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PM$_{2.5}$ chemical composition in five European Mediterranean cities: A 1-year study

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Alexandre Armengaud, Damien Piga, Jean Luc Jaffrezo,
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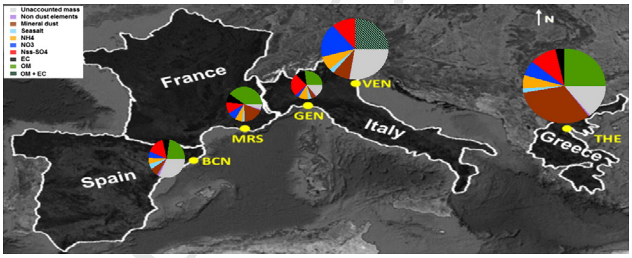

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Highlights

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$PM_{2.5}$ chemical composition in five European Mediterranean cities: A 1-year study

Dalia Salameh [a,b,*], Anais Detournay [a,c], Jorge Pey [a,d], Noemi Pérez [d], Francesca Liguori [e], Dikaia Saraga [f,g], Maria Chiara Bove [h], Paolo Brotto [h], Federico Cassola [h], Dario Massabò [h], Aurelio Latella [e], Silvia Pillon [e], Gianni Formenton [e], Salvatore Patti [e], Alexandre Armengaud [i], Damien Piga [i], Jean Luc Jaffrezo [j], John Bartzis [f], Evangelos Tolis [f], Paolo Prati [h], Xavier Querol [d], Henri Wortham [a], Nicolas Marchand [a,*]

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- PM levels are higher in the Eastern Mediterranean cities.
- Elevated $PM_{2.5}$ concentrations are observed mainly in winter and fall.
- OM was the most abundant component of $PM_{2.5}$ mass except in Thessaloniki.
- PM pollution episodes are characterized by an enrichment of secondary ions.
- Five Mediterranean cities and five different $PM_{2.5}$ pollution situations

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Supplementary material

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ABSTRACT

The seasonal and spatial characteristics of $PM_{2.5}$ and its chemical composition in the Mediterranean Basin have been studied over a 1-year period (2011–2012) in five European Mediterranean cities: Barcelona (BCN), Marseille (MRS), Genoa (GEN), Venice (VEN), and Thessaloniki (THE). During the year under study, PM_{10} annual mean concentration ranged from 23 to 46 μg m^{-3}, while the respective $PM_{2.5}$ ranged from 14 to 37 μg m^{-3}, with the highest concentrations observed in THE and VEN. Both cities presented an elevated number of exceedances of the PM_{10} daily limit value, as 32% and 20% of the days exceeded 50 μg m^{-3}, respectively. Similarly, exceedances of the WHO guidelines for daily $PM_{2.5}$ concentrations (25 μg m^{-3}) were also more frequent in THE with 78% of the days during the period, followed by VEN with 39%. The lowest PM levels were measured in GEN. $PM_{2.5}$ exhibited significant seasonal variability, with much higher winter concentrations for VEN and MRS, in fall for THE and in spring for BCN. $PM_{2.5}$ chemical composition was markedly different even for similar $PM_{2.5}$ levels. On annual average, $PM_{2.5}$ was dominated by OM except in THE. OM contribution was higher in Marseille (42%), while mineral matter was the most abundant constituent in THE (32%). Moreover, $PM_{2.5}$ relative mean composition during pollution episodes ($PM_{2.5} > 25$ μg m^{-3}) as well as the origins of the exceedances were also investigated. Results outline mainly the effect of NO_3^- being the most important driver and highlight the non-negligible impact of atmospheric mixing and aging processes during pollution episodes.

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1. Introduction

Atmospheric particulate matter (PM) is nowadays one of the most challenging environmental issues, mainly because of its adverse effects on human health and its key role in atmospheric processes and climate change (IPCC, 2007; WHO, 2006a). Numerous studies including the Mediterranean region have found that both short- and long-term exposures to ambient $PM_{2.5}$ are associated with increased risk of mortality as well as respiratory illness, lung cancer, asthma and heart disease (Corbett et al., 2007; Dockery, 2009; Perez et al., 2009; Pope and Dockery, 2006; Samoli et al., 2014) and their effects depend on particle size and composition. In order to limit these adverse impacts and to develop efficient strategies for air quality control, the knowledge of $PM_{2.5}$ chemical composition is necessary.

The Mediterranean Sea is bordered by 21 countries, overall accounting for more than 400 million of inhabitants in 2011, ~6–7% of the total World population. These values rank the Mediterranean basin among the most populous regions in the World, akin to the population density found in the Indian subcontinent or in the South–East of China. Moreover, the population is predicted to reach 529 million by 2025 (UNEP/MAP, 2012). The Mediterranean region's population is also concentrated near the coasts. The population of the coastal regions grew from 95 million in 1979 to 143 million in 2000 and could reach 174 million by 2025 (UNEP/MAP, 2012). Furthermore, the Mediterranean Basin has experienced a rapid growth in urbanization (urban population—towns with more than 10,000 inhabitants—increased 1.9% per year during the period 1970–2010, from 152 million to 315 million). The high atmospheric PM loadings in many Mediterranean cities reflect this important urban expansion (Andreae et al., 2002; Gerasopoulos et al., 2011; Güllü et al., 2005; Kanakidou et al., 2011; Querol et al., 2004a; Rodríguez et al., 2001; Saliba et al., 2007).

