Intercomparison campaign (WP3.4) Final Report

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Intercomparison campaign (WP3.4): final Report

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Content

Abstract

Assessing the source contributions of PM by a top down approach requires advanced analytical and statistical approaches. Because no absolute source apportionment approach exists, intercomparison of the different methodologies used by each scientific partners of APICE is a prerequisite for any comparison between the 5 harbors (Barcelona, Genoa, Marseille, Thessaloniki and Venice) involved in the project.

A six weeks intercomparison campaign was organized in Marseille from the 25th of January to the 2nd of March 2011 in an urban background site. The objectives of this field campaign were to intercompare airborne measurements (mass, chemical composition) and source apportionment methodologies in order to converge towards a common methodology.

Regarding measurements, whereas OC, K/K^+ and SO_4^{2-} in the $PM_{2.5}$ fraction resulted in very similar concentrations and temporal evolution for all the partners, some other major components, such as Ca/Ca^{2+}, Mg/Mg^{2+} and NO_3^-, show significant differences for at least one partner. This can be explained by minor analytical and non permanent problems (ie: calibration, contamination). Raw data and analytical conditions will be checked by the partner for whom the data set appears problematic for at least one point. For minor fraction (metals and elements) we observe good agreement, within classical analytical error range, for the most relevant source markers (Pb, Fe, Cu, Zn, Ni).

Regarding source apportionment methodologies, each partner was free to use his own one (measurements and source apportionment model). As expected, significant discrepancies are observed. However these discrepancies regard mostly the average contribution of some sources while the temporal trends are in fair agreements. Differences can also be linked quite easily to the methodology used, either regarding the choice of fitting species or source profiles, either considering biases induced by the dynamic of the atmosphere (particularly important considering the number of observations).

In order to converge towards a homogenous methodology between each pilot area, our recommendations are as follows:

1/ **Use of the same source apportionment approach**. The source apportionment approach chosen is PMF (Positive Matrix Factorization). In consequence, Aix Marseille Univ will also use PMF in addition to CMB,

2/ **Use of a common basis of chemical markers as fitting species**. The chemical markers list will include trace elements/metals and organic markers or at least the different carbon fractions (OC1, OC2,.., Pyrolitic Carbon), in addition to OC, EC, sulfate, nitrate and ammonium. The list of chemical markers will be defined by the partnership after a careful study of the chemical data obtained during the long monitoring campaigns. Some additional markers may be added to the list in each pilot area in order to take into account the specificity of each pilot area,

3/ **Common interpretation of the different factors identified in each pilot area**.

1. Introduction

Source apportionment of atmospheric particulate matter (PM) is far from a straightforward exercise. Atmospheric aerosol consists of a highly complex mixture, in constant evolution in the atmosphere, of mineral and organic materials associated to micron and submicron particles. In urban areas, atmospheric aerosols are emitted to the atmosphere by a multitude of sources and also formed in situ through gas phase oxidation processes of volatile organic compounds (VOC) or gases such as SO2, NOx. Assessing the source contributions of PM by a top down approach requires advanced analytical and statistical approaches. Because no absolute source apportionment approach exists, intercomparison of the different methodologies used by each scientific partners of APICE is a prerequisite for any comparison between the 5 harbors (Barcelona, Genoa, Marseille, Thessaloniki and Venice) involved in the project.

A six weeks intercomparison campaign was organized in Marseille from the 25th of January to the 2nd of March 2011 in an urban background site. The objectives of this field campaign were to intercompare measurements and source apportionment methodologies in order to converge towards a common methodology. The intercomparison campaign gathers all the scientific partners involved in the measurements and source apportionment task. Several instruments were deployed including state of the art instruments such as Aerosol Mass Spectrometer (AMS) for online monitoring of non-refractory submicron particles composition and Proton Transfer Reaction Mass Spectrometer (PTR-MS) for online monitoring of VOCs. Initially planned in autumn 2010, the field campaign was delayed to February/March 2011 for logistical issues and to guarantee its success. A first report discussing of the intercomparison of measurements has been already published1.

The present report summarizes the campaign conditions and the intercomparison of chemical markers measurements used as fitting species in each source apportionment approach. This report focuses on the intercomparison of source apportionment exercise performed by each partner and proposes recommendations to converge towards a common and concerted methodology. Complete source apportionments description and results are presented in Appendix II.

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[1] Progress report can be downloaded here :
http://www.apice-project.eu/dett_news.php?ID1=34&ID=34&ID_NEWS=19&lang=ENG

2. Overview of the field campaign conditions

A complete description of the campaign and campaign conditions is given in the progress report[2]. Only an overview is reported here.

2.1. Sampling site and measurements

The intercomparison campaign took place at Marseilles from the 25th of January to the 2nd of March 2011. The sampling site, called « 5 avenues » (43°18'20'' N, 5°23'40'' E, 64 m a.s.l. – figure 2.1), was located in a urban background environment in a large landscape park.

Figure 2.1 : Sampling site localisation and instrumentation deployed during the APICE intercomparison campaign

The measurement campaign gathered all of the APICE scientific partners on the same sampling site. A large set of instruments was deployed during the whole campaign allowing the constant monitoring of aerosol physico-chemical parameters and associated gas phase (VOC's and regulated pollutants –ie: O_3, NOx, SO_2-) (table 2-1). This instrumentation includes all samplers and analyzers to be used by each scientific partner of APICE as part of the long monitoring campaign carried out in each harbor. State of the art instrumentations (AMS, PTRMS) and ^{14}C analyses have been added to the APICE instrumental setup in order to better constrain the source receptor models outputs.

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[2] Progress report can be downloaded here :
http://www.apice-project.eu/dett_news.php?ID1=34&ID=34&ID_NEWS=19&lang=ENG

Parameters	PMx	Time resolution	Organization/Lab	Instrument/method
Marseille				
Org, SO4, NO3, NH4, (PAH), NR_Cl	PM1	7 min	LCP-IRA (Univ Prov)	HR-ToF-AMS
BC	PM1	5 min	LCP-IRA (Univ Prov)	MAAP5012
particle number, size distr.	PM1	7 min	LCP-IRA (Univ Prov)	SMPS (10-1000 nm)
VOC's (Benz, Tol, isopr, MACR/MVK etc..)		1 min	LCP-IRA (Univ Prov)	HS-PTRMS
OC/EC, majors ions, metals	PM2.5	24h	LCP-IRA (Univ Prov)	Off line HV, OC:EC (EUSAAR2), ions IC, Metals (ICP/MS)
Organic markers (levoglucosan, hopanes, n-alk, sterols, PAH, ..)	PM2.5	24h	LCP-IRA (Univ Prov)	Off line HV, GC/MS
14C	PM2.5	24h	LCP-IRA (Univ-	Off line HV
Wind dir. and speed, HR, T		5 min	LCP-IRA (Univ Prov)	
SO2, O3, NOx, PM10, PM10 FDMS, PM2.5 FDMS		15 min	AtmoPACA	PM by TEOM
Source apportionment by CMB				
Thessaloniki				
OC/EC, majors ions, metals	PM2.5	24h	ETL/UOWM	Off line LV OC:EC (Sunset), ions IC, Metals (ICP/MS or AES)
Organic markers (PAH)	PM2.5	24h	ETL/UOWM	Off line LV, GC/MS
PM concentration	PM2.5	24h	ETL/UOWM	Off line LV, Gravimetric
Source apportionment by PMF				
Venice				
SPAH (total Surface Polycyclic Aromatic Hydrocarbons)	PM1	5 min	ARPAV-ORAR	Photoelectric Aerosol Sensor PAS2000 EcoChem (10-1000 nm)
PM mass	PM2.5	5 min	ARPAV-ORAR	PM2.5 continuous particle sizing monitor / Dual Wavelength Nephelometer
PM particle diameter of mass max concentration	PM2.5	5 min	ARPAV-ORAR	PM2.5 continuous particle sizing monitor / Dual Wavelength Nephelometer
Particle number	PM 0.3-10.0	15 min	ARPAV-ORAR	Handheld 3016IAQ six classes OPC (0.3, 0.5, 1.0, 2.5, 5.0, 10.0)
Organic markers (hopanes, n-alkanes, PAH)	PM2.5	24h	ARPAV-ORAR	Off line LV, DTD-GC-MS
PM2.5	PM2.5	24h	ARPAV-ORAR	PM by TECORA gravimetric
Source apportionment by PMF				
Genoa				
PM2.5	PM2.5	12 h	Dept. of Physics Genoa	sequential sampling on 47 mm quartz and/or teflon filter (porosity 2 micron). Gravimetric, XRF, EC/OC analysis, maybe ions
Particle number concentration in 31 size bins between 0.25 and 18	PM10	1 h	Dept. of Physics	Grimm Optical Particle Counter
BC concentration by optical attenuation measurement	PM10	20 m	Dept. of Physics	Two-wavelength Aethalometer
Source apportionment by PMF				
Barcelona				
Major and trace elements, OC, EC, SO42-, NO3-, Cl- and NH4+	PM10, PM2.5	24h	IDAEA-CSIC	High-vol, quartz filters. ICP-AES, ICP-MS, SUNSET (eusaar_2), IC, Electrode for ammonium
PM mass concentration	PM10,2.5,1	1h	IDAEA-CSIC	GRIMM optical counter
Source apportionment by PMF				
Extern. Partners				
Trace elements, metals	PM10, PM2.5, PM1	2 h	PSI/LAC	RDI (Rotating Drum Impactor), with synchrotron-radiation induced X-ray fluorescence
BC	TSP	5 min	LA/CNRS	Aethalometer 7 lambda

Table 2.1 Overview of the instrumentations deployed during the intercomparison campaign

2.2. Field campaign conditions
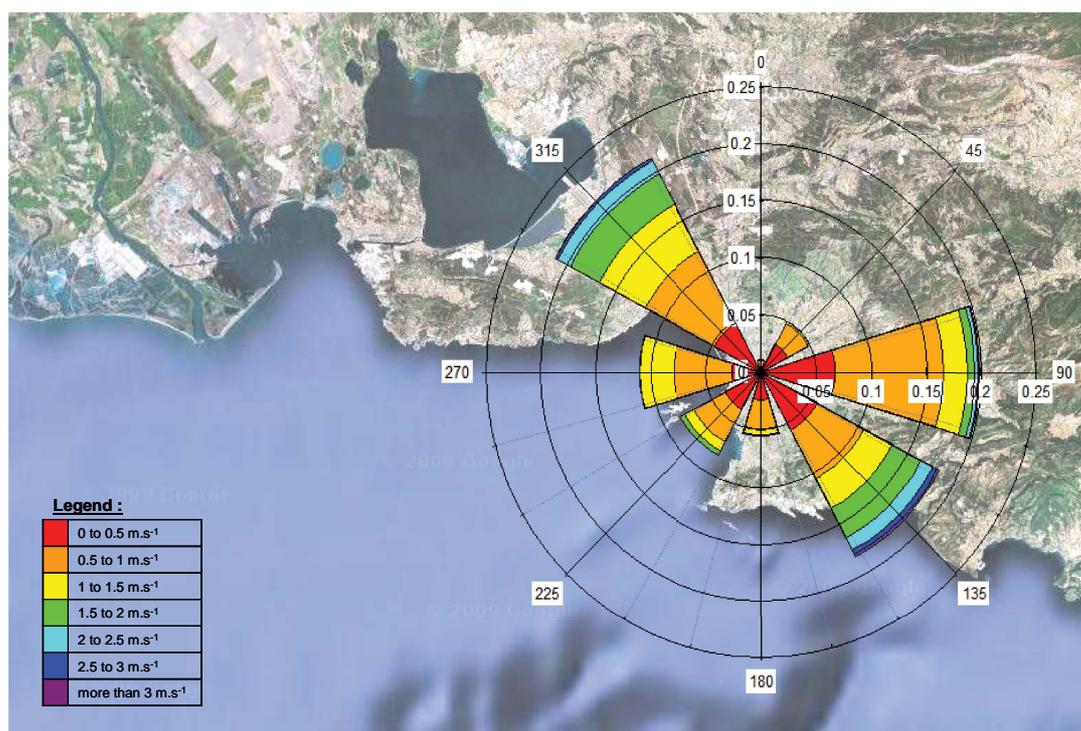
Figure 2.2: Wind direction observed during the intercomparison campaign

Figure 2.2 presents the main local wind directions observed during the measurement campaign. Three wind directions prevailed: north western winds (Mistral), synoptic south eastern winds and eastern winds mainly related to nocturnal land breezes. Western winds have also been observed. Within the framework of APICE north western and western winds are the most important because in those situations the sampling site is downwind the harbors and industrial area.

Air quality observed during the field campaign was typical for the season in Marseille (38 µg m^{-3} for PM10; 25 µg m^{-3} for PM2.5 and 17 µg m^{-3} for PM1). However these average values hide an important variability with periods characterized by high concentrations. Figure 2.3 present the temporal trends of PM10, PM2.5 and PM1 mass concentrations, SO$_2$, total number concentration of submicron aerosol particles and of the major chemical fractions of PM1. Fine particles are dominated by organics (representing 55% of the PM1) followed by nitrate (20%) and BC (9%). Sulfate and ammonium contribute only to 7 and 8% of the PM1, respectively. Then the total carbonaceous fraction (Org + BC) represents approximately 2/3 of the total PM1 mass. This result is not totally surprising in winter, but such a contribution of organic materials indicates a strong influence of combustion sources (oil derivatives and biomass combustions). It is interesting to note that the prevalence of the carbonaceous fraction is particularly marked during the first part of the campaign where sharp increases of their concentration are observed.
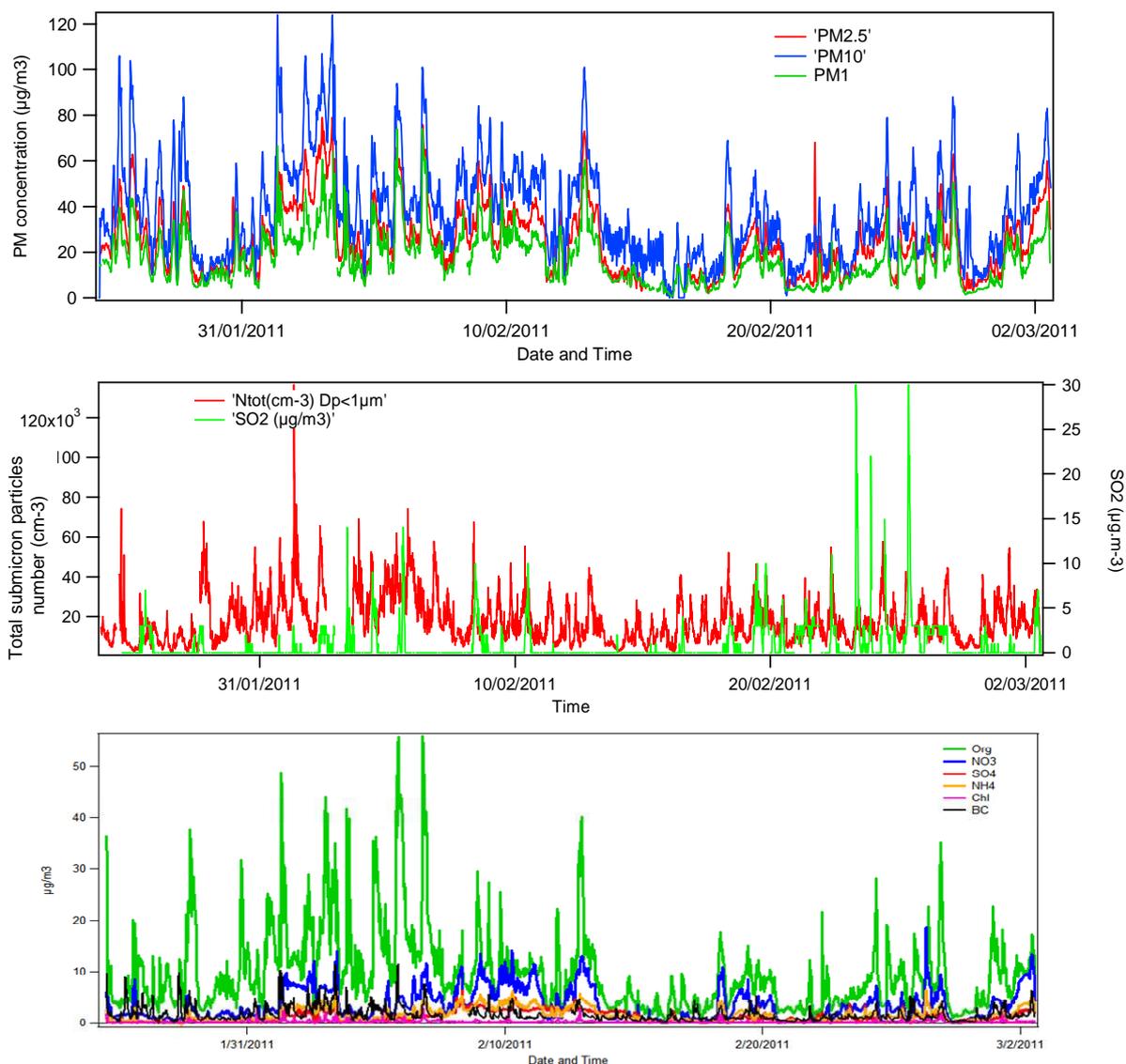
Figure 2.3: a) (up) Temporal trends of PM10, PM2.5 and PM₁; b) (middle) SO₂ , total number of submicron particles; c) (down) major fractions of submicron aerosol particles derived from AMS (Organic, nitrate, sulfate and ammonium) and MAAP (BC).

These sharp increases of organic concentration during the first half of the campaign are related to advection of PM with the onset of nocturnal breezes canalized by the Huveaune valley. The onset of nocturnal breezes is favored by stable and cold conditions such as encountered during the first part of the campaign. As shown by the m/z tracer approach (figure 2.4), also called "poor" PMF approach and based on key organic fragments abundances measured by AMS (see report progress report for more details), the most interesting feature is the abundance of biomass burning organic aerosol. This result is quite unexpected in a Mediterranean city such as Marseille since wood combustion for residential heating is scarce. A more careful look at the temporal trends shows that BBOA is mainly transported by nocturnal breezes from rural areas through the Huveaune valley.
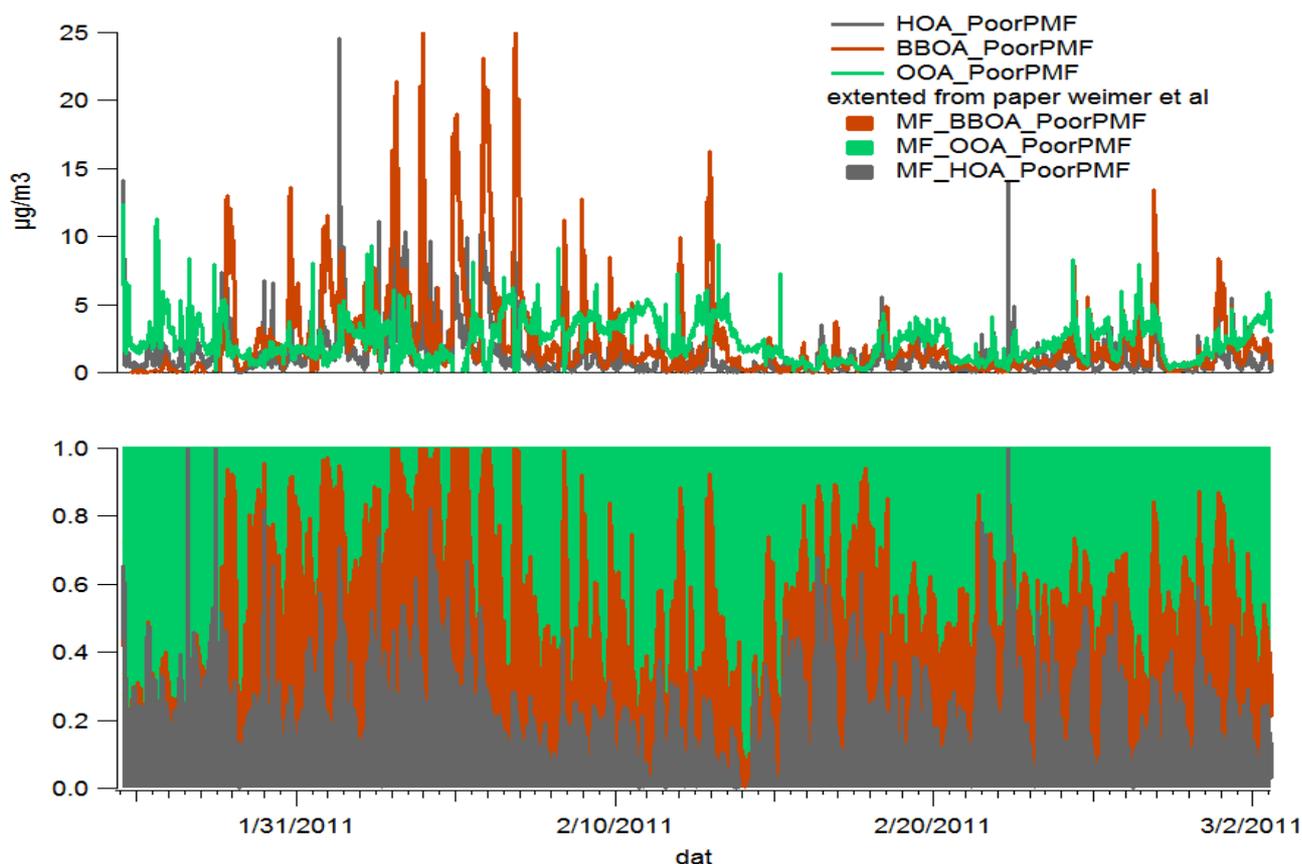
*Figure 2.4: m/z tracer method based on mz57, mz44 and mz60 fragments measured by AMS (from the 29th of January to the 3rd of March 2011); **HOA** (Hydrocarbon like Organic Aerosol) represents the organic fraction coming from fossil fuel combustion (mainly vehicular emissions in urban areas); **BBOA** (Biomass Burning Organic Aerosol) corresponding to organic aerosol emitted by every types of biomass burning (residential heating, lignite combustions, wildfire,..); **OOA** (Oxygenated Organic Aerosol) representing the oxidized fraction of the organic aerosol. This fraction is often assimilated to the traditional secondary fraction of the organic aerosol but we should also consider that this OOA fraction contains a significant amount of oxidized materials coming from primary organic aerosol.*

Events of nano-particles (Dm<50nm) associated to northwestern winds and, most of the time, to SO$_2$ are also observed. Such events can clearly be associated to the advection of air masses impacted by harbors/industrial emissions. Thus even during the first half of the campaign, the influence of harbors and harbors related activities can be highlighted. Their contributions to the total PM concentrations should however remain limited. This influence of harbor related activities sources seems higher during the second half of the campaign.

10

3. Summary of the intercomparison of measurements

During the intercomparison campaign in Marseille each scientific partner participated by using its instrumentation and analytical techniques. In some cases, certain chemical species were determined only by one of the partners, whereas a number of chemical components were analyzed in all the laboratories. In this report we show the intercomparison of those species determined in most of the laboratories (Table 3.1). Please note that UOWM, Univ Provence and ARPAV also analysed organic markers. Results are presented in appendix I.

Table 3.1: Summary of average concentrations obtained by each partners

ng/m^3	U. Genoa	IDAEA-CSIC	U. Provence	UOWM
OC	5895	8333	8196	7994
EC	2109	1366	1984	2422
PAHs			16	9
Al	11	69		
Ca	186	433	972	522
K	149	253	149	161
Na	39	148	123	53
Mg	63	45	23	28
Fe	128	122		
P	5	9		
SO$_4^{2-}$	2967	2963	2663	2353
NO$_3^-$	2594	4740	4060	4989
Cl$^-$	71	340	144	85
NH$_4^+$	1964	1346	1960	6917
Ti	6	5	9	
V	5	3	3	
Cr	2	1	2	
Mn	2	3	4	
Ni	3	2	2	
Cu	15	14	15	
Zn	29	25	25	
Pb	12	10	9	

In all cases the analysis of organic carbon (OC) and elemental carbon (EC) has been made by using a thermo-optical method (SUNSET instrument), although different temperature programmes were used (*eusaar_2* and *niosh*). This difference seems to be not important concerning total concentrations of OC and EC (Figure 3.1) but it may affect the partition of OC and EC peaks. Lower EC levels were determined in the first half of the samples by IDAEA-CSIC, although the quality of the results was checked and 10 of these samples were again analysed (obtaining the same results).
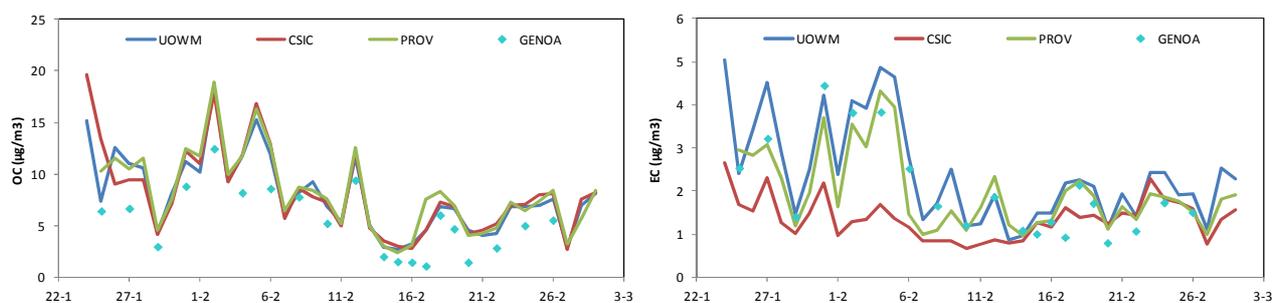
Figure 3.1: Daily concentrations (in µg m^{-3}) of OC (left) and EC (right) determined by the partners during the campaign.

