source apportionment using positive matrix factorization on daily measurements of inorganic and organic speciated PM2.5. *Atmos Environ* 44:2731-2741.
- EN 12341 (1998) Air quality - Determination of the PM 10 fraction of suspended particulate matter- Reference method and field test procedure to demonstrate reference equivalence of measurement methods.
- European Union, 2001. Ambient air pollution by polycyclic aromatic hydrocarbons (PAH). Position Paper. Office for Official Publications of the European Communities. L-2985 Luxembourg. ISBN 92-894-2057-X.
- Henry RC (2000) UNMIX Version 2 Manual, p. 18–19.
- Henry RC (2003) Multivariate receptor modeling by N-dimensional edge detection. *Chemom Intell Lab Syst* 65:179–89.
- Hu SH, McDonald R, Martuzevicius D, Biswas P, Grinshpun SA, Kelley A, Reponen T, Lockey J, LeMasters G, (2006) UNMIX modeling of ambient PM2.5 near an interstate highway in Cincinnati, OH, USA. *Atmos Environ* 40:S378–395.
- Jeong CH, Evans GJ, Dann T, Graham M, Herod D, Zlotorzynska ED, Mathieu D, Ding L, Wang D (2008) Influence of biomass burning on wintertime fine particulate matter: source contribution at a valley site in rural British Columbia. *Atmos Environ* 42:3684-3699.

- Khalili NR, Scheff PA, Holsen TM (1995) PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels and wood combustion emissions. *Atmos Environ* 29(4):533-542.
- Kim E, Hopke P K (2004) Comparison between conditional probability function and nonparametric regression for fine particle source directions. *Atmos Environ* 38:4667-4673.
- Kim E, Hopke PK, Edgeron ES (2004) Improving source identification of Atlanta aerosol using temperature resolve carbon fractions in positive matrix factorization. *Atmos Environ* 38:3349-3362.
- Lee JH, Gigliotti CL, Offenbergh JH, Eisenreich SJ, Turpin BJ (2004) Sources of polycyclic aromatic hydrocarbons to the Hudson River airshed. *Atmos Environ* 38: 5971-5981.
- López JM, Callén MS, Murillo R, Garcia T, Navarro MV, de la Cruz MT, Mastral AM (2005) Levels of selected metals in ambient air PM10 in an urban site of Zaragoza (Spain). *Environ Res* 99:58-67.
- Ma W-L, Li Y-F, Qi H, Sun D-Z, Liu L-Y, Wang D-G (2010) Seasonal variation of sources of polycyclic aromatic hydrocarbons (PAHs) to a northeastern urban city, China. *Chemosphere* 79:441-447.
- Mooibroek D, Schaap M, Weijers EP, Hoogerbrugge R (2011) Source apportionment and spatial variability of PM2.5 using measurements at five sites in the Netherlands. *Atmos Environ* 45(25):4180-4191.
- Moon KJ, Han JS, Ghim YS, Kim YJ (2008) Source apportionment of fine carbonaceous particles by positive matrix factorization at Gosan background site in East Asia. *Environ Internat* 34:654-664.
- Oanh NTK, Pongkiatkul P, Upadhyay N, Hopke PP (2009) Designing ambient particulate matter monitoring program for source apportionment study by receptor modelling. *Atmos Environ* 43:3334-3344.
- Okuda T, Okamoto K, Tanaka S, Shen Z, Han Y, Huo Z (2010) Measurement and source identification of polycyclic aromatic hydrocarbons (PAHs) in the aerosol in Xi'an, China by using automated column chromatography and applying positive matrix factorization (PMF). *Sci Total Environ* 408:1909-1914.
- Paatero P, Tapper U (1994) Positive Matrix Factorization: a non-negative factor model with optimal utilization of error estimates of data values. *Environmetrics* 111-126.
- Paatero P (1997) Least squares formulation of robust non-negative factor analysis. *Chemom Intell Lab Syst* 37:23-35.
- Pant P, Harrison RM (2012) Critical review of receptor modelling for particulate matter: A case study of India. *Atmos Environ* 49:1-12.
- Park SS, Kim YJ (2005) Source contributions to fine particulate matter in an urban atmosphere. *Chemosphere* 59:217-226.
- Polissar AV, Hopke PK, Poirot RL (2001) Atmospheric aerosol over Vermont: chemical composition and sources. *Environ Sci Technol* 35:4604-4621.
- Qin Y, Oduyemi K, Chan LY (2002) Comparative testing of PMF and CFA models. *Chemom Intell Lab Syst* 61:75-87.
- Ramadan Z, Song XH, Hopke PK (2000) Identification of sources of Phoenix aerosol by positive matrix factorization. *J Air Waste Manag Assoc* 50:1308-1320.
- Ravindra K, Sokhi R, Van Grieken RV (2008) Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. *Atmos Environ* 42: 2895-2921.
- Sahu M, Hu S, Ryan PH, Masters GL, Grinshpun SA (2011) Chemical compositions and source identification of PM2.5 aerosols for estimation of a diesel source surrogate. *Sci Total Environ* 409:2642-2651.
- Samoli E, Analitis A, Touloumi G, Schwartz J, Anderson HR, Sunyer J, Bisanti L, Zmirou D, Vonk JM, Pekkanen J, Goodman P, Paldy A, Schindler C, Katsouyanni K (2005) Estimating the exposure-response relationships between particulate matter and mortality within the APHEA Multicity Project. *Environ Health Perspect* 113: 88-95.
- Shrivastava MK, Subramanian R, Rogge WF, Robinson AL (2007) Sources of organic aerosol: Positive matrix factorization of molecular marker data and comparison of results from different source apportionment models. *Atmos Environ* 41:9353-9369.
- Sofowote UM, Hung H, Rastogi AK, Westgate JN, Deluca PF, Su Y, McCarty BE (2011) Assessing the long-range transport of PAH to a sub-Arctic site using positive matrix factorization and potential source contribution function. *Atmos Environ* 45:967-976.
- Song Y, Xie S, Zhang Y, Zeng L, Salmon LG, Zheng M (2006) Source apportionment of PM2.5 in Beijing using principal component analysis/absolute principal component scores and UNMIX. *Sci Total Environ* 372:278-286.
- Vedal S, Hannigan MP, Dutton SJ, Miller SL, Milford JB, Rabinovitch N, Kim SY, Sheppard L (2009) The Denver Aerosol Sources and Health (DASH) study: Overview and early findings. *Atmos Environ* 43:1666-1673.
- Vestenius M, Leppänen S, Anttila P, Kyllönen K, Hatakka J, Hellén H, Hyvärinen A-P, Hakola H (2011)

- Background concentrations and source apportionment of polycyclic aromatic hydrocarbons in south-eastern Finland. *Atmos Environ* 45:3391-3399.
- Viana M, Pandolfi M, Minguillón MC, Querol X, Alastuey A, Monfort E, Celades I (2008) Inter-comparison of receptor models for PM source apportionment: Case study in an industrial area. *Atmos Environ* 42(16):3820-3832.
- Wingfors H, Hägglund L, Magnusson R (2011) Characterization of the size-distribution of aerosols and particle-bound content of oxygenated PAHs, PAHs, and n-alkanes in urban environments in Afghanistan. *Atmos Environ* 45:4360-4369.
- Yubero E, Carratalá E, Crespo J, Nicolás J, Santacatalina M, Nava S, Lucarelli F, Chiari M (2011) PM10 source apportionment in the surroundings of the San Vicente del Raspeig cement plant complex in southeastern Spain. *Environ Sci Pollut Res* 18:64-74.

