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**Intercomparison campaign
(WP3.4)
First Progress Report**

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Colophon

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Main Author(s):

A. Detournay¹, J. Pey², N. Perez², M.C. Bove³, V. Ariola³, E. Cuccia³, D. Massabò³, P. Prati³, J.G. Bartzis⁴, D. Saraga⁴, E. Tolis⁴, K. Filiou⁴, A. Latella⁵, A. De Bortoli⁵, F. Liguori⁵, S. Patti⁵, N. Marchand¹

(1) University of Provence, CNRS, Laboratoire Chimie Provence-Instrumentation et Réactivité Atmosphérique, Marseille, France.

(2) Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, Spain.

(3) University of Genoa - Department of Physics, via Dodecaneso 33, 16146, Genova, Italy

(4) University of West Macedonia, Kozani, Greece

(5) ARPAV Veneto, Padova, Italy

Responsible institution(s):

University of Provence, CNRS, Laboratoire Chimie Provence-Instrumentation et Réactivité Atmosphérique (N. Marchand)

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1. Introduction

Source apportionment of PM (Particulate Matter) 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 an urban area atmospheric aerosol are emitted in 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, NO_x. 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 has thus been 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 are to intercompare measurements and source apportionment methodologies that will be carried out in each harbor under study within APICE. Besides this intercomparison exercise of measurements and source apportionments one of the most important issue of this intercomparison campaign is to assess the ability of each partner to apportion the different harbor sources among the numerous other anthropogenic and natural sources.

The intercomparison campaign gathers all the scientific partners involved in the measurements and source apportionment task. A very large instrumentation have been deployed including state of the art instruments such as Aerosol Mass Spectrometer (AMS) for online monitoring of non-refractory submicron particles composition and Proton Transfert Reaction Mass Spectrometer (PTR-MS) for online monitoring of VOCs. Results obtained within this campaign constitute one of the most important data set ever collected in one point in Europe. It guarantees to fulfill the specific objectives of the campaign and allows going further in our understanding of aerosol particles chemistry and in source apportionment methodologies.

Initially planned in autumn 2010, the field campaign has been delayed in February/March 2011 for logistical issues and to guarantee the success of the campaign.

Thus, **this first progress report focuses on the intercomparison of measurements available in July 2011**. Source apportionments as well as some reaming analyses are in progress in the different laboratories. A comprehensive and critical assessment of this source apportionment intercomparison exercise will be presented in a next progress report. Receptor models analysis will be presented during the meeting in Venice (January 2012) in a targeted day of work besides the official meeting. **The final strategy will be finalized during the meeting and the final report is expected at the end of January 2012.**

The present report details the campaign conditions with a specific focus on harbors/industrial inputs and first intercomparison of PM measurements (mass and chemical composition). Preliminary source apportionments are presented in Appendix II.



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2. Field Campaign Description

2.1. Marseille : situation and figures

Figure 2-1 presents the surroundings of Marseille and the localisation of the sampling site used within the intercomparison campaign. Marseille constitutes an extremely interesting case study to reach the objectives of the campaign. First, being the second city of France, it gathers more than 1.4 millions inhabitants and spreads over 240 km². Then, as Mediterranean first harbor and world third harbor for oil and oil derivatives, Marseille has insured the treatment of over 83 million tons of hydrocarbons and petrochemical products, the transport of 14.5 million tons of miscellaneous goods and over 2 millions passengers in 2009.

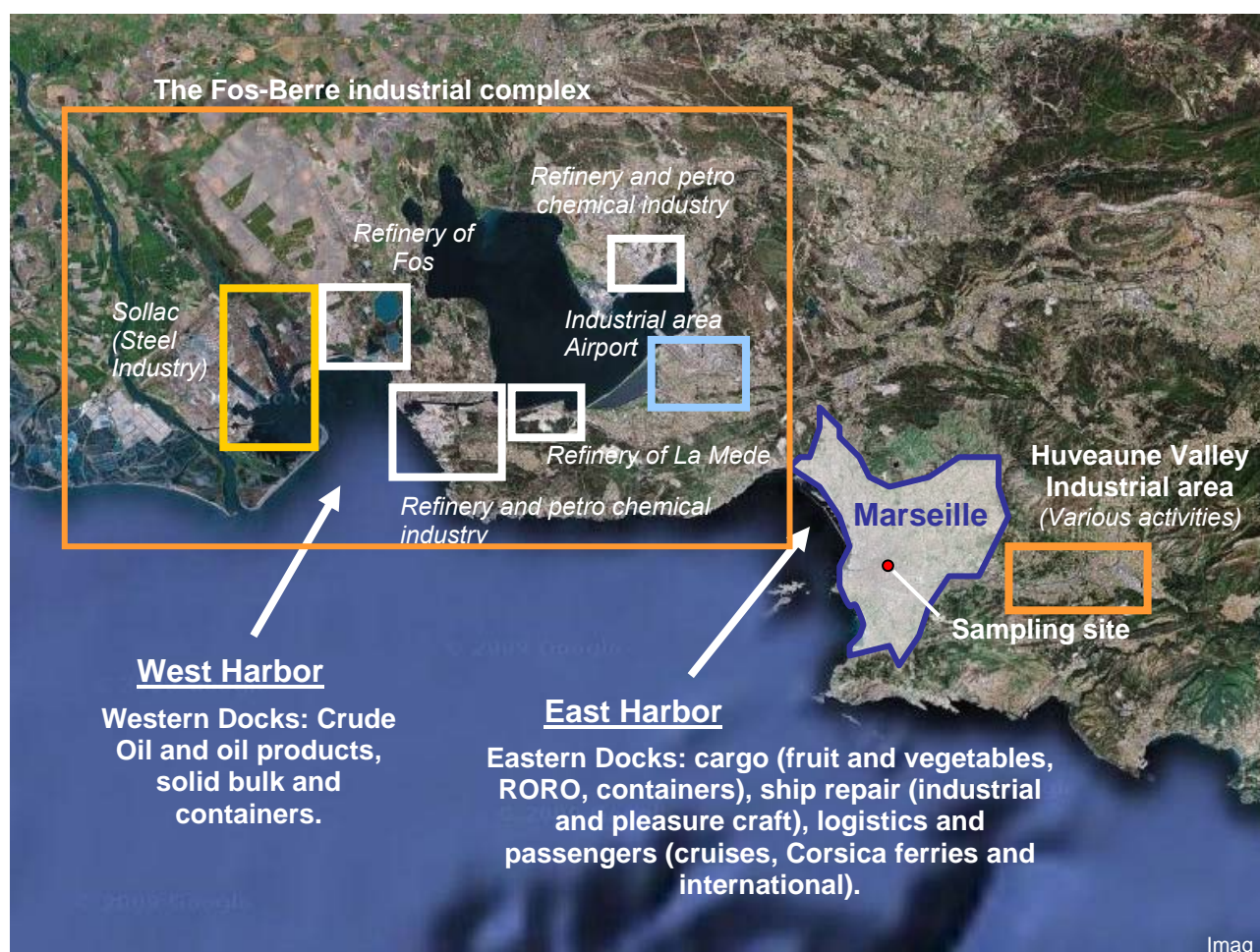


Figure 2-1: Marseille's harbor and industrial areas

Marseille also represents an important industrial area. Thus, the nearby industrial complex of Berre-Fos, located on Marseille eastern side, gathers 4 refineries, representing 32% of the total French oil refining capability; steel industries, petrochemical plants, etc. An additional industrial area, located on Marseille western side (Huveaune Valley), can also impact the atmospheric chemistry over the city.

This area is then well known for its photochemical pollution, especially toward ozone, and evidence of rapid formation of secondary organic aerosols has been pointed out within the framework of the ESCOMPTE and FORMES experiments. Main results regarding the influence of the industrial areas over PM concentrations observed in Marseille are presented in Appendix I.

2.2. Intercomparison campaign: localisation, period and instrumentation

The sampling site selected for the intercomparison campaign, called « 5 avenues » (43°18'20" N, 5°23'40" E, 64 m a.s.l. – cf. figure 2.2.) is located in a large landscape park downtown Marseille. The sampling site is defined as an urban background site.

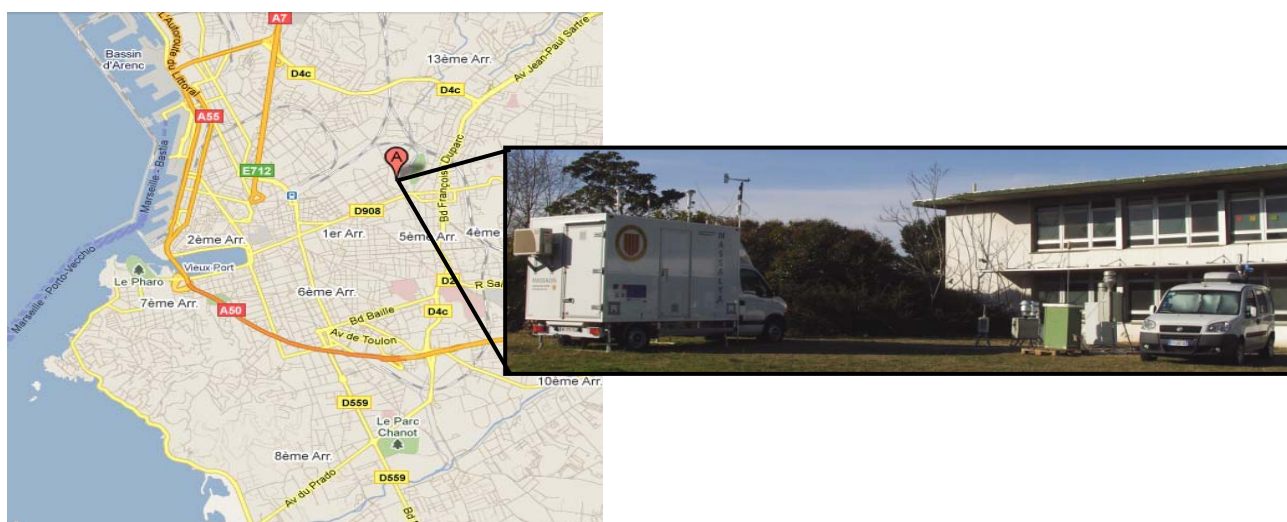


Figure 2-2 : Sampling site localisation and instrumentation deployed during the APICE intercomparison campaign

The measurement campaign took place from the 25th of January to the 2nd of March 2011. It gathered all of the APICE project partners on the same sampling site.

A large instrumentation has been deployed during the whole campaign allowing the constant monitoring of aerosol physico chemical parameters and associated gas phase (VOC's and regulated pollutants –ie: O₃, NO_x, SO₂-) (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 ¹⁴C analyses have been added to the APICE instrumental setup in order to better constrain the source receptor models outputs.

In addition to this very large instrumental setup 2 others European scientific groups joined the campaign in order to go further in our scientific understanding of industrial pollutions over a large Mediterranean city: Paul Sherrer Institute (Villingen, Switzerland) and Laboratoire d'Aérodologie (Toulouse, France).

Results obtained within this campaign constitute one of the most important data set ever collected in one point in Europe. It guarantees to fulfill the specific objectives of the campaign and allows to go further in our understanding of aerosol particles chemistry and in source apportionment methodologies.

Parameters	PM _x	Time resolution	Organization/lab	Instrument/method
Marseille				
Org. SO ₄ , NO ₃ , NH ₄ , (PAH), NR, Cl	PM1	7 min	ICP-IRA (Univ Prov)	HR-TG-AMS
BC	PM1	5 min	ICP-IRA (Univ Prov)	MAAP5012
particle number, size distr.	PM1	7 min	ICP-IRA (Univ Prov)	SMPS (10-1000 nm)
VOCs (Benz, Tol, Isopr, MACR/MVK etc..)	PM1	1 min	ICP-IRA (Univ Prov)	HS-PT-RMS
OC/EC, majors ions, metals	PM2.5	24h	ICP-IRA (Univ Prov)	Off line HV, OC/EC (EUSAAR2), ions IC, Metals (ICP/MS)
Organic markers (levoglucosan, hopanes, n-alk, steroids, PAH, ..)	PM2.5	24h	ICP-IRA (Univ Prov)	Off line HV, GC/MS
14C	PM2.5	24h	ICP-IRA (Univ-)	Off line HV
Wind dir. and speed, HR, T	PM2.5	5 min	ICP-IRA (Univ Prov)	
SO ₂ , O ₃ , NO _x , PM10, PM10 FDMS, PM2.5 FDMS		15 min	AmpoPACA	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	ARPAY-ORAR	Photoelectric Aerosol Sensor PAS2000 EcoChem (10-1000 nm)
PM mass	PM2.5	5 min	ARPAY-ORAR	PM2.5 continuous particle sizing monitor / Dual Wavelength Nephelometer
PM particle diameter of mass max concentration	PM2.5	5 min	ARPAY-ORAR	PM2.5 continuous particle sizing monitor / Dual Wavelength Nephelometer
Particle number	PM 0.3-10.0	15 min	ARPAY-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	ARPAY-ORAR	Off line LV, DTD-GC-MS
PM2.5	PM2.5	24h	ARPAY-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, SO ₄ 2-, NO ₃ -, Cl- and NH ₄ +	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	PS/LAC	RDI (Rotating Drum Impactor), with synchrotron-radiation induced X-ray fluorescence
BC	TSP	5 min	LA/CNRS	Aethalometer 7lambda

Table 2-1: Overview of the instrumentations deployed during the intercomparison campaign

3. Overview of the field campaign conditions

3.1. Wind conditions during the measurement campaign

Figure 3-1 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 (figure 2.1).

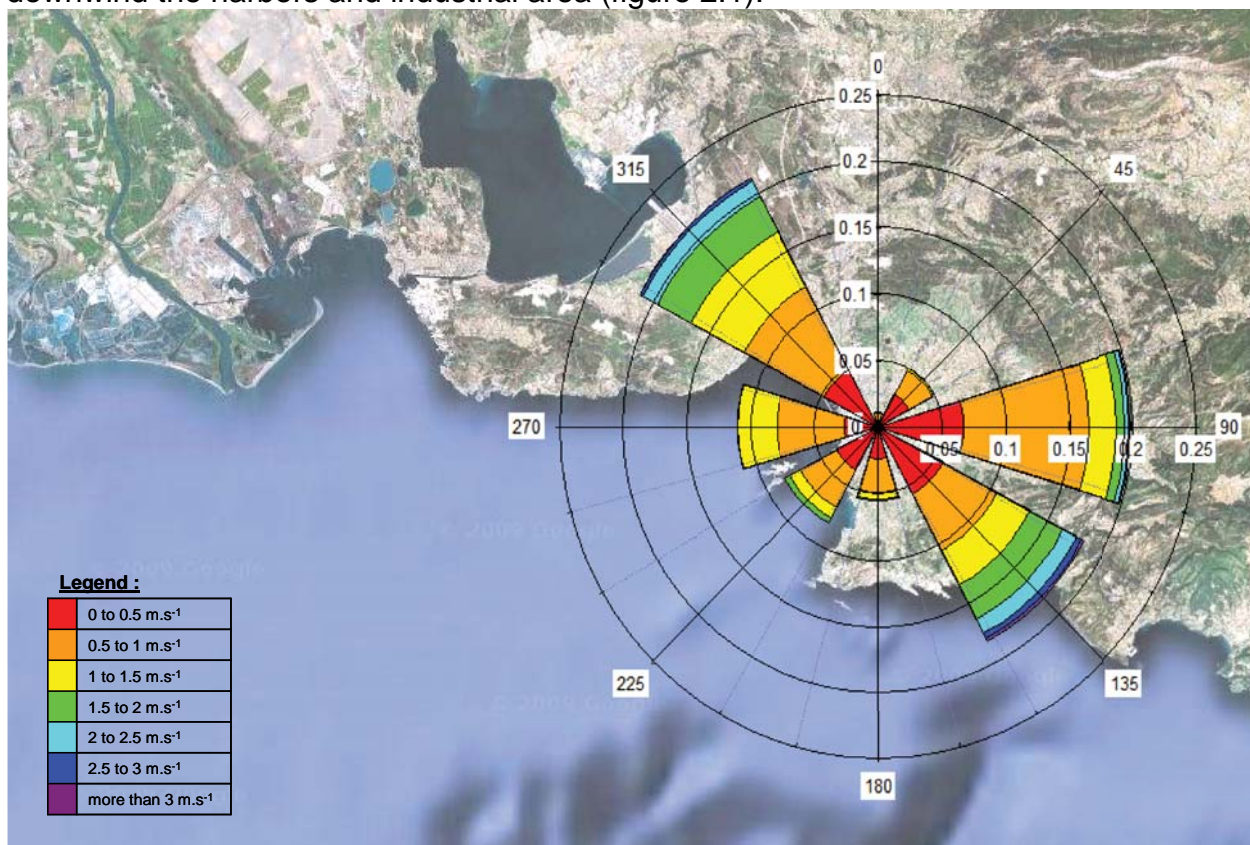


Figure 3-1: Wind direction observed during the intercomparaison campaign

3.2. Mean concentrations and temporal trends

Table 3-1 presents the mean concentrations of several pollutants during the whole measurement campaign.