As regards for the determination of sulphate, nitrate and chloride, Ionic Chromatography was used (Figure 3.2). Sulphate concentrations were equally quantified in all the laboratories whereas some differences where observed for nitrate. Concerning chlorine, the low levels recorded in the PM$_{2.5}$ fraction, in many cases close to the detection limit of the instrument, provoked a relevant divergence between results from the laboratories. In the case of NH$_4^+$, most of the laboratories determined the concentrations by using Ionic Chromatography and one of them by using a specifc electrode. The results present significant divergences for one partner (Figure 3.2) although time-variability is almost the same.
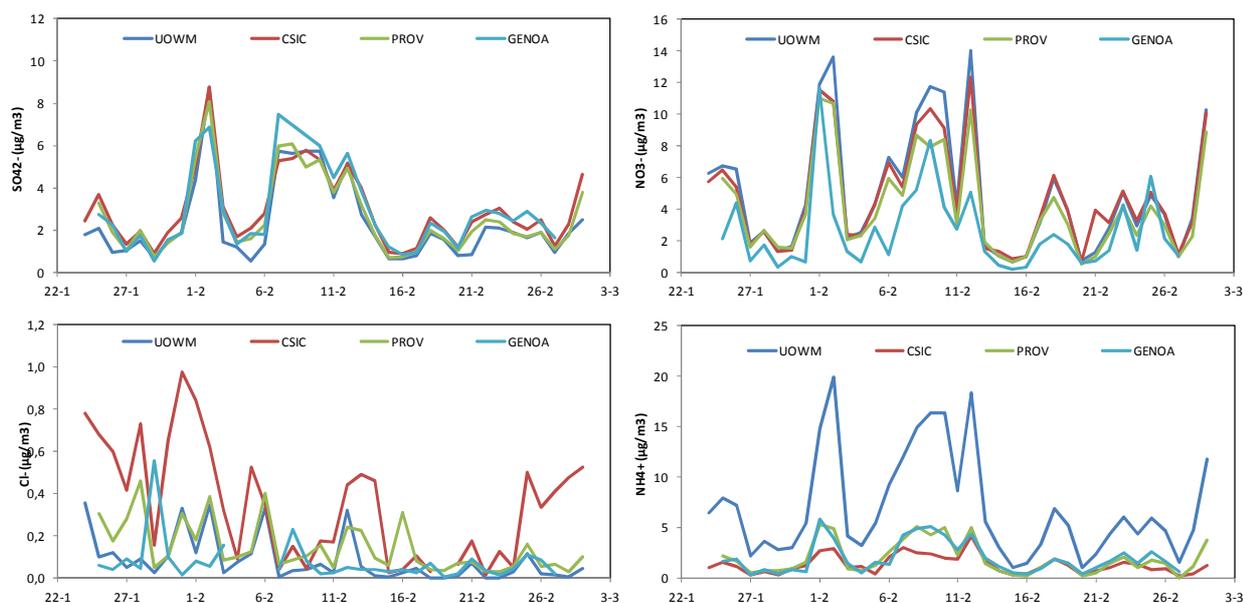
Figure 3.2: Daily concentrations (in µg m^{-3}) of SO$_4^{2-}$ (top-left), NO$_3^-$ (top-right), Cl- (bottom-left) and NH$_4^+$ (bottom-right)determined by the partners during the campaign.

Other major elements and components such as K/K$^+$, Ca/Ca^{2+}, Mg/Mg^{2+}, Na/Na$^+$, were also determined in all the laboratories. In some cases the total and the soluble fraction was analysed but, in general, only one technique was used. Thus, IDAEA-CSIC analysed the total content of the element in the PM$_{2.5}$ samples by using ICP-AES, whereas UOWM and U. Provence determined the soluble fraction of these elements by means of Ionic Chromatography, and the U. Genoa

quantified both the soluble and the total content by Ionic Chromatography and ED-XRF, respectively. Offline analysis of K/K+ resulted in very similar concentrations and temporal evolution for all the laboratories (Figure 3.3), although slightly high concentrations were given by CSIC, but it is attributed to the analysis of total K instead of K^+. As regards for Ca/Ca^{2+}, Na/Na^+ and Mg/Mg^{2+}, some differences have been encountered (Figure 3.3), in some cases attributable to insoluble particles not determined everywhere. In other cases the differences may be due to filter or laboratory contaminations.
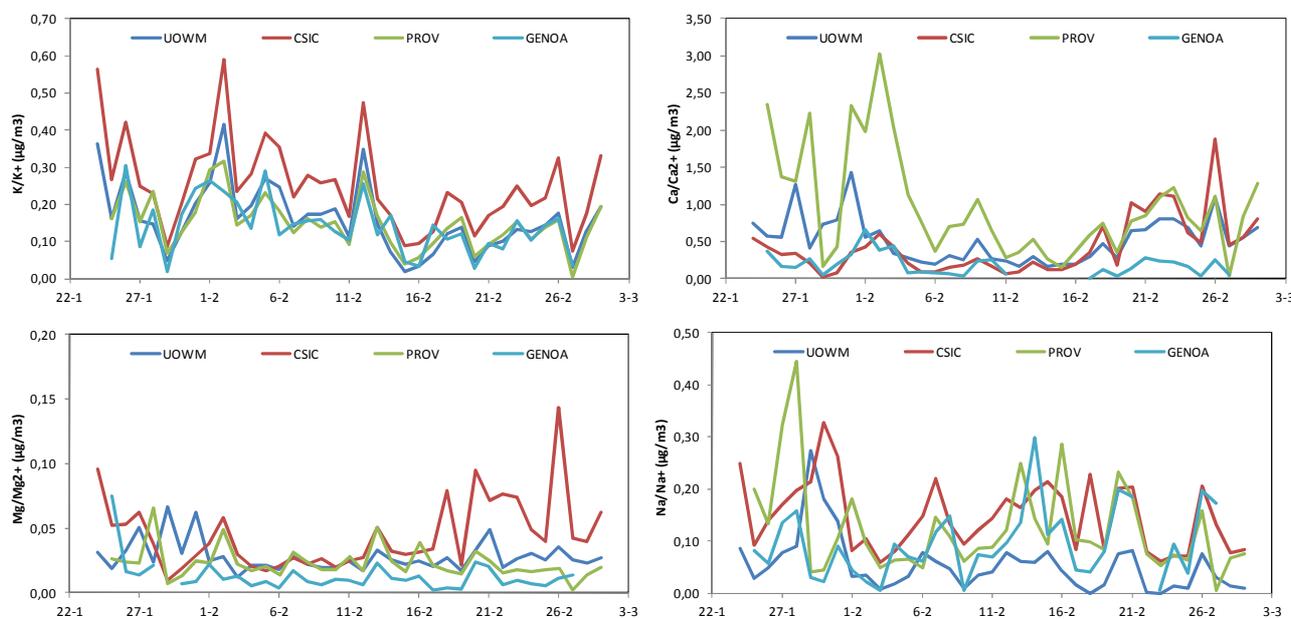
Figure 3.3: Daily concentrations (in µg m^{-3}) of K/K$^+$ (top-left), Ca/Ca^{2+} (top-right), Mg/Mg^{2+} (bottom-left) and Na/Na$^+$ (bottom-right)determined by the partners during the campaign.

Finally, IDAEA-CSIC (by using ICP-AES and ICP-MS), U. Genoa (by means of ED-XRF) and U. Provence (by means of ICP-MS) determined a number of additional elements (P, Fe, Pb, Cu, Zn, Ni, Ti, V, Cr, Mn). For most of these elements the results given by both laboratories are comparable (Table 3.1 and Figure 3.4). Only in few cases (P, V, Cr) some differences may be found. Probably the technique used by IDAEA-CSIC and U. Provence is more sensitive for determining such elements when they are in low concentrations. In Figure 3.4, typical tracers of emissions sources have been plotted: Fe for mineral matter; Cu for road traffic emissions; V for fuel oil combustion; and Pb for industrial emissions. As seen in this Figure 3.4, time variability and daily concentrations given by the partners are rather similar.
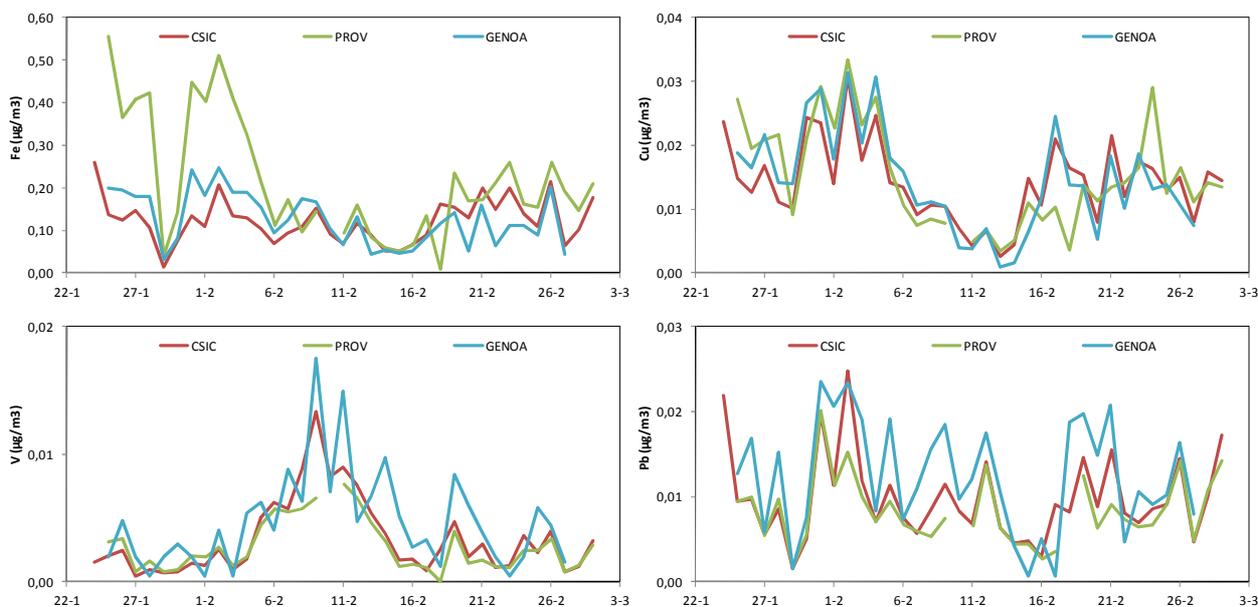
Figure 3.4: Daily concentrations (in µg m^{-3}) of Fe (top-left), Cu (top-right), V (bottom-left) and Pb (bottom-right)determined by the partners during the campaign.

4. Source apportionment intercomparison

4.1. PMF and CMB general description

Source apportionment (SA) models aim to re-construct the contribution of emissions from different sources of atmospheric pollutants, e.g., particulate matter (PM), based on ambient data registered at monitoring sites.
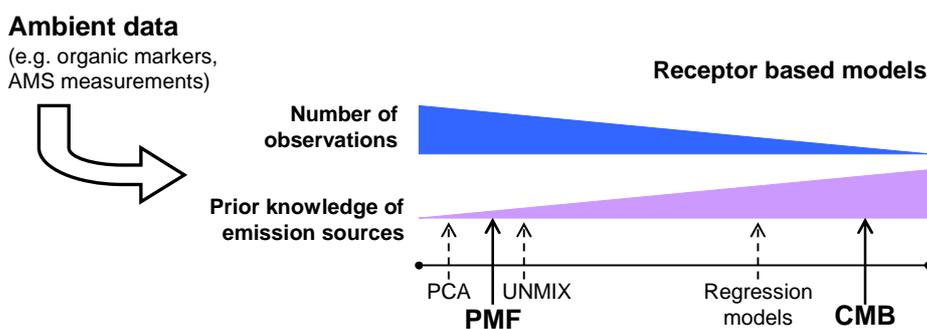
Figure 4.1: Main approaches used in the field of atmospheric chemistry to apportion sources (adapted from Viana et al. 2008). In bold the two approaches used in this study.

Figure 4.1 summarizes the main approaches used to apportion PM. The fundamental principle of receptor modelling is that mass and species conservation can be assumed and a mass balance analysis can be used to identify and apportion sources of airborne PM in the atmosphere (Viana et al, 2008). As shown in figure 4.1, one of the main differences between models is the degree of knowledge required about the pollution sources prior to the application of receptor models. A second major difference between these different approaches is the number of

14

observations (e.g., samples) needed to apportion sources. While **Chemical Mass Balance** (CMB) model can be used, in absolute, with only one sample, approaches such as **Positive Matrix Factorization** (PMF) needs a significant number of samples (at least equal to the number of chemical species included in the model) to provide statistically sound results.

PMF and **CMB** are the two approaches used here. As these two approaches are based on different concepts, direct comparison between these two methods can lead to misunderstandings and misinterpretations of the results presented in section 4.3.

4.1.1 Chemical Mass Balance model (CMB)

CMB modelling estimates source contributions by solving a system of linear equations in which the concentration of specific chemical constituents in a given ambient sample is described as arising from a linear combination of the relative chemical compositions of the contributing sources (Watson et al., 1998). Source-specific individual organic compounds are most often used in conjunction with the CMB model to apportion sources of primary OC. In this approach, the concentration of selected chemical marker i at receptor site k, C_{ik}, can be expressed as the following linear equation:

$$C_{ik} = \sum_{j=1}^{m} f_{ijk} a_{ij} s_{jk} \qquad [1]$$

where m is the total number of emission sources, a_{ij} is the relative concentration of chemical species *i* in fine OC emitted from source *j*, s_{jk} is the increment to total OC concentration at receptor site k originating from source *j* and f_{ijk} is the coefficient of fractionation that represents the modification of a_{ij} during transport from source *j* to receptor *k*. The fractionation coefficient accounts for selective loss of constituent *i* due to atmospheric processes such as chemical aging or gas-particle partitioning related to the dilution of the emissions. Atmospheric oxidation and dilution are non-linear phenomena, depending on numerous conditions including transport time, ambient temperature, oxidant concentration, etc., and can change drastically the fractionation coefficients (f_{ijk}) of the selected markers. These processes represent a very substantial complication to linear source apportionment techniques such as Chemical Mass Balance and the determination of the f_{ijk} coefficient is highly complicated. Accordingly, CMB modelling uses, as fitting species, key markers that are assumed to be non volatile and reasonably stable in the atmosphere, implying fractionation coefficients near unity for such species. In order to solve the set of linear equations generated by equation 1, an effective variance weighted least squares solution is used.

4.1.2 Positive Matrix Factorization (PMF)

PMF is a variant of Factor Analysis with non-negative factor elements. PMF attempts to apportion the sources on the basis of observations and their internal correlations at the receptor site alone. It is a factor analysis method with individual weighting of matrix elements. The PMF approach can be used to analyze 2-dimensional and 3-dimensional matrices. PMF solves the equation 2:

$$X = GF + E \qquad [2]$$

15

where X is the matrix of measured values (time series of the different fitting species), G and F are the factor matrices to be determined, and E is the matrix of residuals, the unexplained part of X. F and G represent respectively the contribution of each fitting species to a factor (e.g., source and/or processes) and the time series of the contribution of the different factors. In PMF, the solution is a weighted Least Squares fit, where the known standard deviations for each value of X are used for determining the weights of the residuals in matrix E. The objective of PMF is to minimize the sum of the weighted residuals. PMF uses information from all samples by weighting the squares of the residuals with the reciprocals of the squares of the standard deviations of the data values.

4.1.3 Summary

CMB model is based on the mass conservation of individual species and carbon from sources to the receptor sites. The mass conservation equations are written as the matrix product of unknown time series of source contributions and known source profiles equaling the time series of known concentrations of a set of marker species observed. Therefore the CMB model assumes knowledge of the chemical fingerprints of the emissions for all relevant sources. This last point is most of the time a critical issue. As CMB model apportion primary sources, the secondary fraction can not be apportioned directly. Secondary fraction of sulfate, nitrate, ammonium and organic aerosol can only be assessed by difference between measured (primary + secondary fractions) and calculated concentrations (primary fraction).

For **PMF**, the mass conservation equations are written as a matrix product of unknown time series of factor (e.g., sources and/or processes) contributions and unknown factors (to be determined and identified) equaling the times series of known concentrations of a set of marker species observed. The most difficult challenge in using PMF is determining the number of factor (ie sources) that are contributing to the PM collected at the receptor site and to identify these factors. The degrees of freedom in the PMF approach are contained inside the different factors and more precisely in the relative contribution of the different fitting species in each factor.

4.2. Methodology used by each partners

The aim of this intercomparison of source apportionment approaches was to keep totally free each partner to choose their own approach and fitting species. Source apportionment results obtained by the different partners of the project are fully described and commented in appendix II. A short description is given below.

4.2.1. Barcelona (IDAEA-CSIC)

The identification of the main PM sources and their contribution to PM_{10} and $PM_{2.5}$ during the intercomparison campaign in Marseille was carried out by a source apportionment analysis with Positive Matrix Factorization (PMF; Paatero and Tapper, 1994), through the computer program PMF2 (Paatero, 1997).

The PMF analysis was performed on 74 cases, including simultaneous daily PM_{10} and $PM_{2.5}$ filter samples, collected from 25/01/2011 to 01/03/2011.

Chemical species were selected according to Signal to Noise ratios (Paatero and Hopke, 2003), to the percentage of values above detection limits and to the database size requirements. For this analysis 22 species analyzed from the filter samples were selected, including Ca, K, Na, Mg, Fe, Mn, SO_4^{2-} (from ICP-AES); V, Ni, Cu, Zn, Sn, Sb, Pb (ICP-MS); NO_3^- (ion chromatography); NH_4^+ (ion selective electrode), and EC and five OC fractions (OC1, OC2, OC3, OC4 and Pyrolitic C) provided by the Sunset OCEC thermo-optical analyzer (EUSAAR2 protocol, Cavalli et al., 2010).

Individual uncertainties were calculated following the procedure described by Amato et al. (2009) and Escrig et al. (2009), taking into account the analytical uncertainty as well as the standard deviations of species concentrations in the blank filters.

Emission sources were identified by taking into account the PMF-resolved chemical profile and the variation explained by each factor for every species. Daily contributions of each source to PM_{10} and $PM_{2.5}$ were calculated by a multilinear regression analysis.

4.2.2. Genoa (Univ Genoa)

The source apportionment approach used by Genoa's group is PMF2 (Positive Matrix Factorization, version 2), an advanced receptor model, developed by Paatero (Paatero et al, 1994) that in the last years has been asserted to international level like most reliable. It is useful, especially, where detailed data do not exist on the composition of the main emission sources, but where large numbers of sampled data are available on ambient concentrations. The important advantage of the positive matrix factorization is the ability to handle missing data and values below the detection limits data by adjusting the error estimates of each data point. In fact, the solution to the PMF problem depends on the uncertainties attributed to each value. The concentrations values and their associated errors were treated according to Polissar et al. (Polissar et al, 1998). PMF was used in "robust mode".

For this approach, PM measured components used for PMF analysis included elements measures by ED-XRF, ions detected by ion chromatography (IC) and organic and elemental carbon measured by thermal-optical transmittance method (TOT). In the PMF data set, OC missing values were replaced using the mean OC/EC ratio with a large uncertainty. Variables were selected according to the signal-to-noise criterion (Paatero and Hopke, 2002) and 15 Variables were finally used in the analysis: Al, Si, P, K, Ca, V, Fe, Ni, Cu, Zn, SO_4^{2-}, NH_4^+, NO_3^-, OC and EC. Na and Cl turned out to be "bad" variables (are present in a low number of samples because of PM2.5 sampling were performed and Na values are available each two days). This prevented the possibility to resolve PM from sea salt.

The number of factors which was examined ranged from three to eight; five sources were resolved and labeled, according to their characteristic tracers, as follows: *Road* (traced by Cu), *Dust* (traced by Al, Si, Ca), *Industrial/Marin* (*Oil Combustion* traced by V, Ni), *Secondary Compound* (*Secondary I* traced by SO_4^{2-} and NH_4^+ and *Secondary II* traced by NO_3^- and NH_4^+).

4.2.3. Marseille (Aix Marseille Univ.)

The CMB source apportionment was computed using United States Environmental Protection agency EPA-CMB8.2 software, in conjunction with the effective variance least squares estimation method.

17

The source emission profiles selected for this study were : vehicular emissions, (El Haddad et al., 2009) ; heavy duty trucks emissions (Rogge et al., 1993a) ; biomass burning emissions (Fine et al., 2002) ; vegetative detritus emissions (Rogge et al., 1993b), and natural gas combustion (Rogge et al., 1993b). Considering the specific case of Marseille area, three industrial-emission-related profiles were also selected: metallurgical coke production (Weitkamp et al., 2005), HFO combustion/shipping (Agrawal et al., 2008) and steel manufacturing (Tsai et al., 2007).

In order to assess contributions from these aforementioned sources, were used as fitting species: levoglucosan, specific marker for biomass burning ; elemental carbon (EC) and three hopanes (*i.e.,* 17α(H),21β(H)-norhopane, 17α(H),21β(H)-hopane and 22S,17α(H),21β(H)-homohopane) as key markers for vehicular emissions ; C27-C32 n-alkanes, since this range demonstrates high odd-carbon preference that is specific to biogenic sources ; and four PAH (benzo[b,k]fluoranthene, benzo[e]pyrene, indeno[1,2,3-cd]pyrene, and benzo[ghi]perylene) and three metals (V, Ni and Pb), to apportion for industrial sources.

To insure a good quality control of CMB calculation results, we make sure that the statistical performance measures usually used in the CMB modeling meet their respective target values (*i.e.* R-square from 0.8 to 1.0, chi-square from 0 to 4.0, t-test above 2 and absence of cluster sources). Another requirement was for the marker's calculated-to-measured ratios (C/M) to match a target value fixed between 0.75 and 1.25, in order to provide reasonable bounds on CMB results.

As CMB can not apportion directly Sea salt and dust contributions, empirical approaches have been used for these two sources. Crustal dust contributions were then estimated using Malm et al. (1994) method based on concentrations of Al, Fe, Ca and Ti in PM samples. Sea salt were calculated according to Putaud et al. (2010) method, based on Cl^- and Na^+ concentrations in PM samples.

4.2.4. Thessaloniki (UOWM)

For the source apportionment analysis conducted from UOWM, Positive Matrix Factorization model (version 3.0) was used. The analysis was performed on 37 PM2.5 samples (provided by CSIC-IDAEA). From the available chemical analysis data, selected species were injected to the model:

- 8 selected PAHs: *Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[e]pyrene, Benzo[a]pyrene, Perylene, Indeno[cd]pyrene, Dibenzo[a,h]anthracene, Benzo[ghi]perylene*. Lighter PAHs were excluded from the analysis because of their volatility.
- 3 selected ions: NO_3^-, SO_4^{2-}, NH_4^+.
- 23 metals: *Al, Ca, K, Na, Mg, Fe, Mn, Ti, P, V, Cr, Ni, Cu, Zn, As, Rb, Sr, Sb, Cd, Sn, Pb, Li, Sb, La.*
- Organic and elemental carbon (*OC, EC*)

Data pre-treatment and analysis of input data included missing data and data below the detection limit replacement. Species with large analytical errors were excluded from the analysis. Species which presented low signal-to-noise ratio were characterized as "weak". The model was run for 3 to 10 factors, in a random seed and the optimal number of factors was six. Finally, bootstrap and Fpeak runs were conducted in order to examine the stability and the rotational ambiguity of the solution, respectively.

4.2.5. Venice (Arpav Veneto)

IDAEA group performed the source apportionment analysis also on the organic species measured by ARPAV. The source apportionment approach used by IDAEA group is PMF2 (Positive Matrix Factorization, version 2), an advanced receptor model, developed by Paatero (Paatero et al, 1994) that in the last years has been asserted to international level like most reliable. It is useful, especially, where detailed data do not exist on the composition of the main emission sources, but where large numbers of sampled data are available on ambient concentrations. The important advantage of the positive matrix factorization is the ability to handle missing data and values below the detection limits data by adjusting the error estimates of each data point. In fact, the solution to the PMF problem depends on the uncertainties attributed to each value. The errors associated to concentrations values were treated according to the procedure described by Amato et al. (2009) and Escrig et al. (2009).