Table 1.

Average PM10, ions, PAH concentrations and meteorological parameters during 2001-2009 sampling in Zaragoza (N=112).

	Average	Standard deviation	Minimum	Maximum
PM10 ($\mu\text{g}/\text{m}^3$)	32.86	15.18	6.64	74.85
Cl ⁻ ($\mu\text{g}/\text{m}^3$)	0.73	0.77	<l.d.	4.21
NO ₃ ⁻ ($\mu\text{g}/\text{m}^3$)	2.86	2.75	0.17	15.38
nmSO ₄ ²⁻ ($\mu\text{g}/\text{m}^3$)	3.58	2.49	0.17	10.28
Na ⁺ ($\mu\text{g}/\text{m}^3$)	0.65	0.41	0.04	2.99
K ⁺ ($\mu\text{g}/\text{m}^3$)	0.29	0.21	<l.d.	1.30
Ca ²⁺ ($\mu\text{g}/\text{m}^3$)	1.18	0.64	0.13	3.52
Phe (ng/m^3)	0.14	0.16	0.03	1.27
An (ng/m^3)	0.02	0.04	0.01	0.32
MePhe24 (ng/m^3)	0.04	0.06	<l.d.	0.38
MePhe9 (ng/m^3)	0.04	0.04	0.01	0.30
MePhe1 (ng/m^3)	0.04	0.04	<l.d.	0.19
DiMePhe (ng/m^3)	0.08	0.09	<l.d.	0.43
Flt (ng/m^3)	0.30	0.34	0.01	1.57
Py (ng/m^3)	0.36	0.35	0.02	1.64
BaA (ng/m^3)	0.37	0.53	<l.d.	3.03
Chry (ng/m^3)	0.47	0.60	<l.d.	3.32
BbjkF (ng/m^3)	0.76	0.99	0.01	5.87
BeP (ng/m^3)	0.33	0.40	<l.d.	2.71
BaP (ng/m^3)	0.33	0.40	<l.d.	1.94
IP+DahA (ng/m^3)	1.00	1.14	<l.d.	6.49
BghiP (ng/m^3)	0.84	0.88	<l.d.	4.61
Cor (ng/m^3)	1.03	1.31	<l.d.	7.57
Precipitation (mm/day)	1.26	4.20	<l.d.	25.6
Temperature (°C)	14.6	7.44	0.49	29.3
Relative humidity (%)	65.4	13.0	37.2	97.1
Solar radiation (W/m^2)	210	105	20.5	365
Wind velocity (m/s)	3.11	1.88	0.70	9.70
Wind direction (°)	232	89	12	357

l.d. = detection limit

Table 2

Source contributions expressed in $\mu\text{g}/\text{m}^3$ and percentage (between brackets) calculated by the two receptor models, Unmix and PMF, for the two sampling campaigns carried out in Zaragoza. (2003-2004, n=50 samples, 2001-2009, n=112 samples).

	Unmix0304	PMF0304	PMF0109	Unmix0109
Industry+traffic	2.90 (9%)	0.57 ^a (1.8%)		
Light-oil comb.			1.77 (5.4%)	0.83 (2.5%)
Heavier-oil comb. ^b	4.84 (15%)	2.25(7.0%)	0.12(0.36%)	2.05 (6.2%)
Marine component	3.22 (10%)	2.20 (7.0%)	2.25 (6.9%)	
Evaporative emissions	0.32 (<1%)	5.65 (18%)		
Soil resuspension ^c	20.95 (65%)	12.56 (39.0%)	18.49 (57.0%)	20.90 (63.5%)
Fossil fuel comb. ^d		1.80 (6%)	0.25 (0.8%)	4.30 (13.1%)
Crustal 2		0.45(1%)		
Biomass combustion		2.10 (6%)	1.07 (3.2%)	
Traffic emissions			6.07 (18.5%)	
Natural gas			0.94 (2.8%)	
PM10 modelled	33.11 (103%)	27.60 (86%)	31.05 (94%)	28.06 (85%)
PM10 experimental	32.24	32.24	32.86	32.86

^a The traffic factor associated with Ba in the PMF0304 model was added to the industry+traffic factor.

^b Heavier-oil combustion factor was named as heavy-duty vehicles in the Unmix0304 and PMF0304

^c Soil resuspension factor was named as crustal 1 in the Unmix0304 and PMF0304

^d Fossil fuel combustion factor was compared to the coal combustion factor obtained by the Unmix0109 and PMF0109 models. To consider that in the Unmix0304, PMF0304 and Unmix0109, the natural gas source was also included in this factor.