Atmospherically, the Mediterranean Basin is a crossroad of air masses coming from Europe, Asia and Africa (Lelieveld et al., 2002). Delimited to the north by the populated and highly industrialized area of southern Europe and to the south by the northern Africa continent, aerosol particle loading is therefore largely affected by a number of natural and anthropogenic sources: Saharan dust (Moulin et al., 1998; Ganor et al., 2010; Israelevich et al., 2012; Querol et al., 2009; Pey et al., 2013b), marine aerosols (Piazzola and Despiau, 1997; Viana et al., 2014b), and anthropogenic emissions from the various urban activities (vehicular traffic, biomass burning, fossil fuel combustion, cooking activities) (El Haddad et al., 2011a,b; Minguillón et al., 2011; Mohr et al., 2012; Pandolfi et al., 2014; Reche et al., 2012), from industries and from the increasing maritime traffic (Eyring et al., 2010; Marmer and Langmann, 2005; Mueller et al., 2011; Pey et al., 2013a; Viana et al., 2014a). Shipping emissions are a significant and growing contributor to air quality degradation in coastal areas. Thereby, emissions of exhaust gases and particles from the oceangoing ships affect the chemical composition of the atmosphere, climate and regional air quality (Eyring et al., 2005). On average, shipping emissions contribute with 1–7% to PM_{10}, 1–20% to $PM_{2.5}$, and with 8–11% to PM_1 in coastal European areas with a maximal contribution in the Mediterranean basin and the North Sea (Viana et al., 2009, 2014a). Furthermore, Pey et al. (2013a) have found that, within shipping emissions, aged products dominated over primary ones even in the vicinity of the source. Forest fires are also a major issue in the Mediterranean area, where an average of 40,000 fires occur per year (period 2000–2009) representing about 300,000 ha of damaged forest each year for, only, France, Spain, Italy and Greece (Schmuck et al., 2013).

The Mediterranean basin is also characterized by a complex meteorology, which favors polluted air masses aging (Artíñano et al., 2001; Millán et al., 1997). During the cold season, atmospheric dynamics in the Mediterranean basin reflect the influence of synoptic conditions characterized by the prevalence of westerly winds. On the contrary, mesoscale processes play a dominant role during the warm season: a) recirculation of air masses in the western side of the basin (Millán et al., 1997; Pey et al., 2009) and b) the prevalence NE winds over the eastern side (Tyrlis et al., 2012). Moreover, as discussed in Querol et al. (2009), Pey et al. (2013b) and Israelevich et al. (2012) Saharan dust outbreaks occur in different seasons in the west (frequently in summer) and in the east (more concentrated in autumn and spring).

With this in mind, the Mediterranean basin is particularly impacted by photo-oxidants. Lelieveld et al. (2002) forecasted summer O_3 concentrations in the Mediterranean planetary boundary layer (PBL) around three times higher than in the northern hemisphere background PBL. In their study, they also pointed out the remarkably high tropospheric concentrations of formaldehyde, methanol and acetone leading to a large in situ production of peroxy radicals. Ozone measurements performed all around the Mediterranean Basin in the last decade have confirmed that the entire Mediterranean region is characterized not only by photochemical episodes in urban pollution plumes, but also by high background ozone concentrations (EEA, 2013). The oxidative capacity of the Mediterranean atmosphere seems also to play an important role in terms of aerosol formation and aging. Hildebrandt et al. (2010, 2011) underlined the high degree of oxidation of the organic aerosol based on Aerosol Mass Spectrometer (AMS) measurements performed in the remote coastal site of Finokalia (island of Crete, Greece) during late summer and winter, respectively. In Mediterranean cities, high contributions of oxygenated organic aerosol (proxy of secondary organic aerosol, SOA) were also observed in Barcelona and Marseille (El Haddad et al., 2013; Minguillón et al., 2011; Mohr et al., 2012). In Marseille, the SOA contribution during summer 2008 was estimated to account for ~80% of the total organic aerosol concentrations (El Haddad et al., 2011b, 2013), with around 80% of such SOA non-fossil in origin despite extensive industrial and urban emissions. The prevalence of non-fossil carbon in the SOA is also observed in Barcelona (February to March 2009), where about 60% of the secondary organic carbon was found to be originated from non-fossil origin (Minguillón et al., 2011). These unexpected results are inextricably linked to the prevalence of regional sources over local anthropogenic emissions.

As part of the APICE project (Common Mediterranean strategy and local practical Actions for the mitigation of Port, Industries, and Cities Emissions; http://www.apice-project.eu/), 1-year monitoring campaigns have been simultaneously organized in five European Mediterranean cities: Barcelona (Spain), Marseille (France), Genoa (Italy), Venice (Italy), and Thessaloniki (Greece). From these long monitoring periods, a detailed characterization of $PM_{2.5}$ in terms of chemical

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composition was obtained. This paper attempts to provide an overview on the aerosol phenomenology, its chemical composition and processes affecting its concentration throughout the Mediterranean basin. Special focus is paid in highlighting similarities and differences concerning PM characteristics among these cities. In the following sections, we investigate the air quality in these five Mediterranean cities during the period of observation (2011–2012), the seasonal and the spatial variability of $PM_{2.5}$ chemical composition.

2. Methodology

2.1. Study areas and sampling strategies

Field campaigns were performed at five urban background (UB) sites west to east across the European Mediterranean coast (Fig. 1): Barcelona (BCN), Marseille (MRS), Genoa (GEN), Venice (VEN), and Thessaloniki (THE). Table 1 specifies site identification codes, geographical coordinates, and $PM_{2.5}$ sampling periods and strategies. Although a detailed description of each site is provided in Appendix A (supplementary data), a brief description on instrumentation and sampling strategies is given here:

BCN: 24 h $PM_{2.5}$ samples (starting at 0 h UTC) were collected onto 150 mm-diameter quartz fiber filters (Tissu quartz, Pall), from February 2011 to December 2011 using a high volume sampler (Digitel DA80) operating at a flow rate of 30 m^3 h^{-1}. Roughly, one filter was collected every 4 days. The total number of samples was 68.

MRS: 24 h $PM_{2.5}$ samples (starting at 0 h UTC) were collected onto 150 mm-diameter quartz fiber filters (Tissu quartz, Pall), from July 2011 to July 2012 using a high volume sampler (Digitel DA80) operating at a flow rate of 30 m^3 h^{-1}. $PM_{2.5}$ sampling was interrupted from 1 to 2 weeks in each month in order to perform the regulatory measurements of PAHs (Polycyclic Aromatic Hydrocarbons). The total number of samples was 216. Most of these samples were grouped together and resulted in 54 composite samples. These composite samples were built according to the $PM_{2.5}$ concentration and air mass origins.