In the presented PMF analysis, PM measured components included elements, ions, organic and elemental carbon measured by IDAEA group and targeted sum of the organic species described in Appendix 1: Even Alkanes (E-ALK: n-C(26-28-30-32)), Odd Alkanes (O-ALK: n-C(27-29-31-33)), Heavy PAH (H-PAH: Benzo(b)fluoranthene, Benzo(j+k)fluoranthene, Benzo(a)pyrene, Indeno(123-cd)pyrene, Dibenz(a,h)anthracene, Benzo(ghi)perylene), Hopanes (HOPA: 17alpha(H)-22,29,30-Trisnorhopane, 17alpha(H),21beta(H)-30-Norhopane, 17alpha(H),21beta(H)-Hopane, 17alpha(H),21beta(H)-22S-Homohopane, 17alpha(H),21beta(H)-22R-Homohopane) and DeHydro Abietic Acid (DHAA) measured by ARPAV.

Variables were selected according to the signal-to-noise criterion (Paatero and Hopke, 2003) and 21 Variables were finally used in the analysis: Ca, Na, Mg, Fe, SO_4^{2-}, V, Ni, Cu, Zn, Sn, Sb, Pb, NO_3^-, NH_4^+, EC, OC, E-ALK, O-ALK, H-PAH, HOPA, DHAA.
Seven sources were resolved and labeled, according to their characteristic tracers, as follows: *Dust* (traced by Ca), *Road* (divided into *Vehicular exhaust + Sea Spray* (traced by Cu, Zn, EC and Na) and *Road Dust* (traced by Sb and Sn), *Industrial/Marine* (*Oil Combustion*, traced by V, Ni), *Secondary Compound* divided into *Secondary I* (*traced* by SO_4^{2-}) and *Secondary II* (traced by NO_3^-) and *Residential* (*Biomass Burning*, traced by DHAA).

4.3. Intercomparison of source apportionment approaches

As described section 4.2 and in appendix II, many sources or source types have been identified and quantified. Some of them can directly be compared some of them not directly. In order to intercompare the results of source contributions or source types have been classified onto 5 source groups. This classification has been elaborated in collaboration with modelers in order to allow a direct comparison of source contributions with models outputs. The 5 source groups are:
- **Road (direct and indirect emissions from traffic),**
- **residential,**
- **primary natural,**
- **Industrial and shipping emissions,**
- **secondary sources** (ie mass of the aerosol formed in the atmosphere from gaseous precursors).

The classification of sources and source types derived from each source apportionment approach onto these 5 source groups is summarized in table 4.1. Table 4.1 also summarizes the model and fitting species used by each partner.

Table 4.1: Summary of source apportionment approaches used by each partner and correspondences between source and source type derived from each source apportionment analysis and source groups.

Pilot area	Barcelona	Genoa	Marseille	Thessaloniki	Venice
Partners	IDAEA-CSIC	Univ Genoa	Aix Marseille Univ.	UOWM	Univ Genoa and IDAEA-CSIC on behalf of ARPA Veneto
Model used	*PMF*	*PMF*	*CMB*	*PMF*	*PMF*
Species included	22 variables : Ca, K, Na, Mg, Fe, Mn, SO_4^{2-} ; V, Ni, Cu, Zn, Sn, Sb, Pb, NO_3^-, NH_4^+, EC and five OC fractions (OC1, OC2, OC3, OC4 and Pyrolitic C)	15 variables : Al, Si, P, K, Ca, V, Fe, Ni, Cu, Zn, SO_4^{2-}, NH_4^+, NO_3^-, OC and EC	23 variables : 4 PAHs, 6 n-alkanes, 3 hopanes, levoglucosan, OC, EC, V, Ni and Pb for CMB and Al, Ca, Fe, Ti, Na^+ and Cl^- for crustal dust and sea salt	37 variables : 8 PAHs, SO_4^{2-}, NH_4^+, NO_3^-, Al, Ca, K, Na, Mg, Fe, Mn, Ti, P, V, Cr, Ni, Cu, Zn, As, Rb, Sr, Sb, Cd, Sn, Pb, Li, Sb, La, OC and EC	21 Variables : Ca, Na, Mg, Fe, SO_4^{2-}, V, Ni, Cu, Zn, Sn, Sb, Pb, NO_3^-, NH_4^+, EC, OC, E-ALK, O-ALK, H-PAH, HOPA, DHAA.
Number of factors/sources	7	5	8 source profiles plus Sea Salt and Dust	6	7

Source group	Source and source types derived from Source Appotionment analysis				
Road	Vehicular exhaust, Road Dust	Road	Vehicular*	Road Dust	Vehicular Exhaust+Sea spray, Road dust
Residential	Biomass burning		Biomass burning vegetative detritus (incomplete combustion of wax alkanes) and natural gas combustion.	Residential combustion	Residential
Industrial and Shipping	Fuel Oil Combustion	Industrial/Marine	Coke Production, HFO Combustion/shipping, Steel manufacturing	Marine-Shiping emissions/industriy	Industrial/marine
Primary natural	Aged Sea Spray, Mineral/industrial	Dust	Sea Salt, Dust	Natural sea salt,	Dust
Secondary	Secondary aerosol	Secondary I Secondary II	Secondary amonium, nitrate and suflate and other OM	Secondary aerosols	Secondary I, Secondary II

PMF approach has been chosen by 4 partners (IDAEA-CSIC, Univ. Genoa, UOWM, and ARPA Veneto) while CMB has been used by one partner (Aix Marseille Univ.). PMF source apportionments also used different set of variables (fitting species, Table 3.1) mixing metals/trace elements, sulfate, nitrate, ammonium, OC (Organic Carbon), EC (Elemental Carbon). Organic markers have also been injected in the ambient data matrix for the pilot area of Venice. Note that IDAEA-CSIC introduced the different fractions of OC derived from thermograms (OC1, OC2,.., pyrolitic carbon) as additional variables in order to provide information on the physico-chemical properties of the organic fraction ; which represents more than 50% of the total PM2.5 mass. CMB approach as been performed using the combination of organic markers and metals as previously developed and optimized in Marseille by El Haddad et al (2011).

Each of these source apportionment approaches allows the characterization and the quantification of all source groups. Only residential source group has not been identified and quantify by source apportionment performed by Univ. Genoa. As discussed below residential sources are, in this case, included in the road source.
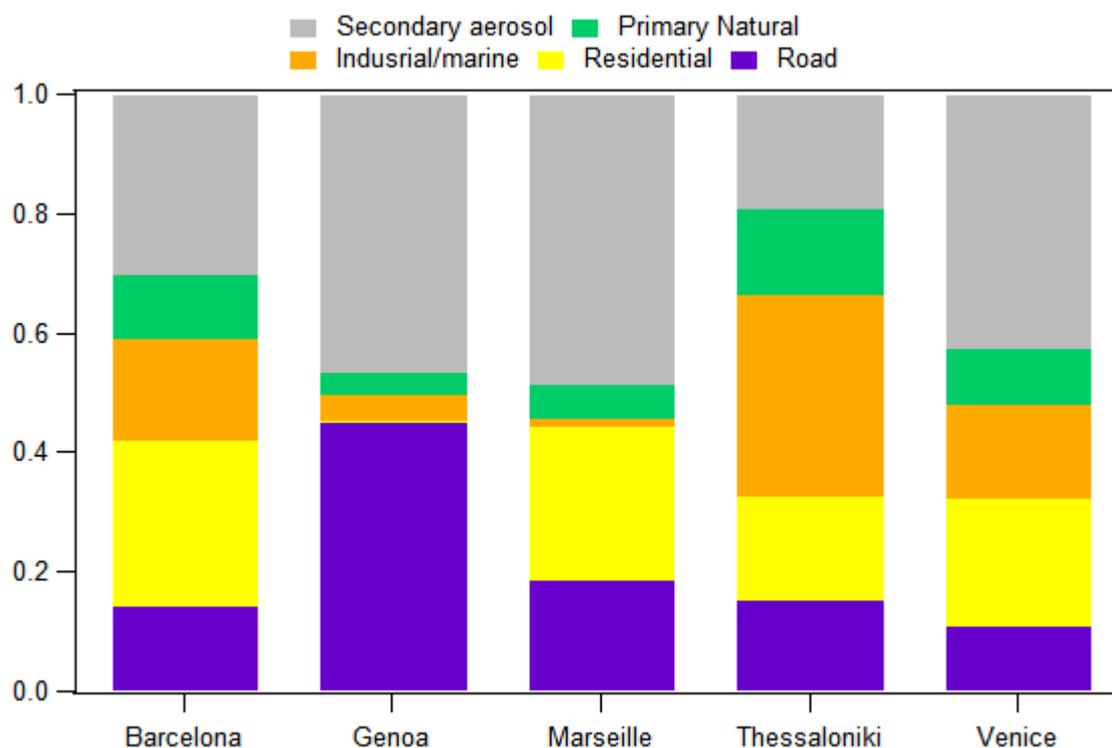
Figure 4.2. : Average relative contributions of source groups to PM2.5

Table 4.2: Absolute concentrations of PM2.5 ($\mu g/m^3$) originating from the different source groups

$\mu g/m^3$	Barcelona	Genoa	Marseille	Thessaloniki	Venice
Road	4.7	11.7	5.0	5.1	3.5
Residential	9.1	nd	6.8	5.6	7.0
Industrial and Shipping	5.6	1.3	0.4	11.2	5.0
Primary natural	3.5	0.9	1.5	4.6	3.1
Secondary	9.9	12.0	13.0	6.3	13.8

Average concentrations and relative contributions of each source group quantified by each partners are presented in table 4.2 and figure 4.2, respectively. An apparent significant discrepancy can be observed. However considering the conditions of the intercomparison exercise (different data set, and partners totally free to use its own methodology), the relatively small number of observations and the difficultly associated to source apportionment assessment, results obtained can be consider in relatively good agreement. Only some sources present significant discrepancy between partners.

Road emission sources (direct and indirect emissions) contributions range from 3.5 to 11.7 $\mu g/m^3$, representing from 11 to 45% of the PM2.5 mass. However this range is biased by the contribution calculated by Univ Genoa (11.7 $\mu g/m^3$). In this case PMF do not allow apportioning any residential sources (wood burning, in particular). Considering that the Road factor identified in this approach (Annex II.2) is mostly driven by organic materials (OC and EC), that vehicular exhaust and wood burning are both largely dominated by organics and that no variables providing

insights into the chemical nature of this fraction have been injected in this specific source apportionment exercise, we can consider that the Road factor represents, in fact, the sum of residential and road sources. This assumption is also supported when comparing the sum of these 2 source groups between all partners. The sum of the contributions of residential and road sources are very homogeneous between partners, ranging from 10.6 to 13.8 µg/m^3.

Residential sources are quasi exclusively related to wood burning sources. The contributions of other sources such as natural gas combustion or cooking activities are negligible when they have been identified. The identification of wood burning is unambiguous since this source is traced by very specific molecular markers (levoglucosan or dehydro abietic acid). A good agreement is found between partners. Contributions of residential sources range from 5.6 to 9.1 µg/m^3. Again a partial overlap between residential and road sources can not be excluded for PMF approaches using no specific markers for wood burning sources. We shall note that the use of the different fractions of OC derived from its thermal properties (OC1, OC2,..,pyrolitic C) provide very promising results to differentiate vehicular emissions from wood burning sources.

Primary natural source group (mainly sea salt and dust) can be regarded as in reasonable agreement between partners taking into account the different approaches and data set used. Contribution of primary natural sources ranged from 0.9 to 4.6 µg/m^3.

For **industrial** and **secondary** factors the situation is a little bit different and these two factors must be considered together in the discussion. Industrial sources contribution shows a high discrepancy between partners and approaches ranging from 0.4 to 11.7 µg/m^3 (ie from 1 to 34% of PM2.5 mass). If 1% can be consider as low and within the uncertainty range of the method used (CMB), 34% can not be regarded as a relevant contribution for industrial and shipping emissions. On the same way, contributions found by IDAEA-CSIC (Barcelona, 17%) and UOWM (Thessaloniki, 15%) should be considered as overestimated taking into account previous studies realized in Marseille and its surroundings. The reason of these higher contributions estimated from the PMF model runs is most probably linked to dynamic processes. As PMF approach is based on the internal variability of the data set, atmospheric dynamics (advection of air masses or boundary layer height) can play a major role on the identification and the quantification of the different factors. Marseille is downwind the industrial area during particular wind conditions: mistral (NW winds). Mistral is canalized by the Rhône valley (a heavily urbanized and industrial area), bringing to Marseille in most cases (when moderate winds) high loads of secondary aerosol particles. Such conditions have been observed during the campaign. Therefore, a significant fraction of the secondary aerosol particles from medium and long range transport episodes have been included in the industrial factor by the PMF approach. As for road and residential sources, this assumption is supported by the fact that the sum of industrial and secondary sources are in pretty good agreement between partners, ranging from 13.4 to 18.8 µg/m^3.

Temporal trends of the contributions of the different source groups are presented in figure 4.3. Taking into account the previous discussion regarding average contributions, we observed a good agreement between partners. Only primary natural sources exhibit significant discrepancy in terms of temporal evolution, but we have to keep in mind that markers for these sources (mainly calcium and sodium) shows the highest variability among all the measured species (see section 3). Temporal trends also support the assumptions of a partial or total overlap of road and residential sources, in one hand, and industrial and secondary sources, in the other hand. The road source contribution calculated by Univ. Genoa is indeed particularly high during the first two weeks of the field campaign; period in which residential sources are at their highest (impact of nocturnal breezes, see section 2). For industrial and secondary sources we also observed that the highest

contribution of industrial sources correspond to high loadings of secondary aerosol (especially from 02/05 to 02/15/2011, figure 4.3).
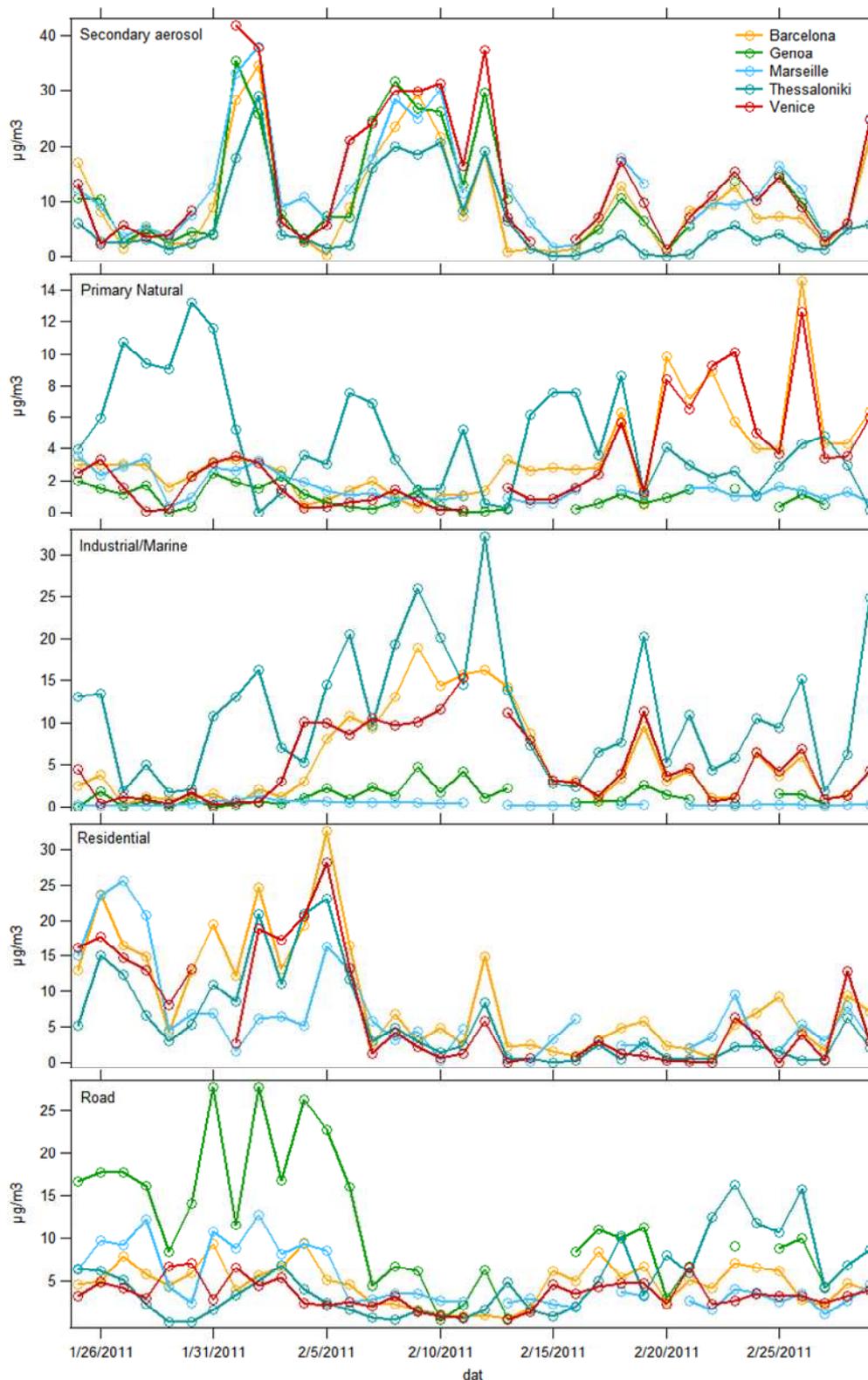
Figure 4.3.: temporal evolution of the contributions ($\mu g/m^3$) of the different source groups quantified.

5. Conclusions and perspectives

Within the framework of APICE the aim of the intercomparison campaign was to compare the source apportionment outputs of each scientific group involved in the long monitoring campaign carried out in each pilot area. Each partner was totally free to use his own methodology (measurements and source apportionment model). As expected, significant discrepancies are observed. However these discrepancies regard mostly the average contribution of some sources while the temporal trends are in fair agreements. Differences can also be linked quite easily to the methodology used, either regarding the choice of fitting species or source profiles, either considering biases induced by the dynamic of the atmosphere (particularly important considering the number of observations).

In order to converge towards a homogenous methodology between each pilot area, our recommendations are as follows:

1/ **Use of the same source apportionment approach**. The source apportionment approach chosen is PMF (Positive Matrix Factorization). In consequence, Aix Marseille Univ will also use PMF in addition to CMB,

2/ **Use of a common basis of chemical markers as fitting species**. The chemical markers list will include trace elements/metals and organic markers or at least the different carbon fractions (OC1, OC2,.., Pyrolitic Carbon), in addition to OC, EC, sulfate, nitrate and ammonium. The list of chemical markers will be defined by the partnership after a careful study of the chemical data obtained during the long monitoring campaigns. Some additional markers may be added to the list in each pilot area in order to take into account the specificity of each pilot area,

3/ **Common interpretation of the different factors identified in each pilot area**.

Currently, a vast intercomparison exercise of source apportionment approaches is conduced at the European level, in which some partners of the project APICE are associated. The results obtained within APICE long monitoring campaigns will also directly benefit from this European intercomparison exercise in terms of methodological harmonization.

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Appendix I : Intercomparison of organic markers

The quantification of organic markers completes the chemical characterisation of the daily PM$_{2.5}$ samples (from 14:00 to 14:00) collected in Marseille from the 25th of January to the 1st of March presented in the first progress report.

Several organic markers were measured by the partners according to their specific detection list:

1. University of Provence: 15 PAH, 15 linear alkanes (from n-C19 to n-C33) and 12 others (6 hopanes, 5 phthalates and levoglucosan);

2. UOWM Thessaloniki: 27 PAH;

3. ARPAV ORAR: 22 PAH, 24 linear alkanes (from n-C17 to n-C40) and 14 others (6 hopanes, 6 steranes and 2 biomass burning tracers as estimate).

The common quantification technique was Gas Chromatography Mass Spectrometry (GC-MS) for all the partners, but sample preparation and organic marker extraction were different. UOWM Thessaloniki and University of Provence Marseille performed liquid extraction (LE) and Accelerated Solvent Extraction (ASE) respectively, whereas ARPAV ORAR adopted the Direct Thermal Desorption (DTD) of the sample without any preparation.

A numerical overview of the obtained results is presented in Table AI.1 where the daily average concentrations (ng/m^3) of the 32 organic markers commonly measured by each partner are presented. The concentration level of the PAH and the lighter linear alkanes (up to n-C22) was relatively small and indicatively below 1 ng / m^3. The highest concentrations were recorded for the heavier alkanes from n-C23 onward. Furthermore the highest average concentrations were those of the odd carbon number alkanes (n-C27 to n-C33, last raws in the table). The concentration of these odd number alkanes was 2.6 times greater than the corresponding even carbon number alkanes (n-C26 to n-C32) revealing the typical emission profile, and significant presence, of biomass burning sources. The hopanes concentrations were relatively small according to the background nature of the sampling site. They are diagnostic biomarker indicators and useful as proof of the origin in oil spill analysis, oil waste analysis and in our case in the assessment of the airborne particulates originated from combustion processes of heavy fuels or lubricants.

Class	Organic Marker	All Labs	Univ. Provence Marseille	ARPAV Venice	UOWM Thessaloniki
	PM$_{2.5}$ Sampling volume		High	Low	High
	Extraction technique		ASE*	DTD*	LE*
		Average daily concentration (ng/m^3)			
PAH	Phenanthrene	0.2	0.1	0.3	0.2
	Anthracene	0.0	0.0	0.1	0.0
	Fluoranthene	0.4	0.3	0.4	0.5
	Pyrene	0.4	0.3	0.4	0.4
	Benzo[a]anthracene	0.6	0.6	0.5	0.6
	Chrysene / Triphenylene	0.9	1.0	0.7	0.8
	Benzo[b,k]fluoranthene	1.4	1.1	1.3	1.9
	Benzo[e]pyrene	0.8	1.4	0.5	0.7
	Benzo[a]pyrene	0.7	1.1	0.4	0.6
	Indeno[1,2,3 - cd]pyrene	1.0	1.8	0.2	0.8
	Dibenzo[a,h]anthracene	0.3	0.7	0.1	0.1
	Benzo[ghi]perylene	0.6	1.2	0.1	0.6
Alkanes	Nonadecane (C19)	0.3	0.3	0.4	
	Eicosane (C20)	0.5	0.4	0.6	
	Heneicosane (C21)	0.7	0.7	0.7	
	Docosane (C22)	1.7	1.9	1.6	
	Tricosane(C23)	3.2	3.1	3.2	
	Tetracosane (C24)	3.4	3.3	3.6	
	Pentacosane (C25)	4.2	4.5	4.0	
	Hexacosane (C26)	3.4	4.1	2.6	
	Octacosane (C28)	3.8	4.9	2.8	
	Triacontane (C30)	4.0	5.4	2.6	
	Dotriacontane (C32)	3.9	6.0	1.9	
	Heptacosane (C27)	5.1	6.7	3.6	
	Nonacosane (C29)	10.2	13.7	6.7	
	Untriacontane (C31)	12.9	17.9	7.9	
	Tritriacontane (C33)	11.6	18.6	4.6	
Hopanes	17α(H) trisnorhopane (C27)	0.2	0.3	0.1	
	17α(H) - 21β(H)- norhopane (C30)	0.5	0.7	0.3	
	17α(H) - 21β(H)- hopane (C29)	0.5	0.6	0.4	
	17α(H) - 21β(H)-22S - homohopane (C31)	0.4	0.5	0.3	
	17α(H)-21β(H)-22R-Homohopane (C31)	0.3	0.4	0.2	

Table AI.1. Organic markers commonly measured by partners in the intercomparison campaign.