Those different pollutants displayed classical concentrations for the season in Marseille. ($37.5 \mu\text{g m}^{-3}$ for PM₁₀; $24.9 \mu\text{g m}^{-3}$ for PM_{2.5} and $17.3 \mu\text{g m}^{-3}$ for PM₁). However these average values hide an important variability with periods characterized by high concentrations. For example, maximal value (15 min average) for PM₁₀ was $124 \mu\text{g m}^{-3}$ – for note: according to the French law n° 96-1236, the daily mean of $50 \mu\text{g m}^{-3}$ can't be

exceeded more than 35 times a year-. For PM2.5 and PM1 highest concentrations were $79 \mu\text{g m}^{-3}$ and $74.1 \mu\text{g m}^{-3}$, respectively.

	Mean value	Maximal value	Minimal value
PM10 ($\mu\text{g m}^{-3}$) ^a	37.5	124	1
PM2.5 ($\mu\text{g m}^{-3}$) ^a	24.9	79	2
PM1 ^(a) ($\mu\text{g m}^{-3}$) ^b	17.3	74.1	0.6
Total number of submicron particles (cm^{-3}) ^c	17485	107931	1896
SO ₂ ($\mu\text{g m}^{-3}$) ^d	0.81	30	0
NO ($\mu\text{g m}^{-3}$) ^d	14.8	409	0
NO ₂ ($\mu\text{g m}^{-3}$) ^d	44.5	154	2
O ₃ ($\mu\text{g m}^{-3}$) ^d	30.3	88	0
BC (PM1) ($\mu\text{g m}^{-3}$) ^e	1.6	11.6	0.1

a : TEOM-FDMS, b : Sum of BC (MAAP) and organic, nitrate, sulfate and ammonium (AMS), c : Particle size from 10 to 1013nm measured by SMPS, d : Air Quality Network(ATMOPACA) measurements, e : Black Carbon measured by MAAP5012

Table 3-1: Concentrations observed during the intercomparison campaign

The concentrations variability is illustrated in figure 3-2-a and 3-2-b for selected parameters.

A contrast can be observed between the beginning of the campaign (from the 25th of January to the 11th of February), when higher concentrations of PM were observed, and the last part of the campaign (from the 12th of February to the 2nd of March). This dichotomy is explained by a change in weather conditions, which were characterized by sunny conditions and low wind speed at the beginning of the campaign enabling the accumulation of pollutants over the city and rains and winds episodes during the last part.

The same kind of variation can be observed for the total number of particles. However, SO₂ concentration displays a different behavior, with higher concentrations observed during the second part of the measurement campaign. This specific behavior of SO₂ can be linked to an increase of the occurrences of north western and western winds during the second part of the campaign. In such conditions Marseille is downwind the harbors and Fos-Berre industrial area.

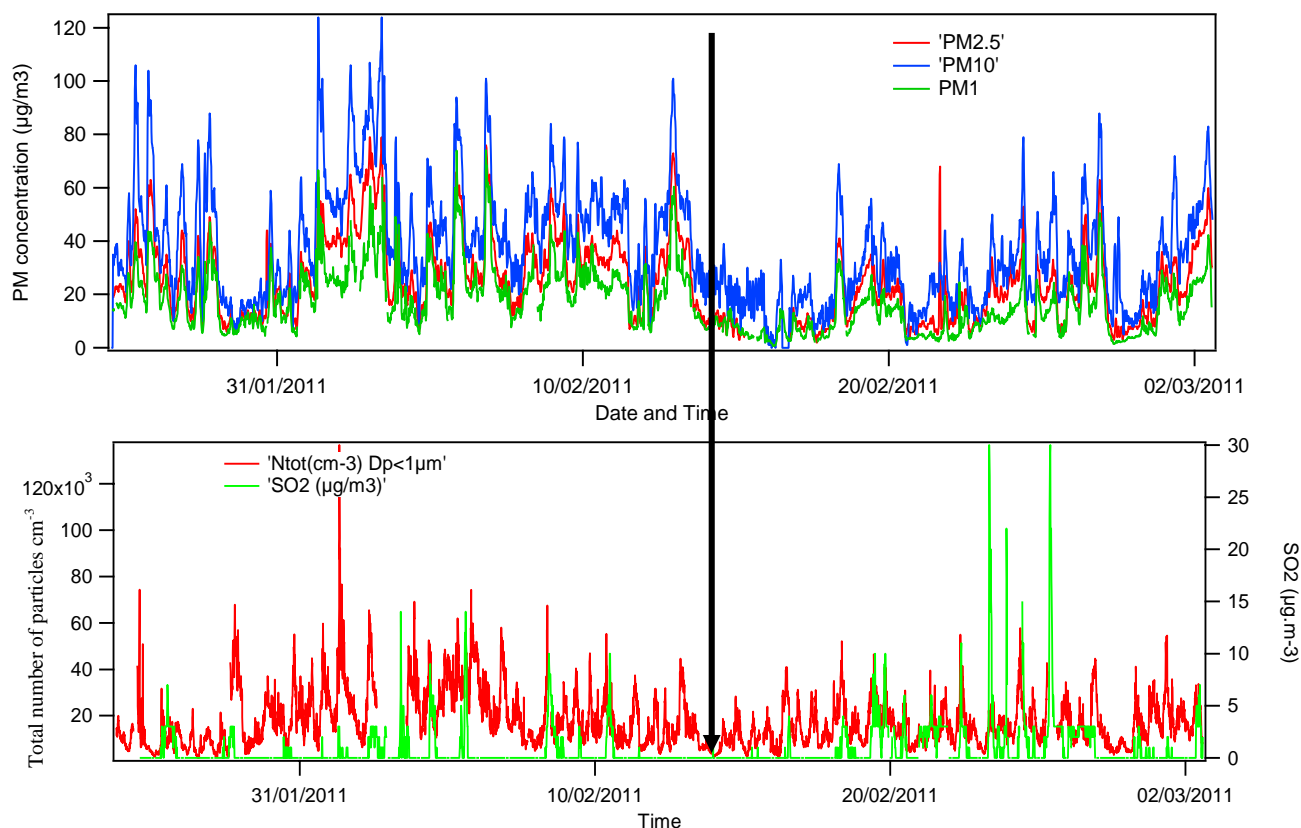


Figure 3-2-a (up) and 3-2-b (down): Temporal trends of PM₁₀, PM_{2.5} and PM₁ (up) and SO₂ and total number of particles (down)

3.3. PM₁ Composition

Figure 3-3-a and 3-3b present the temporal trends and the average contributions of the major 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.

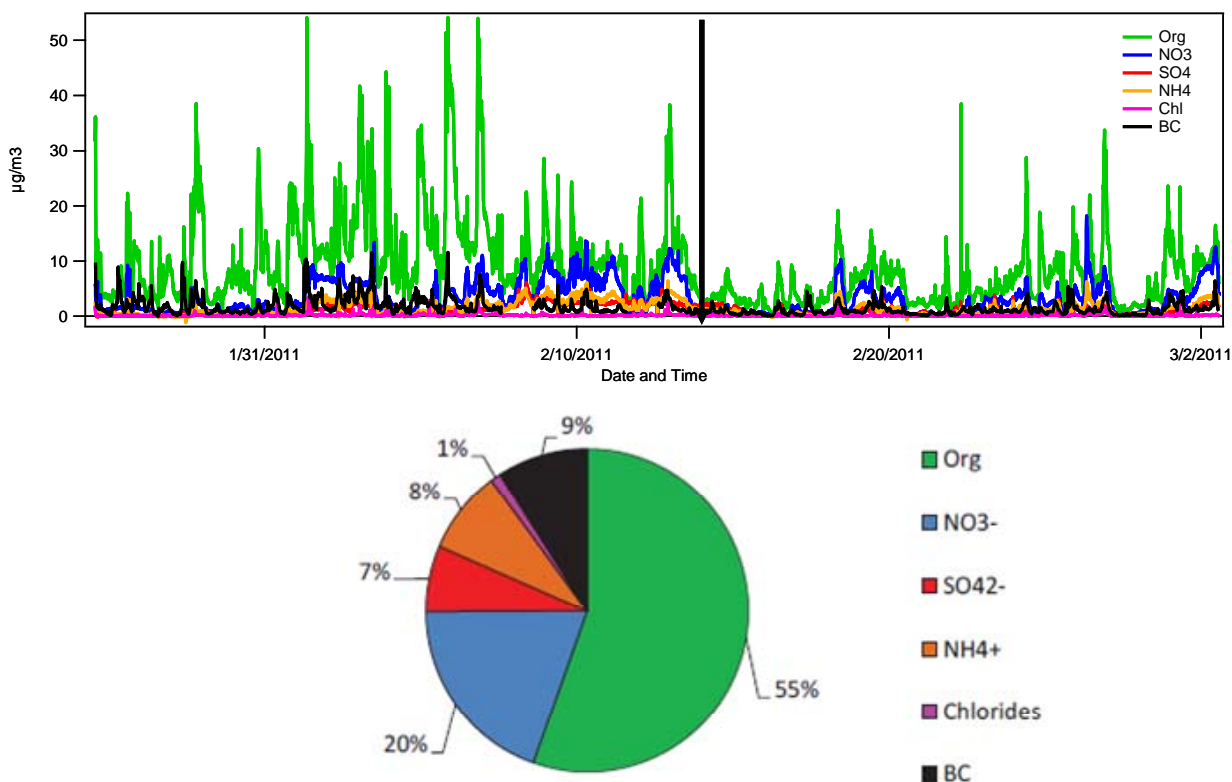


Figure 3-3-a (up) and 3-3-b (down): Temporal trends of PM1 major fraction (Organics –Org, Sulfate, Nitrate, ammonium and BC-Black Carbon-) measured by AMS and MAAP (up); average contributions (down)

3.4. Diurnal trends

Three different categories of diurnal evolutions can be distinguished. First, as shown figure 3-4 for the total number of submicron particles (N_{tot}) and toluene, some pollutant display slightly lower concentrations during the day than during the night, with strong morning (about 8:00) and evening (about 19:00) peaks. This kind of evolution is characteristic of urban traffic emission processes.

As shown on figure 3-4 for organic fraction and acetonitrile, several other pollutants display a different diurnal evolution, with strong concentrations at night (from about 18:00 to 06:00), associated to the morning traffic related peak. The sharp increases during night can't be explained solely by a decrease of the boundary layer heights. Such behavior, particularly marked for organic and black carbon, is more likely related to an additional emission source or to air masses advected over Marseille at night.

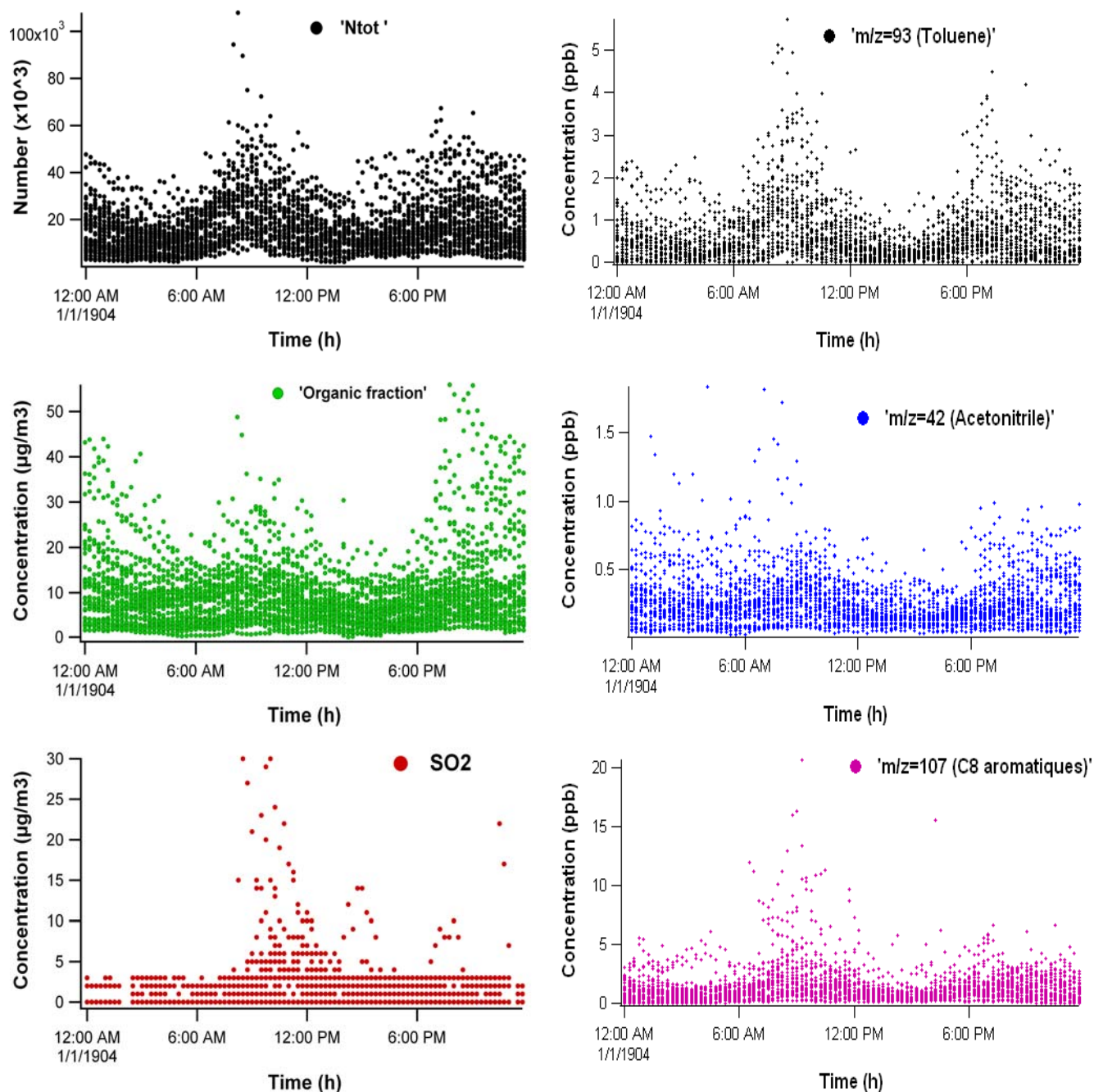


Figure 3-4: Diurnal trends of the total number of submicron particles (N_{tot}), organic aerosol, SO_2 and selected VOC's (Toluene, Acetonitrile and C8 aromatics).