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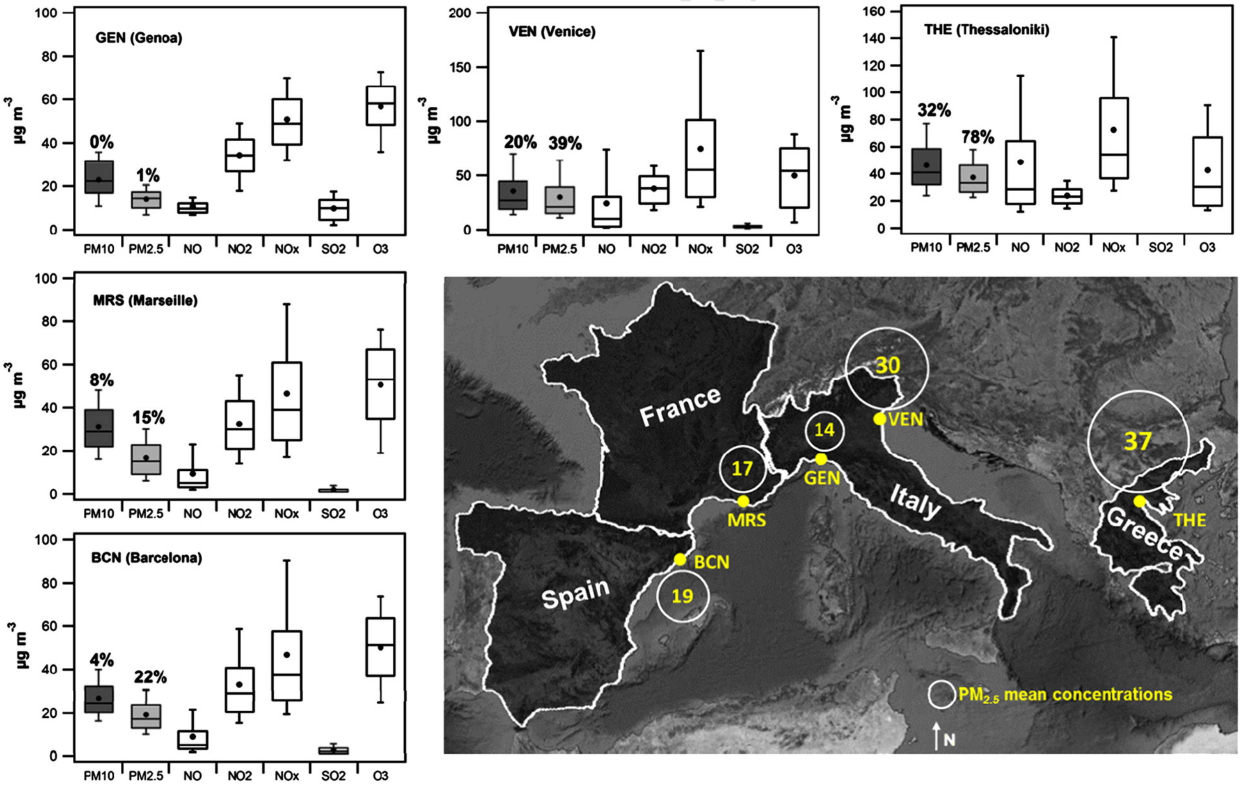

Fig. 1. Map of the sites: *BCN* Barcelona, *MRS* Marseille, *GEN* Genoa, *VEN* Venice, and *THE* Thessaloniki. Yellow circles: $PM_{2.5}$ mean concentration (2011–2012). Box-whisker plots represent PM and main gaseous pollutants daily concentrations observed at each sampling site during the study period (Table 1). Each box plot shows mean (marker), median (solid line of the box), 25th and 75th percentile (bottom and top lines of the box, respectively), as well as 10th and 90th percentile (lower and upper end of the whisker lines, respectively). PM data capture during this 1-year period (see Table 1) was over 85%, for BCN (86% for PM_{10} and $PM_{2.5}$), MRS (91% for PM_{10} and 95% for $PM_{2.5}$), VEN (87% for PM_{10} and 85% for $PM_{2.5}$) while lower data coverage was reported for GEN (59% for PM_{10}; 50% for $PM_{2.5}$) and for THE (62% for PM_{10} and 40% for $PM_{2.5}$). Gaseous pollutants data capture was over 82%, for BCN (82%), MRS (95%), VEN (99%) and THE (84%) while it covers only 64% for GEN, and for THE no SO_2 data available. Values listed above the PM box plots represent the percentage of days exceeding the limit value of 50 µg m^{-3} and 25 µg m^{-3}, for PM_{10} and $PM_{2.5}$ respectively, during the period under study.

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Table 1
The study site locations, the time period and the $PM_{2.5}$ sampling in the five Mediterranean cities.

City (Code)	Sampling sites (UB) (latitude; longitude)	Time period	$PM_{2.5}$ sampling (N)[a]	$PM_{2.5}$ measuring method
Barcelona (BCN)	Palau Reial (41°23′14″N; 2°06′56″E)	February 2011 to December 2011	HVS (500 L/min), every 4 days, Quartz (68)	GRIMM-OPC corrected with gravimetric data
Marseille (MRS)	Cinq avenues (43°18′18.84″N; 5°23′40.89″E)	July 2011 to July 2012	HVS (500 L/min), daily, Quartz (216)	TEOM–FDMS
Genoa (GEN)	Corso Firenze (44°25′5.69″N; 8°55′38.97″E)	March 2011 to September 2011	LVS (38.3 L/min), daily, Teflon/quartz (184)	gravimetric
Venice (VEN)	Parco Bissuola (45°29′58.71″N; 12°15′40.55″E)	January 2011 to December 2011	LVS (38.3 L/min), daily, Quartz (312)	gravimetric
Thessaloniki (THE)	City hall (40°62′36.25″N; 22°95′38.27″E)	June 2011 to May 2012	LVS (38.3 L/min), 7–28 days/month, Quartz (149)	gravimetric

[a] (N): number of collected $PM_{2.5}$ filters.

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Note that all the available samples corresponding to a daily $PM_{2.5}$ concentration exceeding 25 µg m^{-3} were analyzed individually.