PAH

A comparative time series of the total PAH daily concentration of the compounds reported in Table AI.1 (omitting Phenantrene and Anthracene) is shown in figure AI.1. The results of each partner are plotted along with the PAH concentration estimate obtained with the on line instruments available during the monitoring campaign: the High Resolution Time of Flight Aerosol Spectrometer (AMS) and the Photoelectric Aerosol Sensor (PAS), their continuous measurements were averaged to appropriate 24 hours values.
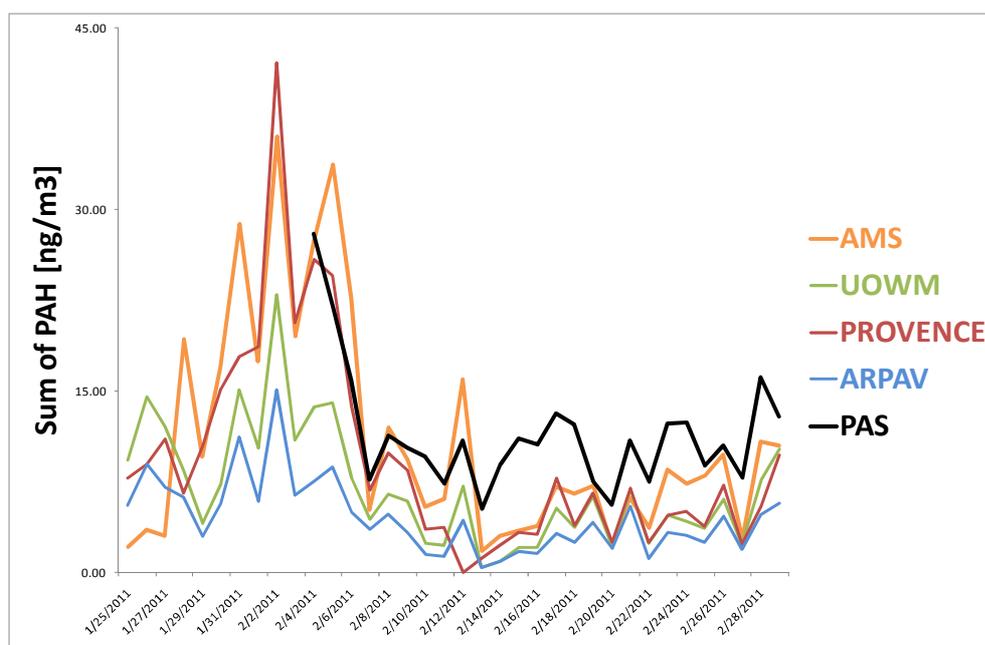
Figure. AI.1. Time trends of the sum of PAH concentration values provided by different measurements including the average daily values obtained with the online analysers AMS and PAS

A common time trend is shared among all instruments and technique for the entire period of the campaign, however during the days from the 28th of January to the 6th of March concentrations obtained by UOWM and ARPAV are clearly lower than those measured by the University of Provence, such a discrepancy is not found in the rest of the monitoring campaign. A specific matrix effect of the samples that lowered the extraction efficiency of PAH (and n-alkanes see below) of both the liquid extraction and the direct thermal desorption could be a key factor. Since The AMS values support the results from the University of Provence and already revealed (see section 2) those days as the richest in organic fraction of all the campaign, the hypothesis of a sample matrix effect gains confidence. The PAS concentration values are intrinsically higher as the sensor measure also heavier (larger) PAH that cannot be determined with the other techniques.

Alkanes and hopanes

A common time trend was found by ARPAV and the University of Provence for alkanes and hopanes. Similarly to the the PAH a marked matrix effect affected the alkanes concentrations in the first half of the campaign resulting in higher concentration obtained on samples processed with the accelerated solvent extraction. In the second half of the monitoring period a very good agreement was found (Figure AI.2). The hopanes concentration values were in good agreement for the entire campaign and did not suffer of the overestimation showed by PAH and alkanes.
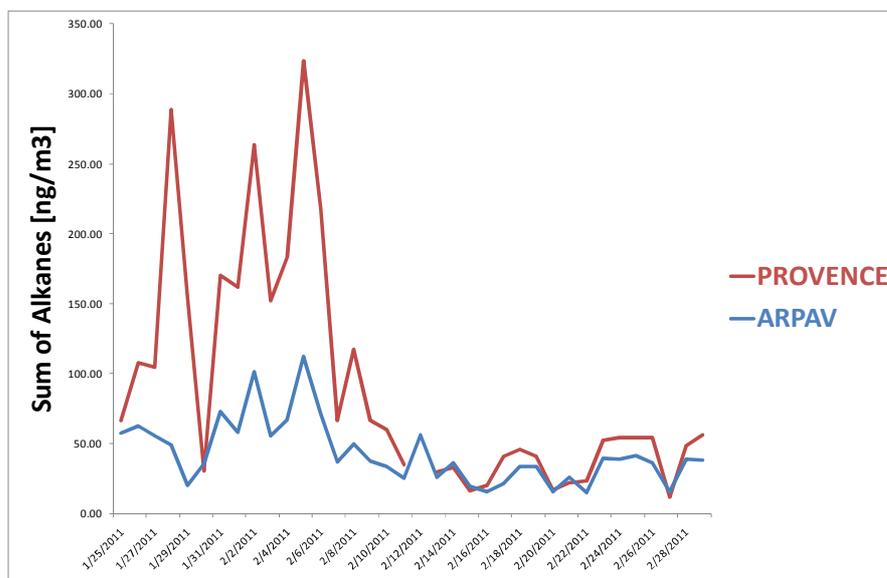
Figure. AI.2. Time trends of the sum of the linear alkanes from n-C19 to n-C33
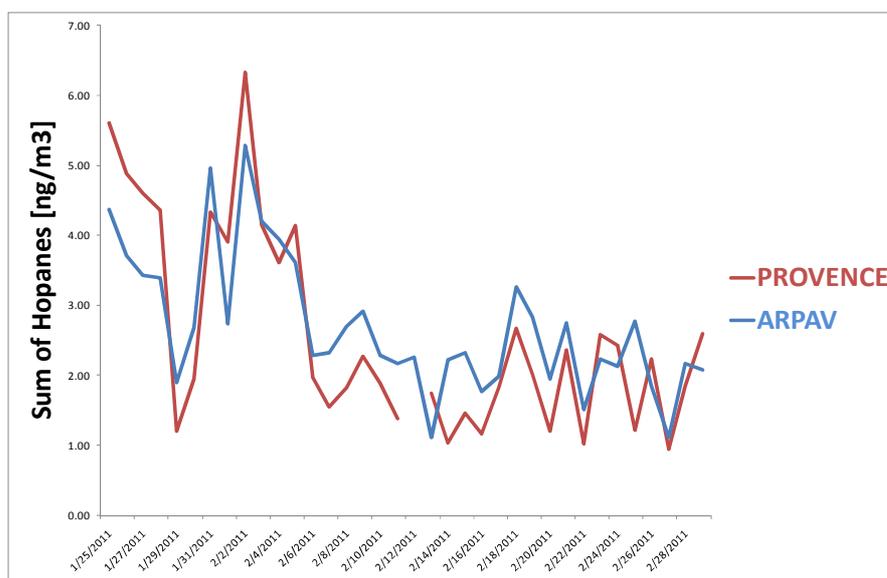
Figure. AI.3. Time trends of the sum of the 5 hopanes concentration values.

Appendix II.1 : Source apportionment results (IDAEA-CSIC, Barcelona)

1. Identification of emission sources

Emission sources were identified by taking into account the PMF-resolved chemical profile and the variation explained by each factor for every species. Since the PMF analysis was performed on a single dataset including simultaneous PM_{10} and $PM_{2.5}$ data, the same source profiles were obtained for both size fractions. The source profiles identified, together with the explained variation for each species by each factor are shown in Figure AII.1.1.

The best solution was found for 7 factors, including:

- Vehicular exhaust, representing emissions from vehicle engines. This factor is traced by EC, the three organic carbon fractions with higher volatility (OC2, OC3 and OC4), and Cu.
- Road dust, characterized by the presence of Ca, Mg, Fe, Mn, Cu, Zn, Sn and Sb. This factor is attributed to the resuspension of particles deposited on the road pavement by traffic. These particles originate from the degradation of the road pavement and vehicle components, such as brake pads or tires.
- Biomass burning, identified by the presence of K and all the OC fractions (OC1, OC2, OC3, OC4 and pyrolitic C), being the explained variances higher for the more volatile OC fractions.
- Fuel oil combustion, traced by the presence of V and Ni. This factor reflects emissions from industrial combustion processes, such as refinery activities, as well as shipping exhaust emissions. A high contribution from secondary sulfate was also found, probably representing emissions of sulfate precursors from the same source.
- Mineral/industrial, characterized by the presence of crustal elements, such as Ca and Mg, but also Pb, EC and some OC fractions (OC2, OC3 and OC4). This factor probably acounts for several sources of natural (soil resuspension) and anthropogenic mineral matter (excluding road dust). Pb appears in this factor probably because it accounts for mineral matter mixed with tracers from the industrial areas. To clarify this a more detailed analysis on wind directions should be done.
- Aged sea spray, traced by Na. Sea spray emissions were higher than the sum of Na and Cl^- concentrations because of the contribution of secondary aerosols to this factor. Aging is caused by the interaction of sea spray and gaseous pollutants during transport of air masses to the monitoring site.
- Secondary aerosols, characterized by the presence of SO_4^{2-}, NO_3^-, NH_4^+, and the most volatile OC fractions (OC1 and pyrolitic C).
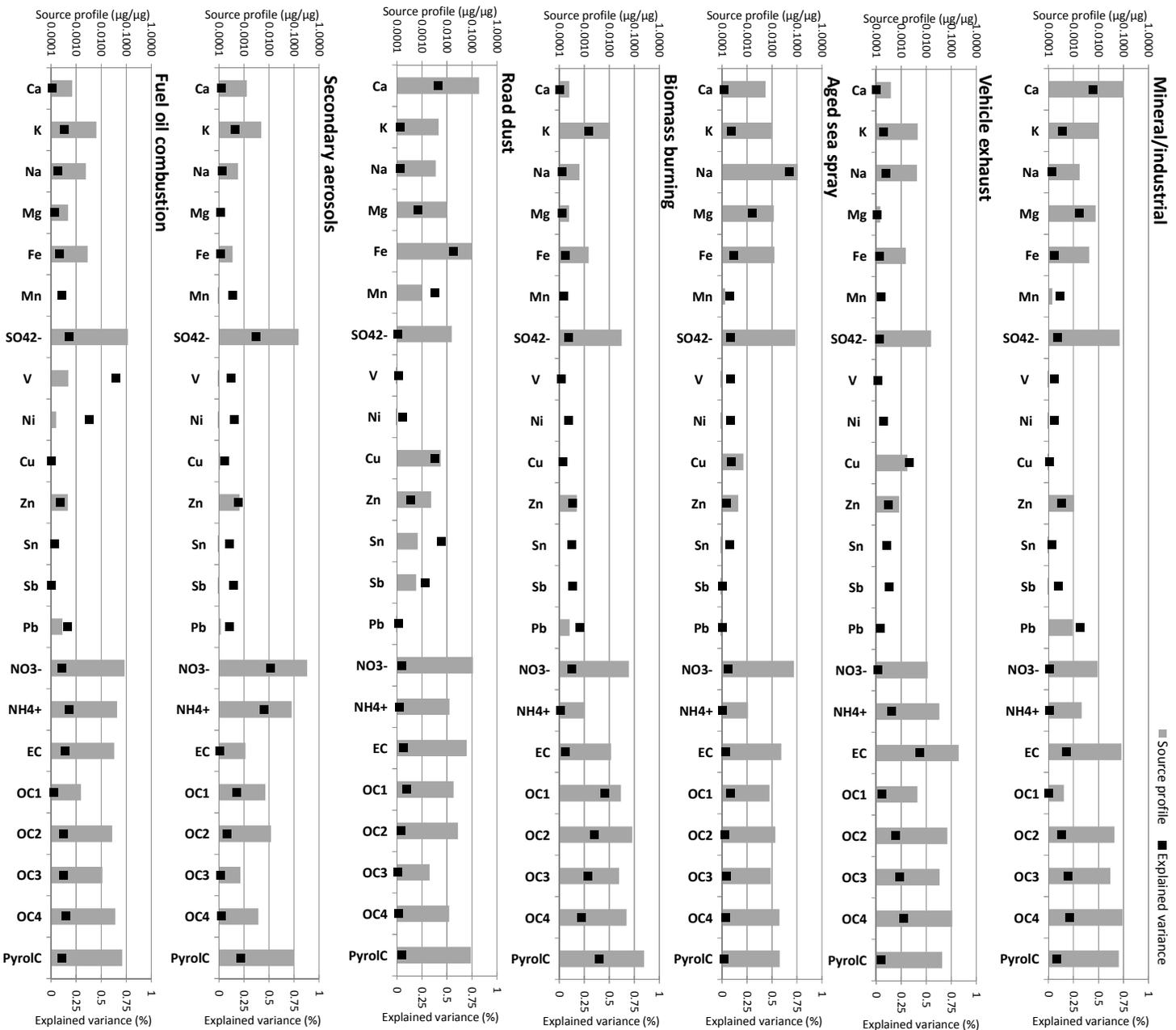
Figure AII.1.1. Source profiles for the seven factors obtained in the analysis

2. Quantification of source contributions

Daily contributions of each source to PM_{10} and $PM_{2.5}$ were calculated by a multilinear regression analysis. There was a good correlation between PM concentrations simulated by PMF and the measured gravimetric PM_{10} and $PM_{2.5}$ levels (Figure AII.1.2). Almost 100% of the PM_{10} and $PM_{2.5}$ mass was simulated in the analysis.
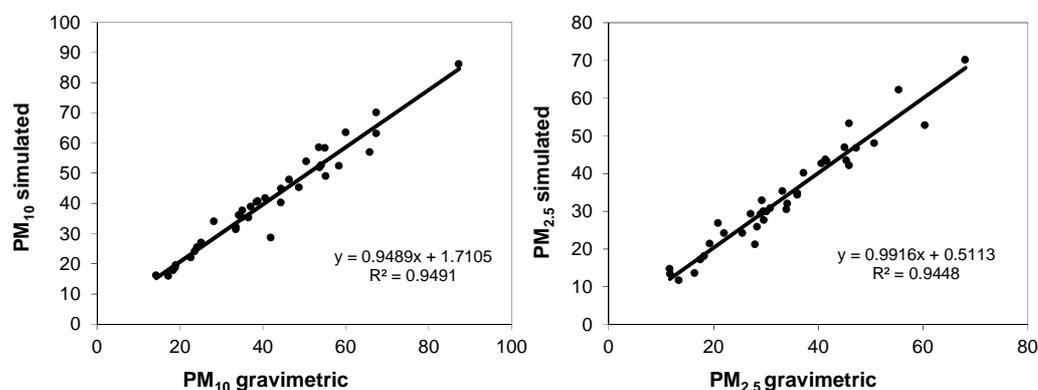
Figure AII.1.2. Correlation between PM_{10} and $PM_{2.5}$ concentrations measured and simulated with PMF

The average contributions of the factors obtained for PM_{10} and $PM_{2.5}$ are shown in Table AII.1.1 and Figure AII.1.3. Residential emissions (biomass burning) and secondary aerosols presented the highest contributions, being mostly in the $PM_{2.5}$ size range. Biomass burning was 19% of PM_{10} and 30% of $PM_{2.5}$, while secondary aerosols were 25-29%. Emissions from road traffic, including vehicular exhaust and road dust emissions, presented also high contributions, with vehicle exhaust being mostly in $PM_{2.5}$ (10-13%) and road dust in the coarse size range (9% in PM_{10} and 2% in $PM_{2.5}$). Fuel oil combustion was mostly fine, presenting also a high contribution (14-16%) owing to the presence of secondary aerosols in this factor. Primary natural emissions were coarser in size, being mineral/industrial 12% of PM_{10} and 8% of $PM_{2.5}$, and aged sea spray 10% of PM_{10} and 3% of $PM_{2.5}$.

Table AII.1.1. PMF average contributions of the seven factors obtained grouped by main categories

		PM_{10}		$PM_{2.5}$	
		µg/m³	%	µg/m³	%
Road	Vehicle exhaust	4.2	10	4.2	13
	Road dust	3.7	9	0.6	2
Residential	Biomass burning	7.8	19	10.0	30
Industrial/marine	Fuel oil combustion	5.9	14	5.5	16
Primary Natural	Mineral/industrial	4.9	12	2.7	8
	Aged sea spray	4.3	10	0.9	3
Secondary inorganic	Secondary aerosols	10.2	25	9.8	29
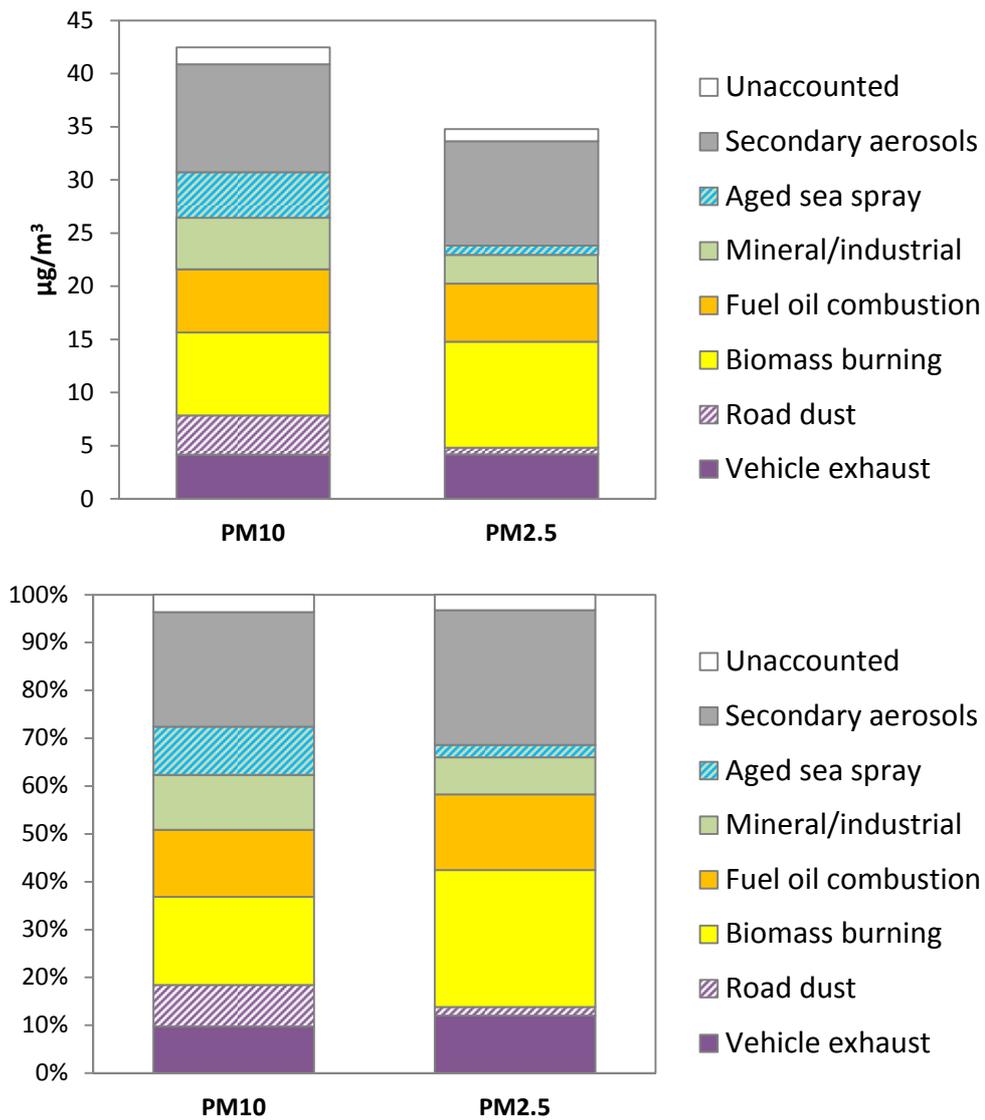
Figure AII.1.3. Average contributions of the seven sources obtained to PM$_{10}$ and PM$_{2.5}$

3. Temporal trends

The temporal variation of the source contributions to PM_{10} and $PM_{2.5}$ are shown in Figure AII.1.4. The Biomass burning and Secondary aerosol sources presented higher contributions in the first half of the campaign and they were reduced towards the end. The contribution of fuel oil combustion emissions increased during the central part of the campaign. The contribution of road traffic emissions, including vehicular exhaust emissions and road dust, were higher at the beginning and the end of the campaign, but reduced during the central part. The contributions of the mineral/industrial factor were higher at the beginning and the end of the campaign for PM_{10}, but the levels increased towards the end of the campaign for $PM_{2.5}$. Further analysis of wind directions should be done in order to understand the possible origins of the pollutants that reached the monitoring site during the intercomparison campaign.
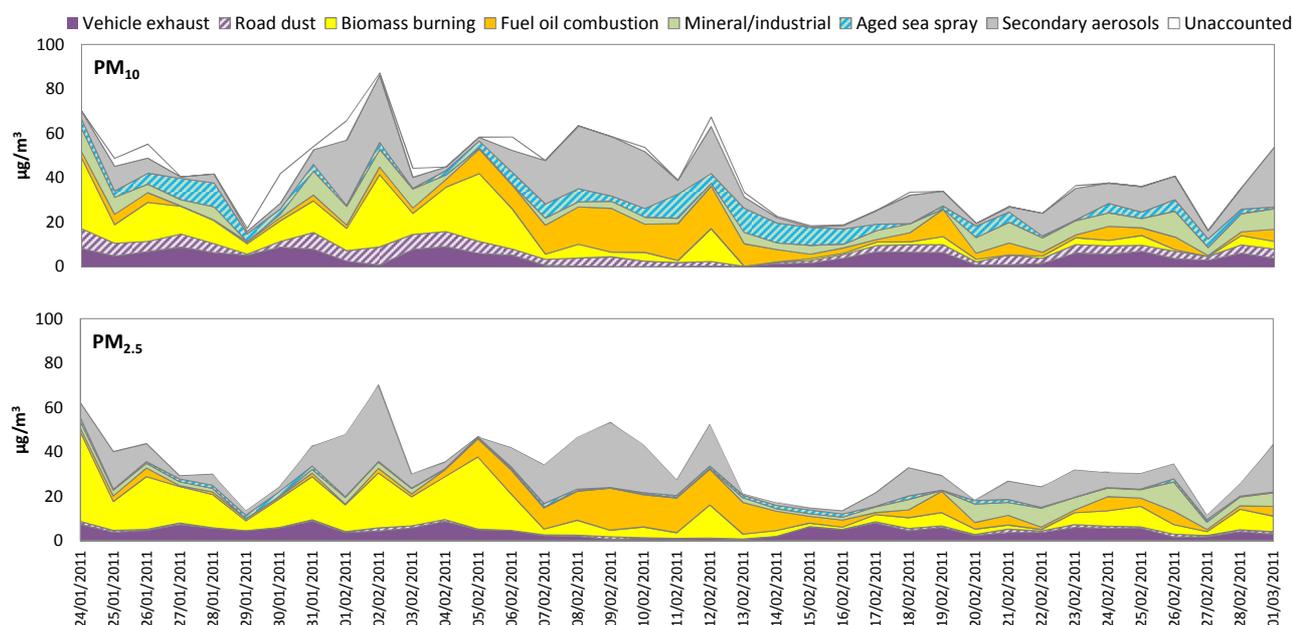
Figure AII.1.4. Temporal trends of the contribution of the main sources obtained in the PMF analysis

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Appendix II.2 : Source apportionment results (Univ Genoa, Genoa)

1. Methodology of sampling and methods of analysis

During the experimental campaign, carried out in Marseille from 25/1/2011 to 28/02/2011, PM2.5 sampling was performed. The filters (54 samples) were collected by standard Low Volume (Tecora), on 47 mm Quartz and Teflon filters, changed and alternated every 12 hours still beginning at 2.00 pm. Our sampling are different from all the other groups/Institutions for the type of filters and the time-basis of PM sampling.

The compositional analysis, performed by Genoa's group for samples collected in this campaign, was conducted with different chemical-physical methods and PM compounds measured are:

- **18 elements:** *Na, Mg, Al, Si, P, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Mo, Pb*
- **8 ions:** Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^+, Ca^{2+}
- **Organic & Elemental Carbon:** *OC, EC*

Elemental concentrations were obtained with Energy Dispersive X- ray Fluorescence, **ED-XRF**, a widespread and versatile technique for the quantification of the elements present in a sample, and even traces therefore (Tsuji et al, 2004) but with atomic number Z>10. ED-XRF is based on the ionization of the inner atomic shells obtained by irradiating the samples with electromagnetic radiation: inner shell vacancies get promptly filled by outer shell electrons, with the release of radiant energy. During the de-excitation, energy is released under the form of fluorescence in the X-band: emitted photon energies equal the energy differences between outer and inner shells, and thus carry the signature of the emitting atom. The peak positions in the energy spectrum allow the identification of the elements present in the sample and the peak areas are proportional to concentrations.

Ionic fraction was analysed with **Ion Chromatography**, in collaboration with "Dipartimento di Chimica Inorganica, Metallorganica e Analitica dell'Università degli Studi di Milano". Ion Chromatography (IC) is a physical-chemical separation technique that provides quantitative analysis of inorganic ions from a complex mixture. IC combines features of ion exchange, liquid chromatography, eluent suppression, and quantitative detection. IC has multispecies capabilities, small sample requirements, and the detectors have high sensibility, variable selectivity, good stability and high linearity of response.

The quantification of OC and EC fractions was obtained by the **Thermal-Optical Transmittance** method (SUNSET system - Birch and Cary, 1996) consisting of two main steps. In the first part of the analysis, during the evolution in inert atmosphere, pyrolysis of the material deposited on the filter can occur and in extreme condition to form EC (Chow et al, 2007). In this condition, pyrolysed OC (PyC) cannot evolve in the inert atmosphere anymore, thus an underestimation of OC and an overestimation of EC are registered. Pyrolysis leads to the variation of the optical proprieties of the sample as PyC is light-adsorbing; thus, in the TOT analysis, the optical transmission of a laser thought the filter is continuously monitored. Due to pyrolysis, the transmittance of the filter decreases during the first part of the analysis (He atmosphere). When oxygen is injected into the line, EC (both originally present on the filter and derived from OC pyrolysis) evolves causing an increase of the laser transmission. When the filter transmittance

reaches the values registered at the beginning of the analysis, the method assumes that a quantity of EC equal to the one formed by pyrolysis has combusted and therefore all the carbon evolved up to this point has to be considered OC. All remaining carbon is considered EC. This method does not physically separate the two fraction, but it simply corrects the measured concentration using EC optical proprieties.