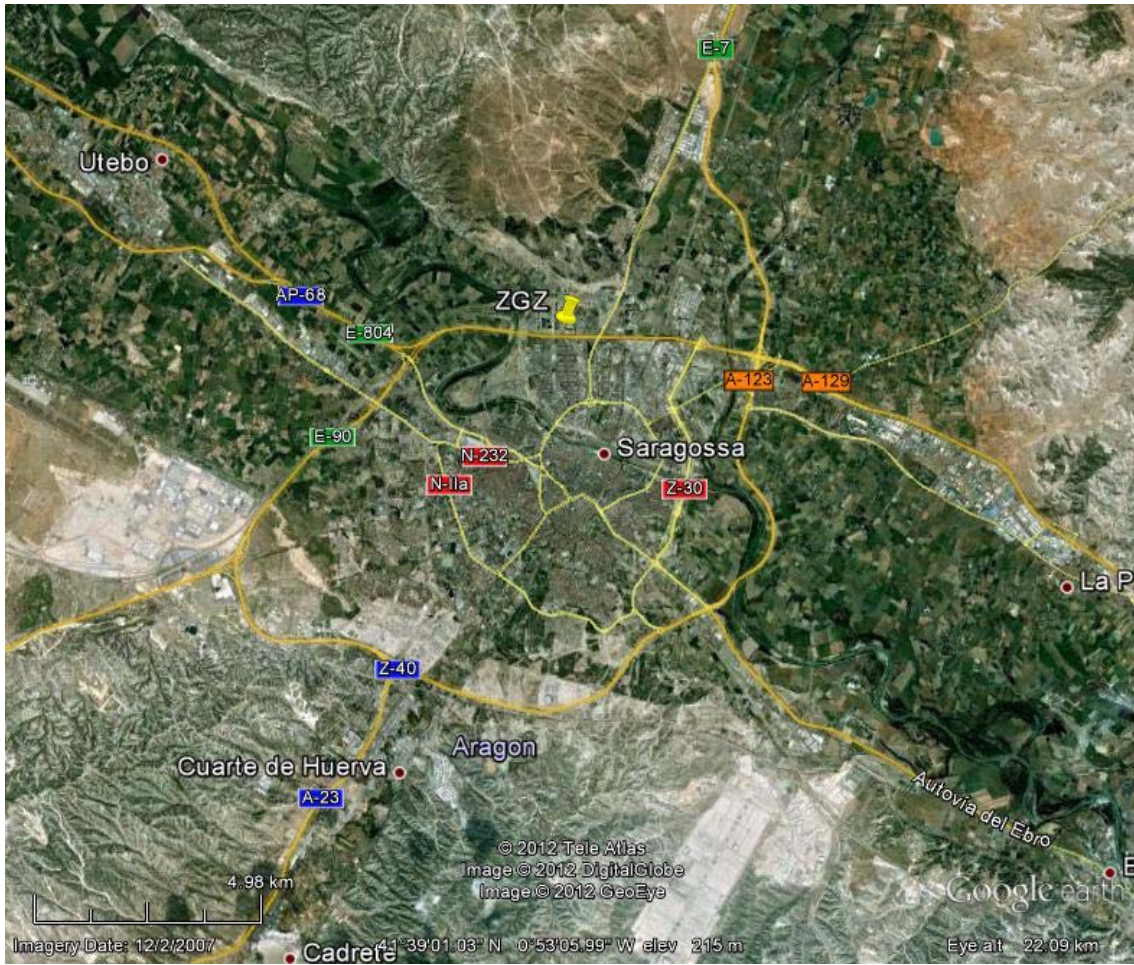
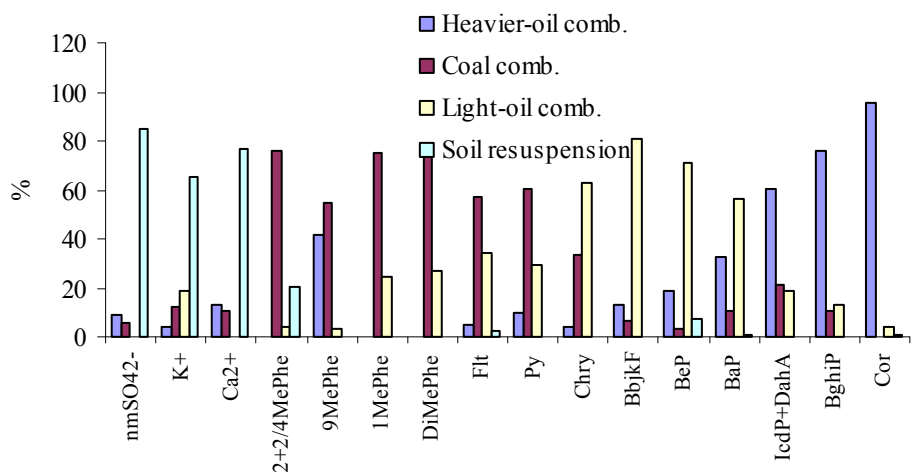
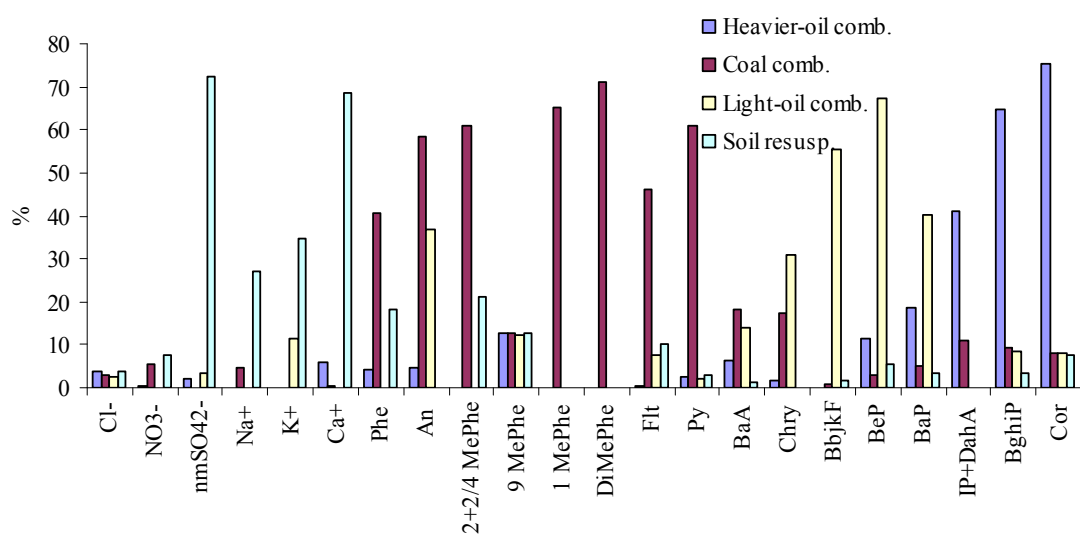


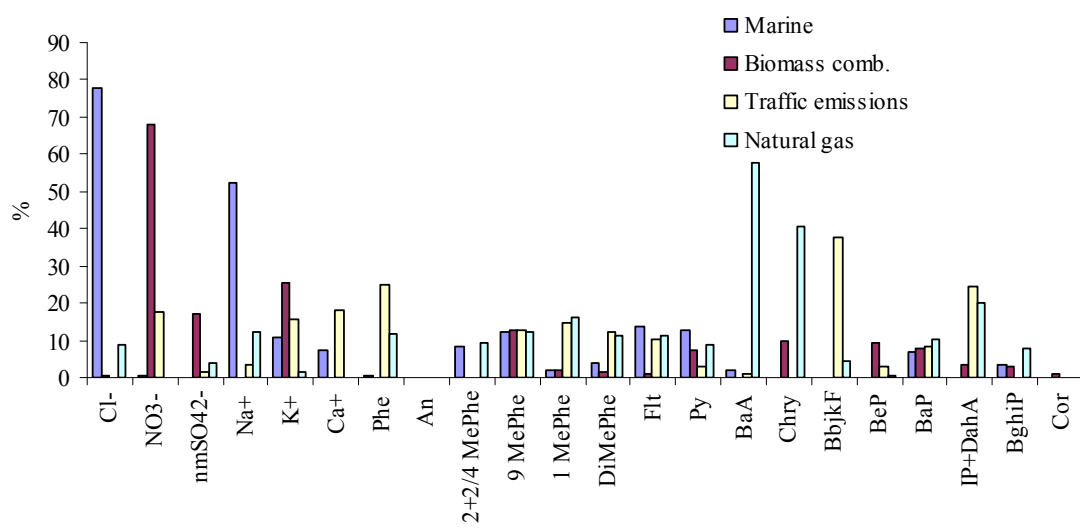
Figure 1. Location of the sampling point in Zaragoza (ZGZ= sampling point)



a)