GEN: 24 h $PM_{2.5}$ samples were collected using a low volume sampler (Skypost by TRC TECORA), which was designed according to the CEN standards at Corso Firenze site, selected based on the direction of the prevailing winds. The sampler was operated almost continuously from March 2011 to September 2011 (with only three samples collected in February 2011 and three other in October 2011), every 24 h beginning at midnight, and alternating between Teflon (PTFE, Pall: R2PJ047) and quartz fibers (Pallflex, 2500QAO UP) filter membranes (47 mm). The number of collected samples was 184.

VEN: 24 h $PM_{2.5}$ samples (starting at 0 h local time) were collected continuously from January 2011 to December 2011 onto 47 mm-diameter quartz fiber filters (Whatman QMA, GE Healthcare) according to the EN 14907:2005 (CEN, 2005a) standards, using a low volume sampler (Zambelli Explorer Plus). The total number of samples was 312.

THE: 24 h $PM_{2.5}$ samples were collected onto 47 mm-diameter quartz fiber filters (Whatman), mounted in a low volume air sampling system (Derenda LVS3.1/PMS3.1-15 with a $PM_{2.5}$ inlet). The air flow rate was set to 2.3 m^3 h^{-1} for daily sampling, beginning at approximately 09:00 pm and the total sampled volume per filter was approximately 55 m^3. A hundred forty-nine samples corresponding to about 7–28 filters per month were collected from June 2011 to May 2012.

PM_{10} and $PM_{2.5}$ daily concentrations were obtained in GEN, VEN and THE by gravimetric analysis on pre-weighted and pre-conditioned filters for 48 h in a controlled room (temperature: 20 ± 1 °C, relative humidity: 50 ± 5%). Before and after conditioning, the filters were weighted using an analytical balance (sensitivity: 0.1–1 µg). In BCN daily PM measurements were achieved using a GRIMM-OPC corrected with the gravimetric levels obtained similarly as in the other sites, and in MRS a TEOM-FDMS (Tapered Element Oscillating Microbalance equipped with a Filter Dynamic Measurement System) was used to measure PM concentrations.

Concentrations of gaseous pollutants were measured using the chemiluminescence analyzer for NO and NO_2; the UV fluorescence analyzer for SO_2; and the UV photometry analyzer for O_3.

2.2. Analytical techniques

Different laboratory procedures and analytical techniques (Appendix B, supplementary data) have been applied for a comprehensive chemical characterization of $PM_{2.5}$ composition. Briefly, they are summarized as follows:

- Organic carbon (OC) and elemental carbon (EC)
  For BCN, MRS and GEN, OC and EC fractions were quantified using the thermal optical transmittance (TOT) method, with a Sunset Lab analyzer, following the EUSAAR2 temperature protocol (Cavalli et al., 2010), while, in THE, the TOT analyzer was operating with the NIOSH 5040 temperature protocol (Chow et al., 2001). These protocols differ in their temperature set point, higher for NIOSH 5040 (up to 850 °C for the analysis of OC in 100% He and to 940 °C for the analysis of EC in 98% He + 2% O_2) than EUSAAR2 (up to 650 °C for the analysis of OC in 100% He and to 850 °C for the analysis of EC in 98% He + 2% O_2), and in the residence time (longer steps for EUSAAR2). Both thermal protocols gave similar concentrations of total carbon (Chiappini et al., 2014; El Haddad et al., 2009). However, the EC (respectively OC) contribution to the TC measured by the EUSAAR2 method was higher (respectively lower) than the one measured by the NIOSH method, due to the lower temperature used for the last OC step in the EUSAAR2 protocol (Cavalli et al., 2010; El Haddad et al., 2009). Thus, a difference of about 20% for OC and EC is expected between these two methods (El Haddad et al., 2009).
  In VEN, only the total carbon (TC) fraction was analyzed using a TOC analyzer (Shimadzu, V-CPH model) coupled with a SSM-5000A module. TC was quantified by a catalyzed oxidative conversion to CO_2 at 900 °C, then analyzed with a NDIR (no dispersive infrared detector).
- Ionic species
  Major ions (SO_4^{2-}, NO_3^-, Cl^- NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}) were analyzed by ionic chromatography after extraction of a fraction of the samples in ultra-pure water for MRS, GEN, VEN and THE (El Haddad et al., 2011a; Pey et al., 2013a; Tolis et al., 2014; Bove et al., 2014). For BCN only anions were analyzed by IC. Quantification of NH_4^+ was achieved by a selective electrode.

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- Metals and trace elements

  For the determination of the elemental compositions, a second fraction of the filter was digested using a different mixture of inorganic acids (e.g. HNO_3–HF–$HClO_4$ for BCN; HNO_3–HF for MRS; HNO_3–HCl for VEN and THE). The quantitative analysis of metals and trace elements was performed using: a) ICP–AES (inductively coupled plasma–atomic emission spectrometry) for major elements (Al, Ca, Na, Mg, K, Fe, P) and an ICP–MS (inductively coupled plasma–mass spectrometry) for trace elements (Cu, Ni, Pb, V, Zn) in BCN (Pey et al., 2013a) ; b) an ICP–MS in MRS; c) and a GFAAS (graphite furnace atomic absorption spectrometry) in VEN and THE (Tolis et al., 2014). For GEN, elemental concentrations were directly measured by ED-XRF (energy dispersive–X-ray diffraction) technique (Ariola et al., 2006).

Finally, to guarantee the quality and the accuracy of the analytical determinations, blank filters were also analyzed following the same methodology, as well as small amounts of reference material.

2.3. Chemical mass closure

Chemical components of PM were grouped into nine classes as follows: organic matter (OM), elemental carbon (EC), non-seasalt sulfate (nss-SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), sea-salt, mineral dust, non-dust elements and unaccounted mass.