This experimental sampling strategy presented some problems: the light elements (Na to P) were not detectable by ED-XRF on quartz filters and EC/OC concentration values were available each two days (i.e. only on quartz filters). For this reason, the light absorption and thence the BC content in the PM collected with the PTFE filters, was measured off-line by a simple, fully automatic and non-destructive **new optical system** developed in our laboratory.

2. Source apportionment approach

The source apportionment approach used by Genoa's group is the Positive Matrix Factorization version 2 (PMF2). PMF2 is an advanced receptor model, developed by Paatero and Hopke (Paatero et al, 1994). In the last years this approach has been asserted like most reliable to international level. It is useful, especially, where detailed data do not exist on the composition of the main emission sources, but where large numbers of sampled data are available on ambient concentrations. The important advantage of the positive matrix factorization is the ability to handle missing data and values below the detection limits data by adjusting the error estimates of each data point. In fact, the solution to the PMF problem depends on the uncertainties attributed to each value.

The concentrations values and their associated errors were treated according to Polissar et al. (Polissar et al, 1998). Values corresponding to one half of detection limit were used for data below detection limits in the calculations of geometric means (Table AII.2.1).

Table AII.2.1: approach suggested by Polissar et al, 1998 for the concentration values and their associated error estimates

$$\text{Determined values}: \quad x_{ij} = c_{ij}, \quad s_{ij} = \sigma_{ij} + \frac{MDL_{ij}}{3}$$

$$\text{Values below MDL}: \quad x_{ij} = \frac{MDL_{ij}}{2}, \quad s_{ij} = \frac{\overline{MDL_j}}{2} + \frac{MDL_{ij}}{3}$$

$$\text{Missing values}: \quad x_{ij} = c_j, \quad s_{ij} = 4\tilde{c}_j \quad \text{con } \tilde{c}_j \text{ media geometrica}$$

Another important aspect of data points weighting, is the handling of extreme values. Environmental data typically show a positively skewed distribution; often with a long tail. Thus, there can be extreme values in the distribution as well as true "outliers". In either case, such high values would have significant influence on the solution: this influence will generally distort the solution and thus, an approach to reduce their influence can be an useful tool. In this approach, we used PMF in "robust mode": the robust factorization, based on the Huber influence function (Huber, 1981), is a technique of iterative reweighing of the individual data values.

Mass apportionment was calculated both performing a linear regression between the temporal trends of sources resolved by PMF and the time trends of mass concentrations (Ramadan et al., 2000) and including PM mass concentration as an independent variable in PMF

model analysis (Qin et al, 2006). In the second case, the PM mass data were down-weighted in the analysis by setting the uncertainties to 5 times their actual value. No differences between the two approaches were found within the calculation uncertainties (typically a few per cent of the percentual source weights).

Among the output of the model, important parameters to consider are the explained variations (EV). They indicate to what extent a source explains the temporal trend of an element. The higher is the EV of an element in a source, the more this element is specifically "contained" in that source if compared to the others. This, high EV for an element in a source identify that element as a good tracer for the source. EV are a good help to associate factors with real chemical – physical processes that emitted PM.

In PMF analysis, the choice of the best number of factors (particle sources) derivers from a compromise: using too few factors will combine sources of different nature together, while using too many factors it could happen that a real factor is dissociated into two or more non – existing sources. In this work the criteria used to choose the best number of factors are:

1) The study of Q; the theoretical Q parameter should be equal to the number of degree of freedom, or equal to the total number of data points in the data array: in fact, if the errors are properly estimated, it will result that the fit of each data point reproduces the value within the estimated error value, contributing with a value of about 1 to the Q value. Thus, it is suggested to examine the estimated Q value as a function of the number of factors to determine the number of factors to retain. However, this approach can be misleading if the data point uncertainties are not well determined.

2) The study of residuals; typically the distributions of the residuals are plotted for each measured species: it is desirable to have symmetric distributions and to have all residuals within ± 3 standard deviations. If there is a larger spread of residuals, then the number of factors should be re-examined.

3) Study of the standardized residual matrix (R); *IM* is the maximum individual column mean and *IS*, the maximum individual column standard deviation. IM and IS serve as indicators to identify the species having the least fit and the most imprecise fit, respectively. When the number of factors increases to a critical value, *IM* and *IS* show a drastic drop.

4) Study of Rotmat; Rotmat, a matrix resulting from each PMF computation, is used for detecting the degree of rotational freedom of the factors; it can be used to reveal if factors have excessive rotational freedom. Where the largest element in *Rotmat* is plotted against the number of factors, there is a minimum value in correspondence of the best number of x factors (Paatero et al., 2002).

In the PMF analysis here presented, PM measured components used included elements measures by ED-XRF, ions detected by ion chromatography (IC) and organic and elemental carbon measured by thermal-optical transmittance method (TOT). In the PMF data set, OC missing values were replaced using the mean OC/EC ratio with a large uncertainty.

Variables were selected according to the signal-to-noise criterion (Paatero and Hopke, 2002) and then 15 variables were finally used in the analysis: Al, Si, P, K, Ca, V, Fe, Ni, Cu, Zn, SO_4^{2-}, NH_4^+, NO_3^-, OC and EC. Na and Cl turned out to be "bad variables" (they are present in a low number of samples because of PM2.5 sampling were performed and Na values are available each two days, i.e. only on Teflon filters). This prevented the possibility to resolve the source sea salt.

3. Results

The number of factors which was examined ranged from three to eight. Finally, five sources were resolved and labeled, according to their characteristic tracers, as follows: *Road* (traced by Cu), *Dust* (traced by Al, Si, Ca), *Industrial/Marin* (*Oil Combustion* traced by V, Ni), *Secondary Compounds* (*Secondary I* traced by SO_4^{2-} and NH_4^+ and *Secondary II* traced by NO_3^- and NH_4^+). PMF applied to a time series of elemental concentration values resolved, over the number, the profiles of PM sources at the sampling site (Figure AII.2.1) and their contribution to PM2.5 levels (Figure 2). In Figure 3 the correlation between measured and calculated mass is shown to validate the results of PMF analysis.

The source profiles deserve some specific comments:

- **Road**: This source is linked to *road traffic*.
- **Secondary:** Species measured in this experiment (ions, organic and elemental carbon) make it possible to separate *Secondary Compounds* into two different sources, the first traced by sulfates and ammonium (hereinafter called *Secondary I*) and the second one traced by nitrates (hereinafter called *Secondary II*). The concentration ratio SO_4^{2-}/NH_4^+ in *Secondary I* is 2.3 ± 0.2, in agreement with the stoechiometric ratio. Secondary II presents a concentration ratio NO_3^-/NH_4^+ of 2.8 ± 0.3, in partial agreement with stoechiometric ratio.
- **Industrial/Marine:** This source is linked to *Oil Combustion* and the V/Ni concentration ratio in the profile is 2.5 ± 0.3. This profile presents an high contribution of SO_4^{2-} and NH_4^+ (concentration ratio SO_4^{--}/NH_4^+ is 2.2 ± 0.2), due to an only partial separation obtained by PMF analysis between this source and *Secondary I*.
- **Dust**: PMF analysis resolves a source partially natural. It is a source that includes both soil and soil re-suspended from road traffic. In fact, the concentration ratios of soil tracers (Al:Si and Al:Ca) in the profile are in disagreement with the literature values (Mason, 1966). This confirms the hypothesis that this source is only partially natural and that its composition is significantly contaminated by anthropogenic source emissions.
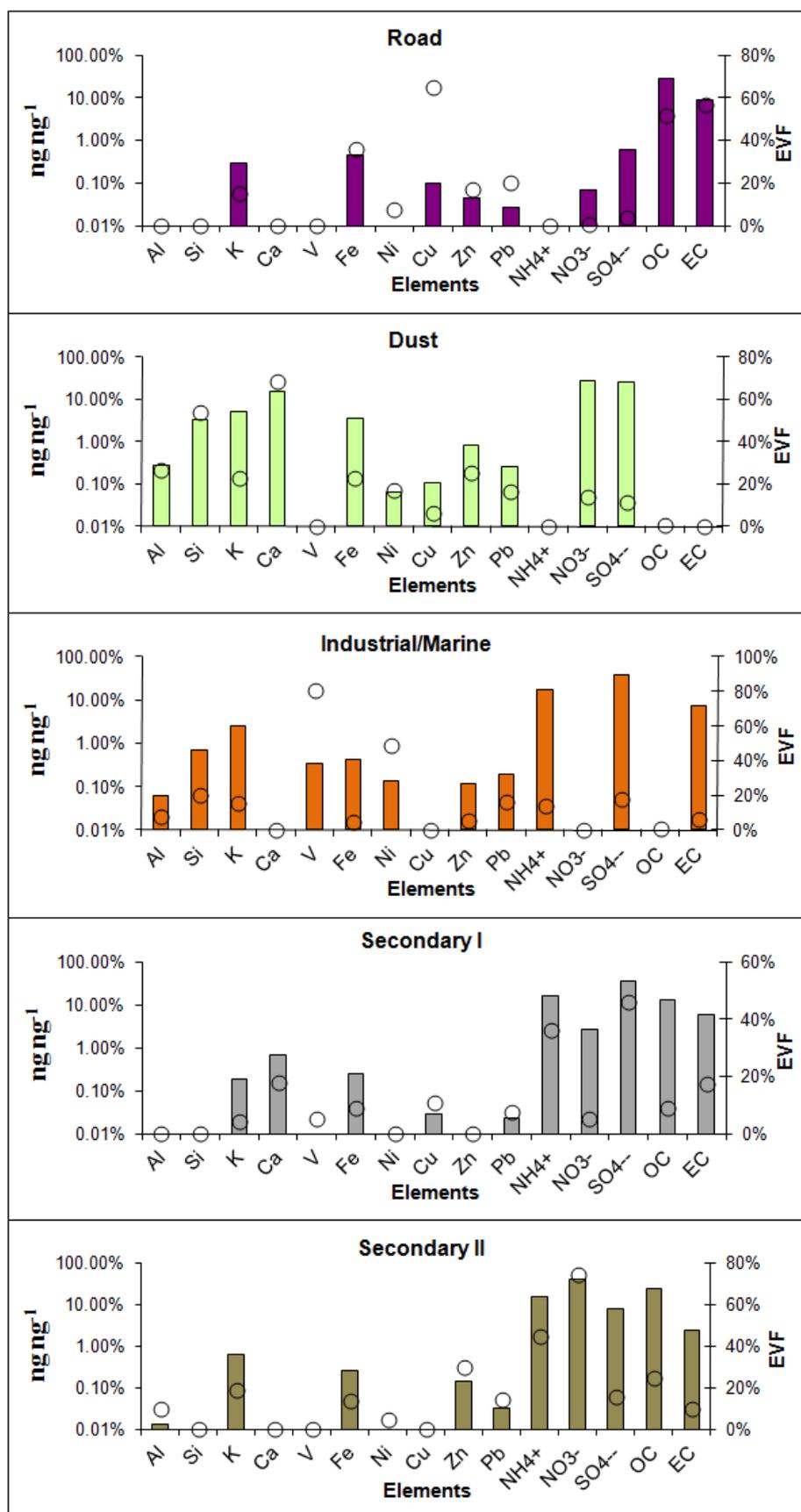
Figure AII.2.1. Profiles (bars) of the five PM2.5 sources identified by PMF on PM2.5. Values on the y-axis (ng ng^{-1}) are the relative weight of the concentration of each element to the mass of each source. Dots represent Explained Variations.
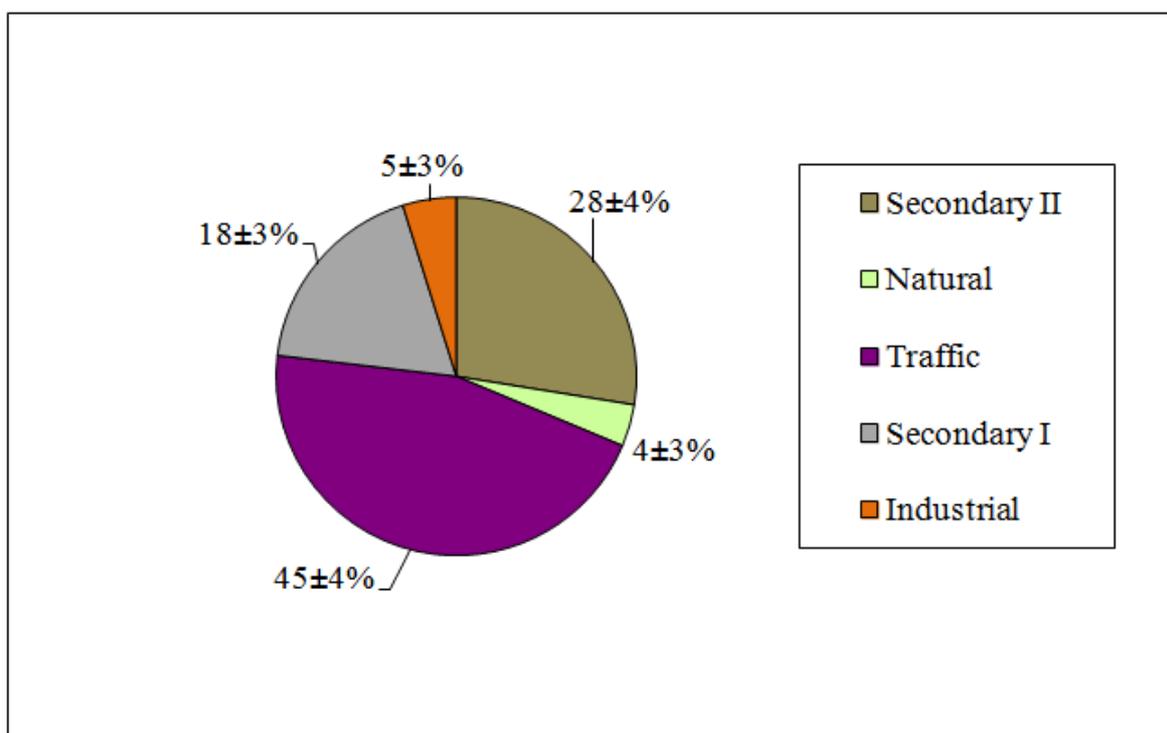
Figure AII.2.2: PM2.5 mass apportionment deduced by the PMF analysis.
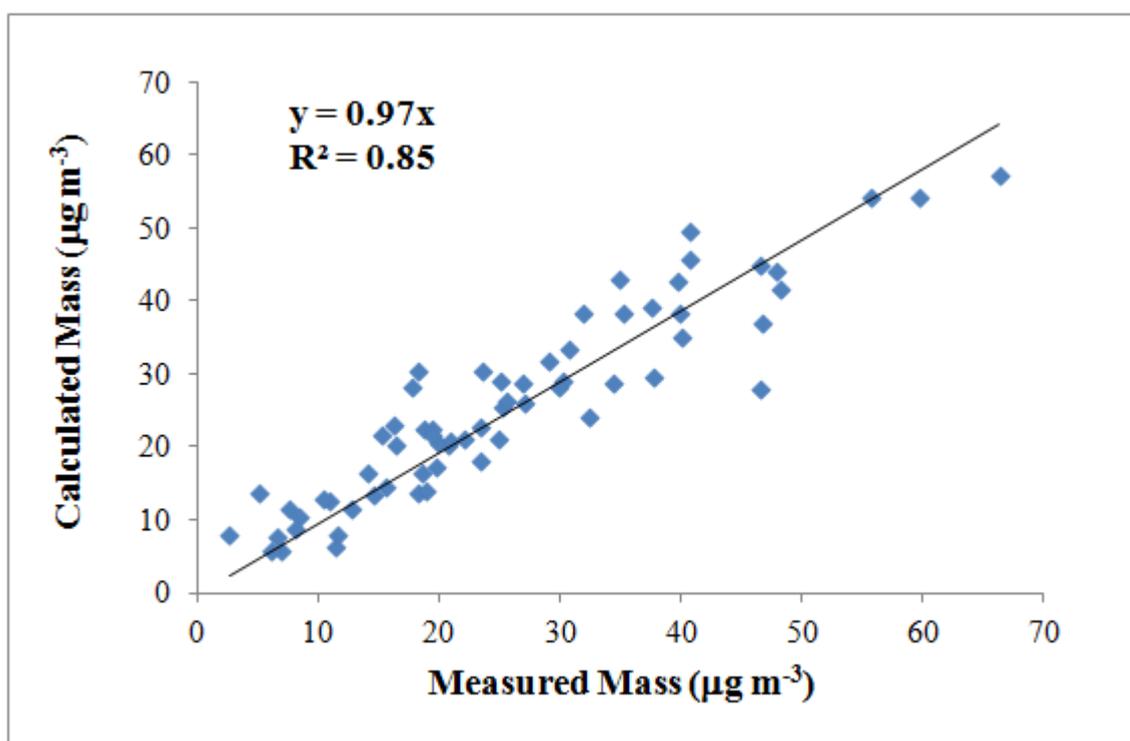
Figure AII.2.3: Correlation between measured and calculated (by PMF) PM2.5 concentration.

In Figure AII.2.2 the mass apportionment is shown; *Dust* and *Industria/Marine* were resolved with a considerable error due to them low mass contribution. The time trends of sources resolved by PMF are shown in Figure AII.2.4. In the first part of intercomparison campaign a main

contribution of *Road* and *Dust* is present, while the central part of sampling campaign is caracterised by the high contribution of *Secondary Compounds (both Secondary I and Secondary II)*. *Industrial/Marine* source presents a time trend similar to *Secondary Compounds* because of the only partial separation between this sources and S*econdary I*. In Figure AII.2.5 the apportionment of each single PM compounds is shown. Crustal element (Al, Si, Ca) are mainly linked to *Dust*, while V and Ni, tracer of *Oil Combustion,* are mainly emitted by *Industrial/Marine*. Zn, Pb, Fe and K are emitted by different sources because of the different processes that emitted them. Regarding ions, SO_4 is prevalently associated to *Secondary I* and NO_3 to *Secondary II*. Ammonium, instead, is emitted by both the *Secondary compounds*.
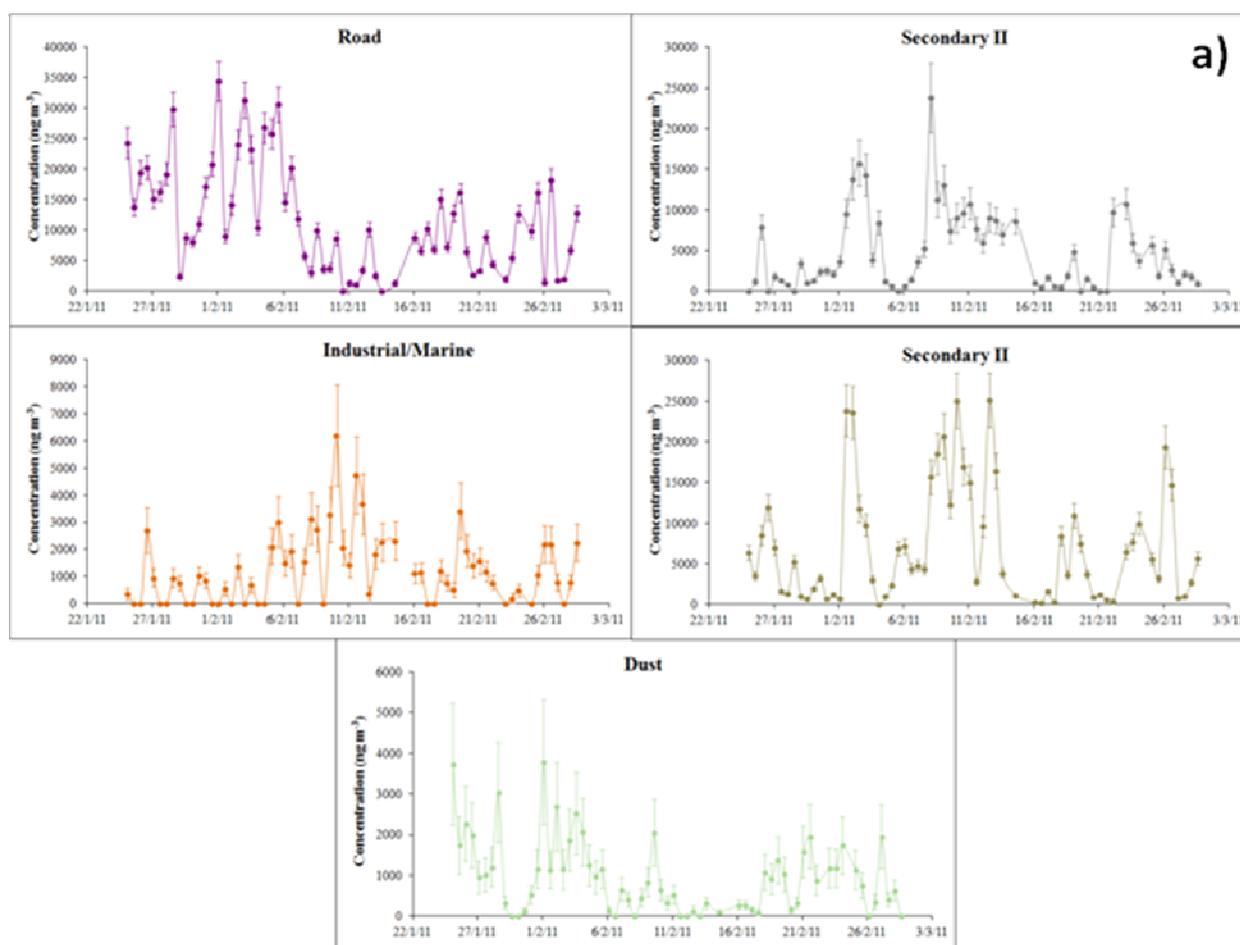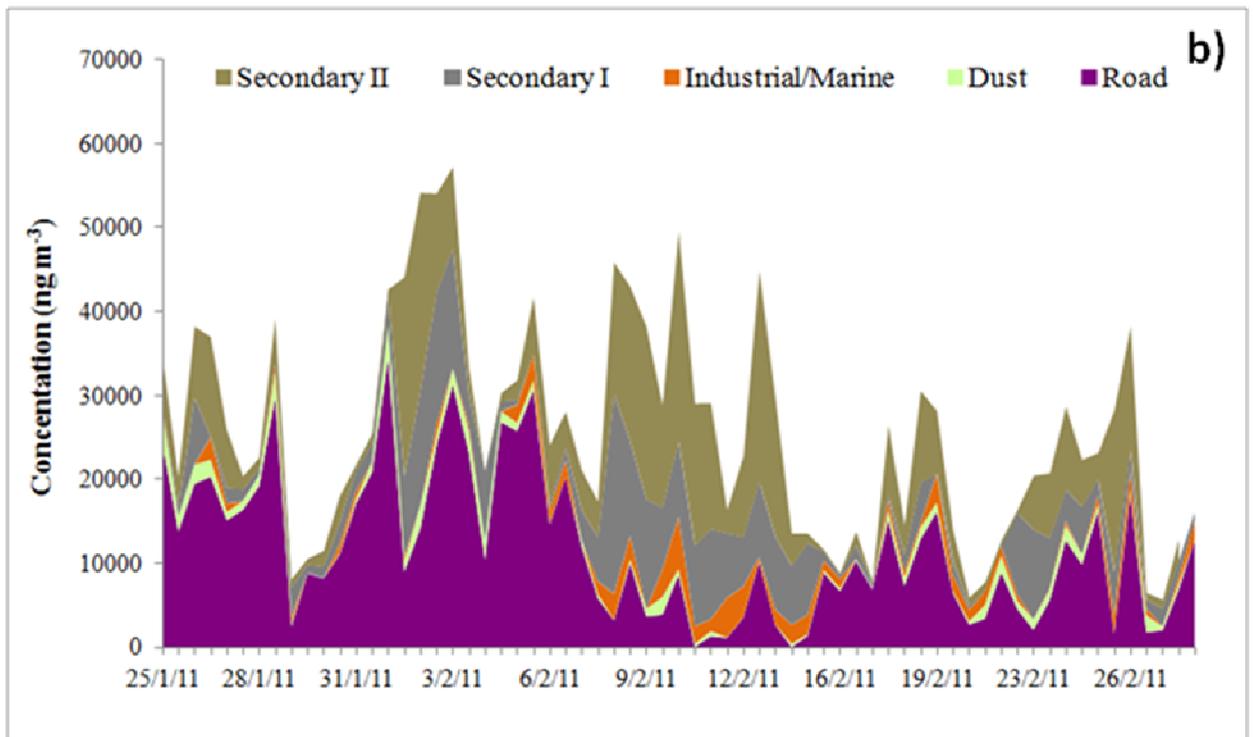
Figure AII.2.4: a) Temporal trends of each source b) Temporal trends of all sources.
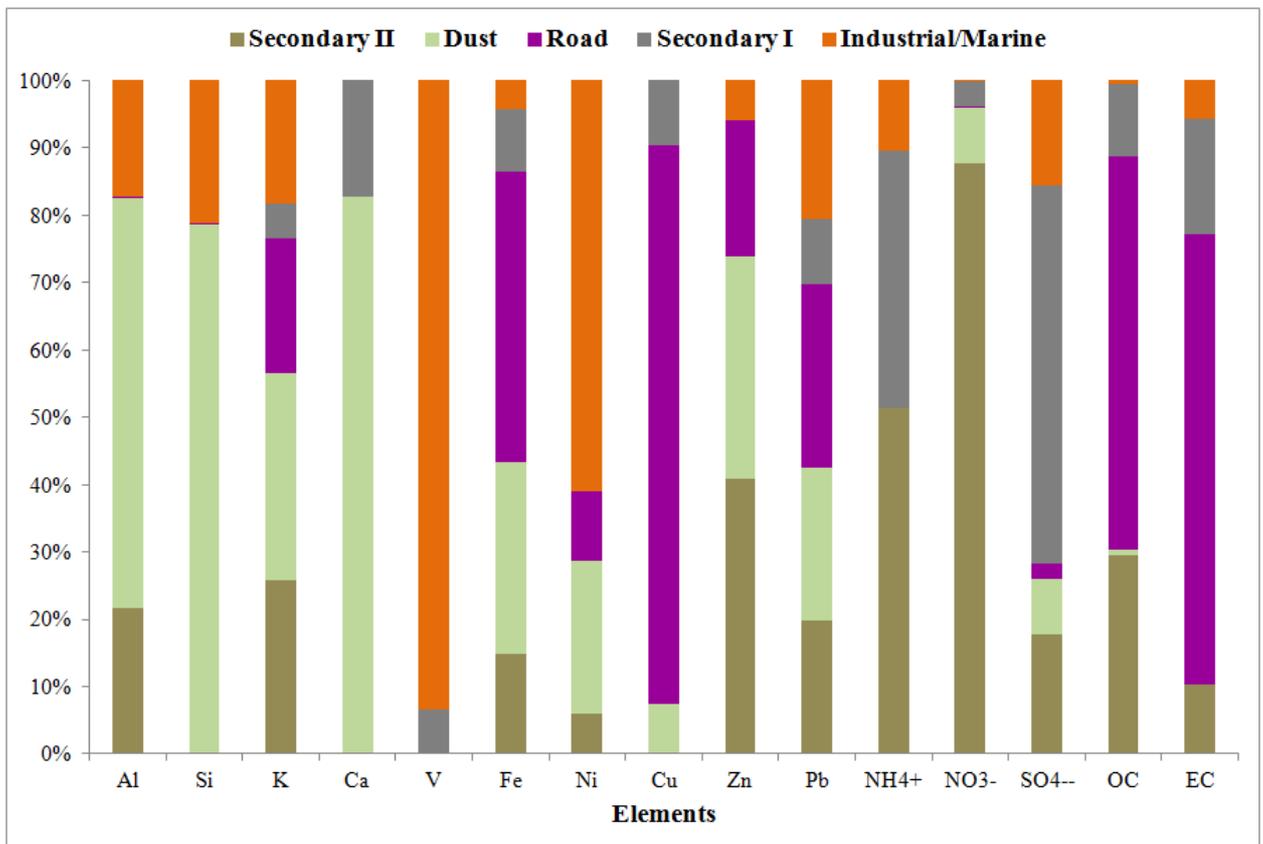
Figure AII.2.5: Mass apportionment of single PM compounds deduced by the PMF analysis in PM$_{2.5}$.