Finally some pollutants, represented by SO_2 and C₈ aromatic compounds (xylenes and ethyl benzene) display no significant diurnal evolution. Their evolutions are mostly driven by specific events usually occurring in the morning (between 9:00 and 12:00). The same behavior is observed for Styrene and C₉ aromatic compounds. This kind of evolution can be associated to occasional release and advection of compounds over Marseille; those pollutants are more likely emitted from industrial /harbors areas.

3.5. Principal emissions areas

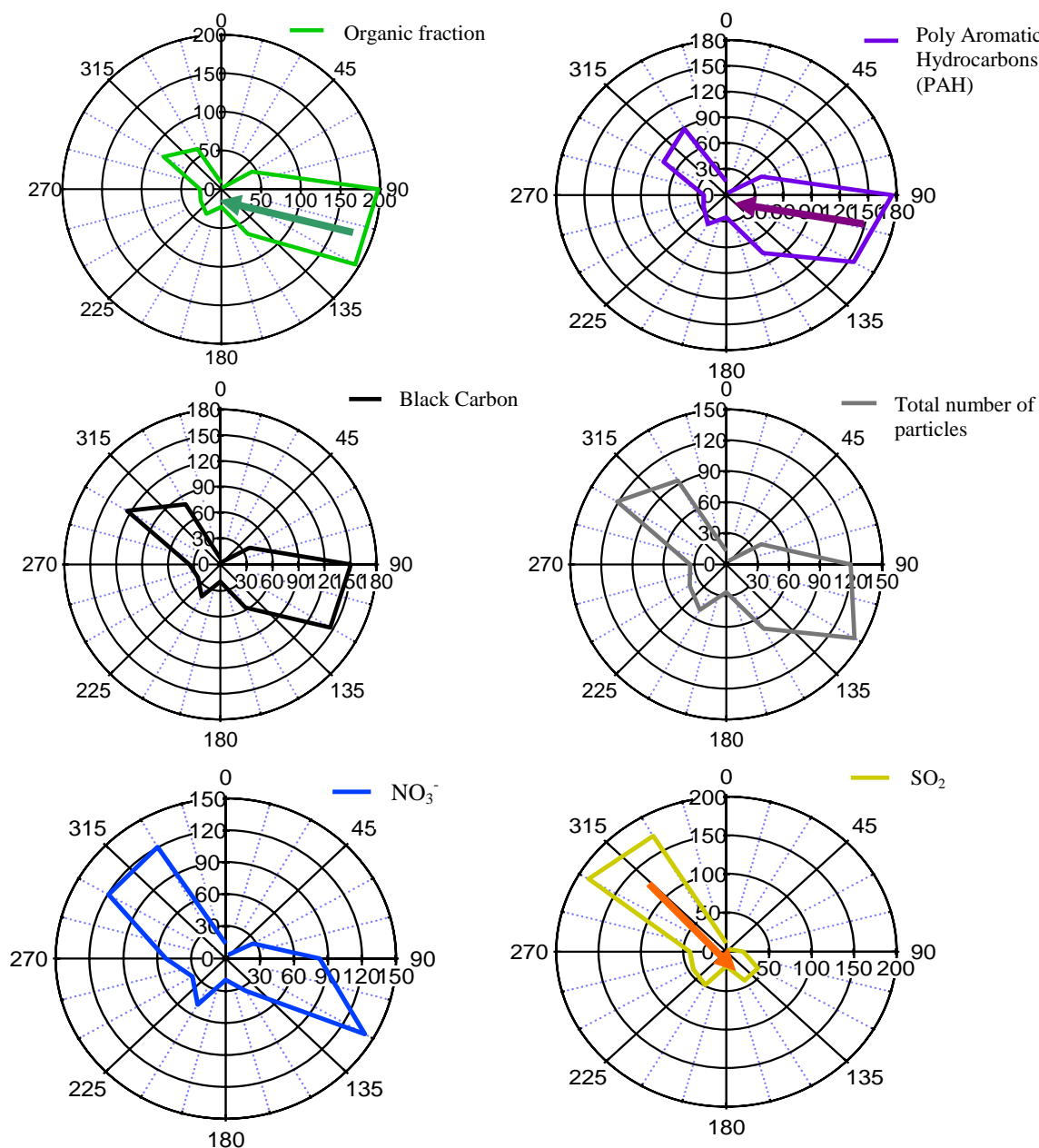


Figure 3-5: Conditional Function Probability (CPF) calculated for several measured pollutants

In order to determine the geographical origin of the air masses impacting Marseille during the measurement campaign, an analysis using Conditional Function Probability (CPF) have been performed. It consisted in determining the occurrence of the highest concentrations of a pollutant (basically values over the 75th percentile) for a wind sector. On figure 3-5 are presented several CPF, calculated for selected measured parameters.

These CPF clearly highlight the prevalence of two wind directions regarding atmospheric pollution: north-west and south-east. However, if both wind directions can be associated to high concentrations for the majority of pollutants (NO_3^{2-} , particle number, Black carbon, ...), it can be observed that higher SO_2 concentrations are encountered under north-western wind influence only; whereas higher concentrations of organic aerosol and PAH are observed preferentially under south-eastern wind direction.

These results highlight that pollution over Marseille during the field campaign was mainly driven by two processes: advection from the harbor and industrial area of Fos-Berre (north-west); and advection with the onset of nocturnal breezes canalized by the Huveaune valley. The onset of nocturnal sea breezes is favored by stable and cold conditions such as encountered during the first part of the campaign. The dichotomy between the two parts of the campaign is confirmed by CPF analysis. As shown in figure 3-6 this influence advection from east is clearly more marked during the first part of the campaign whereas advection from north-west are prevalent during the second half of the campaign. Thus if the influence of harbors and harbors related activities are expected during the second half of the campaign the question is: What about the first half of the campaign?

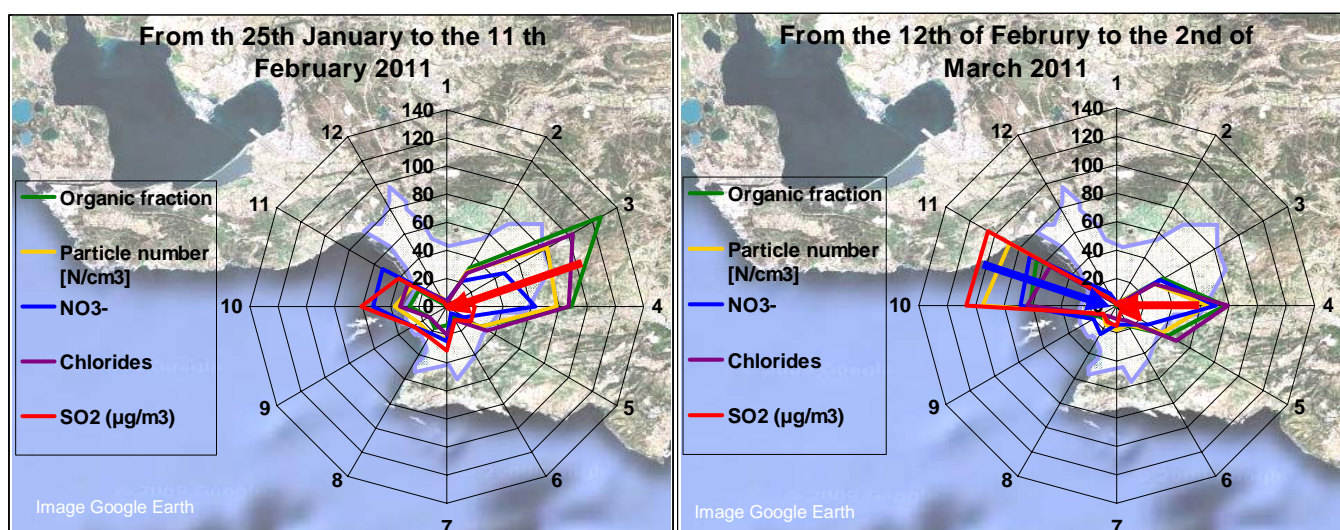


Figure 3-6: CPF calculated for the first (25th of January to 11th of February) and last part of the campaign (12th of February to 2nd of March) for the organic aerosol (PM₁), total submicron particles number (10-1000nm), Nitrate, non refractory chlorides (PM₁) and SO₂.

In order to analyze thoroughly the different events occurring during the first part of the measurement campaign, a focus on this period is presented in figure 3.7.

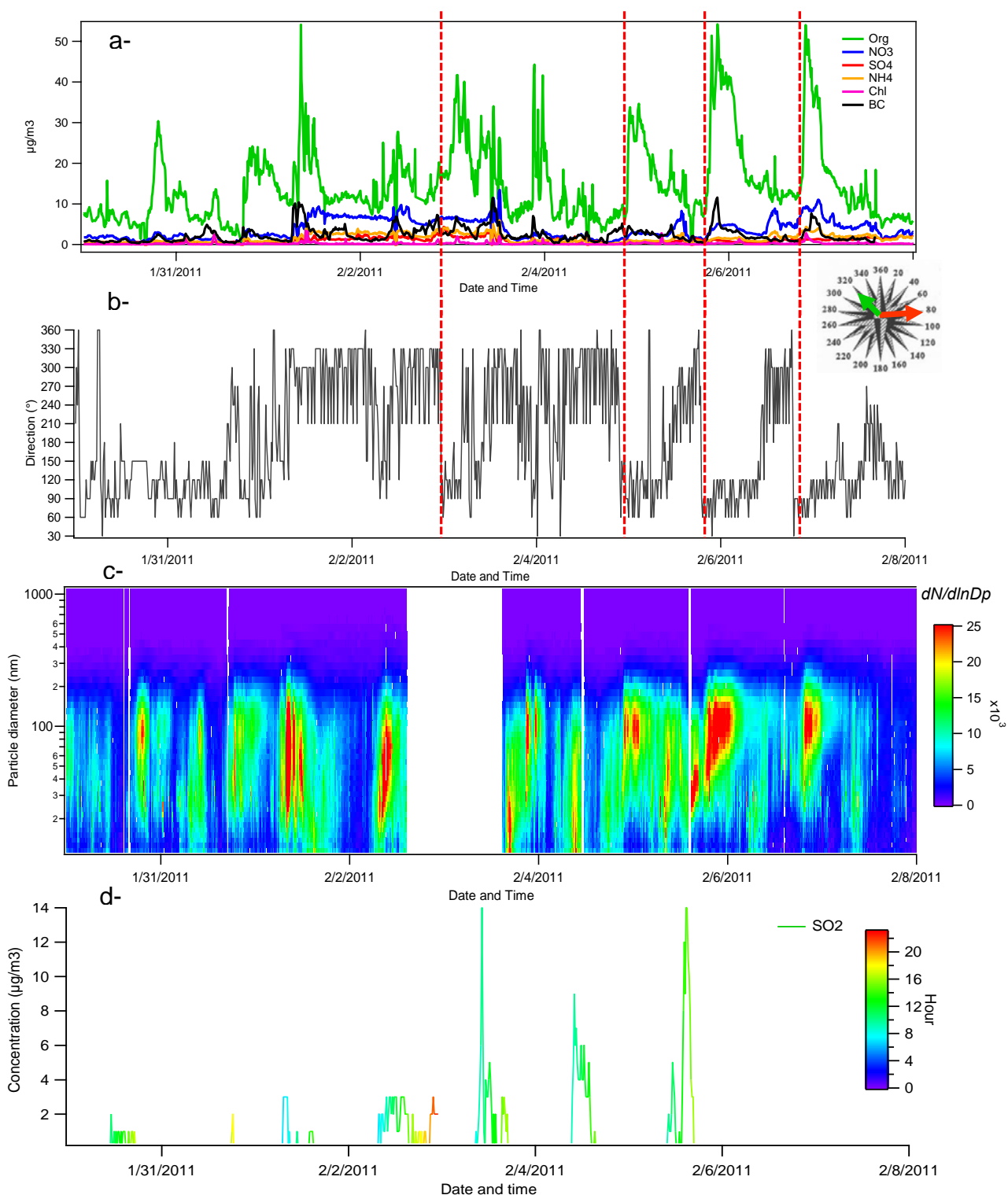


Figure 3-7: Temporal evolution of particulate matter from 10 to 1000nm (up) and SO₂ (down) during the first part of the measurement campaign

The specific pattern of organic aerosol concentrations with sudden and sharp increases at sunset is clearly related to wind direction changes (from north-west to east) and the onset of nocturnal breezes. These events are associated to particles with mobility

diameters from about 70 nm to 150 nm (figure 3-7-c). Main sources influencing these high concentrations of organic aerosol are not precisely known for now, but a preliminary source apportionment analysis performed on AMS data shows that biomass burning (residential heating, green waste combustion, ..) is most probably one of the major sources (see Appendix II).

Events of small particles ($D_m < 50\text{nm}$) 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 (Appendix I). 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. Within the framework of the intercomparison this constitutes an excellent case study.

4. Intercomparison of aerosol mass concentration (PM10 and PM2.5)

4.1. Instrumentation and strategies

During the inter-comparison campaign in Marseille, several PM samples were collected by standard Low Volume (LVS) and High Volume (HVS) Samplers. On line monitors, namely Optical Particle Counters (OPC), Tapered Element Oscillating Microbalance (TEOM) and Thermo-DataRAM, were used as well. Thus, PM concentration values were obtained both by off-line gravimetric analyses and by on-line monitors. The main scope of the inter-comparison of PM physical parameters is to identify possible systematic differences.

The list of the PM samplers and monitors used by each laboratory and/or organization during the inter-comparison exercise in Marseille is given in **Table 4.1**. Note that only methodology in bold in table 4-1 will be used during the long monitoring campaigns carried out in each harbour under study.