To account for associated oxygen and hydrogen mass, OM was obtained by multiplying the measured concentration of organic carbon (OC) by a conversion factor, which is the ratio of the average molecular mass to the carbon mass for the organic aerosol. In order to be consistent in our comparative study, a single 1.4 conversion factor (Lonati et al., 2005; Putaud et al., 2010; Sillanpää et al., 2006) was applied. Nevertheless, we are aware that this simplicity might introduce some uncertainties in the overall estimations of OM, since the OM-to-OC ratio is very dependent on site location (higher for oxidized and aged aerosol), aerosol sources and seasons. For VEN, only TC (total carbon) concentration was measured. To balance properly the $PM_{2.5}$ mass, TC measured values needed to be corrected. Therefore, for the other sites involved in this study (except VEN), we have calculated the concentrations of measured TC ($TC_{measured} = OC + EC$), and corrected TC ($TC_{corrected} = OM + EC = 1.4 \times OC + EC$). Then, we have determined the $TC_{corrected}$-to-$TC_{measured}$ ratios for each season, and the average ratio of the four cities (1.28 ± 0.06) was used to roughly estimate the corrected TC concentrations in VEN.

The non-sea salt sulfate (nss SO_4^{2-}) was calculated from the measured SO_4^{2-} minus the sea-salt fraction of SO_4^{2-} (ss $SO_4^{2-} = 0.252 \times Na^+$) (Seinfeld and Pandis, 1998).

Sea-salt concentrations were calculated from soluble sodium concentrations, assuming that sea-salt mass is equal to $3.252 \times Na^+$ (Grythe et al., 2014).

Mineral dust was considered as the sum of Al_2O_3, SiO_2, CO_3^{2-}, Ca, Fe, K, Mg, Mn, Ti and P, where Al_2O_3, SiO_2 and CO_3^{2-} were indirectly determined using empirical equations ($Al_2O_3 = 1.89 \times Al$; $SiO_2 = 3 \times Al_2O_3$; $CO_3^{2-} = 1.5 \times Ca$) (Pérez et al., 2008; Querol et al., 2001). However, since only Fe concentrations were determined in VEN, mineral dust in VEN was determined using the ratio Fe-to-dust content calculated in the other four cities. This ratio ranged between 0.04 and 0.246, thus an average ratio of 0.143 was applied to reconstruct dust concentrations in VEN from Fe values.

Non-dust elements correspond to the sum of the common measured trace elements (i.e., Cu, Ni, Pb, V, Zn) other than geological ones.

The unaccounted mass is obtained as the difference between measured PM mass concentration and the reconstructed mass (i.e., the sum of aerosol component concentrations). This fraction could be attributed to analytical errors, such as the underestimation of the OM contribution; as well as to the estimation of mineral dust (e.g. VEN). Moreover, a part of the unaccounted PM mass is likely to be ascribed to particle-bound water, especially if mass concentrations are determined at relative humidity (RH) > 30% (Putaud et al., 2010). The water content in PM samples will vary for different samples and measurement sites, depending on the particle composition and the ambient RH (e.g. average RH during the study period was 63% in MRS and 67% in BCN) and temperature. It was estimated to vary between 20% and 35% of the $PM_{2.5}$ mass (Tsyro, 2005). Indeed, some of the inorganic species (e.g. ammonium nitrate and ammonium sulfate) present in the ambient aerosol are mostly hygroscopic by nature and exhibit the property of deliquescence in humid air (Tang and Munkelwitz, 1994). They can retain water if the RH is increased which thus affects the physical and chemical properties of aerosol particles. (Perrino et al., 2013).

2.4. Intercomparison campaign

Before long monitoring campaigns in each city, a 6-week intercomparison campaign was organized in Marseille from 01/25/2011 to 03/02/2011 at the urban background site “Cinq Avenues”. During this intercomparison exercise, all the partners of the project deployed the same instruments and/or samplers used thereafter within the framework of the long monitoring campaigns. Analyses of the samples were performed as described above (see Section 2.2). The main objective of that intensive campaign was to guarantee the consistence of the results as different instruments and analytical techniques were used by the different groups.

For PM concentration measurements, an excellent agreement was observed between partners with a standard deviation lower than 10% and a correlation coefficient (R^2) greater than 0.9 ($n = 42$). Sulfate, nitrate and OC showed also a very good agreement between groups with a standard deviation lower than 15% ($R^2 > 0.85$). For EC, an excellent agreement was observed, but only between 3 groups (SD < 10%, $R^2 > 0.9$). The 4th group, which reported EC concentrations ~2 times lower, encountered an analytical issue, fixed thereafter, during the analysis of samples collected during the intercomparison campaign. Ammonium exhibited more discrepancies. Two groups measured the same concentrations of ammonium (±3%) and very close to the ammonium concentrations which can be predicted considering a full neutralization of sulfate and nitrate (±10%). The other two groups reported values 1.4 times lower and three times higher (on average) than the concentrations reported by the first two groups. For these two later groups, the ionic balance was thus not respected during the intercomparison campaign. Therefore, a special care has been taken for the ammonium data series and

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their consistency with sulfate and nitrate concentrations provided by the two later groups for the long monitoring campaigns. Only one dataset has been corrected by applying a correction coefficient of 2.7 obtained from the intercomparison campaign measurements.

Finally, the levels of trace metals showed a good agreement between partners, within a classical analytical error range (30%).

3. Results and discussions

3.1. Levels of PM_{10}, $PM_{2.5}$, and gaseous pollutants

Taking into consideration the $PM_{2.5}$ sampling time periods performed at each site (Table 1), we have plotted the daily PM and the main gaseous air pollutant (NO, NO_2, NO_x, SO_2 and O_3) concentrations in Fig. 1. During this 1-year period, PM data coverage was over 85%, i.e., for BCN (86% for PM_{10} and $PM_{2.5}$), MRS (91% for PM_{10} and 95% for $PM_{2.5}$), and VEN (87% for PM_{10} and 85% for $PM_{2.5}$). However, lower data coverage is reported for GEN (59% for PM_{10}; 50% for $PM_{2.5}$) and for THE (62% for PM_{10} and 40% for $PM_{2.5}$). Regarding the gaseous pollutants, the data covered more than 82%: for BCN (82%), MRS (95%), VEN (99%), and THE (84%) while in GEN it only covered 64%.