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Appendix II.3 : Source apportionment results (Univ. Provence, Marseille)

Within the framework of the intercomparison campaign, the Chemical Mass Balance model has been used in order to apportion sources.

1. CMB modeling set up

1.1. CMB modeling: Definition

In this approach, ambient chemical concentrations are expressed as the sum of products of species abundances and source contributions. These equations are solved for the source contributions when ambient concentrations and source profiles are supplied as input. Source-specific individual organic compounds of primary origin are then most often used in conjunction with the CMB model to apportion sources of primary OC (Organic Carbon). Then, C_{ik}, the concentration of a selected chemical marker i at a receptor site k, can be expressed as the following linear equation:

$$(1) \qquad C_{ik} = \sum_{j=1}^{m} f_{ijk}\, a_{ij}\, s_{jk}$$

Where **m** is the total number of emission sources, **aij** is the relative concentration of chemical species i in fine OC emitted from source j, **sjk** is the increment to total OC concentration at receptor site k originating from source j and **fijk** is the coefficient of fractionation that represents the modification of aij during transport from source j to receptor site k.

This fractionation coefficient accounts for selective loss of constituent i due to atmospheric processes such as chemical aging or gas-particle partitioning related to the dilution of the emissions. Those are nonlinear phenomena, depending on numerous conditions, and can change drastically the fractionation coefficients (fijk) of the selected markers. Determinate the fijk coefficient is then highly complicated. Therefore, CMB modeling uses as fitting species key markers that are assumed to be non-volatile and reasonably stable in the atmosphere, implying fractionation coefficients near unity for such species.

To solve the set of linear equations generated by eq. (1), the effective variance least squares estimation method, which remains the most commonly used in studies, has been selected. The CMB source allocation was computed using United States Environmental Protection agency EPA-CMB8.2 software.

1.2. Choice of profile sources and Markers

A critical issue generally encountered in CMB modeling is the selection of source profiles, which relies heavily on several implicit assumptions. First, we have to assume that the different emissions resulting from a given source class can be represented by an average source profile, with known marker-to-OC ratios (a_{ij}). This average profile would then have to reflect precisely the emission sources influencing the receptor site. Finally, all of the major sources of the different marker compounds have to be included in the model.

Carbonaceous matter (µg.m^{-3})			
OC	8.2 (2.43 ; 18.93)	EC	1.98 (0.97 ; 4.32)
Major ions (µg.m^{-3})			
Cl$^-$	0.14 (0.03 ; 0.46)	Na$^+$	0.12 (0.01 ; 0.45)
NO$_3^-$	4.06 (0.55 ; 11.02)	NH$_4^+$	2.94 (0.05 ; 7.95)
SO$_4^{2-}$	2.66 (0.69 ; 8.07)	Ca^{2+}	0.97 (0.04 ; 3.03)
Polyciclics Aromatics Hydrocarbons (PAH - ng.m^{-3})			
*benzo[b,k]fluoranthene	1.13 (0.13 ; 4.57)	indeno[1,2,3 - cd]fluoranthene	0.79 (0.11 ; 3.58)
benzo[j]fluoranthene	0.12 (<dl ; 0.74)	*indeno[1,2,3 - cd]pyrene	1.81 (0.23 ; 8.14)
*benzo-e-pyrene	1.38 (0.17 ; 5.69)	dibenzo[a,h]anthracene	0.7 (<dl ; 4.14)
benzo-a-pyrene	1.08 (<dl ; 5.03)	*benzo - ghi - perylene	1.15 (<dl ; 3.94)
n-Alkanes (ng.m^{-3})			
Pentacosane (C25)	5.78 (0.7 ; 19.38)	*Nonacosane (C29)	14.74 (2.05 ; 55.74)
Hexacosane (C26)	5.95 (0.88 ; 35.23)	*Triacontane (C30)	6.39 (<dl ; 35.08)
*Heptacosane (C27	8.69 (1.9 ; 52.95)	*Untricontane (C31)	17.51 (1.56 ; 73.61)
*Octacosane (C28)	6.64 (0.57 ; 54.05)	*Dotriacontane (C32)	6.08 (<dl ; 18.21)
Hopanes (ng.m^{-3})			
17α(H) trisnorhopane	0.27 (<dl ; 1.03)	*17α(H) - 21β(H)-22S - homohopane	0.51 (0.18 ; 1.17)
*17α(H) - 21β(H)- norhopane	0.68 (0.16 ; 1.72)	*17α(H)-21β(H)-22R-homohopane	0.37 (<dl ; 1.02)
*17α(H) - 21β(H)- hopane	0.64 (0.25 ; 1.6)	17α(H)-21β(H)-22S-bishomohopane	0.3 (<dl ; 0.66)
Phtalathes esters (ng.m^{-3})			
di-isobutyl phtalate	0.37 (<dl ; 1.38)	benzyl butyl phtalate	0.07 (<dl ; 0.16)
di butyl phtalate	0.18 (<dl ; 0.39)	bis (2-ethyl hexyl) phtalate	0.74 (0.26 ; 2.03)
Sugar and derivatives (ng.m^{-3})			
*Levoglucosan	471.2 (17.36 ; 1626.87)		
Main element (ng.m^{-3})			
Al	170.65 (63.55 ; 404.42)	Ti	8.88 (0.81 ; 22.4)
Cu	14.92 (3.38 ; 33.46)	Ca	893.89 (29.85 ; 2691.07)
*Ni	2.07 (<dl ; 3.46)	Fe	213.38 (7.57 ; 555)
*Pb	8.25 (<dl ; 20.21)	Mn	3.4 (<dl ; 7.88)
*V	2.79 (<dl ; 7.68)	Zn	24.35 (4.2 ; 57.81)

* compounds included in the CMB modelling

*Table A.II.3.1: Principal organic markers and elements measured during the APICE intercomparison campaign, * included as fitting species in CMB modeling.*

The selection of the source profiles for non-industrial emissions in France and the sensitivity of the CMB model results with respect to the selected profiles are detailed in Favez et al. (2010). All calculations include vehicular emissions derived from a tunnel study held in Marseille (El Haddad et al., 2009), heavy duty trucks emissions (Rogge et al., 1993a), biomass burning emissions (Fine et al., 2002), vegetative detritus (Rogge et al., 1993a) and natural gas combustion (Rogge et al., 1993b). Considering the specific case of Marseille area, and as discussed elsewhere (El Haddad et al., 2011), three industrial-emission-related profiles were selected: metallurgical coke production (Weitkamp et al., 2005), HFO combustion/shipping (Agrawal et al., 2008) and steel manufacturing (Tsai et al., 2007).

In order to assess contributions from the aforementioned sources, we have used in this particular model as fitting species (cf. table A.II.3.1): levoglucosan as a specific marker for biomass burning, and elemental carbon (EC) and three hopanes (*i.e.,* 17α(H),21β(H)-norhopane, 17α(H),21β(H)-hopane and 22S,17α(H),21β(H)-homohopane) as key markers for vehicular emissions (Table A.II.3.1). In addition, a series of C27-C32 n-alkanes were selected since this range demonstrates high odd-carbon preference that is specific to biogenic sources. In order to apportion industrial emissions, four PAH (benzo[b,k]fluoranthene, benzo[e]pyrene, indeno[1,2,3-cd]pyrene, and benzo[ghi]perylene). V, Ni and Pb (Table 1) were included as fitting species in the CMB.

1.3. Quality control

Statistical performance measures usually used in the CMB modeling as a quality control check of the CMB calculation generally includes the use of R-square (target 0.8–1.0), chi-square (target 0–4.0), t-test (target >2) and the absence of cluster sources (Watson et al., 1998). The CMB solutions presented here meet these 4 criteria for all of the samples.

Another requirement for a good fit is the marker's calculated-to-measured ratios (C/M) with a target value that we fixed between 0.75 and 1.25 in order to provide reasonable bounds on CMB results.
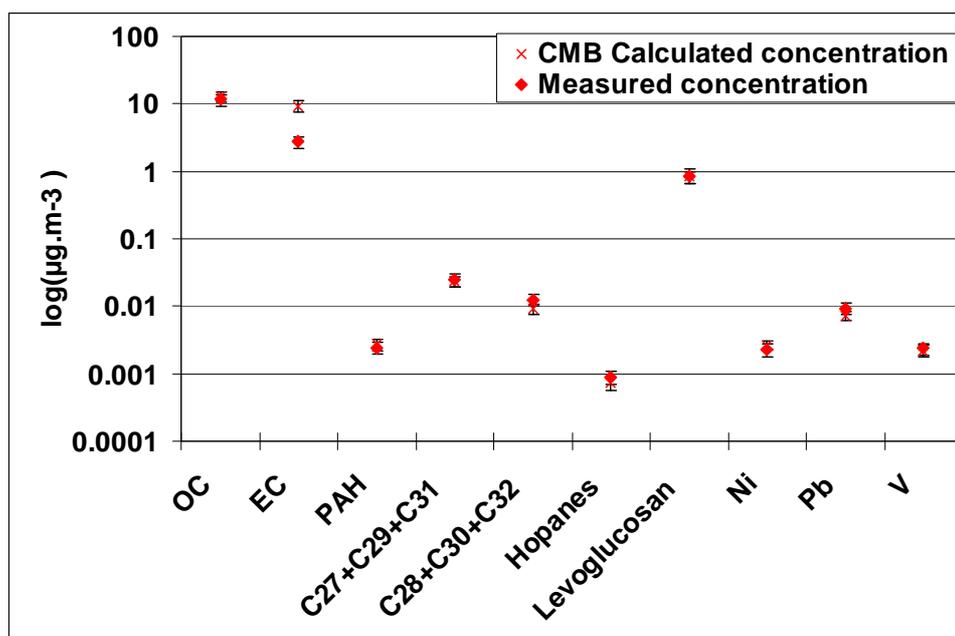
Figure A.II.3.1: Comparison between measured and modeled concentration for several groups of markers EC, hopanes (sum of 17_(H)- trisnorhopane, 17_(H),21_(H)-norhopane, 17_(H),21_(H)-hopane and 22S,17_(H), 21_(H)-homohopane), odd carbon number alkanes (C27+C29+C31), even carbon number alkanes (C28+C30+C32), PAH (sum of benzo[b,k]fluoranthene, benzo[e]pyrene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene), levoglucosan, V, Ni and Pb.

As shown in figure A.II.3.1, a good agreement can be observed for most of these values. Nevertheless, discrepancies can be observed in the case of EC. This bias can be partially explained by a difference between the methods used 1.) for the measurement of EC and OC (measure by thermo-optical transmission – TOT- method on a Sunset Lab analyzer, following the EUSAAR II analysis parameters) and 2.) for the determination of EC in source profiles (calculated using measures performed with the NIOSH analysis method). Nevertheless, the different source profiles selected for this analysis seems to reflect satisfactorily the emission in the study area.

2. Estimate of sea salts and crustal dust apportionment

As CMB can not apportion directly Sea salt and dust contributions, empirical approaches have been used for these two sources.

2.1. Sea salt

Marine aerosol represents a significant fraction of the global aerosol loading. Among its various components, sea salt is quantitatively the major contributor to marine aerosol mass and is therefore the one to be considered when evaluating the natural contribution of marine aerosol to PM loadings. However, there is no existing profile in the literature for this source. Marine aerosol contribution to PM has then been estimated using the calculation method proposed by Putaud et al. (2010) (eq. 2).

(2) $\quad [sea\ salt] = [Cl^-] + [Na^+] \times (1 + (K^+/Na^+)_{SW} + (Mg^{2+}/Na^+)_{SW} + (Ca^{2+}/Na^+)_{SW} + (SO_4^{2-}/Na^+)_{SW})$

$$\Leftrightarrow [sea\ salt] = [Cl^-] + [Na^+] \times 1.47$$

Where: [Cl-] is the concentration of chloride, [Na+] is the concentration of sodium, and $(K^+/Na^+)_{SW}$, $(Mg^{2+}/Na^+)_{SW}$, $(Ca^{2+}/Na^+)_{SW}$ and $(SO_4^{2-}/Na^+)_{SW}$ are typical ions ratios encountered in sea water.

2.2. Crustal dust

This term refers to the fraction of mineral aerosols, except for sea salt; fraction which also could represent a significant fraction of PM. Considering the important variability of dust composition, no real source profile exists for this parameter. It has been estimated using Malm et al. (1994) method, based on the measure of metals and elements constituting the aerosol (eq. 3):

(3) $\quad [Crustal - Dust] = 2.20[Al] + 2.49[Si] + 1.63[Ca] + 2.42[Fe] + 1.94[Ti]$

Where [Al], [Si], [Ca] [Fe] and [Ti] respectively are the mass concentrations of aluminum, silicon, calcium, iron, and titanium in particulate matter.

Since no measurement of Si was performed during the measurement campaign, we estimated its concentration according to Malm et al. (1994) method (eq. 4):

(4) $\quad [Si] = 0.10[Fe]$

2.3. Contribution to PM 2.5

On table A.II.3.2 are presented the estimated mean contribution of sea salt and crustal dusts to PM2.5. Figure A.II.3.2 displays these contributions temporal evolution during the whole measurement campaign.

Table A.II.3.2: Statistical distribution of sea salt and crustal dust contribution to PM2.5

Concentration (µg.m⁻³) of PM due to	Sea salt	Crustal dust
Mean contribution	1.71	5.15
Standard deviation	1.76	3.07
Max. contribution	8.16	11.64
Min. contribution	0.44	0.26
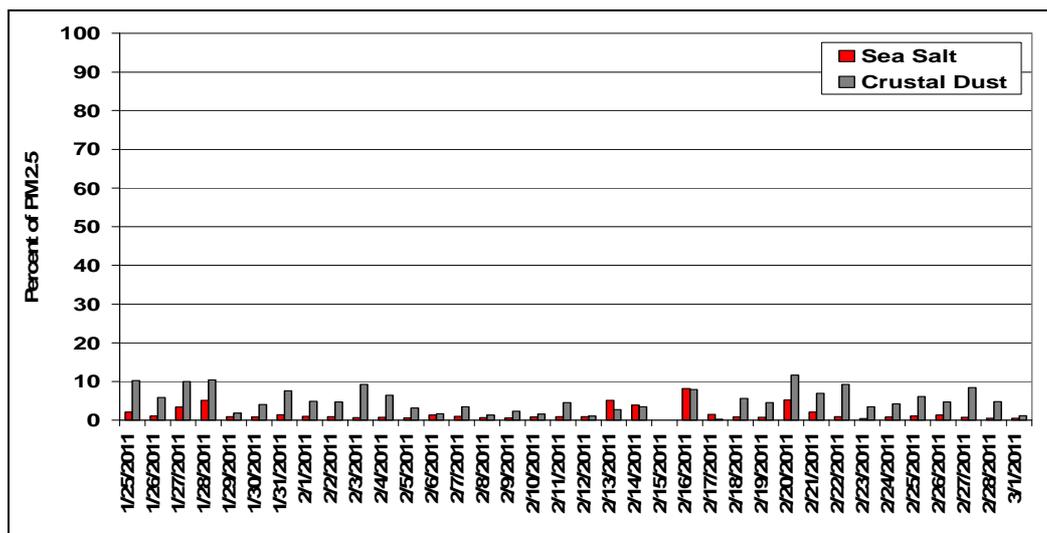
Figure A.II.3.2: Temporal evolution of sea salt and crustal dust contribution to PM$_{2.5}$

We can observe that crustal dust and sea salt contribute to a small yet significant fraction of PM 2.5 (from about 1 to 12%). However, this information still have to be handled with care, as it is an estimation, based on calculation that doesn't take any specific environmental parameters into account. A comparison with PMF results might provide a better perspective upon this concern.

3. CMB modeling results

3.1. Primary sources contribution assessed by the CMB
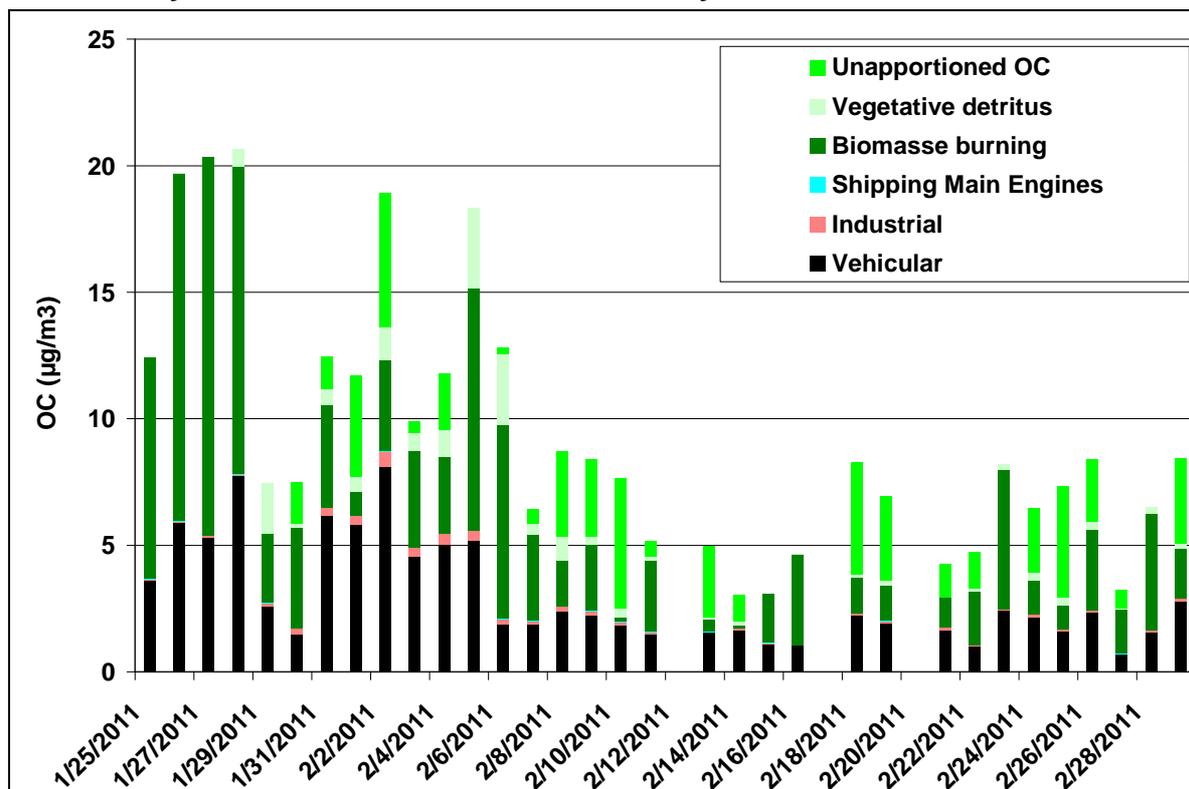
Figure A.II.3.3: Source contribution to ambient organic carbon (OC), as determined by CMB modeling, throughout the measurement campaign.

On figure A.II.3.3 are presented the primary contributions of the different sources to Organic Carbon (OC) according to the CMB outputs.

Biomass burning is the most important OC source considered during the whole measurement campaign, accounting for about 49% of the measured OC in average. Biomass burning, including wood combustion processes, has often been described as an important emission source in winter (domestic heating), especially in mountains or remote areas. However, this situation was therefore quite unexpected in a Mediterranean city such as Marseille. This observation is consistent with the preliminary results obtained during the preliminary study of the AMS dataset, which listed biomass burning as an important source for 1µm organic fraction (cf. section 2 and progress report, appendix II).

The second most important OC source is vehicular emissions, which represents about 32% of the measured OC. Vegetative detritus and un-apportioned OC are less important sources, representing respectively about 6 and 18% of the total mass of OC. Industrial sources and Shipping main engines are the least important sources, representing respectively 1.5 and 0.2% of the measured OC.

Finally, it can be observed that the sum of the calculated OC only account for 82% of the measured OC, leaving 18% of unapportioned OC. This unapportioned fraction is classically associated to Secondary OC, but can also be linked to others sources not considered here (ie : cooking sources, for example). It has been reported to be rather important in several studies (about 78% in Marseille, summer 2009, El Haddad et al., 2011). An 18% percentage is then

perfectly consistent with a winter time situation, where atmospheric photoreactivity is at its lowest level.

3.1.1. Sources contribution to PM 2.5

To determine the contributions from primary sources to PM$_{2.5}$ mass, OM mass associated with each source is calculated applying an OM-to-OC conversion factor specific for each source, as summarized in table A.II.3.3.

Table A.II.3.3: OC-to-OM conversion factors applied in this study

Vehicular emission Natural gas combustion Industrial emissions Main shipping engines	1.2	Aiken et al., 2008 ; Mohr et al., 2009
Biomass burning	1.7	Puxbaum et al., 2007 and references therein
Vegetative detritus	2	Kunit and Puxbaum, 1996

El Haddad et al., 2011

The result is then combined with the corresponding EC, sulfate, nitrate and ammonium concentrations, as given in the source profiles. Secondary sulfate, nitrate and ammonium are then deduced by subtracting from the measured ionic species the primary emissions of these species. CMB unexplained OM can be calculated as the difference between the measured OM, determined by applying an OM-to-OC conversion factor of 1.6 (derived from AMS measurements performed here), and the apportioned OM attributed to primary sources.