Lab/organization	Instrument	Measurement	Flow rate
IDAEA-CSIC Barcelona	HVS – PM10	Off line	500 l/min
	HVS – PM2.5	Off line	500 l/min
	OPC (no dryer)	On line	1 l/min
UNIVERSITY Genoa	LVS – PM2.5	Off line	38.3 l/min
	OPC (with dryer)	On line	1.2 l/min
UNIVERSITY Provence and ATMOPACA Marseille	TEOM FMDS	On line	3 l/min
	HVS PM2.5	Off line	500 l/min
	SMPS	On line	0.3 l/min
UNIVERSITY of West Macedonia ^a Thessaloniki	LHS - PM2.5	Off line	38.3 l/min
ARPAV Venice	LVS PM2.5	Off line	38.3 l/min
	DataRAM PM2.5	On line	1-3 l/min

Table 4-1. List of the instruments deployed for PM sampling/monitoring during the inter-comparison campaign. ^{a)} due to a technical problem with the sampler, portions of the PM2.5 samples collected by IDAEA-CSIC have been provided to UOWM for chemical analyses. In Bold : Methodology to be used during the long monitoring campaigns

IDAEA-Barcelona, sampled both PM10 and PM2.5 by HVSs and PTS, PM10, PM2.5 and PM1 by a GRIMM-OPC (ENVIRONcheck MODEL107). **Department of Physics-Genoa** sampled PM2.5 with the use of a standard LVS (model skypost by TCR TECORA) and PM2.5 and PM10 by a GRIMM-OPC (ENVIRONcheck MODEL107), the same instrument of the Barcelona group but equipped with a *drying denuder*. **University of Provence with ATMOPACA**, used 2 TEOMs (Tapered Element Oscillating Microbalance by Thermo) equipped with a FDMS (Filter Dynamics Measurement System) module to monitor both PM10 and PM2.5. The TEOM-FDMS measures the core and volatile fractions of the collected mass by using a self referencing technique (TEOM-FDMS is the methodology used in France by air quality networks to monitor PM mass); **University of Provence-Marseille** deployed a HVS to collect PM2.5 (actually, not used for subsequent gravimetric analysis but for chemical speciation only). **ARPAV-Venice**, collected PM2.5 using an On line instrument (DataRAM4 by Thermo) and of a standard LVS for the sampling of PM2.5. Finally, **UOWM-Thessaloniki** used a LVS sampler for the collect of PM2.5. Unfortunately a technical problem with this sampler occurred at the beginning of the campaign and therefore punches of filters have been provided by IDAEA-CSIC to UOWM for the chemical analyses and source apportionment exercise only.

During the campaign, PM samples were collected independently by each group following different strategies (see **Table 4-2**). In particular, major differences between University of Genoa and all the other groups/Institutions were the type of filters and the time-basis of PM sampling. Actually, PM concentration was determined using Quartz membranes and the sampling time was always 24 h starting at 2 pm for all the groups but University of Genoa which collected PM2.5 on 47 mm Quartz and Teflon filters, changed and alternated every 12 hours still beginning at 2.00 pm.

Lab/organization	Instrument	PMx	Time Resolution
IDAEA-CSIC Barcelona	HVS	PM10	24 h
	HVS	PM2.5	24 h
	OPC - no dryer	PM10, PM2.5, PM1	1 h
UNIVERSITY Genoa	LVS	PM2.5	12 h
	OPC - dryer	PM10, PM2.5, PM1	1 h
UNIVERSITY Provence and ATMOPACA Marseille	TEOM FMDS	PM10, PM2.5	15 min
	HVS	PM2.5	24 h
	SMPS	PM1 (10-1000 nm)	7 min
ARPAV Venice	LVS	PM2.5	24 h
	DataRAM	PM2.5	5 min

Table 4-2. Sampling/monitoring strategies adopted by each research group during the inter-comparison campaign. In bold : methodology to be used during the long monitoring campaigns

ARPAV-Venice, adopted a PM2.5 sampling strategy fully consistent with the Standard method (EN 14907:2005) for the determination of the PM2.5 mass fraction of suspended particulate matter quoted in the “European Directive 2008/50/EC on ambient air quality and cleaner air for Europe”. For this reason, ARPAV concentration values are here taken as a reference to compare the PM2.5 values obtained by the other groups. Note that TEOM-FDMS instruments have been proved to be equivalent to the European

reference gravimetric method (EN 12341 and 14907 respectively for PM10 and PM2.5) by various studies.

The main outputs of this part of the inter-comparison campaign are summarized in the following.

4.2. Results

The mean and the standard deviation of the PM2.5 concentration values obtained by off-line gravimetric analyses and on-line monitors between January 25 and February 28 2011 are reported in **Table 4-3**. The PM2.5 results are in fair agreement with the Barcelona values only which differ for more than 10% from the ARPAV-Venice mean taken as reference. In **Figure 4-1**, the time series of concentration values obtained by off line gravimetric (**Figure 4-1a**) and on line measurements (**Figure 4-1b**) are shown. Note that OPCs will not be used within the framework of the long monitoring campaigns. This instrumentation was deployed during the intercomparison campaign only for comparison with more robust and accurate methodologies.

GROUP / Institution	Mean ($\mu\text{g}/\text{m}^3$)	σ ($\mu\text{g}/\text{m}^3$)
HVS BARCELONA	32.5	13.3
OPC BARCELONA	18.7	11.7
LVS GENOA	24.1	13.1
OPC GENOA	25.0	12.3
TEOM FDMS MARSEILLE	24.3	11.5
LVS VENICE	26.6	13.9
DataRAM VENICE	29.5	19.7

Table 4-3. Mean and standard deviation of the PM2.5 concentration values obtained by off line gravimetric and on line monitors. In Bold : Methodology to be used during the long monitoring campaigns

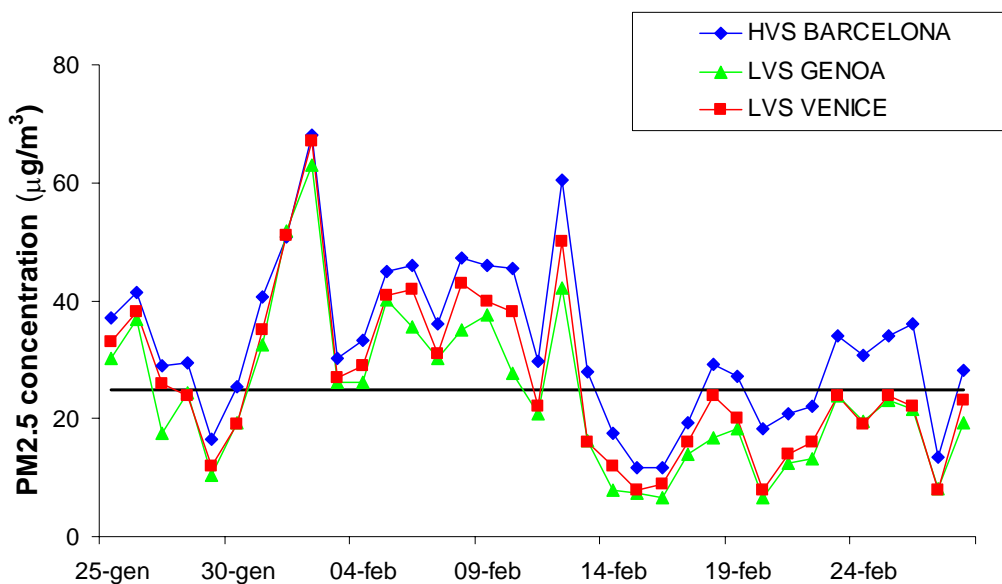


Figure 4-1a. Time series of PM_{2.5} concentration values obtained by off-line gravimetric analyses: the horizontal continuous line indicates the European limit of 25 µg/m³ – annual average - (European Directive 2008/50/EC).

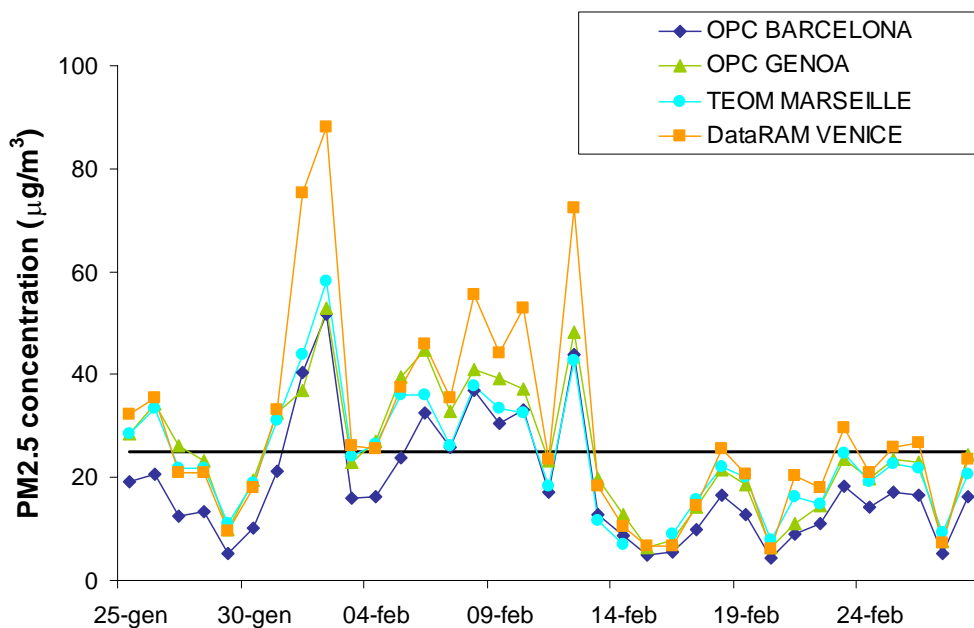


Figure 4-1b. Time series of PM_{2.5} concentration values provided by on-line monitors: the horizontal continuous line indicates the European limit of 25 µg/m³ – annual average - (European Directive 2008/50/EC).

The time series of concentration values are well correlated (**Figure 4-2a-b**, respectively for off-line and on-line data) with the Barcelona- HVS data only which seem to show an offset.

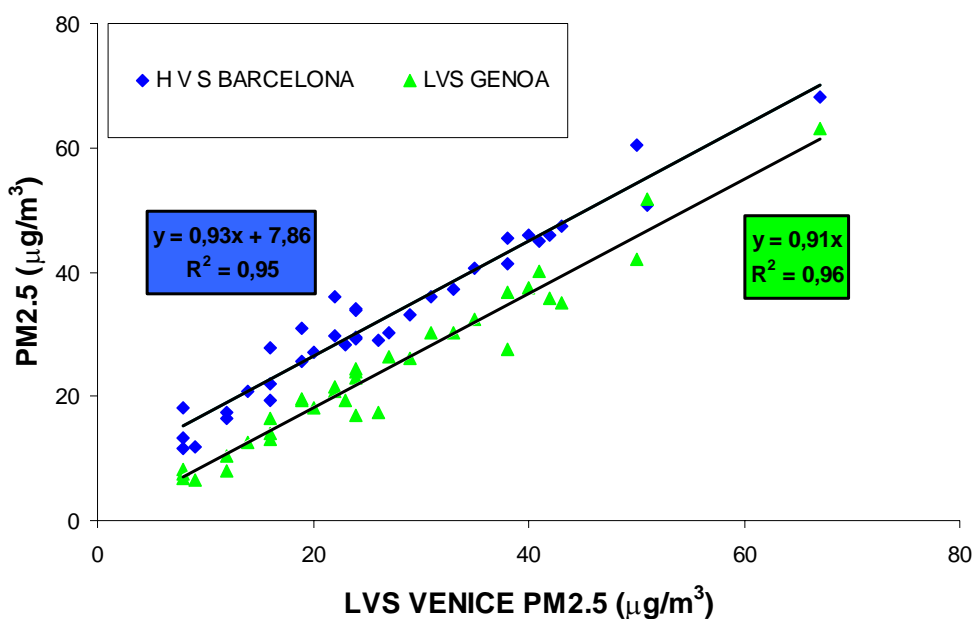


Figure 4-2a. Correlation study among the off-line sets of PM2.5 values.

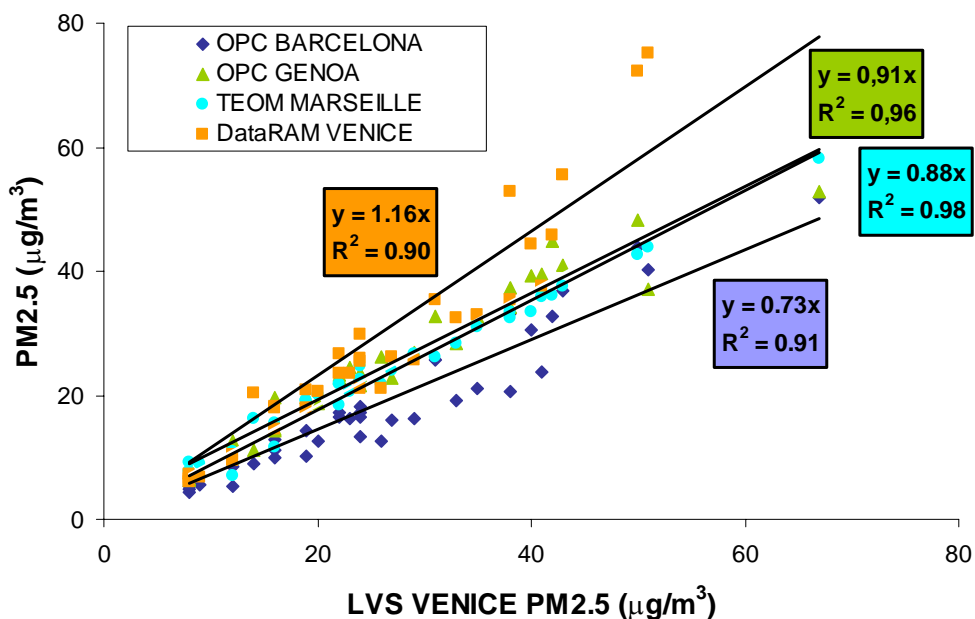


Figure 4-2b. Correlation study among the on-line sets of PM2.5 values

4.2.2. PM10

The mean PM10 concentration values measured by OPCs (Genoa and Barcelona), HVS (Barcelona) and TEOM (Marseille) are reported in **Table 4.4**. The four values are in acceptable agreement, being the OPC and HVS Barcelona data respectively the lowest and highest figures. The time series of PM10 values are shown in **Figure 4-3**.

Instrument	Mean ($\mu\text{g}/\text{m}^3$)	σ ($\mu\text{g}/\text{m}^3$)
HVS BARCELONA	40.3	16.7
OPC BARCELONA	26.6	13.6
OPC GENOA	31.4	13.8
TEOM FDMS MARSEILLE	36.8	15.9

Table 4.4. Mean and standard deviation of the PM10 concentration values obtained by different groups and equipment during the inter-comparison campaign. In Bold : Methodology to be used during the long monitoring campaigns

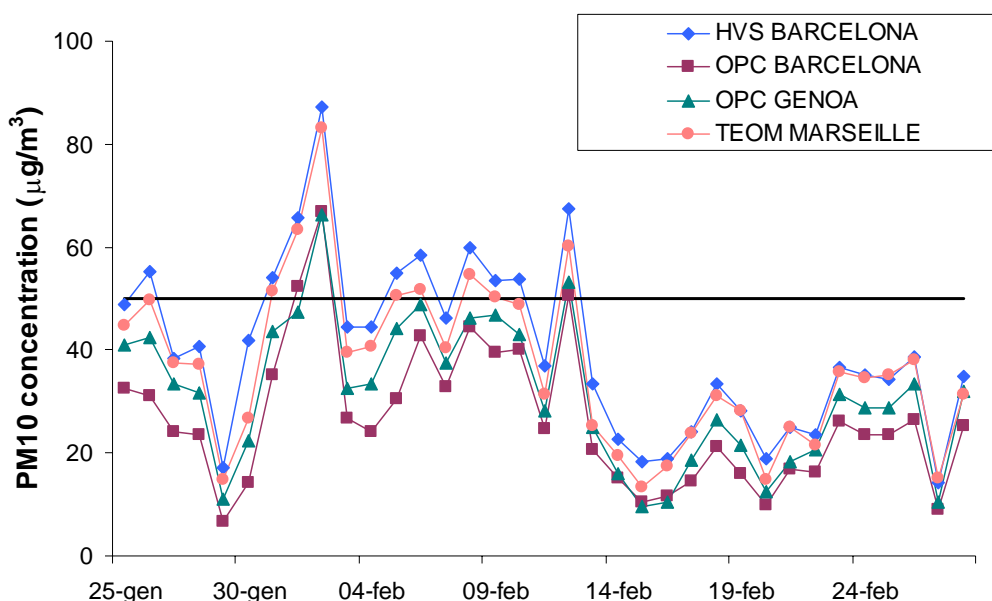


Figure 4.3. Time trends of PM10 concentration values provide by different measurements: the horizontal line indicates the European daily limit of $50 \mu\text{g}/\text{m}^3$ (European Directive 2008/50/EC).