PM_{10} mean concentrations ranged from 23 to 46 μg m^{-3}, with THE (46) > VEN (36) > MRS (31) > BCN (27) > GEN (23). Hence, the annual EU PM_{10} limit value of 40 μg m^{-3} is only exceeded in THE. As reported in Fig. 1, exceedances of PM_{10} concentration over the EU PM_{10} 24-h limit value of 50 μg m^{-3} were more frequent in THE and VEN (more than 35 times), where 32% and 20% of the days had a PM_{10} concentration greater than 50 μg m^{-3}. Only GEN complied the PM_{10} EU short-term air quality standard. However, owing to the relatively low data coverage in some of the cities, the 90.4 percentile is also assessed following the recommendations included in the Directive 2008/50/EC. Results were in accordance with the abovementioned exceedance days and the PM_{10} 90.4 percentile ranged from 35 to 77 μg m^{-3}, in the following order: THE (77) > VEN (70) > MRS (48) > BCN (40) > GEN (35).

Similarly, the average $PM_{2.5}$ concentration was significantly higher in THE (37 μg m^{-3}) and VEN (30 μg m^{-3}), than that observed in BCN (19 μg m^{-3}), MRS (17 μg m^{-3}), and GEN (14 μg m^{-3}). Moreover, $PM_{2.5}$ levels recorded in THE and VEN, were 1.2–1.5 times the EU annual target value for $PM_{2.5}$ (25 μg m^{-3}), breaching then the EU long-term air quality standard. Regarding the $PM_{2.5}$ 24-h guideline of 25 μg m^{-3} (WHO, 2006a), it is well exceeded at all sites. The highest number of days for which $PM_{2.5}$ concentration was greater than 25 μg m^{-3}, is recorded in THE (78% of the days), followed by VEN (39%), BCN (22%), MRS (15%), and GEN (1%). It is worthy to note that in the case of GEN, roughly 7 months of $PM_{2.5}$ measurements are reported (data coverage 50%), which might explain the lowest number of PM exceedances recorded at this site. Nevertheless, the $PM_{2.5}$ 90.4 percentile ranged from 20 to 64 μg m^{-3}, in the following order: VEN (64) > THE (58) > BCN (30.8) ≈ MRS (30.7) > GEN (20).

Furthermore, in order to frame the state of particulate pollution in these five Mediterranean cities, PM levels are compared with previous measurements performed in the same study areas, as well as with those from other European cities over the past years as reported in Table 2. We remarked that PM concentrations observed during this study exhibited various behaviors in the five cities as follows: (i) close levels to those recorded previously are noted for MRS and GEN; (ii) lower levels for BCN; (iii) lower PM_{10} and similar $PM_{2.5}$ levels for VEN; (iv) while higher levels for both PM fractions are observed in THE. The absence of the PM decreasing trend in Thessaloniki could be attributed to the metro construction activities started in 2007, and which were, indeed, in progress during the campaign. The comparison of these data shows that PM concentrations in BCN, MRS and GEN fall within the mean annual ranges reported in the different European UB sites (Table 2), while in THE and VEN cities, PM concentrations were relatively higher and of the same order of magnitude of the most polluted cities in central Europe, such as Budapest and Prague. Moreover, recent studies (Cusack et al., 2012; Karanasiou et al., 2014; Masiol et al., 2014; Querol et al., 2014) on long-term PM trends across the Mediterranean basin revealed a significant decreasing trend for PM levels. These reductions can be attributed to the implementation of emission abatement strategies, such as the introduction of the IPCC: Climate Change (2007) or the EURO standards on road traffic emission (1998/69/EC, 2002/80/EC, 2007/715/EC), but also to meteorological conditions. Nevertheless, the present study emphasizes that PM concentrations in THE and VEN were still relatively high compared to the other European cities (Table 2), and this may require appropriate control strategies for the reduction of PM emissions and the abatement of the public health hazard due to PM-associated morbidity and mortality.

Table 2
Average concentrations of PM_{10} and $PM_{2.5}$ (for at least 1-year data) in different European cities in comparison with this study (μg m^{-3}).

Location	Sampling period	PM_{10}	$PM_{2.5}$	Reference
Madrid (Spain)	2005	32	14	Kassomenos et al. (2014)
Valencia (Spain)	2004–2006	33	23	Pascal et al. (2013)
Barcelona (Spain)	**2011–2012**	**27**	**19**	**This study**
Barcelona (Spain)	2004–2006	37	27	Pascal et al. (2013)
Paris (France)	2009–2010	–	15	Bressi et al. (2013)
Lyon (France)	2004–2006	25	16	Pascal et al. (2013)
Marseille (France)	**2011–2012**	**31**	**17**	**This study**
Marseille (France)	2004–2006	30	18	Pascal et al. (2013)
Grenoble (France)	2000–2001	–	19	Götschi et al. (2005)
Amsterdam (Netherland)	2002–2004	31	21	Lianou et al. (2011)
Basel (Switzerland)	2005–2008	21	16	Putaud et al. (2010)
Zurich (Switzerland)	2008	20	15	Putaud et al. (2010)
Genoa (Italy)	**2011**	**23**	**14**	**This study**
Genoa (Italy)	2009–2010	22	15	Cuccia et al. (2013)
Roma (Italy)	2006–2010	28	18	Karanasiou et al. (2014)
Venice (Italy)	**2011–2012**	**36**	**30**	**This study**
Venice (Italy)	2009–2010	43	30	Pecorari et al. (2013)
Prague (Czech republic)	2004–2005	37	–	Schwarz et al. (2008)
Thessaloniki (Greece)	**2011–2012**	**46**	**37**	**This study**
Thessaloniki (Greece)	2007–2008	36	21	Kassomenos et al. (2011)
Budapest (Hungary)	2004–2006	48	34	Pascal et al. (2013)
Bucharest (Romania)	2004–2006	55	38	Pascal et al. (2013)
London (UK)	2004–2006	25	13	Pascal et al. (2013)
Birmingham (UK)	2002–2004	22	13	Lianou et al. (2011)

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Regarding the levels of gaseous air pollutants (Fig. 1), NO and NO_x annual average concentrations were also higher in THE (49 and 72 μg m^{-3}, respectively) and VEN sites (24 and 75 μg m^{-3}, respectively), than in BCN (9 and 47 μg m^{-3}, respectively), MRS (9 and 46 μg m^{-3}, respectively) and GEN (11 and 51 μg m^{-3}, respectively). However, NO_2 annual mean concentration was the highest in VEN (38 μg m^{-3}) and the lowest in THE (24 μg m^{-3}). The annual limit fixed by the European Union (40 μg m^{-3}; EU, 2008) for NO_2 has been complied at all the sites. O_3 presented annual mean concentrations ranging between 43 μg m^{-3} (in THE) and 57 μg m^{-3} (in GEN), with maximum daily values up to 134 μg m^{-3} in THE, 117 μg m^{-3} in VEN, 104 μg m^{-3} in MRS, 99 μg m^{-3} in BCN and 91 μg m^{-3} in GEN during summer.