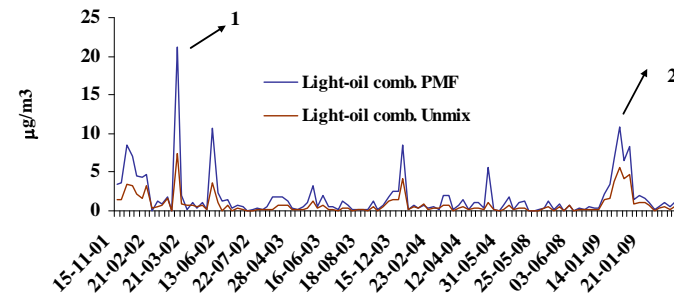
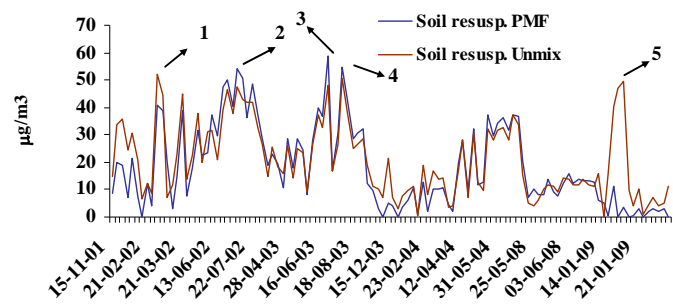
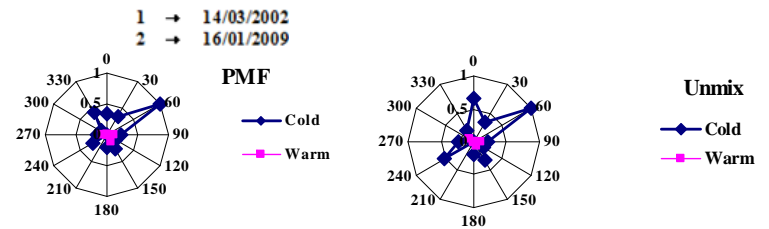
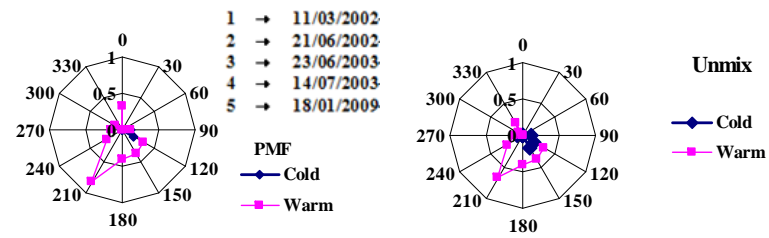
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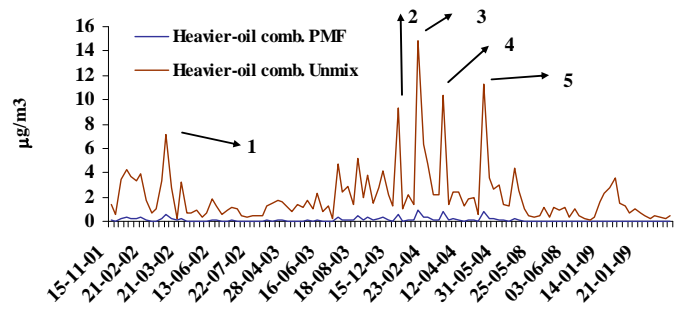
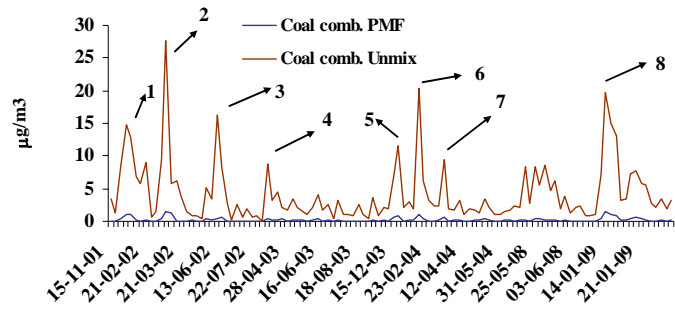
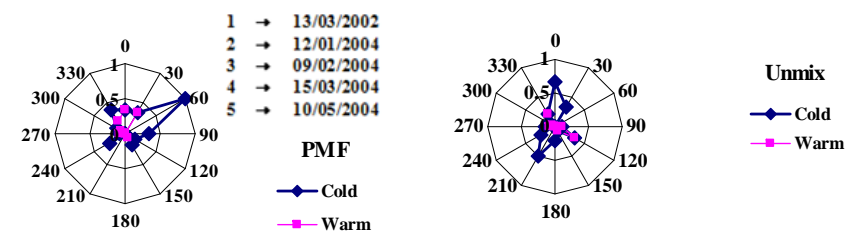
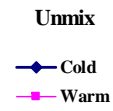
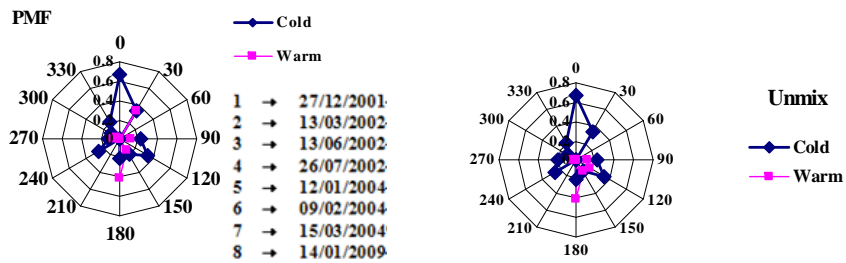


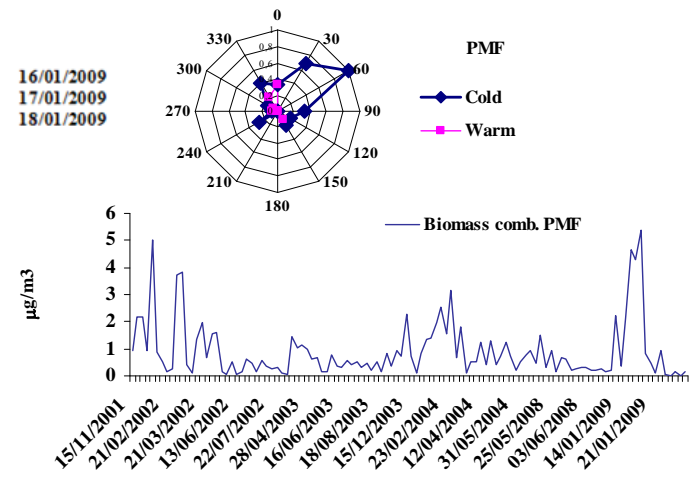
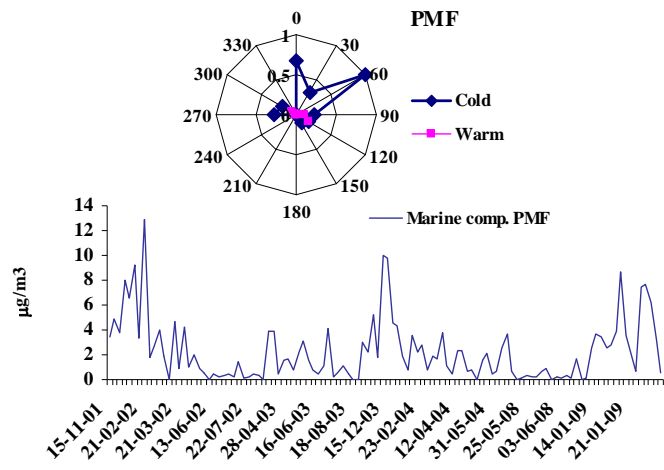
c)

Figure 2. Percentage of species apportioned to each source obtained by both

receptor models. For a) the Unmix, b) and c) the PMF model in the 2001-2009 campaign carried out in Zaragoza.