Figure 4-4 shows the correlation study between PM10 time series provided by the on-line monitors and the gravimetric Barcelona data set (HVS).

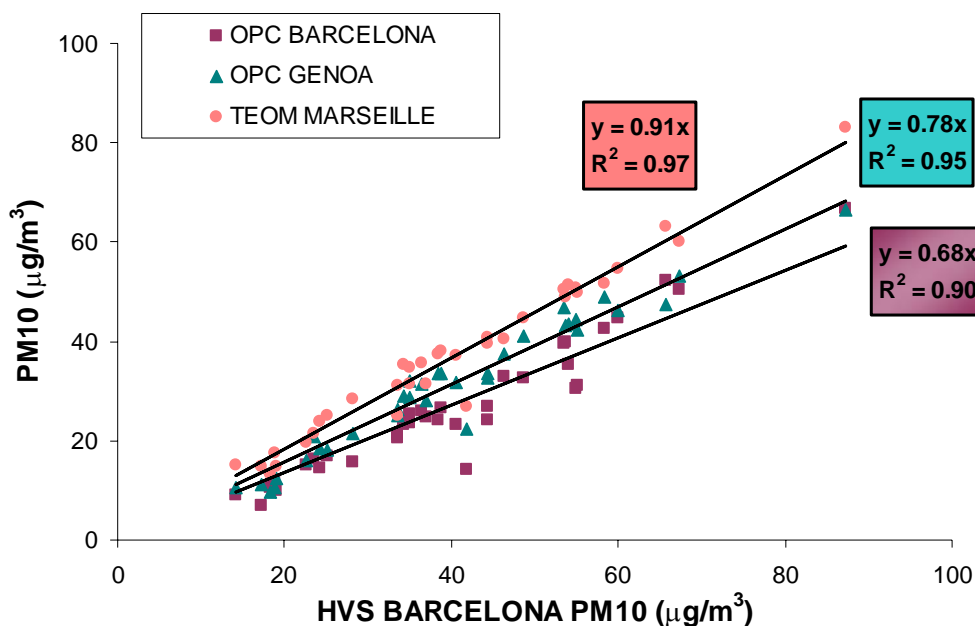


Figure 4-4 . Correlation study among the PM10 data provided by on-line monitors and the HVS-Barcelona gravimetric data.

4.3 Summary

The analysis of the temporal variations of the PM10 and PM2.5 concentration levels measured during about one month of continuous measurements at the urban background site selected for the inter-comparison campaign of Marseille, allows some conclusions:

- The inter-comparison of PM2.5 and PM10 concentration levels and time series shows a good agreement among the data sets delivered by each participating Group/Institution; the agreement is particularly good with PM2.5 data. The PM2.5/PM10 concentration ratio turns out to be practically constant for all the techniques/instruments.
- The presence of a possible offset in High Volume Samplers data was appreciated but it is not such to produce significant differences in the data reduction phase, in particular in the source apportionment.

In summary, no major discrepancies and/or artefacts could be observed in the PM concentration data sets delivered by the participating Groups/Institutions.

5. Intercomparison of PM chemical composition

This intercomparison exercise relates to data available in July 2011. Complementary analysis, in particular organic speciation and metals/elements for some groups, were still in progress at this date. A comprehensive intercomparison of these remaining data will be presented in the next progress report.

5.1. Participants and techniques

The chemical parameters measured by each partner in the intercomparison campaign carried out in Marseille from 24th January to 2nd March are presented in the following table 5.1, together with the PM fraction measured, the analysis technique, dates or measurement, time resolution and mean concentrations.

Parameter	PM fraction	Partner	online/ offline	Technique / Instrument	Time resolution	Start	End	Mean conc. (ng/m ³)			
BC (880 nm)	PM _{2.5}	UNIV Genoa	ON	Aethalometer	5-minutes	24/01/2011	01/03/2011	3332			
BC (370 nm)								3467			
BC (670 nm)	PM ₁	U. Provence Marseille	ON	MAAP	15-minutes	24/01/2011	02/03/2011	1593			
OC				AMS	15-minutes	25/01/2011	02/03/2011	9527			
NO ₃ ⁻								3417			
NH ₄ ⁺								1551			
SO ₄ ²⁻								1185			
nss Cl ⁻								183			
PAHs								16			
OC				PM _{2.5}	U. Provence Marseille	OFF	Thermo-optic (Eusaar_2)	24-hours	25/01/2011	02/03/2011	8196
EC							Ionic Chromatography	24-hours	25/01/2011	02/03/2011	1984
Cl ⁻											144
NO ₃ ⁻	4060										
SO ₄ ²⁻	2663										
Ox	153										
Na ⁺	123										
NH ₄ ⁺	2941										
K ⁺	149										
Mg ²⁺	23										
Ca ²⁺	972										
PAHs	PM _{2.5}	ARPAV Venice	ON	PAS2000	15-minutes	25/01/2011	04/03/2011	11			
Na	PM _{2.5}	UNIV Genoa	OFF	ED-XRF	12-hours	25/01/2011	01/03/2011	40			
Mg								60			
Al								109			
Si								74			
P								8			
K								151			
Ca								192			
Ti								5			
V								5			
Cr								1.6			

Mn								2
Fe								128
Ni								2.9
Cu								15
Zn								29
Br								9
Mo								9
Pb								12
Na ⁺				Ionic Chromatography	12-hours	25/01/2011	01/03/2011	97
NH ₄ ⁺								1964
K ⁺								144
Mg ²⁺								13
Ca ²⁺								204
Cl ⁻								71
NO ₃ ⁻								2594
SO ₄ ²⁻								2967
OC				Thermo-optic	12-hours	25/01/2011	01/03/2011	6600
EC								2300
TC								8900
PAHs				GC/MS	24-hours	24/01/2011	01/03/2011	9
Cl ⁻				Ionic Chromatography	24-hours	24/01/2011	01/03/2011	85
NO ₃ ⁻								4979
SO ₄ ²⁻								2353
Na								53
NH ₄ ⁺	PM _{2.5}	UOWM Thessaloniki	OFF					6917
K								161
Mg								28
Ca								522
OC				Thermo-optic	24-hours	24/01/2011	01/03/2011	7994
EC								2422
OC	PM _{2.5}	IDAEA-CSIC Barcelona	OFF	Thermo-optic (Eusaar_2)	24-hours	24/01/2011	01/03/2011	8333
EC								1366
Al				ICP-AES	24-hours	24/01/2011	01/03/2011	69
Ca								433
K								253
Na								148
Mg								45
Fe								122
P								9
SO ₄ ²⁻				Ion Chromatography	24-hours	24/01/2011	01/03/2011	2963
NO ₃ ⁻								4740
Cl ⁻								340
NH ₄ ⁺				Selective electrode	24-hours	24/01/2011	01/03/2011	1346
Li				ICP-MS	24-hours	24/01/2011	01/03/2011	0.08
Ti								4.5
V								3.4
Cr								1.0
Mn								2.6
Co								0.10
Ni								1.8
Cu								14

Zn								25
Ga								0.05
As								0.5
Se								0.17
Rb								0.4
Sr								1.0
Y								0.06
Zr								3.5
Cd								0.22
Sn								1.4
Sb								2.8
Cs								0.03
Ba								3.4
Pb								10
Bi								0.08
Th								0.01
U								0.06
Rare earths								0.5

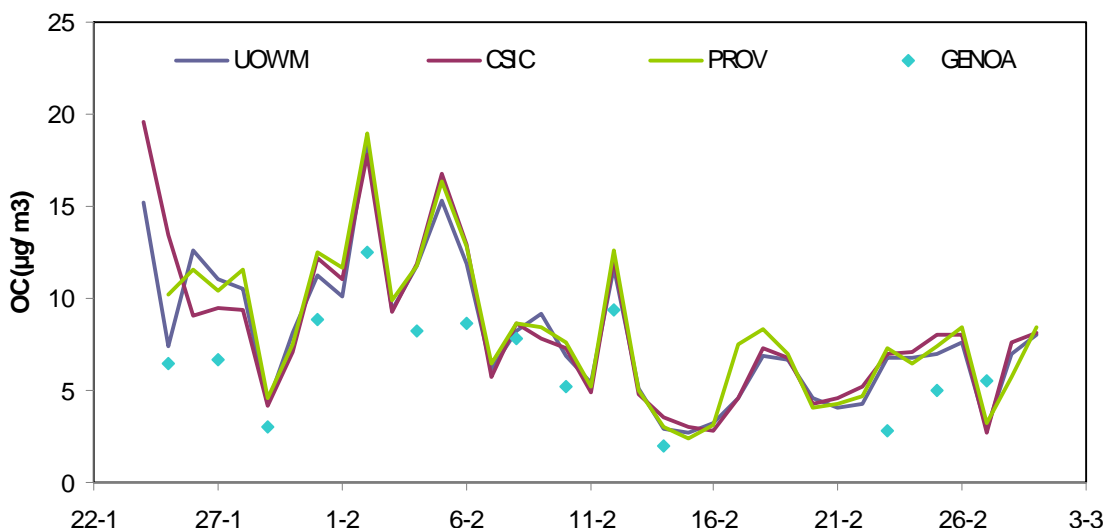
Table 5.1. chemical parameters measured by each partner in the intercomparison campaign

5.2. Chemical results of major components in PM_{2.5} samples

The next figures show the daily variability of the concentrations for different major components in PM_{2.5}, from analysis carried out in filters collected during the Marseille campaign. All the graphs present results of offline analysis carried out by each laboratory: University of Western Macedonia (UOWM), IDAEA-CSIC (CSIC), University of Provence (PROV) and University of Genoa (GENOA).

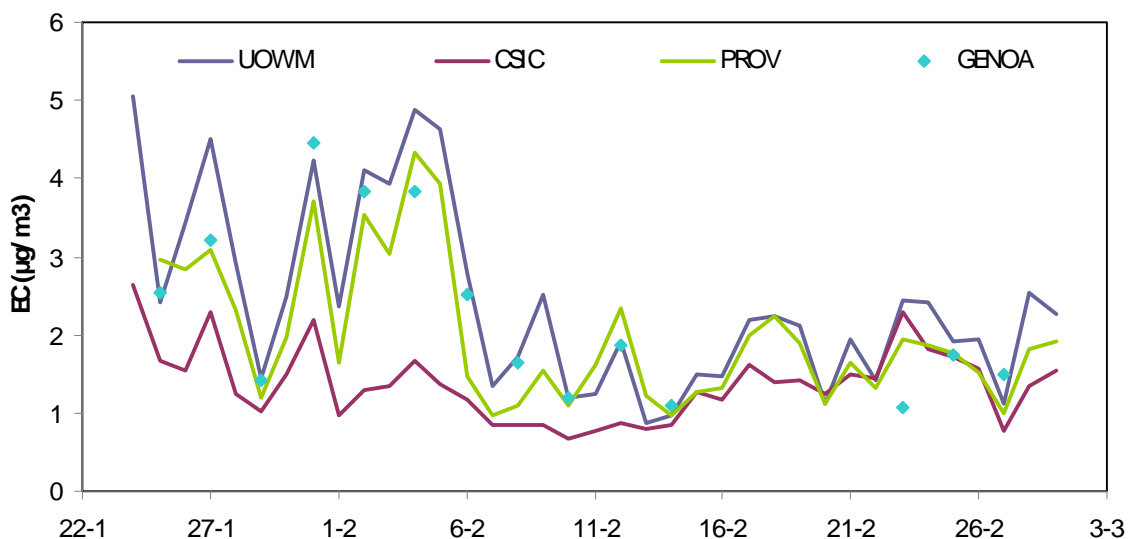
Organic carbon (OC)

This component has been analyzed in all the laboratories with the same type of instrumentation, a SUNSET OC/EC analyzer, although not all the partners have used the same temperature protocol and data from Univ-Genoa is not homogeneous with the other time series. Nevertheless, as seen in the graph, there is a very good agreement between the results reported by each group.



Elemental carbon (EC)

This component has been analyzed in all the laboratories with the same type of instrumentation, a SUNSET OC/EC analyzer, although not all the partners have used the same temperature protocol and data from Univ-Genoa is not homogeneous with the other time series. Measurements reported by CSIC are quite different from the other partners, at least in some samples.

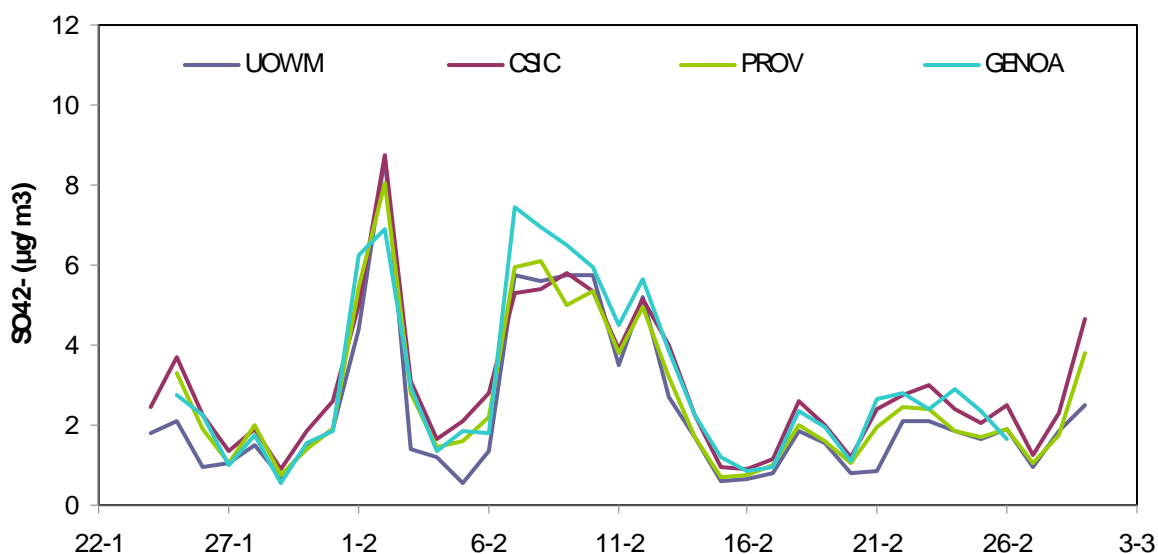


Sulphate (SO₄²⁻)



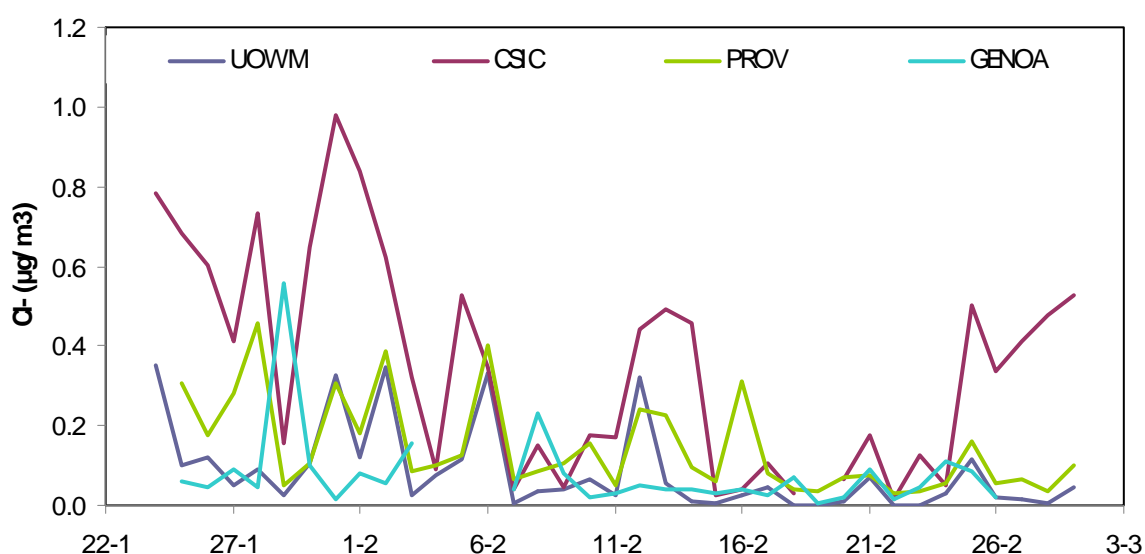
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Sulphate concentrations have been determined by ionic chromatography in all the laboratories. As for OC, there is a very good correlation between offline analysis for all the laboratories.