SO_2 annual average concentration recorded in GEN (10.5 μg m^{-3}) was significantly higher than those observed in the four other cities (2–3 μg m^{-3}). Such differences can be explained because the Corso Firenze site is located immediately outside of the harbor area and is more influenced by heavy fuel oil combustion (e.g. shipping emissions). However, high SO_2 concentrations appear as a peculiarity of the atmospheric pollution over GEN, since high SO_2 concentrations (12.3 μg m^{-3} on average) were also observed in another site located in the city of GEN during the same period (data not shown).

3.2. $PM_{2.5}$ seasonal and spatial variation

Fig. 2 illustrates the seasonal distribution of $PM_{2.5}$ concentrations (mean, median and percentiles). In order to compare the seasonal differences in $PM_{2.5}$, a one-way ANOVA approach was used. The results showed that $PM_{2.5}$ exhibited the strongest seasonality in VEN, with a much higher mean concentration in winter (53 μg m^{-3}) than in summer (15 μg m^{-3}) or fall (34 μg m^{-3}) ($p < 0.05$). Likewise, significant seasonal variability was evident in MRS, with higher concentrations observed during winter (24 μg m^{-3}) than during summer (14 μg m^{-3}) ($p < 0.05$). Likewise, THE and BCN showed clear seasonal variations but $PM_{2.5}$ maxima are shifted to fall (45 μg m^{-3}) and spring (25 μg m^{-3}) seasons, respectively. On the other hand, $PM_{2.5}$ concentrations in GEN were relatively steady along the year and no significant statistical differences can be highlighted. These differences can be assigned to the variability of local source strengths in combination with the influence of specific meteorological conditions. Moreover, the increased $PM_{2.5}$ concentrations in winter and fall compared to the summer can be generally ascribed to the enhancement of some particular anthropogenic activities (e.g. heating sources or agricultural fires) associated with lower boundary layer heights. For instance, in the case of Thessaloniki, elevated PM levels recorded during cold season were mostly due to the burning of the less expensive wood/biomass, which was widely used during the period of economic crisis in Greece (Saffari et al., 2013). In summer, lower $PM_{2.5}$ concentrations are generally observed, as sea and land breezes are intensified and the mixing layer height is wider, both processes favoring atmospheric dispersion (Kassomenos et al., 2011).

Fig. 2 also presents the number of days with $PM_{2.5}$ concentrations higher than 25 μg m^{-3} for the whole period (Table 1), and for collected and analyzed $PM_{2.5}$ samples. As expected, the highest frequency of exceedances is observed in VEN and THE. With respect to the seasonality, the number of exceedances in THE, was relatively similar in all seasons, whereas for VEN and MRS most of the exceedances occurred in winter and fall. For BCN, the exceedances were more frequent in spring while for GEN, only two exceedances were noted during the same season (Fig. 2) Once again, the data coverage in GEN (50%) prevents from drawing final conclusions regarding the occurrence of $PM_{2.5}$ pollution events over the year.

3.3. $PM_{2.5}$ chemical composition and mass balance

During this 1-year period, a total of 68, 216, 184, 312 and 149 daily filters were collected in BCN, MRS, GEN, VEN, and THE, respectively (Table 1). These samples do not cover all the episodes of high concentration of $PM_{2.5}$ ($PM_{2.5} > 25$ μg m^{-3}) (Fig. 2). Therefore, for statistical representativeness purpose, we have determined the percentage of days presenting

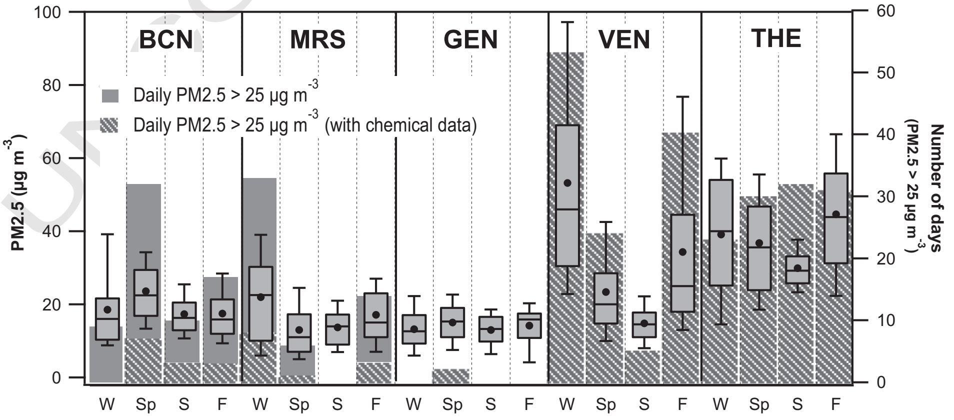

Fig. 2. Seasonal $PM_{2.5}$ concentrations (left y-axis) at the five study sites. The boxes and whiskers denote the 10th, 25th, medians, 75th and 90th percentile; the dots denote the mean value. The bars (right y-axis) represent the number of days whose daily $PM_{2.5}$ concentrations measured is above 25 μg m^{-3} both, for the whole study year (solid bars) and for the collected samples for which we have chemical data (dashed bars). It should be reminded that in the case of BCN and MRS, even if not all the samples belonging to the episodes of high $PM_{2.5}$ concentrations were collected and analyzed, online $PM_{2.5}$ measurements were carried out along the study period. Further details on $PM_{2.5}$ data coverage can be found in Section 3.1 and Fig. 1.