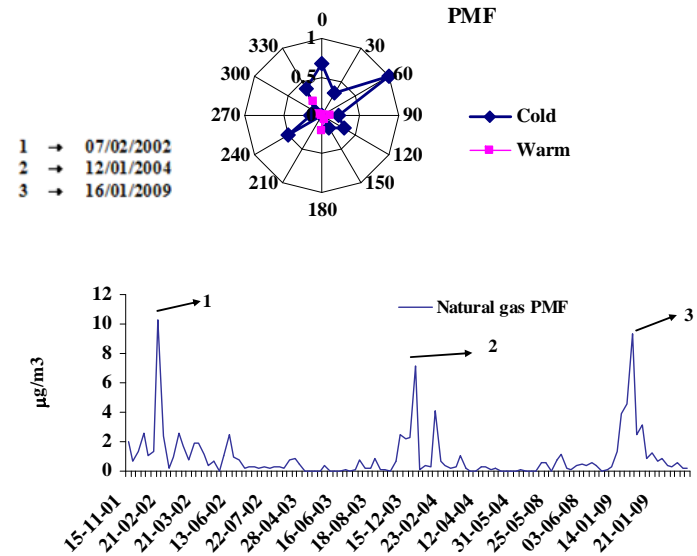
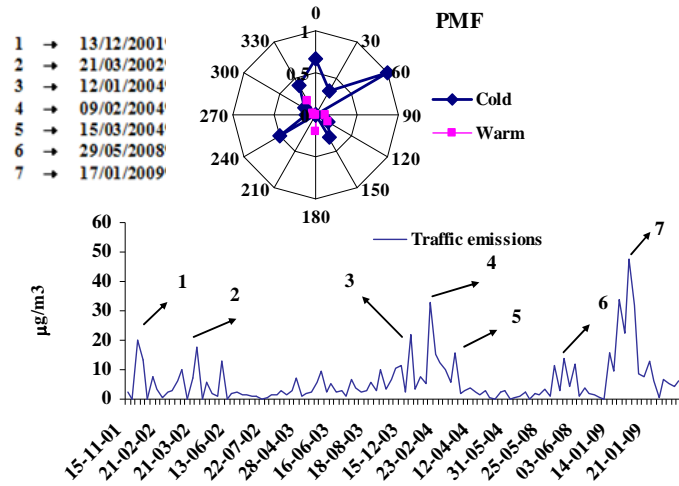
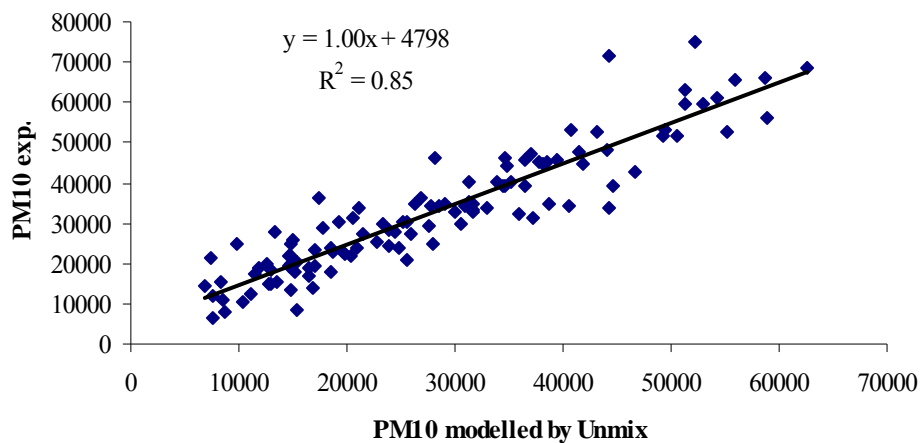


Figure 3. Source contribution time series and wind direction using CPF. Results are shown by each factor obtained by the PMF and Unmix models for the 2001-2009 campaign carried out in ZGZ during the warm and cold seasons.

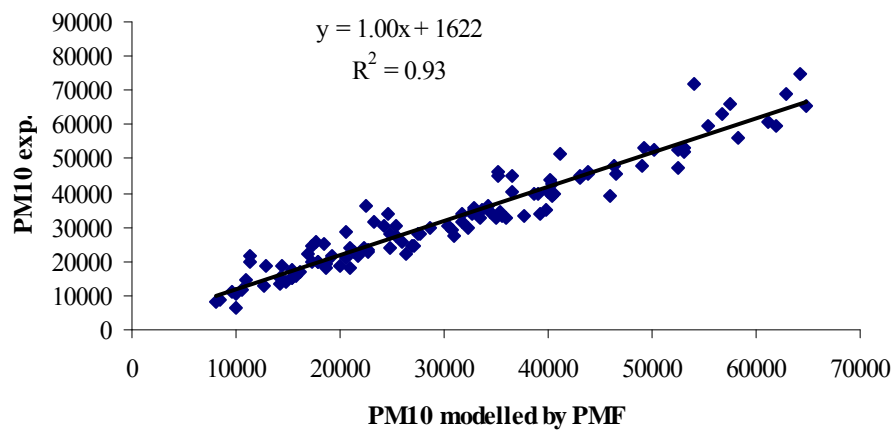
SUPPLEMENTARY DATA

Table 1S. Concentration of each chemical component in ng/m³ (µg/m³ for the PM10, nmSO₄²⁻, K⁺, Ca²⁺ and Na⁺) obtained experimentally and by the corresponding model: Unmix and PMF for the 2001-2009 sampling campaign carried out in Zaragoza (R²= correlation coefficient).

	Experimental	Unmix		PMF		R ²	% Error
		Modelled		Modelled			
PM10	32.86	28.06	0.85	-14.6	31.05	0.93	-5.8
nmSO ₄ ²⁻	3.58	4.24	0.82	18.5	3.90	0.89	8.2
K ⁺	0.29	0.31	0.68	8.3	0.32	0.70	9.1
Ca ²⁺	1.18	1.14	0.71	-3.5	1.14	0.82	-3.5
2+2/4 MePhe	0.05	0.08	0.75	69.8	0.06	0.52	23.5
9 MePhe	0.04	0.04	0.74	-8.3	0.08	0.67	45.3
1 MePhe	0.04	0.04	0.87	14.7	0.04	0.82	6.3
DiMePhe	0.08	0.08	0.80	-8.6	0.07	0.75	-22.8
Flt	0.30	0.33	0.87	9.4	0.38	0.91	19.1
Py	0.36	0.24	0.88	-33.2	0.37	0.98	2.4
Chry	0.47	0.48	0.82	2.1	0.49	0.89	3.9
BbjkF	0.76	0.74	0.94	-2.6	0.80	0.98	4.0
BeP	0.33	0.33	0.92	0.2	0.33	0.99	-2.1
BaP	0.33	0.37	0.94	11.2	0.39	0.95	13.2
IcdP+DahA	1.00	1.14	0.88	14.4	1.07	0.94	6.9
BghiP	0.84	0.86	0.93	2	0.79	0.99	-5.9
Cor	1.03	1.16	0.94	12.4	1.12	0.95	7.3
BaA	0.37				0.40	0.99	7.0
Cl ⁻	0.73				0.81	0.98	10.2
NO ₃ ⁻	2.86				2.87	0.97	0.3
Phe	0.14				0.13	0.32	-1.5
An	0.02				0.03	0.62	20.3
Na ⁺	0.65				0.42	0.36	-56.8