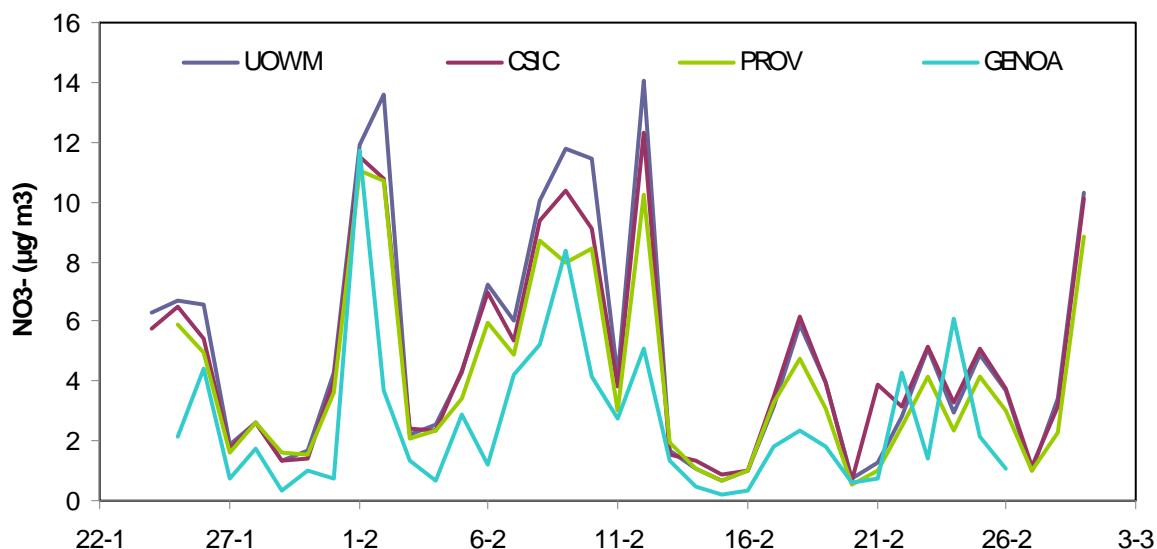
Chlorine (Cl⁻)

As for the previous two components, chlorine concentrations have been determined by ionic chromatography in all the laboratories. Nevertheless, big discrepancies have been found in the reported results among groups. Whereas UOWM and PROV report similar levels and temporal variability, CSIC reports much higher levels than the others, and GENOA and CSIC trends are not coetaneous, neither among them or with respect to the others. It should be noted that the concentration of chlorine remains low but this discrepancy between groups involved in APICE can induce the same variability for the apportionment of sea salt.



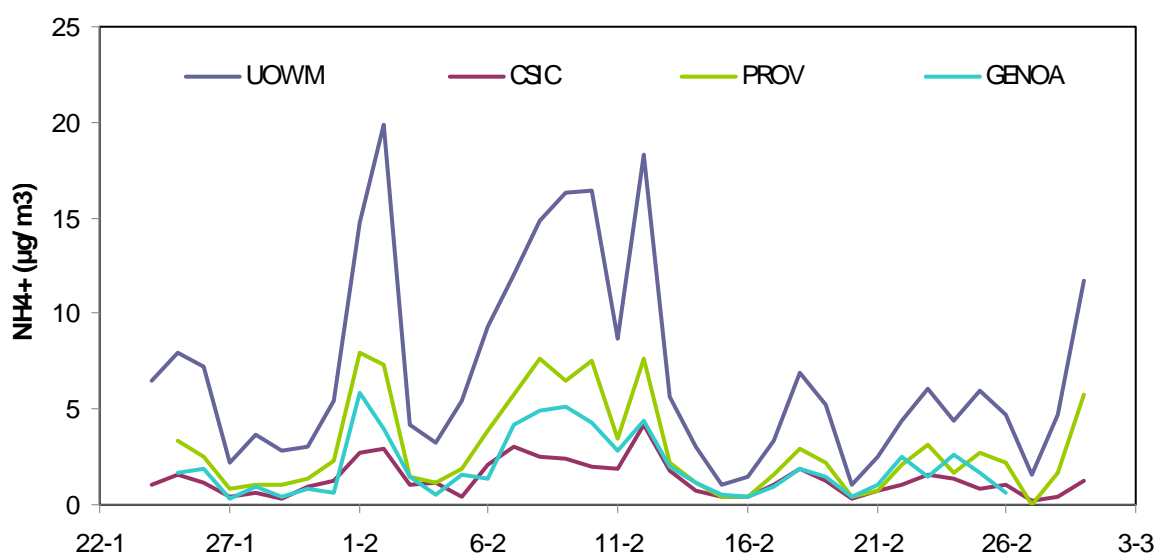
Nitrate (NO₃⁻)

As for sulphate, nitrate concentrations have been determined by ionic chromatography in all the laboratories. Some differences have been found (around 30%) between groups. UOWM, CSIC and PROV measured similar levels, whereas GENOA measurements were slightly lower.



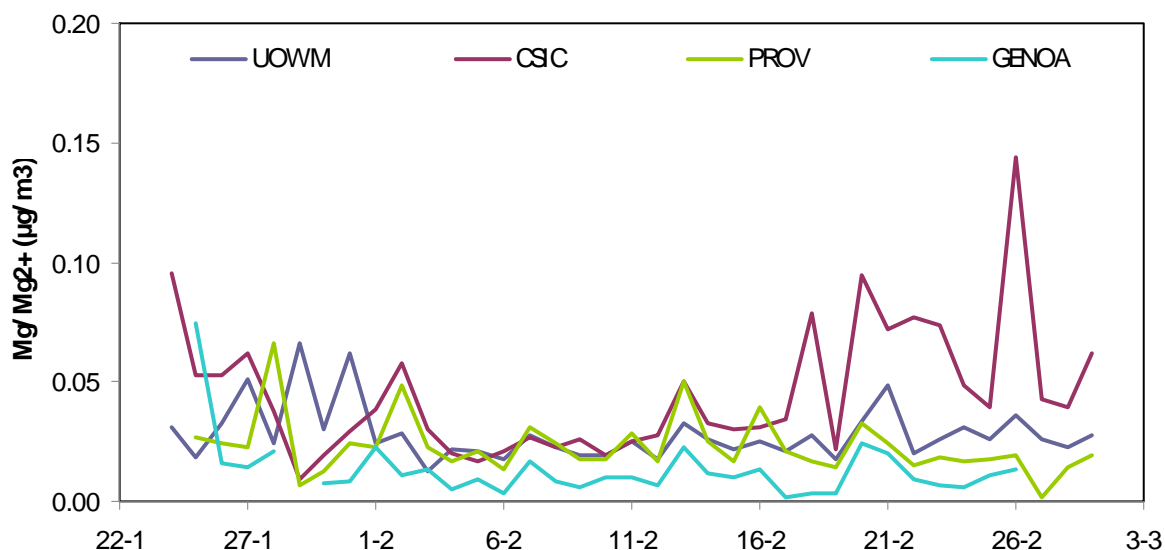
Ammonium (NH₄⁺)

Ammonium levels have been determined by ionic chromatography by 3 groups (UOWM, PROV and GENOA) and by using a selective electrode in the case of CSIC. Important discrepancies in the concentrations measured have been found although the temporal trends are very similar. UOWM is measuring much over the other partners and CSIC is under the rest of the measurements. Probably PROV and GENOA are right in the concentrations reported.



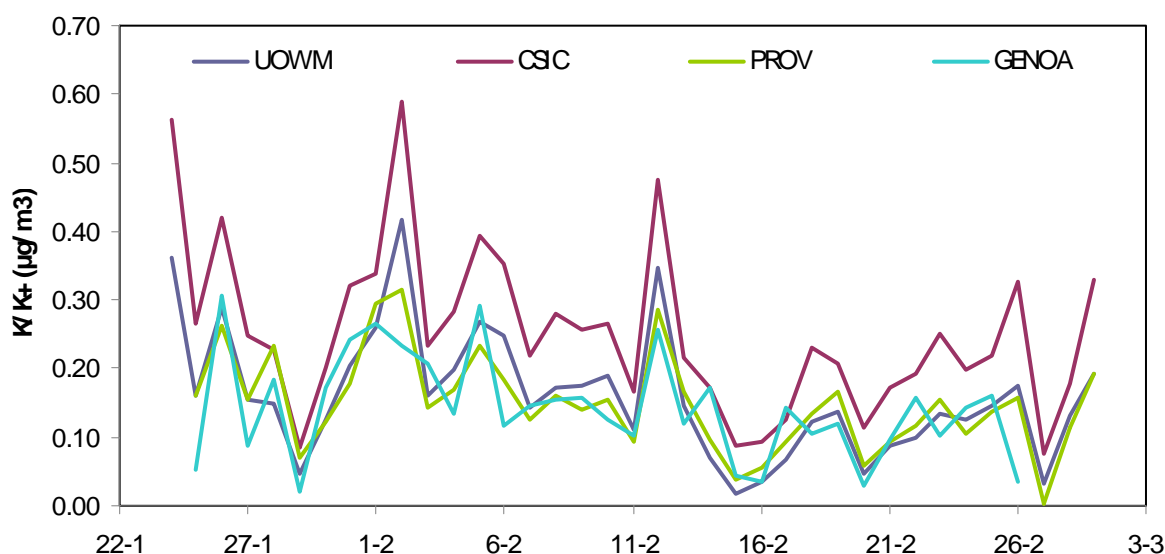
Magnesium (Mg/Mg²⁺)

Magnesium concentrations have been determined by ionic chromatography (soluble Magnesium = Mg²⁺) by 3 groups (UOWM, PROV and GENOA) and by ICP-AES (total Magnesium = Mg) in the case of CSIC. Temporal trends are rather similar with the exception of sporadic peaks determined by UOWM. Concentrations reported by CSIC are usually higher than the others, probably because of the coexistence of soluble and insoluble Mg in the aerosols. This observation is more evident at the end of the campaign. Note that PROV will also provide elemental concentration of Mg determined by ICP/MS.



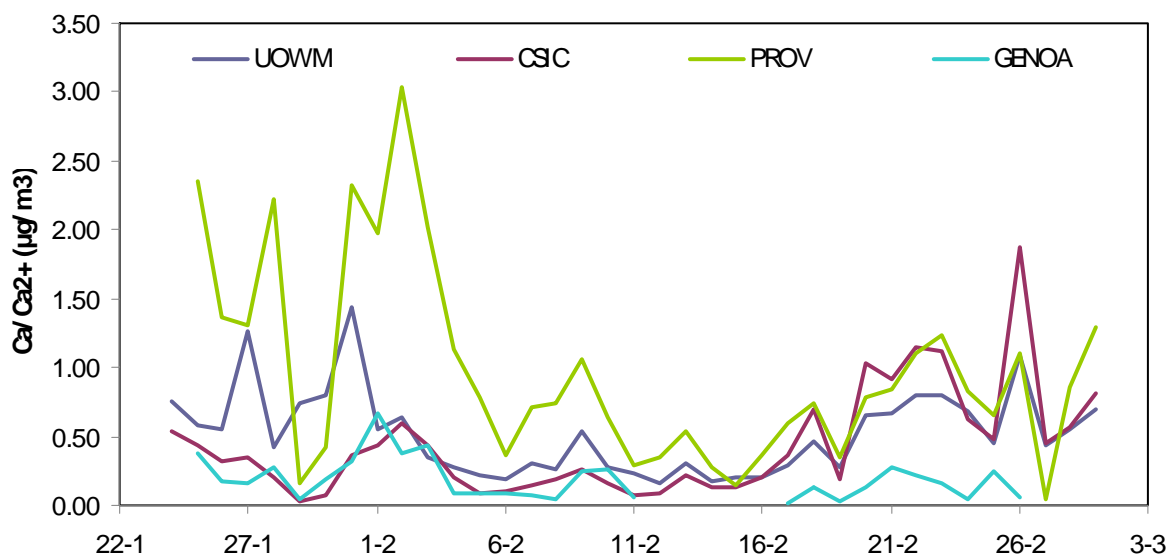
Potassium (K/K⁺)

Potassium concentrations have been determined by ionic chromatography (soluble Potassium = K⁺) by 3 groups (UOWM, PROV and GENOA) and by ICP-AES (total Potassium = K) in the case of CSIC. Temporal trends are very similar. Concentrations reported by CSIC are consistently 30% higher than the others, probably because of the coexistence of soluble and insoluble K in the aerosols.



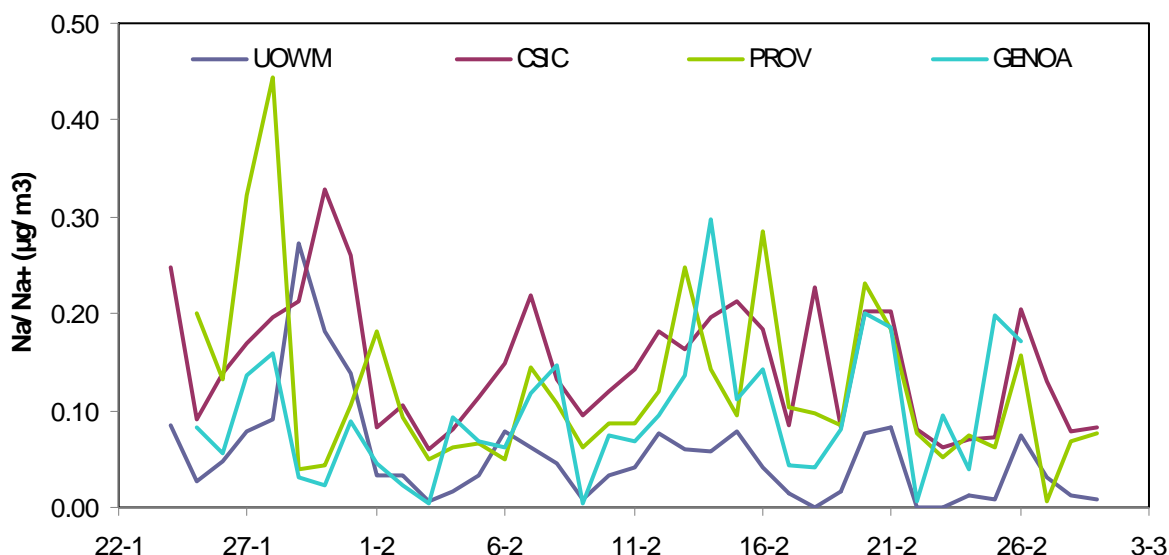
Calcium (Ca/Ca²⁺)

Calcium concentrations have been determined by ionic chromatography (soluble Calcium = Ca²⁺) by 3 groups (UOWM, PROV and GENOA) and by ICP-AES (total Calcium = Ca) in the case of CSIC. Temporal trends are generally coincident with the exception of PROV data that are much higher at the beginning of the campaign. Concentrations reported by GENOA are usually under the other groups, specially from the middle of the campaign to the end.