This unexplained OM is classically associated to CMB SOA (Secondary Organic Aerosol calculated by the CMB model). Actually the most important levels of unapportioned OM are encountered when wind speed is at its lowest level, *i.e.* when meteorological conditions are favorable to atmospheric compounds accumulation.

Figure A.II.3.4 shows a time series of the ambient PM2.5 mass apportioned by CMB. Black dots on the figure stand for the daily average of measured PM2.5. It should be noted that measured PM2.5 and apportioned PM2.5 are in good agreement, with the exception of the 4 first days of the measurement campaign, where higher PM2.5 levels have been calculated.
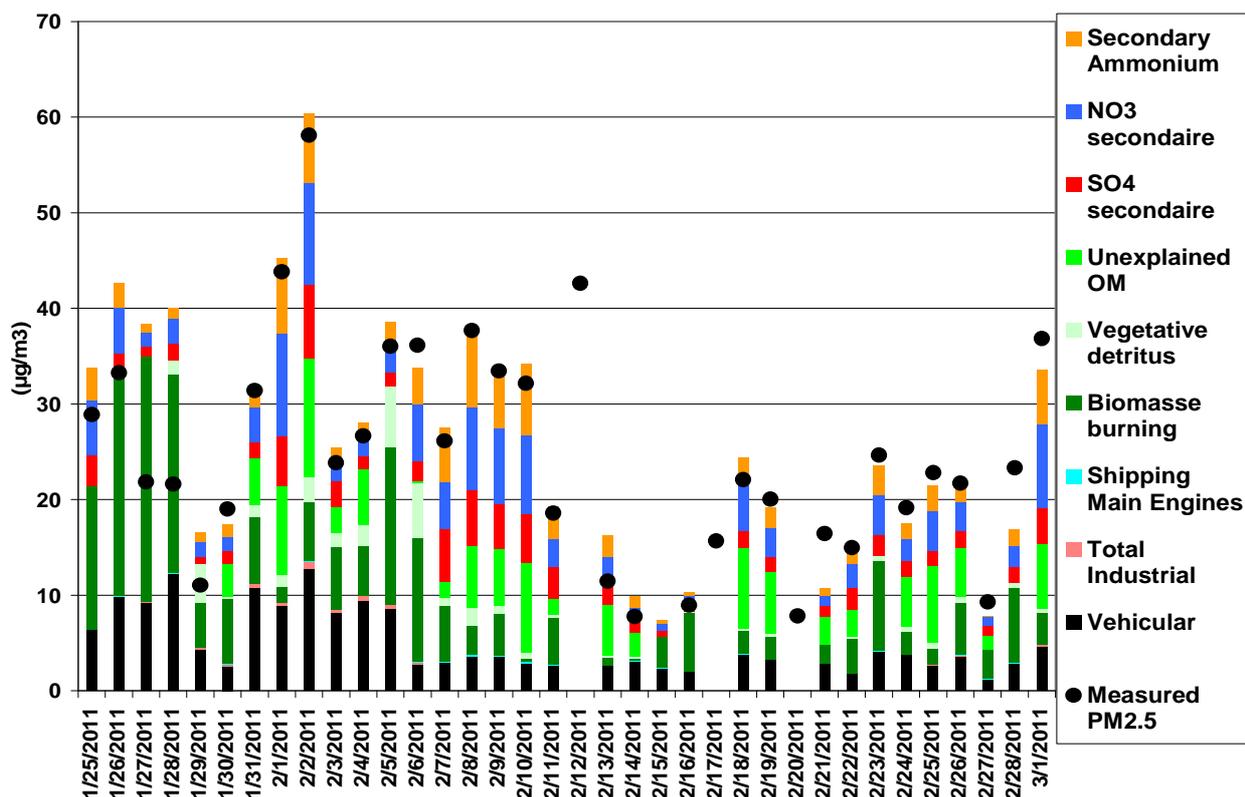
Figure A.II.3.4: Temporal evolution of source contribution to PM2.5 concentrations throughout the measurement campaign

4. PM2.5 average composition

Figure A.II.3.5 presents the average composition of PM2.5 calculated for the whole measurement campaign. Primary contributions to PM2.5 (sum of the contributions of all primary sources) represent about 49.7% of PM2.5 measured mass; whereas secondary sources (*i.e.* unexplained OM and secondary ions) account for 50.3% of PM2.5 mass. The importance of secondary sources is then lower than what have been previously described for Marseille area in summertime (El Haddad et al., 2011); this observation is perfectly consistent with winter time data.
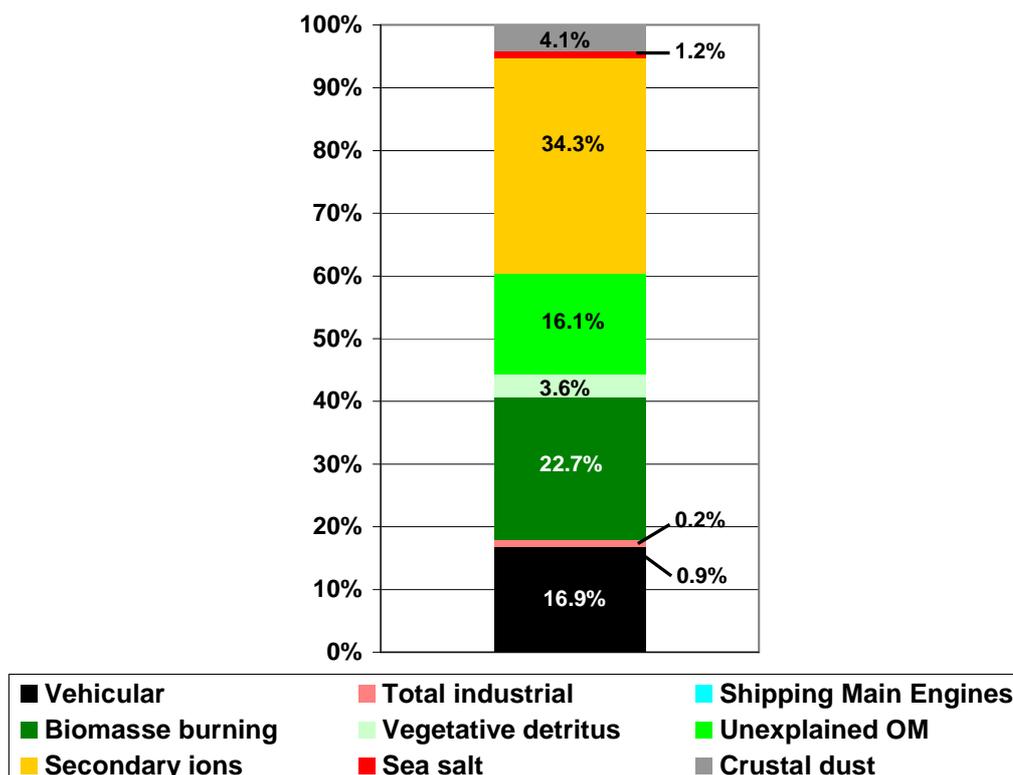
Figure A.II.3.5: Calculated PM2.5 average composition throughout the measurement campaign

Among primary sources, biomass burning, representing 22.7% of PM2.5 mass, is the most important, followed by vehicular emission (16.9%), crustal dust (4.1%) and vegetative detritus (3.6%)

Industrial sources and Shipping main engines are the least important primary sources observed. Thus, shipping main engines account for 0.2% of PM2.5 mass. If this result might seem low for an area such as Marseille, it remains consistent with the importance of this source as described it further studies (El Haddad et al., 2011 and references therein).

Industrial sources represent 0.9% of PM2.5 mass. This value is lower than expected. Actually, APICE intercomparison campaign data-set preliminary analysis had underlined several events characterized by SO_2 peaks, which had been interpreted as industrial events. However, those events are not visible in this very analysis. This can be explained as the most influent marker for Industrial source is Pb, which displays a different temporal evolution than SO_2, as shown on figure A.II.3.6. The comparison with PMF results might provide a new perspective upon this concern.
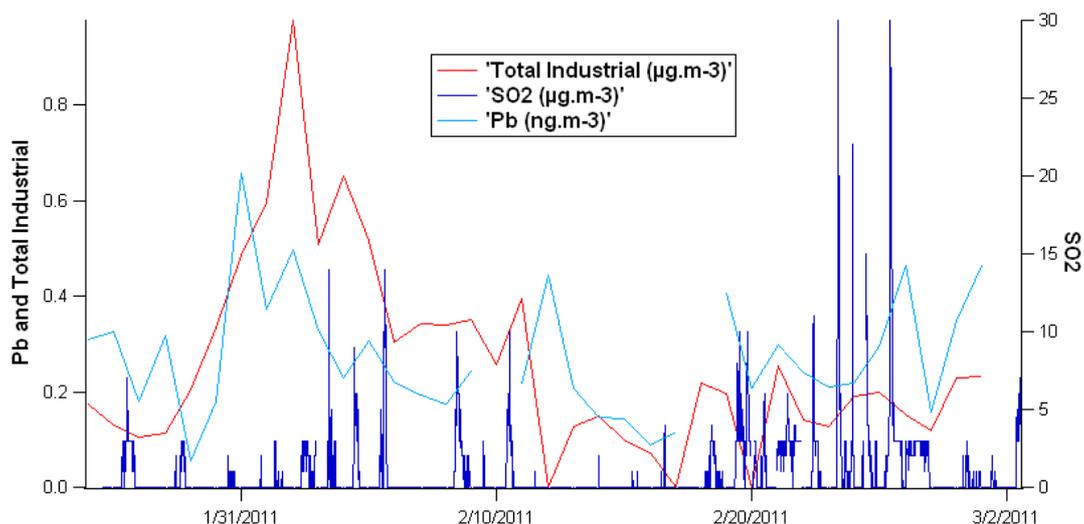
Figure A.II.3.6: Temporal evolution of SO_2, Pb and the Industrial emission source contribution

5. Conclusion

The CMB analysis described here displayed quite interesting results. Biomass burning, accounting for 22.7% of PM2.5, is the most important primary emission source influencing the measurement site; followed by vehicular emissions (16.9%), crustal dusts (4.1%), vegetative detritus emissions (3.6%), and sea salt (1.2%). Those results are consistent with preliminary analysis (cf. progress report) and other studies leaded in the same area (El Haddad et al., 2011). The lowest impacting primary sources are shipping main engines and industrial emission (respectively 0.2% and 0.9%). If those values seem rather low on a first sight, they are nevertheless quite consistent considering the selected source profiles. Those primary emissions account for about 49.6% of all PM2.5. Unexplained OM, which can be related to Secondary Organic Aerosol, represents 16.1% of the total PM2.5 mass. This result is consistent with winter time conditions (lower photoreactivity, leading to lesser SOA production). Together with secondary ions (representing about 34.3% of PM 2.5), they constitute PM2.5 secondary fraction, which represent 50.4% of the total PM2.5 mass.

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Appendix II.4 : Source apportionment results (UOWM, Thessaloniki)

1. Introduction

The determination of the impact of different air pollution sources is an important step in the development of efficient air quality control strategies. Source apportionment models are mathematical (statistical) procedures for identifying and quantifying the sources of air pollutants at a receptor location (receptor models). A group of these models, generally termed as factor analysis tools, require little or no a priori knowledge of sources or their emission profiles, and can therefore point out unexpected sources. A widely used model is Positive Matrix Factorisation (PMF) which is a new variant factor analysis method developed by Dr. Paatero at the University of Helsinki in Finland in the mid 1990's (Paatero 1997).

Results from Positive Matrix Factorization (PMF) model application on the data collected from Marseille's intercomparison campaign (conducted from 25/1/2011 to 1/3/2011) in the frame of APICE project are presented. The present study was conducted by the University of West Macedonia (UOWM).

2. Methodology

2.1. Available data from chemical analysis

The available data for the source apportionment analysis were data from **PM2.5** samples chemical analysis for 27 **Polycyclic Aromatic Hydrocarbons (PAHs)**, 8 major **ions (**Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^+, Ca^{2+}), **organic and elemental carbon (OC/EC)** and **metals** (Al, Ca, K, Na, Mg, Fe, Mn, Ti, P, V, Cr, Ni, Cu, Zn, As, Rb, Sr, Cd, Sn, Sb, Pb, Li, Sb, La). *Analysis for PAHs, ions, OC, EC was conducted in UOWM laboratory while data for metals were provided from CSIC-IDAEA).*

EPA PMF model version 3.0 was used. The model was run with several cases of data; however the best solution was achieved with the following input data:

- **8 selected PAHs**: *Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[e]pyrene, Benzo[a]pyrene, Perylene, Indeno[cd]pyrene, Dibenzo[a,h]anthracene, Benzo[ghi]perylene.* Lighter PAHs were excluded from the analysis because of their volatility.
- **3 selected ions**: NO_3^-, SO_4^{2-}, NH_4^+. Chlorine (Cl^-) and sodium (Na^+) ions were excluded due to large analytical errors. The other ions were excluded as their pair elemental species were used in the analysis (to avoid double counting mass).
- **23 metals**: *Al, Ca, K, Na, Mg, Fe, Mn, Ti, P, V, Cr, Ni, Cu, Zn, As, Rb, Sr, Sb, Cd, Sn, Pb, Li, Sb, La.*
- **Organic and elemental carbon** (*OC, EC*)

2.2. Data pre-treatment and analysis of input data

An input concentration matrix of 37 samples and 37 species was created. A corresponding matrix of sample-specific uncertainty values was also injected in the model. Concentration data below the detection limit (the maximum reported detection limit was used as a conservative limit for all samples) was substituted with one-half of the detection limit and missing concentration data were substituted with the median value. Correspondingly, uncertainty for data below the detection limit was set equal to 5/6 of the detection limit while uncertainty for missing data were set equal to 4 times the median concentration (Polissar et al., 2001).

As mentioned, species with large analytical errors were excluded from the analysis. From the data included, none of the species presented high percentage of data below the detection limit. Finally, Cr and NI species which presented low signal-to-noise ratio (<2) were characterized as "weak". Finally, before the model base runs, scatter plots between species were examined for correlations indicating potential common influencing factors (e.g. strong correlation among all PAHs, or between PAHs and OC/EC).

2.3. Statistical parameters

The model was run for 3 to 10 factors and a random seed. For each factor 20 runs were conducted, in order to obtain Q-value stability. All runs converged and Q values ranged between ±1.2%. In each case, the Q-robust value was lower than 1.5 times the Q-true value, indicating that outliers are not significantly impacting the Q value. Furthermore, many scale residuals for Sb were <-3 and >3 and this specie was characterizes as weak and the model was re-run.

A critical step in PMF analysis is the determination of the number of factors which correspond to particle sources. The optimal number of factors was determined by examining the Q values for PMF solutions resulting from a range of the -number of factors- values without excluding the solution's physical validity (Reff et al., 2007). The optimal number of factors in this analysis was six. The two final steps were the bootstrap and Fpeak runs in order to examine the stability and the rotational ambiguity of the solution, respectively. The chosen solution was bootstrapped 100 times with a seed of 25, block size of 10 and r^2=0.6. Fpeak values between -2 and +2 were examined by a step of 0.1 and the optimal Fpeak value was -0.1 (independence of factors increase without significantly increasing the Q value).

3. Results and discussion

PMF analysis lead to a solution of six factors, which correspond to six sources or groups of sources. Figures A.II.4.1a-f present the six factor profiles. Figures A.II.4.2 and A.II.4.3. present the temporal trends of factors contribution and the factors relative contribution to PM2.5 mass concentration respectively. A factor-to-source correspondence is obtained:

- The dominant specie (~60%) in the first factor is Na indicating particles origin *from the sea*, possibly through sea-breeze circulation (**Sea-salt source**)
- The second factor is strongly connected with Ca, Al, Sr (>60%) and in a lower percentage with the other metals implying that this source is possibly **road dust**.

- The strong presence (~70%) of V and Ni, tracers which indicate fuel oil combustion in combination with NO_3^-, SO_4^{2-}, NH_4^+ ions and Na, Mg (sea-origin) connects possibly the third factor with a **marine-shipping emissions** source.
- The fourth factor is strongly associated with NO_3^-, SO_4^{2-}, NH_4^+ implying a correspondence with **a secondary aerosols** related source.
- For the fifth factor, the dominant species are the PAHs and several metals as Cr, Zn, Pb, V, Sb indicating a **mineral/industrial** source.
- The last factor is characterized by elevated contribution to all PAHs (>60%) and organic and elemental carbon (>40%), tracers of **combustion sources**.

Concluding, the present PMF analysis indicated PM2.5 origin from six sources or groups of sources: a source related to marine-shipping emissions, a group of combustions-related sources, a secondary aerosols-source, a road dust source, a sea-salt source and an industry emissions-related source. The quantitative contribution of each source to PM2.5 concentration was estimated by the model (Figure A.II.4.3). However, a critical interpretation and assessment of the analysis should include several parameters which can affect the quantitative results accuracy. In PMF (and generally in receptor models), uncertainty derives from both inaccuracy in the input data and model assumptions and ambiguities. The former includes the assumptions made for missing values and values below the detection limit, the analytical uncertainty, the outliers etc. The uncertainty associated with factor analysis performance is strongly connected with the number of the relevant factors determination and their correspondence with sources (which is based on both mathematical criteria and user's subjectivity). Furthermore, another contribution to overall uncertainty in factor analysis is the lack of a unique solution due to the large number of unknown variables (rotational uncertainty), although this is partially eliminated by the non-negativity constraints in PMF.

Last but not least, the limitation of the short duration of the experimental campaign (a 6-week campaign, 37 samples injected in the model) has influenced the PM2.5 source apportionment result. The source apportionment analysis based on the long monitoring campaign in Marseille's city (larger number of samples, more seasons covered) will give a more complete picture of the sources identification and contribution to particles concentration.