1

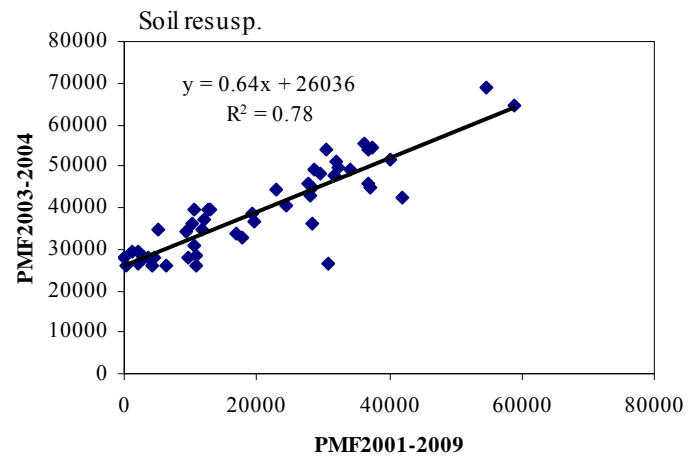
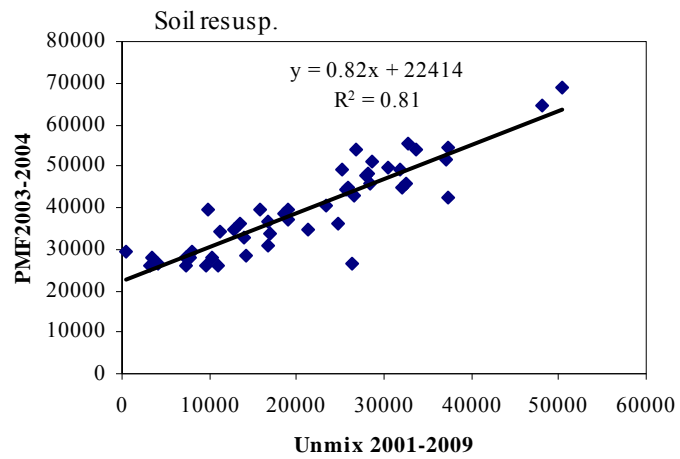


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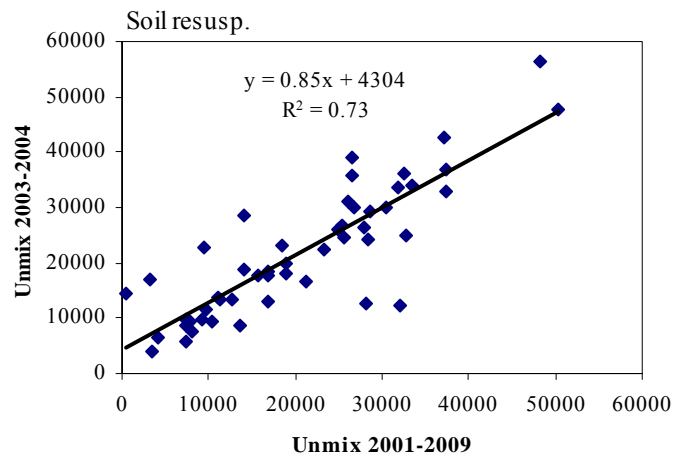
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Figure 1S. Plot between the experimental and the modelled PM10 (ng/m^3) obtained by the Unmix and the PMF models for the 2001-2009 sampling campaign carried out in Zaragoza.