Sodium (Na/Na⁺)

Sodium concentrations have been determined by ionic chromatography (soluble Sodium = Na⁺) by 3 groups (UOWM, PROV and GENOA) and by ICP-AES (total Sodium = Na) in the case of CSIC. Both temporal trends and concentrations are rather different among the groups.



5.3. Summary table: mean concentrations

	OC	EC	Ca	K	Na	Mg	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺
UOWM	8.0	2.4	0.52	0.16	0.05	0.03	2.35	4.98	0.08	6.92
CSIC	8.3	1.4	0.43	0.25	0.15	0.04	2.96	4.74	0.35	1.35
U. Genoa	6.6*	2.3*	0.19	0.15	0.04	0.06	2.97	2.59	0.07	1.96
U. Provence	8.2	2.0	0.97	0.15	0.12	0.02	2.66	4.06	0.14	2.94

Table 5.2. Average concentration of major fraction of PM_{2.5} (µg/m³). *Please note that data from U. Genoa is not homogeneous with the other time series.

Offline analysis of OC, K/K⁺ and SO₄²⁻ in the PM_{2.5} fraction resulted in very similar concentrations and temporal evolution for all the laboratories. Only high concentrations of K were given by CSIC, but it is attributed to the analysis of total K instead of soluble K. Some other major components showed similar concentrations among most of the laboratories, such as Ca/Ca²⁺, Mg/Mg²⁺ and NO₃⁻. Other components however need to be checked as deduced from the high divergences found. This is the case of Na/Na⁺, EC, Cl⁻ and NH₄⁺. In the meeting held in Thessaloniki we discussed about this and each partner knows which components have to be corrected or re-analyzed.

	Al	Fe	Pb	Cu	Zn	Ni	Ti	V	Cr	Mn
CSIC	132	120	10	14	25	1.8	4.5	3.4	1.0	2.6
U. Genoa	109	128	12	15	29	2.9	5.9	4.7	1.6	2.0

Table 5.3. Average concentration of trace metals/elements (ng/m³)

Concentrations of Al, Fe, Pb, Cu, Zn, Ti and Mn showed standard deviations lower than 20% between analysis carried out at CSIC and University of Genoa. Its is important to remark that these elements are mainly tracers of traffic (Cu, Zn), mineral (Al, Fe, Ti, Mn) and industrial sources (Pb). Levels of Ni, V and Cr presented divergences up to 35% between both laboratories. It is important to highlight that these elements have been found in much lower concentrations, and in this case the ICP-MS technique, used at CSIC, is more adequate for their determination. Soon the results of trace elements from Univ Provence measured by ICP/MS will be available.



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6. Conclusions and workplan

A six weeks intercomparison campaign has been performed 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 that will be carried out in each harbor under study. Results obtained within this campaign constitute one of the most important data set ever collected in one point in Europe. It guarantees to fulfill the specific objectives of the campaign and allows to go further in our understanding of aerosol particles chemistry and in source apportionment methodologies. In addition various and interesting conditions, within the scope of the project, were observed during the campaign.

More than **80% of the data set was available in July 2011**. Only organic markers were still under analyze (Univ-Provence – ARPA Veneto). These kinds of analysis are complex and time consuming. The full database will be available in the first weeks of November.

The PM_{2.5} and PM₁₀ inter-comparison shows very a good agreement among the data sets produced by each participating partners. We noted a potential offset for PM mass determined with filters collected by high volume. However this slight discrepancy is within the incertitude range. The PM_{2.5} data collected by on-line monitors are also in good agreement with the standard method (EN 14907:2005). Only some differences are found between the two OPC possibly due to presence or absence of a dryer system upstream the particles counters. OPC instruments will not be used during the long monitoring campaign.

More differences are observed for particles chemical composition. If OC, K/K⁺ and SO₄²⁻ 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/Ca²⁺, Mg/Mg²⁺ and NO₃⁻, 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).

A complete intercomparison of measurements, including missing data (not available in July 2011) will be performed in the next weeks. Source apportionments, still in progress in the different laboratories, will be finalized by all the partners in December 2011. Receptor models analysis will be presented and discussed during the meeting in Venice (January 2012) in a targeted day of work besides the official meeting. **Then a comprehensive final report of source apportionments intercomparison will be finalized in early February 2012.**



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Appendix I : Previous studies in the measurement site

This sampling site have been used for the set up of different previous studies, including the FORMES Campaign, in summer 2008, which aimed at characterizing particulate matter over Marseille.

This previous study allowed first to define precisely the major wind condition over Marseille (cf. figure A-I-1).

Three principal wind directions can then been underlined. First, strong north western winds (red pointer on the map) are induced by Mistral winds (important air flows coming from Rhône valley). North-eastern winds, channelled trough Huveaune valley, are also well represented (purple pointer on the map). Southern synoptic winds can also be observed (blue pointer on the map).

In summer conditions, when the previous wind sectors are not important, composition of sea breezes (orange pointer on the map) and Mistral can be observed. However, this phenomenon, linked to the important temperature difference between the land and the sea, is unlikely to occur in winter time and not expected during the intercomparaison campaign.

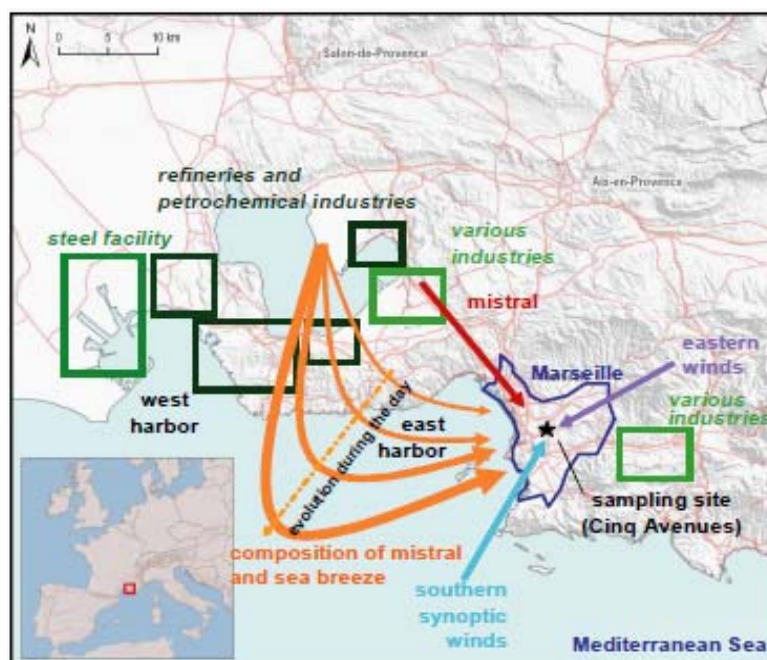


Figure A-I-1 Characterization of the different wind direction affecting Marseille

The FORMES campaign also allowed distinguishing several industrial events, which have been associated to Fos-Berre area influence. As shown on figure A-I-2, industrial events are characterized by high level of SO_2 , in addition to high levels of fine particles (below $1\mu\text{m}$). This aerosol was mostly constituted of PAHs, metals and bisulfate (HSO_4^-). An analysis of these data trough source apportionment models estimated that industrial and port activities from the Fos-Berre area contribute to 30% of the total sub micrometer particles number concentration, and 7% of $\text{PM}_{2.5}$.

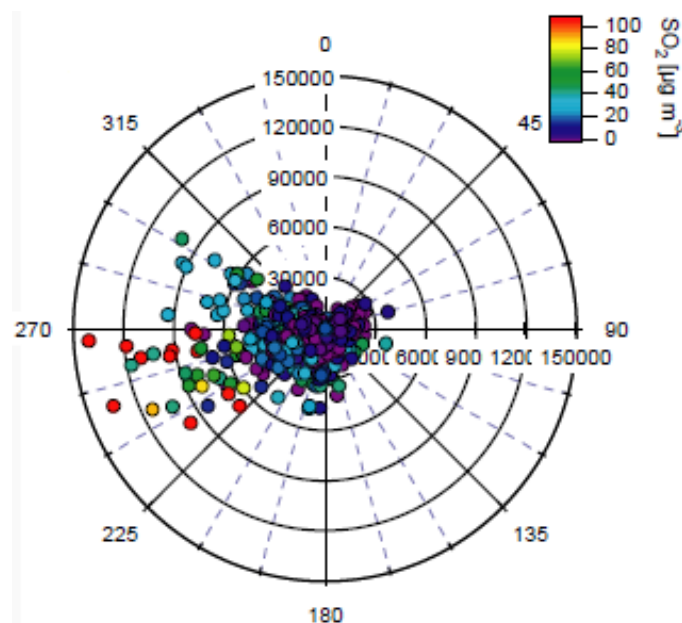


Figure A-I-2: Total number of submicron particles (from 10nm to 1000nm) regarding wind direction and SO₂ concentration (markers' colour)

More details can be found in El Haddad et al 2001a and 2011b¹.

¹ El Haddad I., Marchand N., Wortham H., Piot C., Besombes J.L., Cozic J., Chauvel C., Armengaud A., Robin D., Jaffrezo J.L. Primary sources of PM_{2.5} organic aerosol in an industrial Mediterranean city, Marseille. *Atmos. Chem. Phys.*, 11, 2039-2058, 2011a.
 El Haddad I., Marchand N., Temime-Roussel B., Wortham H., Piot C., Besombes J.L., Baduel C., Voisin D., Armengaud A., Jaffrezo J.L. Insights into the secondary fraction of the organic aerosol in a Mediterranean urban area: Marseille. *Atmos. Chem. Phys.*, 11, 2059-2079, 2011b.

Appendix II : Preliminary source apportionment

I. Tracer m/z approach (AMS-PM1)

The tracer m/z approach, also called “poor” PMF approach, is an empirical method based on the comparison between key organic fragments abundances measured by AMS and main factors derived from full PMF analysis performed on the whole organic mass spectra detected by AMS. With this approach only three factors can be assessed:

- **HOA** (Hydrocarbon like Organic Aerosol) representing the organic fraction coming from fossils 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.

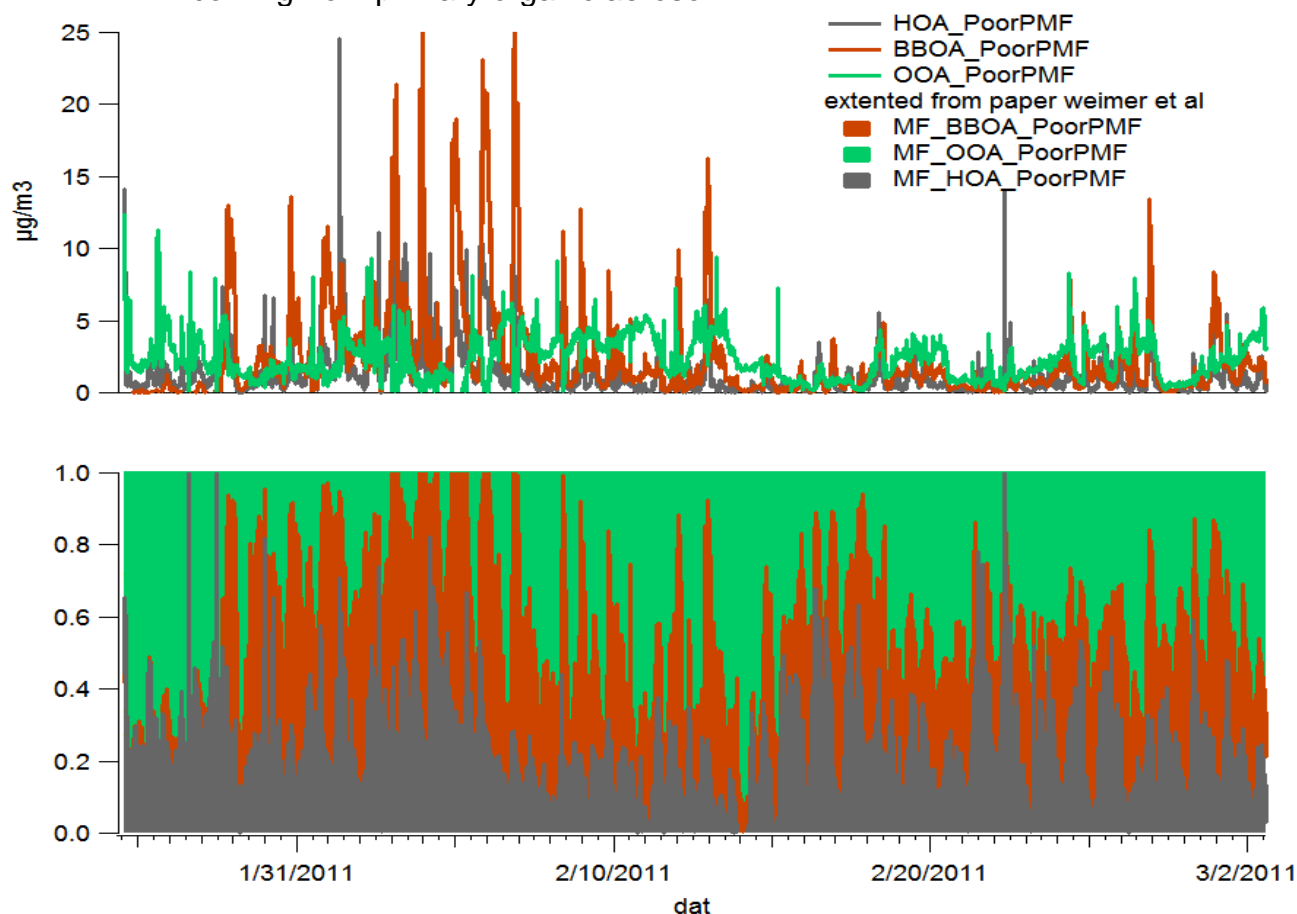


Figure A-II-1: Preliminary source apportionment by the m/z tracer method based on m/z57, m/z44 and m/z60 fragments measured by AMS (from the 29th of January to the 8th of February)

This easy-to-use approach based on 3 key ions ($m/z57$, $m/z44$, $m/z60$) is a first evaluation tool allowing first order estimate of the 3 main sources usually encountered in urban areas during winter. Results are presented in figure A-II-1

From this preliminary analysis 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. However a more careful look at the temporal trends shows that BBOA is mainly advected by nocturnal breezes from more rural areas through the Huveaume Valley (see 3.5). The analysis of aerosols samples (collected on filters) may provide further information, with the study of several specific tracers of biomass burning. Full PMF analysis will also provides more information on these 3 sources and others sources.