Natural-sea salt

Road dust

Marine-shipping emissions
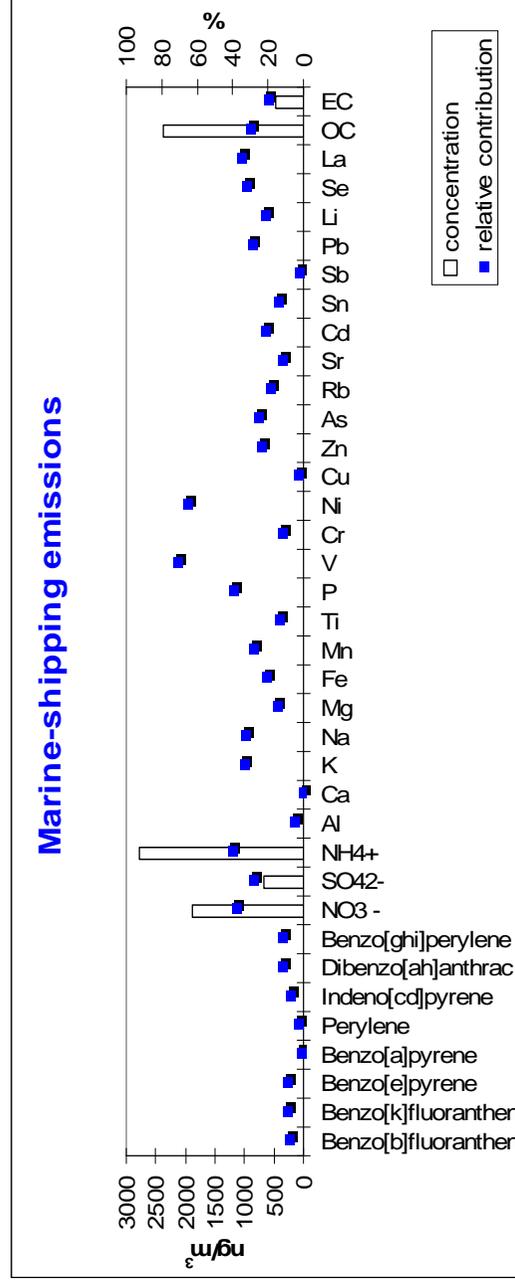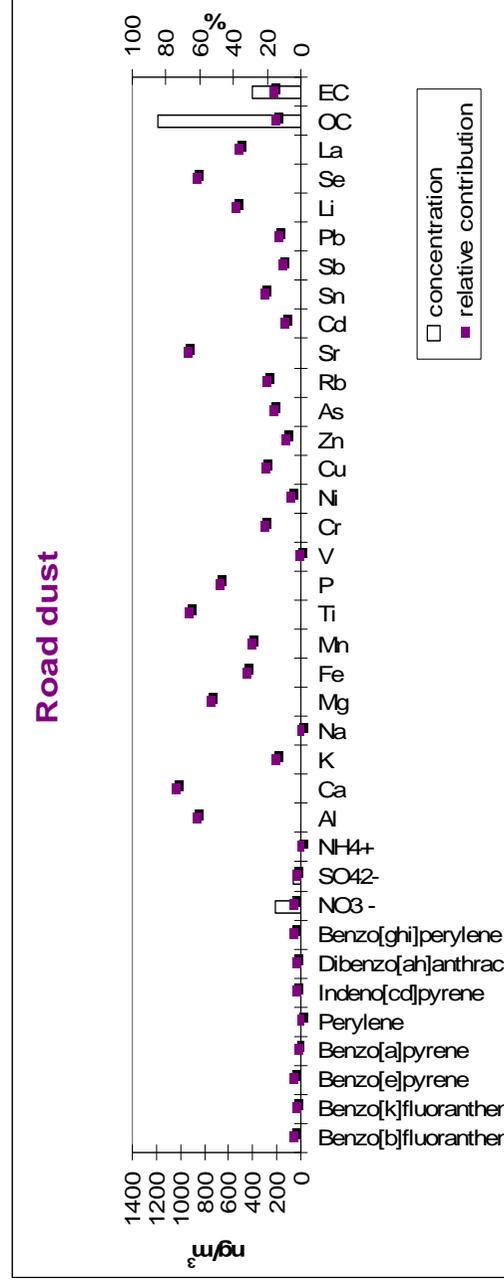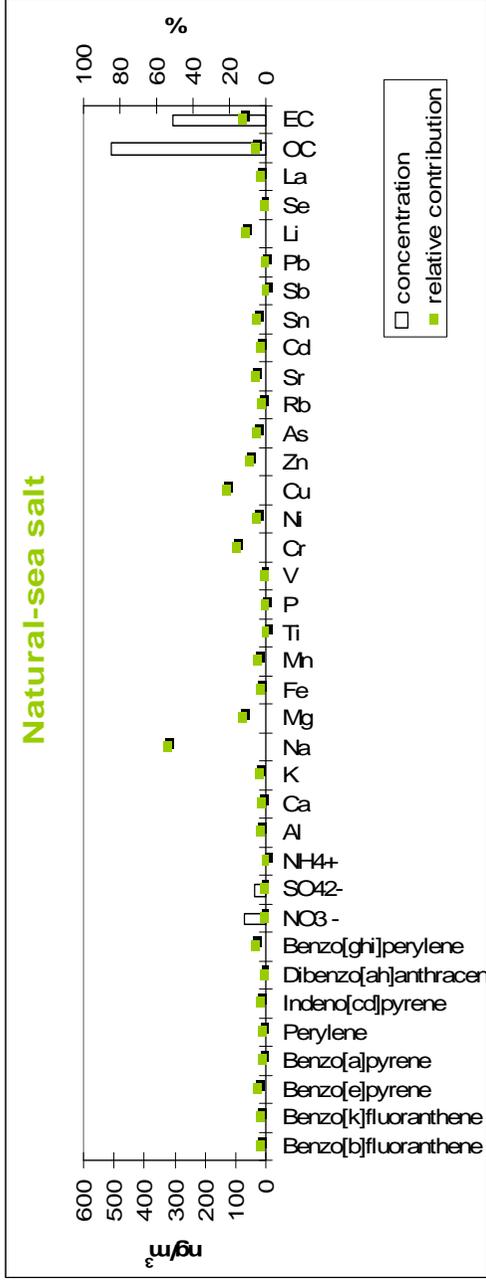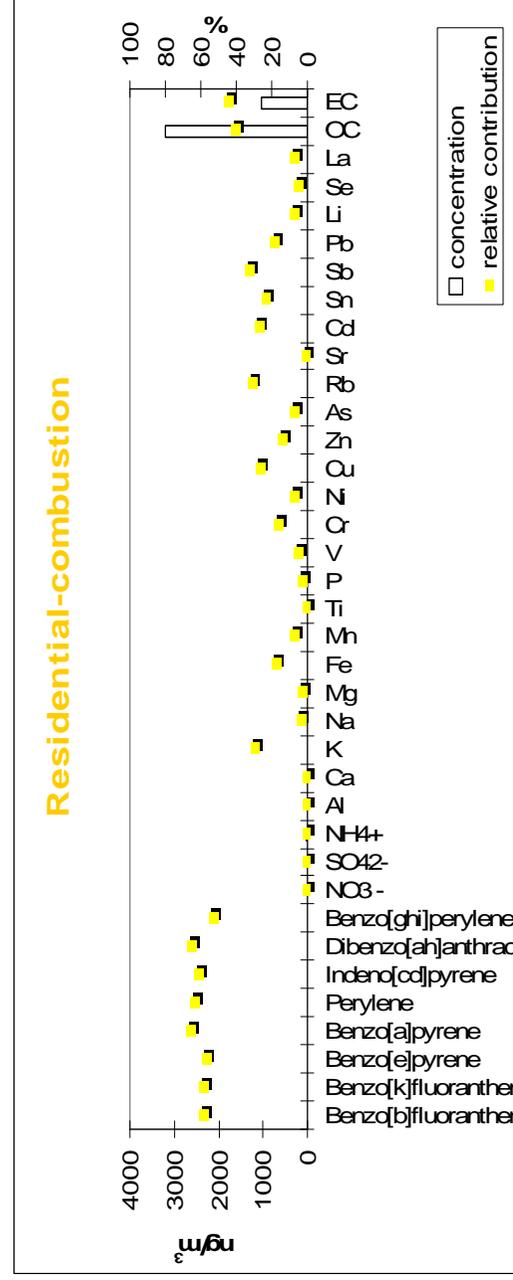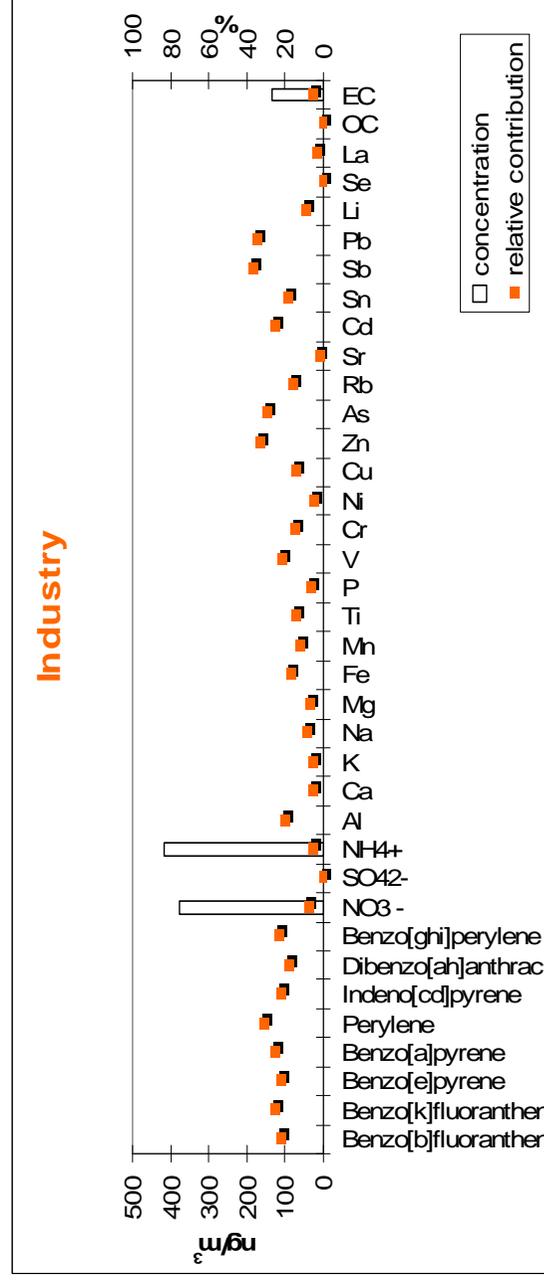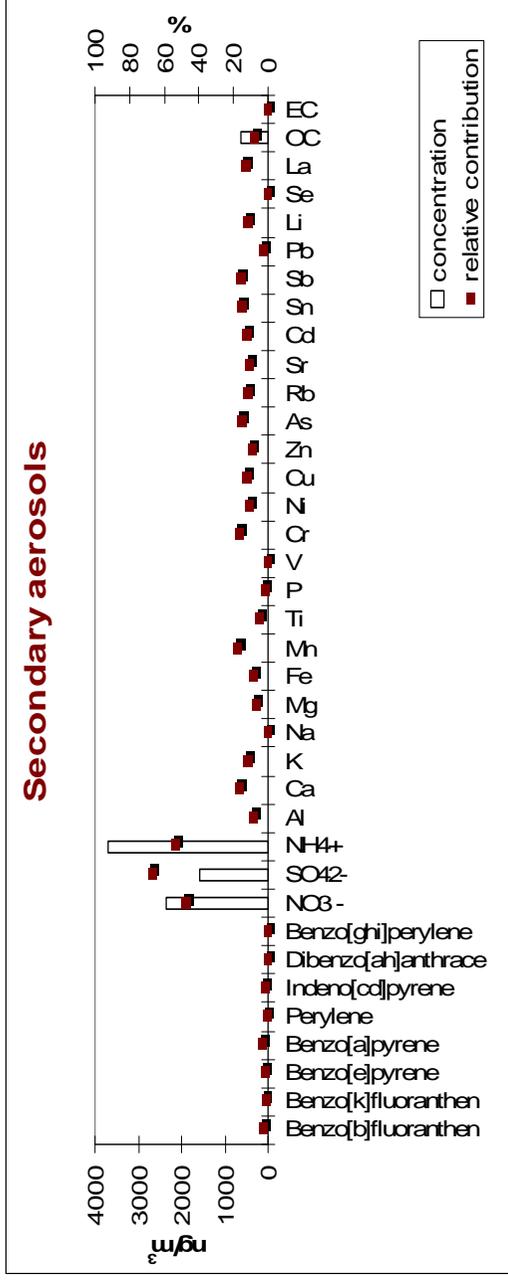
Figures A.II.4.1a-f: Factor profiles (absolute concentration and relative contribution to species)
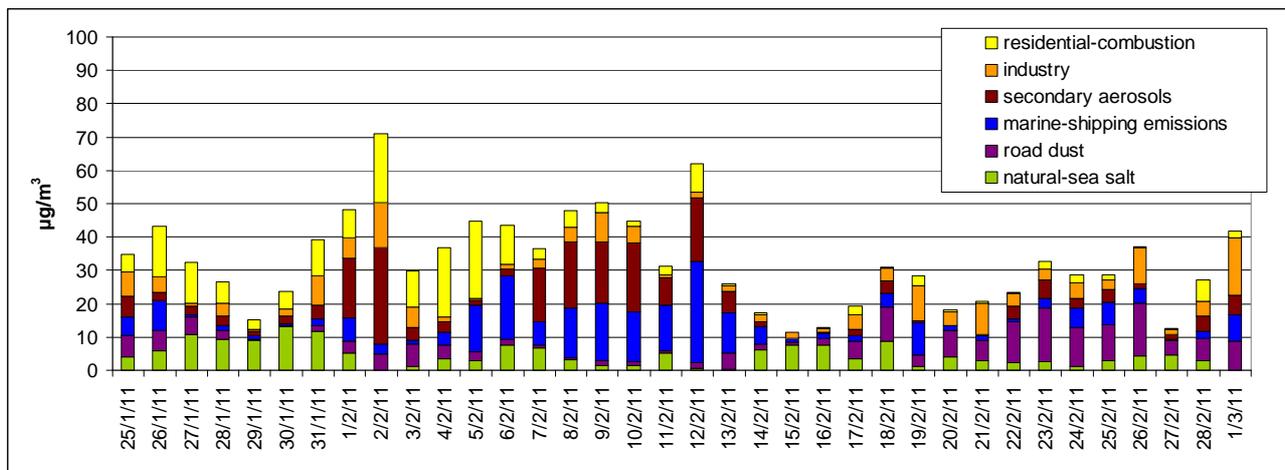
Figure A.II.4.2. Temporal trends of the factors contribution to PM2.5 mass concentration.
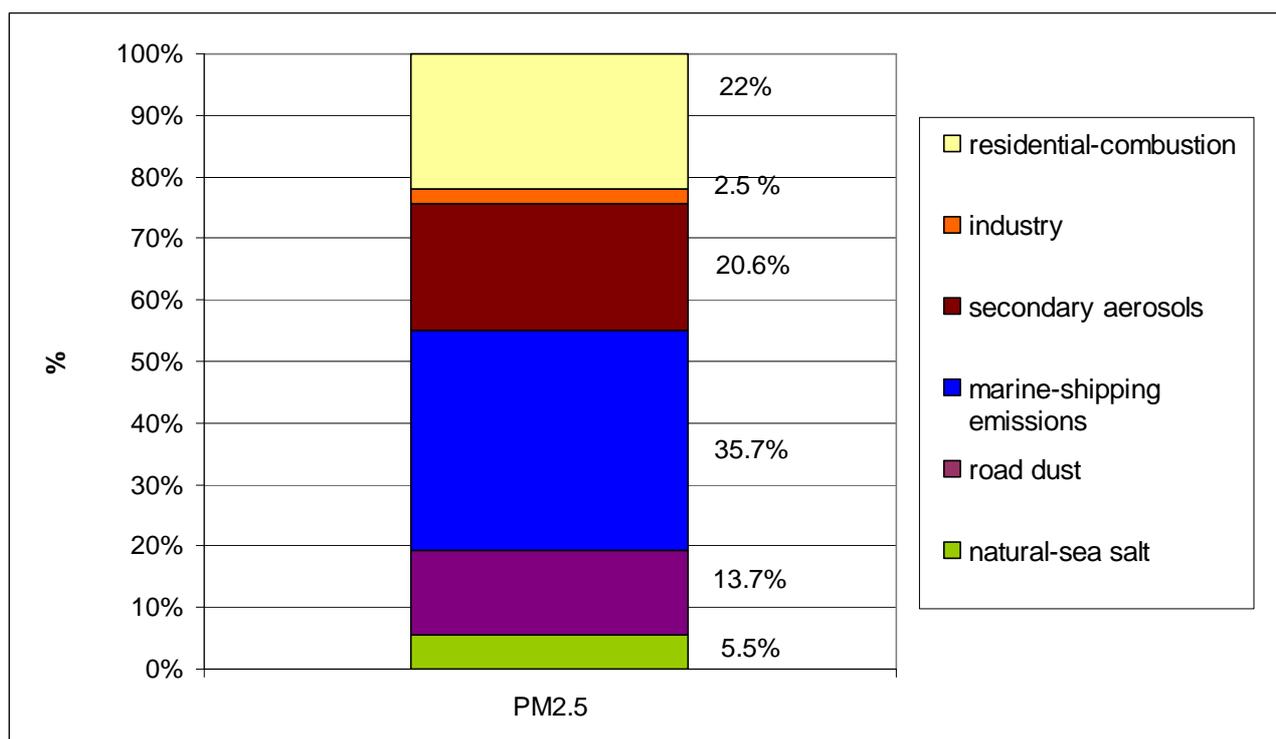
Figure A.II.4.3: Relative contribution of the six factors to PM2.5 mass concentration.

Acknowledgements

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Appendix II.5 : Source apportionment results (IDAEA-CSIC/U. Genoa, Venice)

1. Source apportionment approach

The source apportionment approach used by IDAEA group is PMF2 (Positive Matrix Factorization, version 2), an advanced receptor model, developed by Paatero (Paatero et al, 1994) that in the last years has been asserted to international level like most reliable. It is useful, especially, where detailed data do not exist on the composition of the main emission sources, but where large numbers of sampled data are available on ambient concentrations. The important advantage of the positive matrix factorization is the ability to handle missing data and values below the detection limits data by adjusting the error estimates of each data point. In fact, the solution to the PMF problem depends on the uncertainties attributed to each value.

The errors associated to concentrations values were treated according to the procedure described by Amato et al. (2009) and Escrig et al. (2009).

Mass apportionment was calculated performing a linear regression between the temporal trends of sources resolved by PMF (Ramadan et al., 2000).

Among the output of the model, important parameters to consider are the explained variations (EV). They indicate to what extent a source explains the temporal trend of an element. The higher is the EV of an element in a source, the more this element is specifically "contained" in that source if compared to the others. This, high EV for an element in a source identify that element as a good tracer for the source. EV are a good help to associate factors with real chemical – physical processes that emitted PM.

In the presented PMF analysis, PM measured components included elements, ions, organic and elemental carbon measured by IDAEA group and and targeted sum of the organic species described in Appendix 1: Even Alkanes (E-ALK: n-C(26-28-30-32)), Odd Alkanes (O-ALK: n-C(27-29-31-33)), Heavy PAH (H-PAH: Benzo(b)fluoranthene, Benzo(j+k)fluoranthene, Benzo(a)pyrene, Indeno(123-cd)pyrene, Dibenz(a,h)anthracene, Benzo(ghi)perylene), Hopanes (HOPA: 17alpha(H)-22,29,30-Trisnorhopane, 17alpha(H),21beta(H)-30-Norhopane, 17alpha(H),21beta(H)-Hopane, 17alpha(H),21beta(H)-22S-Homohopane, 17alpha(H),21beta(H)-22R-Homohopane) and DeHydro Abietic Acid (DHAA) measured by ARPAV.

Variables were selected according to the signal-to-noise criterion (Paatero and Hopke, 2003) and 21 variables were finally used in the analysis: Ca, Na, Mg, Fe, SO_4^{2-}, V, Ni, Cu, Zn, Sn, Sb, Pb, NO_3^-, NH_4^+, EC, OC, E-ALK, O-ALK, H-PAH, HOPA, DHAA.

2. Results

Seven sources were resolved and labeled, according to their characteristic tracers, as follows: *Dust* (traced by Ca), *Road* (divided into *Vehicular exhaust + Sea Spray* (traced by Cu, Zn, EC and Na) and *Road Dust* (traced by Sb and Sn), *Industrial/Marine* (*Oil Combustion*, traced by V, Ni), *Secondary Compound* divided into *Secondary I* (*traced* by SO_4^{2-}) and *Secondary II* (traced by NO_3) and *Residential* (*Biomass Burning*, traced by DHAA). PMF applied to a time series of elemental concentration values resolved, over the number, the profiles (Figure AII.5.1) of PM sources at the sampling site and their contribution to PM2.5 levels (Figure AII.5.2).
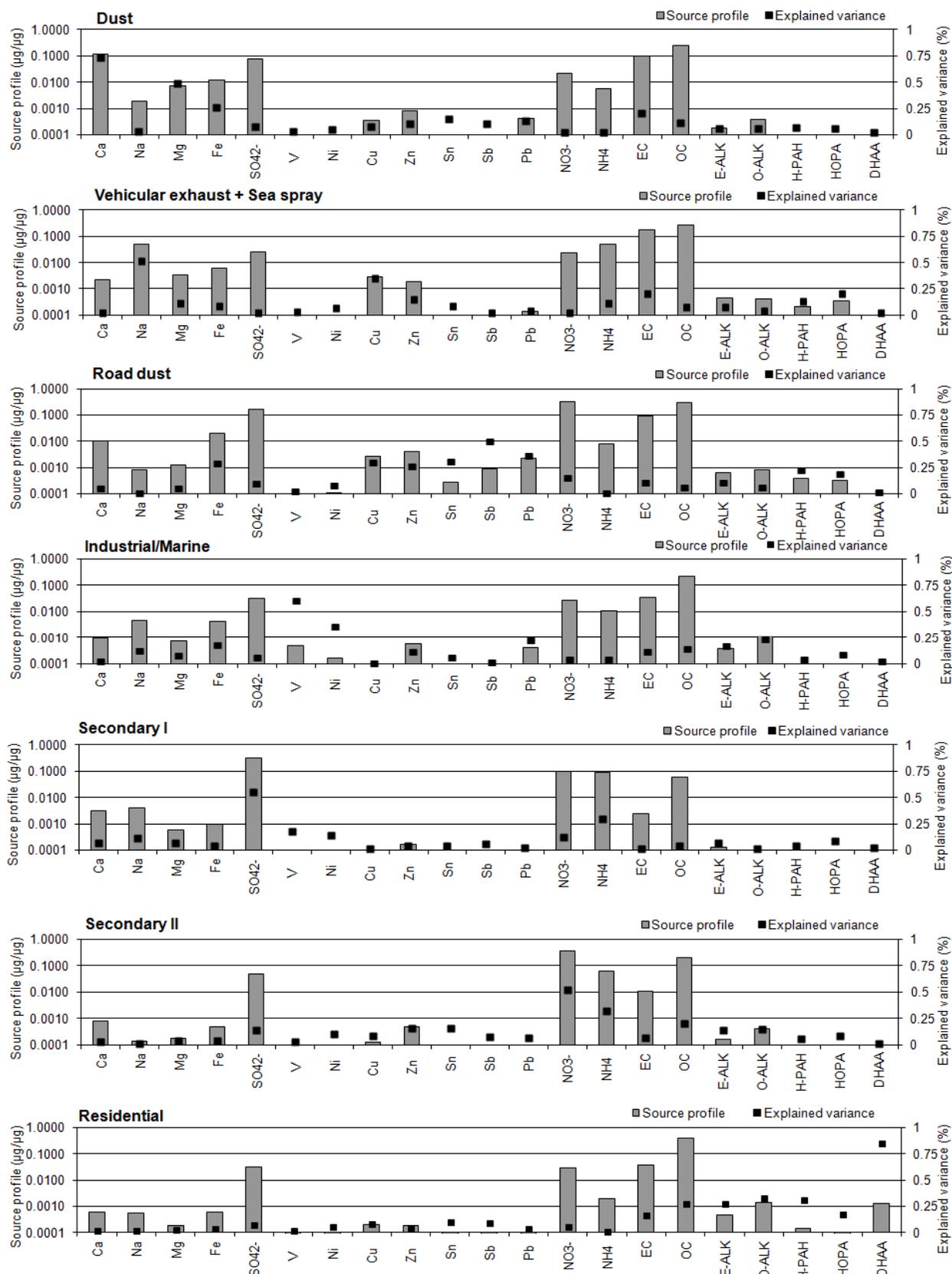
Figure AII.5.1. Profiles (bars) of the seven PM2.5 sources identified by PMF. Values on the y-axis (µg/µg) are the relative weight of the concentration of each element to the mass of each source in the PM2.5 fraction. Squares represent Explained Variations.
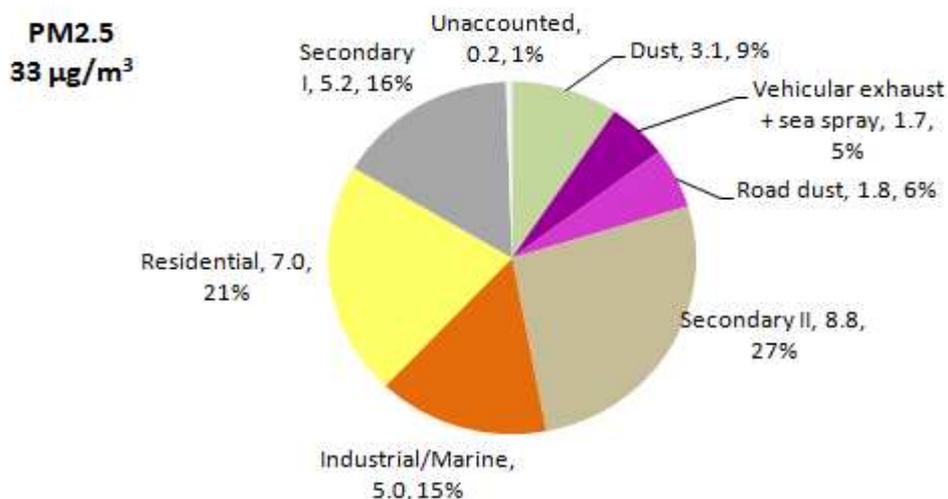
Figures AII.5.2: PM2.5 apportionment mass deduced by the PMF analysis (reported as absolute contribution in µg/m³ and as relative contribution).

In Figure AII.5.2 the mass apportionment is shown. The time trends of sources resolved by PMF are shown in Figure AII.5.3. In the first part of intercomparison campaign *Residential* present an high contribution to the total mass, while the central part of sampling campaign is caracterised by the high contribution of *Secondary I, Secondary II and Industrial/Marine.*

In Figures AII.5.4 the apportionment of each single PM compounds is shown.

66
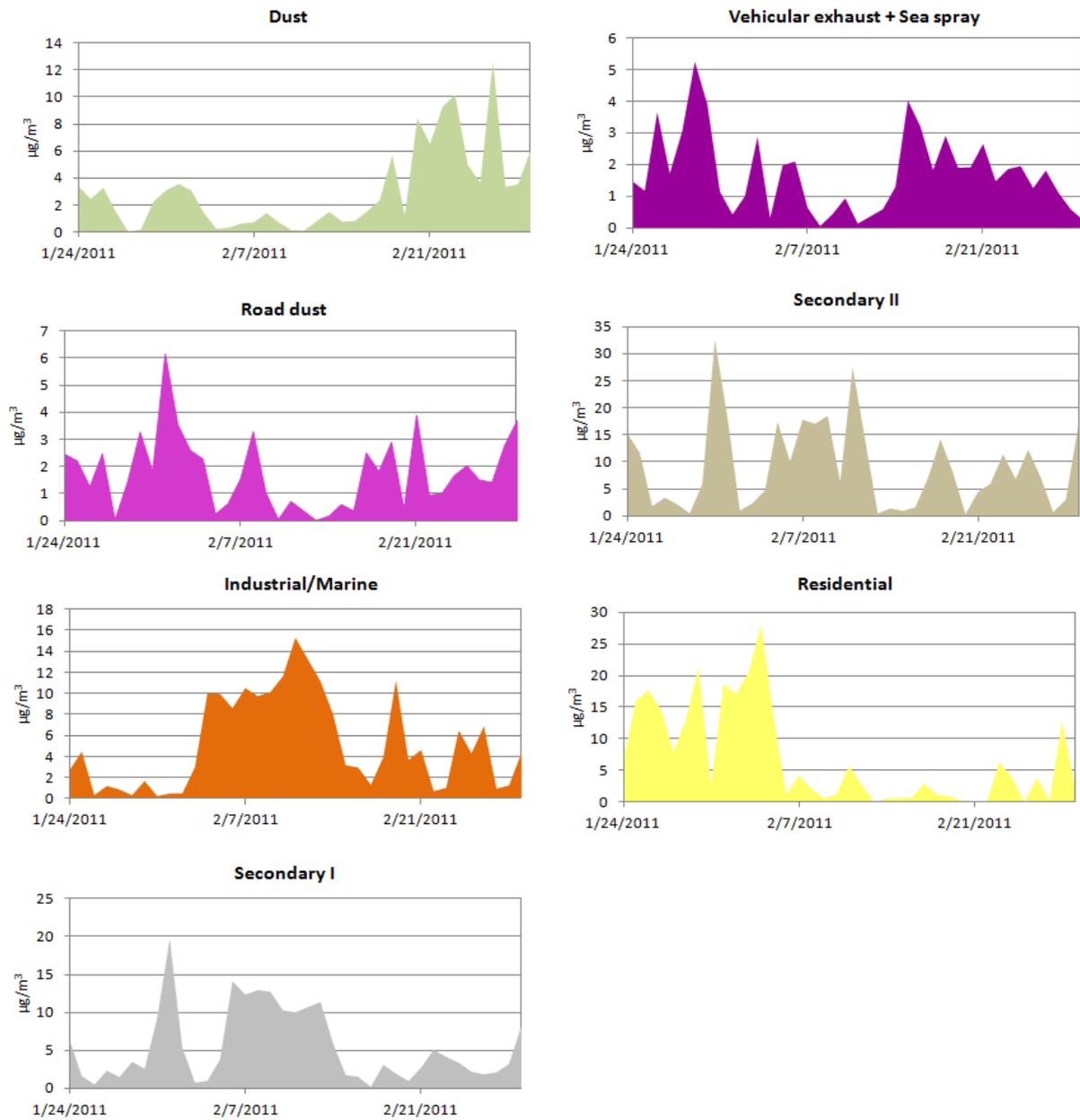
Figure AII.5.3: Temporal trends of each source resolved by PMF in PM2.5.
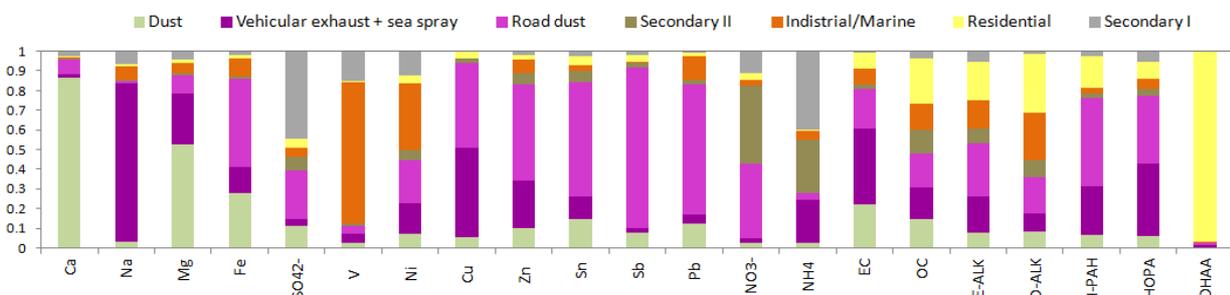
Figure AII.5.: Mass apportionment of single PM compounds deduced by the PMF analysis in PM2.5.

67