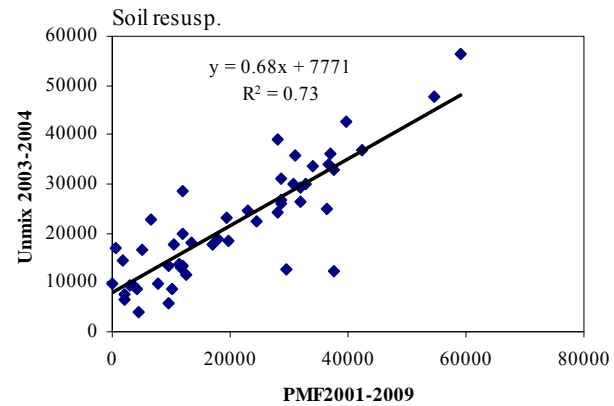
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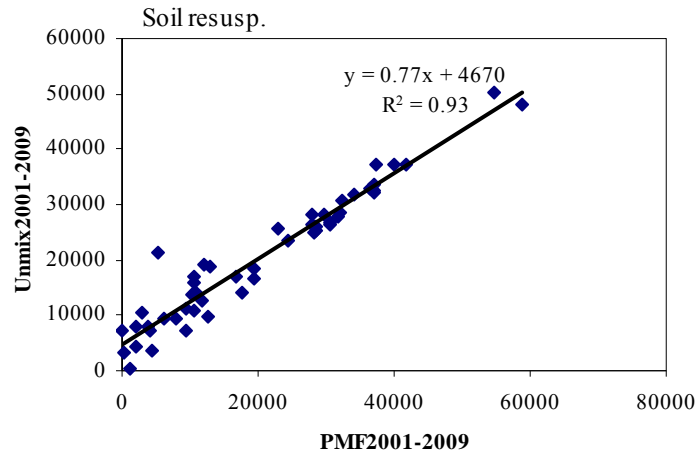
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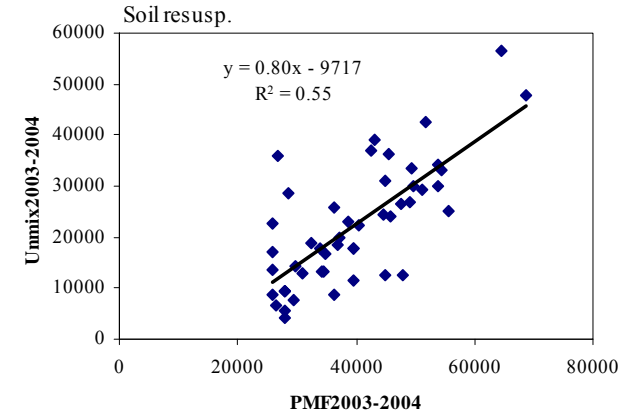
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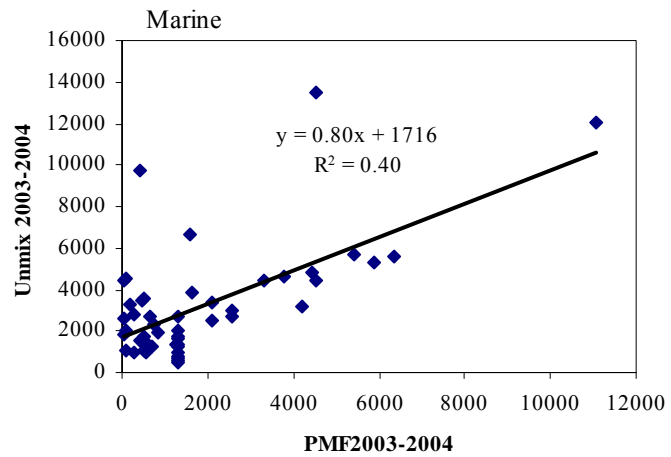
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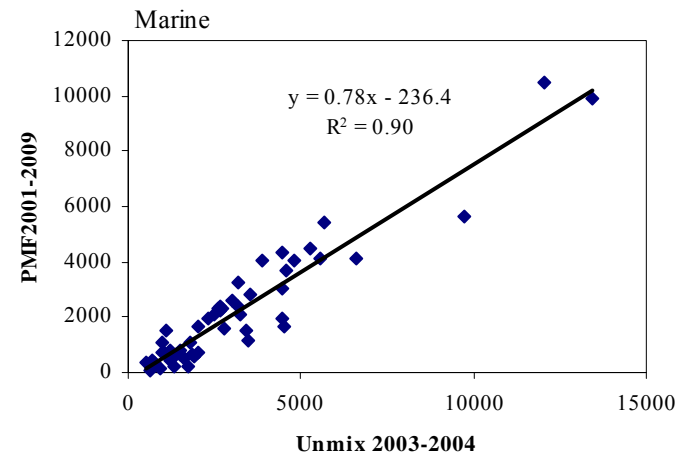
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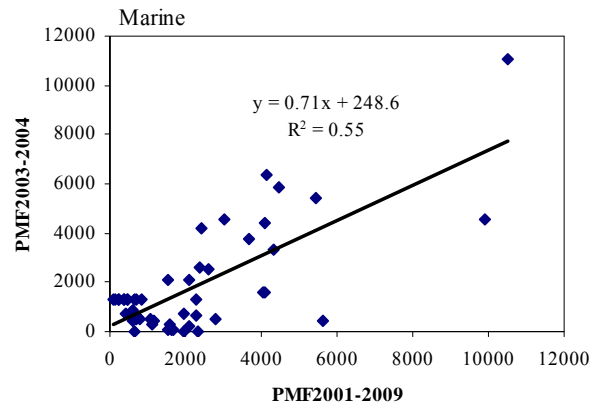
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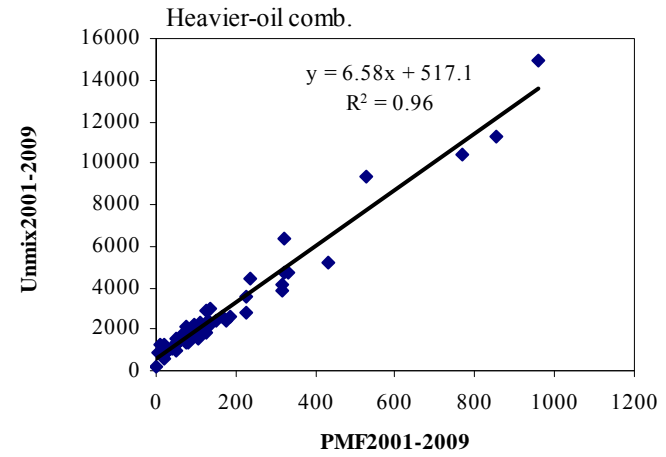
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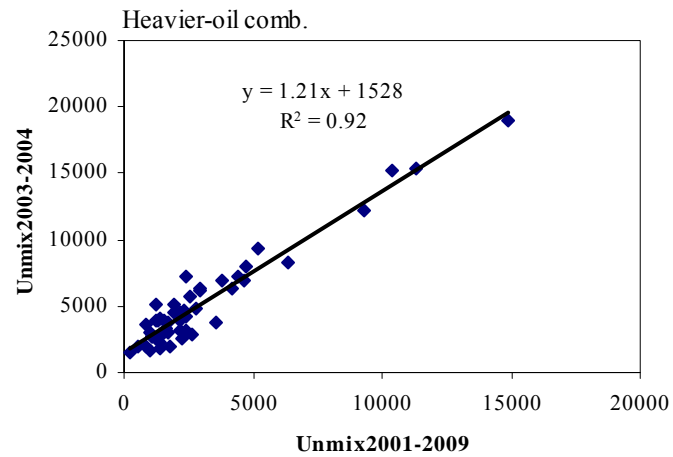
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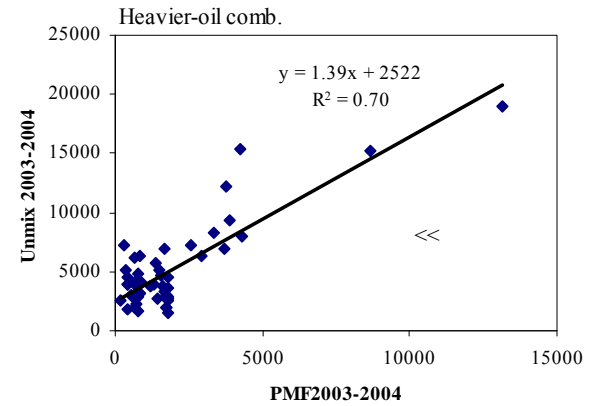
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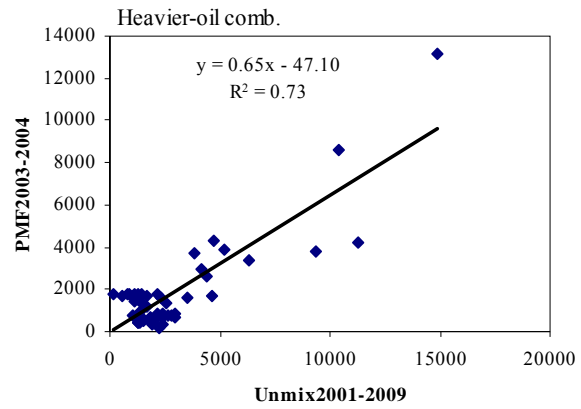
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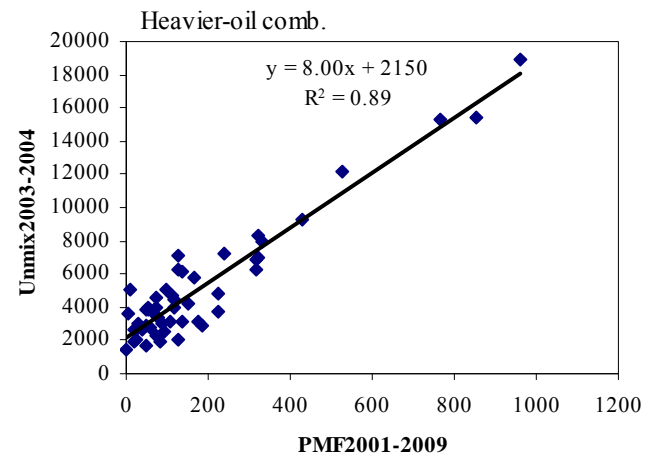
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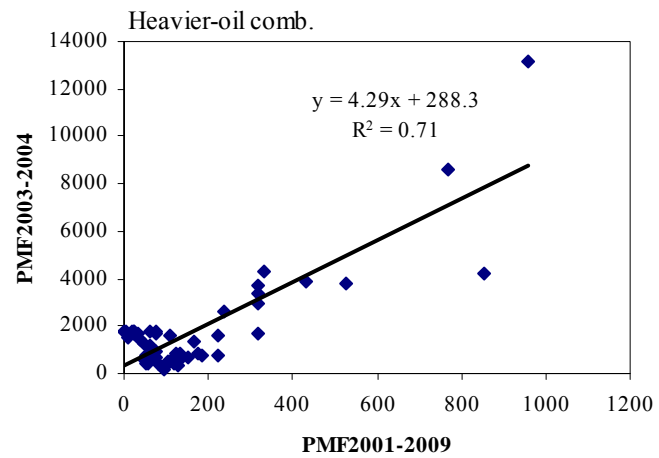
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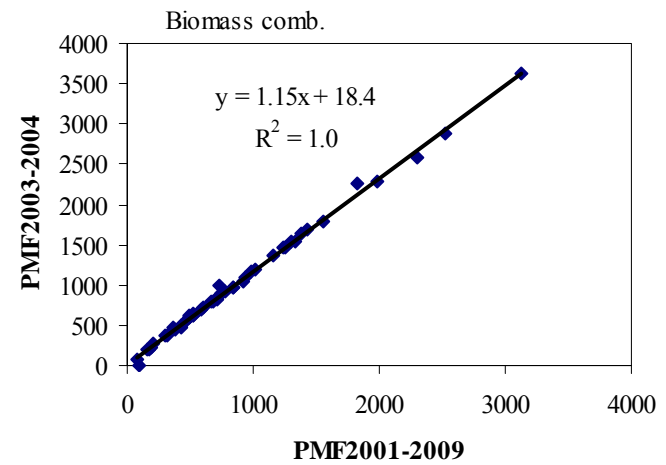
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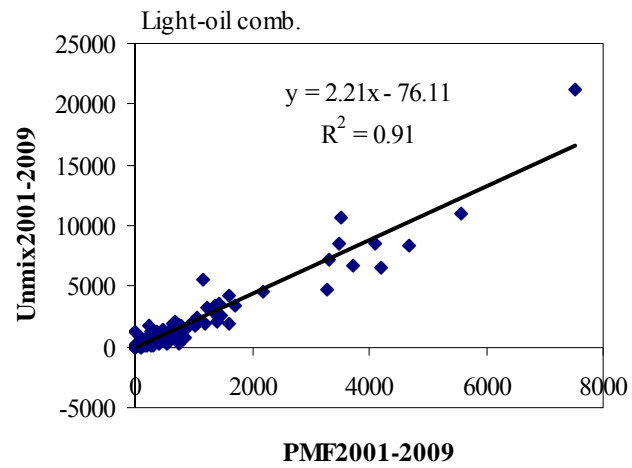
m)