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Appendix II : Preliminary source apportionment

II. Results from Positive Matrix Factorization model -UOWM- Preliminary

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 model application on the data collected from Marseille's campaign in the frame of APICE project are presented. The present study was conducted by University of Western Macedonia (UOWM) and comprises a part of WP3 source apportionment intercomparison report.

Methodology

The experimental (intercomparison) campaign of PM_{2.5} physico-chemical data sampling took place in Marseille's city from 25/1/2011 to 2/3/2011. The filters (samples number 37) collected were analysed at UOWM laboratory for major ions, polycyclic aromatic compounds, organic and elemental carbon. In particular, the chemical analysis by UOWM was conducted for:

- **27 PAHs:** *Naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, 2,6-dimethylnaphthalene, Acenaphthylene, 1,2-dimethylnaphthalene, Acenaphthene, 2,3,5-trimethylnaphthalene, Fluorene, Dibenzothiophene, Phenanthrene, Anthracene, 2-methylphenanthrene, 1-methylphenanthrene, 3,6-dimethylphenanthrene, Fluoranthene, Pyrene, benzo[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[e]pyrene, Benzo[a]pyrene, Perylene, Indeno[cd]pyrene, Dibenzo[a,h]anthracene, Benzo[ghi]perylene.*
- **8 ions:** *Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Mg⁺, Ca²⁺* and
- **Organic & Elemental carbon:** *OC, EC.*

PMF model was applied on three combinations of data:

- data including all PAHs, ions and OC/EC
- data including ions and OC/EC values and
- data including selected (8) PAHs, ions and OC/EC

In the first case, input data included more variables (species) than samples, which is problematic for a PMF analysis. From the conducted runs, the third case lead to more clear results, which are discussed in the present report. In particular, a data set including (as species) all the measured ions, OC/EC values and 8 selected (based on literature) PAHs: Fluorene, Phenanthrene, Fluoranthene, Pyrene, benzo[a]pyrene, Indeno[cd]pyrene,

Dibenzo[a,h]anthracene and Benzo[ghi]perylene (Cao et al., 2011; Vestenious et al., 2011, Wang et al., 2009).

A critical step in PMF analysis is the determination of the number of factors which correspond to particle sources. It is a fact that choosing too few factors may lead to non-well separated sources, whereas too many factors may essentially lead to a split up of a true source into two or more non-existing sources. In this work, the number of factors which was examined ranged from two to eight. The optimal number of factors was five. Finally, regarding the uncertainty's calculation, a data set including unique uncertainty values of each data point was created and inserted to the model.

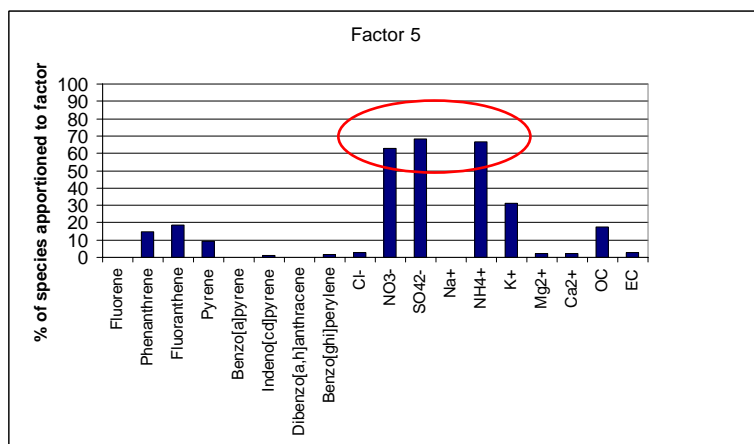
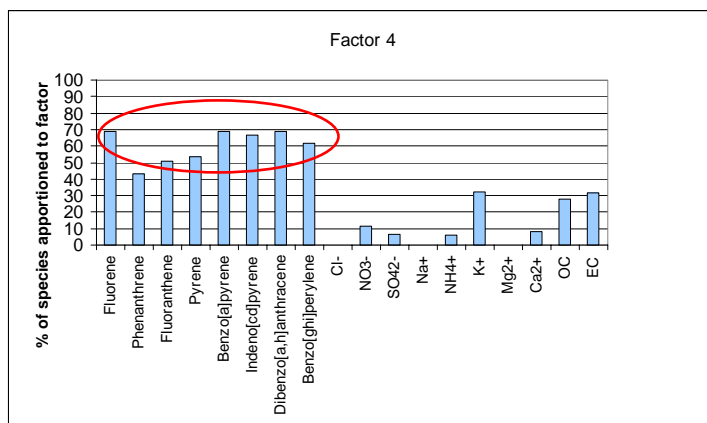
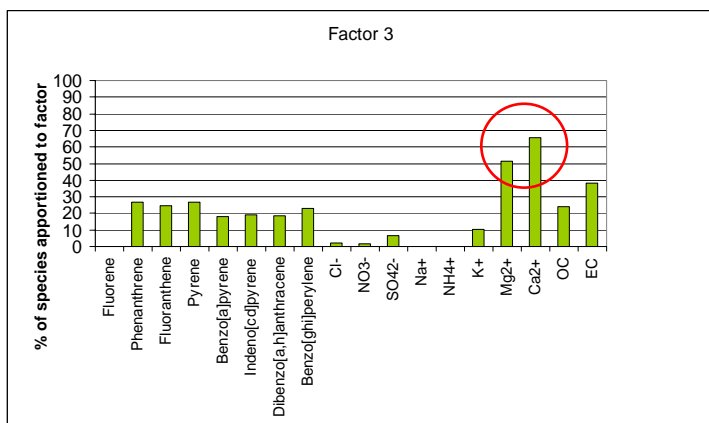
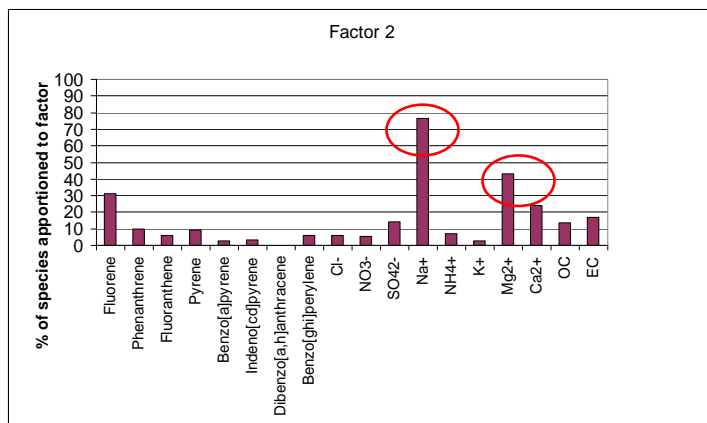
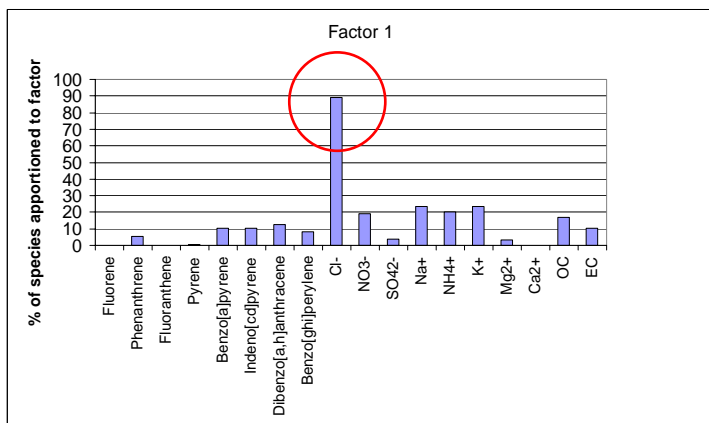
Concluding remarks

PMF analysis lead to a solution of five factors, which correspond to five sources or groups of sources. The main output of PMF is the percentage of the species (chemical species) apportioned to each factor (source) and the time variation of each factor (figures A.II.2a-e and A.II.3a-e). From this information, a factor-to-source correspondence is obtained:

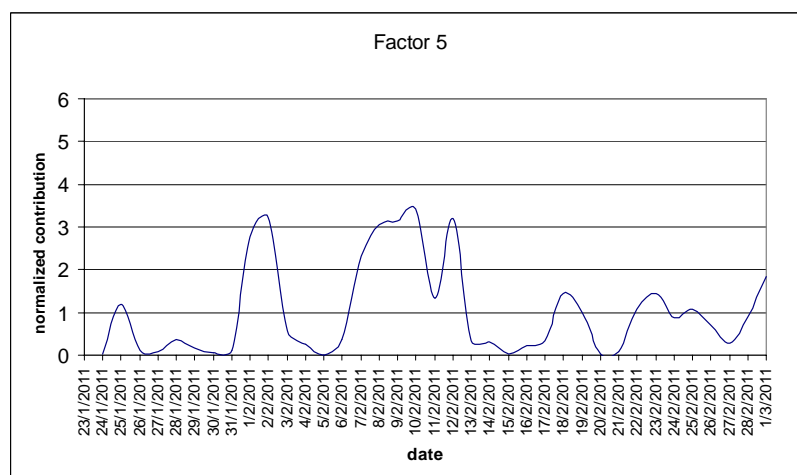
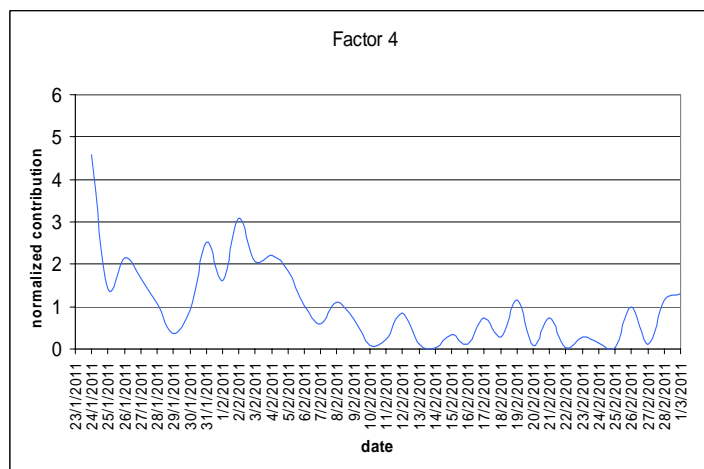
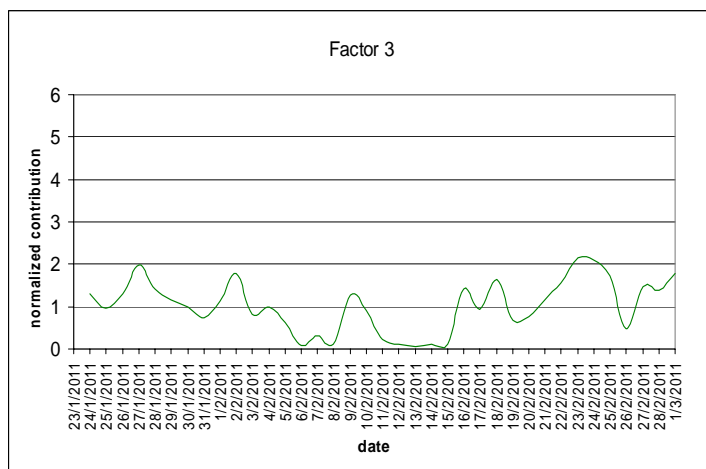
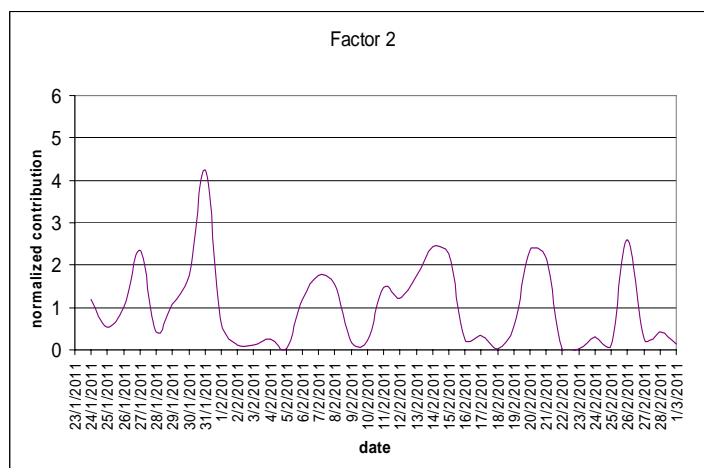
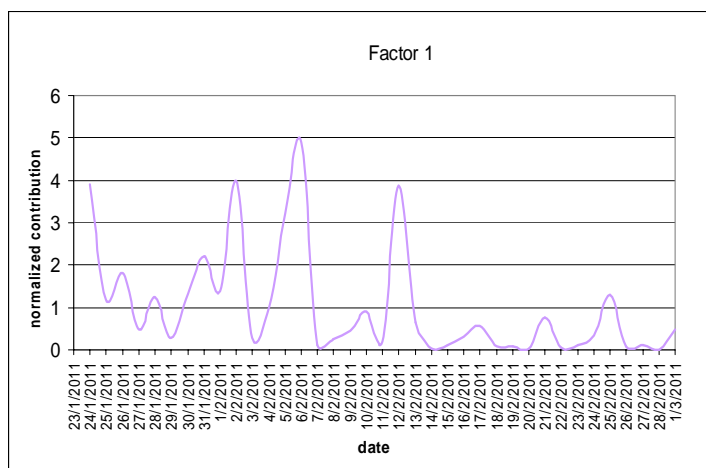
- The dominant specie (~90%) in **Factor 1** is **Cl⁻** which indicates particles **origin from the sea**, possibly through sea-breeze circulation. Peaks of the time variation of this factor (figure A.II.3a) are noticed during all the sampling period; however, during three days (2/2, 6/2 and 12/2) peaks are significantly higher. It is important to notice that **Na⁺** was among the elements with the most significant discrepancy between partners (see Table 5.1 in the main report). Consequently, factor 1 should be confirmed by other source apportionment studies.
- The dominant species in **Factor 2** are **Na⁺ and Mg⁺**, which are connected with **sea salt and crustal dust origin**. Peaks of the time variation of this factor (figure A.II.3b) are noticed during all the sampling period, too. **Na⁺** was also among the elements with the most significant discrepancy between partners.
- Over the 50% of **Mg⁺** and **Ca²⁺** correspond to **Factor 3** implying **soil and mineral rock origin**. This factor presents less sharp peaks during all the sampling period.
- The dominant species in **Factor 4** are all **PAHs** examined (>40%), **K⁺, OC and EC**. These components are associated with **wood burning, vehicles exhausts and in general combustion sources**. It is characteristic that this factor presents higher peaks during the first period (25/1-11/2) of the campaign.
- Over the 50% of **NO₃⁻, SO₄²⁻** and **NH₄⁺** correspond to **Factor 5**. This factor seems to be connected with **transport/regional background, industrial sources, secondary aerosols**. Peaks of the time variation of this factor (figure A.II.3e) are noticed during all the sampling period.



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Figures A.II.2a-e: Percentages of species apportioned to each factor



Figures A.II.3 a-e: Time variation of each factor

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