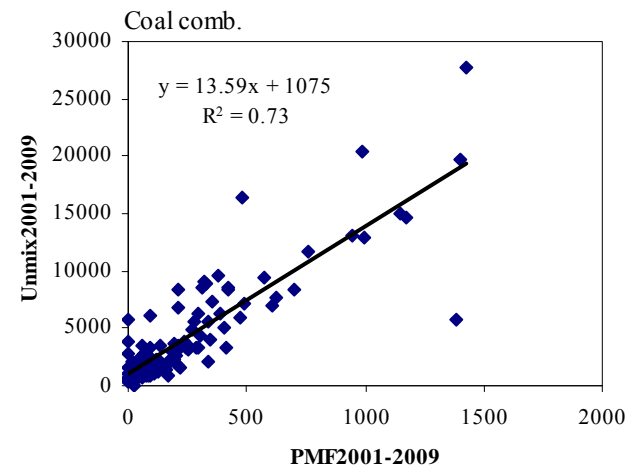
n)



o)



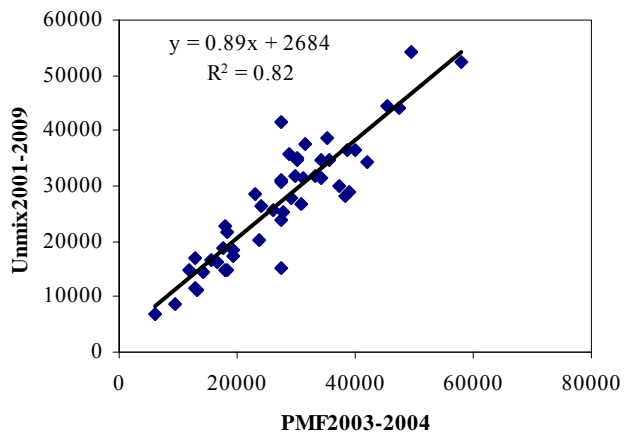
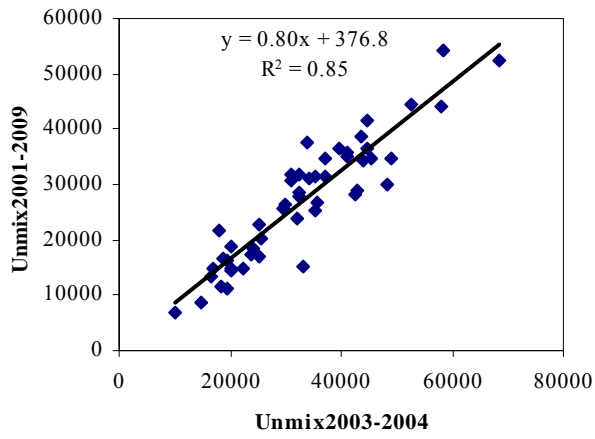
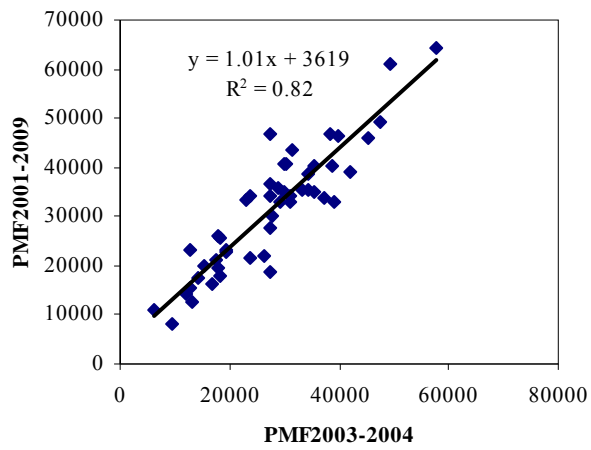
p)



q)

r)

Figure 2S. Plot between the common sources (ng/m^3) obtained by the two receptor models: Unmix and PMF and by the two sampling campaigns: 2003-2004 and 2001-2009 carried out in Zaragoza.



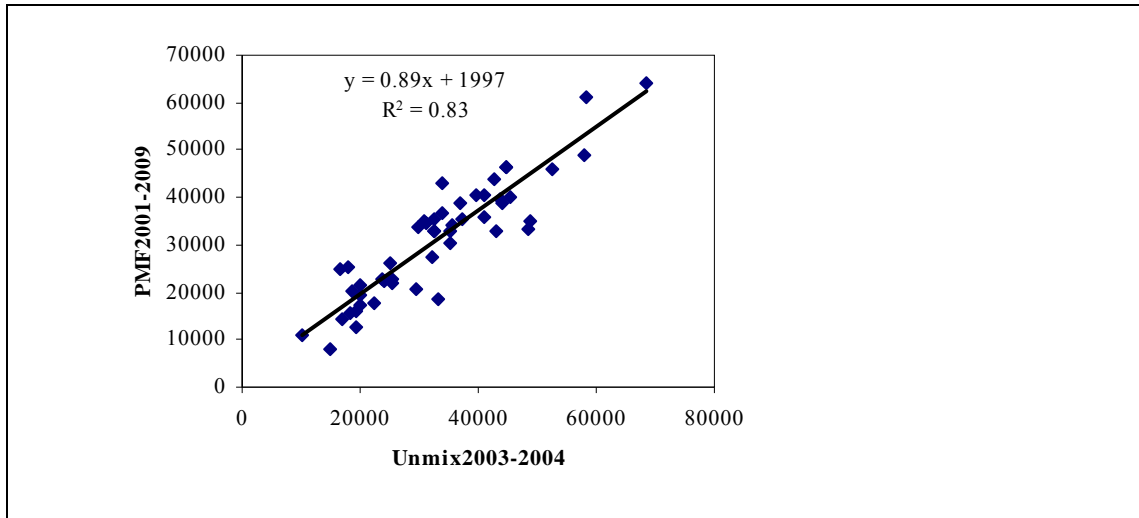


Figure 3S. Plot between the modelled PM10 (ng/m³) obtained by the different models: Unmix and PMF and by the sampling campaigns: 2003-2004 and 2001-2009 carried out in Zaragoza.