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$PM_{2.5} > 25$ µg m^{-3}, whose filters were collected and analyzed with respect to the total number of days showing high $PM_{2.5}$ concentrations during the study period. In BCN, from the 68 days presenting $PM_{2.5}$ concentrations higher than 25 µg m^{-3} along the study period, 13 daily filters have been collected and analyzed (i.e. 19.1%). In MRS, among the 53 days with high $PM_{2.5}$ concentrations, 12 samples have been collected and analyzed (i.e. 22.6%). For GEN, VEN and THE where gravimetric methods have been used to determine $PM_{2.5}$ concentrations, 100% of the high $PM_{2.5}$ concentration events have been analyzed, but the data coverage for $PM_{2.5}$ concentrations were lower than that in BCN and MRS.

The statistical presentation of the analytical results for major and trace components content in $PM_{2.5}$ samples is reported in Table 3, whereas the seasonal $PM_{2.5}$ chemical composition is depicted in Fig. 4(a–b).

3.3.1. Carbonaceous fraction

On an annual basis, OM mean concentration accounted for 4.2 µg m^{-3} (23% of the $PM_{2.5}$ mass) in BCN, 8.6 µg m^{-3} (42%) in MRS, 3.8 µg m^{-3} (27%) in GEN, and 9.2 µg m^{-3} (25%) in THE. OM constituted the most important fraction of $PM_{2.5}$ in MRS and this contribution was comparable to the highest values reported for urban sites in Europe (Putaud et al., 2010).

EC mean concentration ranged between 1.2 and 1.8 µg m^{-3}, and contributed between 3.5% (in THE) and 10% (in GEN) to the $PM_{2.5}$. These results were in agreement with those reported in other European urban sites (1.3–1.7 µg m^{-3} for larger cities or those influenced by shipping emissions; Querol et al., 2013). However, EC presented homogeneous concentration compared to OM. This can be due to the existence of various sources of OM, including direct particle emissions and atmospheric oxidation of reactive organic gases; whereas EC is emitted from primary combustion sources (Lonati et al., 2005).

Significant seasonal variations were observed for the carbonaceous fraction (OM + EC) in VEN, MRS, THE, and BCN as observed for $PM_{2.5}$. OM + EC concentrations increased markedly during winter and fall seasons in MRS, VEN, and THE, whereas they raised during springtime in BCN (Fig. 4).

3.3.1.1. OC-to-EC ratios seasonal variation. OC-to-EC ratio has been used in several studies as a useful tool that provides information on the origins of the carbonaceous fraction (Pio et al., 2011; Plaza et al., 2011; Na et al., 2004; Turpin and Huntzicker, 1991; Viana et al., 2007). The OC-to-EC ratios are strongly source dependent and quite variable for the different sources. Hence, the variation in this ratio may be used to determine changes in emission sources, aging evolution and the presence of secondary organic aerosol. EC is exclusively derived from primary combustion sources (e.g. fossil fuel combustion and biomass burning) and contains compounds with graphite-like structures, which can absorb light (warming effect) (Pöschl, 2005). OC has similar sources but also results from primary biogenic emissions such as leaf abrasion or sea spray and from secondary processes in the atmosphere involving volatile or semi-volatile organic compounds and oxidants (O_3, OH, NO_3, and NO_2). OC fraction includes organic molecules and polymers, e.g. organic acids, which do not generally absorb visible light (cooling effect). OC-to-EC values can be used to evaluate the relative scattering and absorption and to estimate the radiative forcing induced by carbonaceous aerosols (Novakov et al., 2005).

Table 3

Arithmetic mean (AM), geometric mean (GM), minimum (Min), and maximum (Max) concentration of major and trace components of $PM_{2.5}$ obtained at each sampling site during the study period.

	BCN				**MRS**				**GEN**				**VEN**				**THE**			
	AM	GM	Min	Max	AM	GM	Min	Max	AM	GM	Min	Max	AM	GM	Min	Max	AM	GM	Min	Max
µg m^{-3}																				
$N^{(a)}$	68				54				184				312				148			
$PM_{2.5}^{(b)}$	18.6	17.1	7.8	49.6	19.6	17.2	4.5	56.0	14.0	13.0	3.3	31.4	30.0	23.5	4.0	159	**37.2**	**34.5**	12.9	82.6
OC	3.0	2.7	0.9	9.9	6.2	5.1	1.6	20.9	2.7	2.4	0.7	6.2	na	na	na	na	6.6	5.6	1.6	17.7
EC	1.2	1.0	0.3	4.3	1.8	1.6	0.6	3.8	1.4	1.3	0.4	4.1	na	na	na	na	1.3	1.2	0.4	3.7
OC/EC	2.9	2.7	1.0	11.2	3.5	3.1	1.3	10.7	2.1	1.9	0.4	5.0	na	na	na	na	5.2	4.8	2.2	12.8
TC	4.2	3.7	1.3	11.4	7.9	6.8	2.2	23.8	3.4	2.9	0.4	7.9	5.8	4.5	1.7	27.0	7.9	6.9	2.3	20.3
TC/PM2.5 (%)	24.1	21.8	7.5	66.8	41.3	39.9	19.7	64.5	26.7	22.9	4.5	85.3	19.1	18.1	3.6	44.7	21.0	19.9	8.5	41.8
Nss-SO_4^{2-}	2.8	2.3	0.4	7.9	2.2	1.8	0.4	7.2	3.6	2.9	0.04	9.9	3.4	2.8	0.2	13.3	3.9	3.3	0.1	11.3
NO_3^-	1.0	0.4	0.01	10.5	1.7	0.9	0.2	6.9	0.5	0.3	0.1	6.1	5.4	1.8	0.2	60.2	2.4	1.9	0.1	10.2
NH_4^+	1.0	0.7	0.1	5.4	1.5	1.1	0.1	5.2	1.4	1.2	0.02	4.4	2.3	1.4	0.1	18.6	2.1	1.6	0.1	6.4
Nss-K^+	na	na	na	na	0.1	0.08	0.02	0.3	0.06	0.05	0.004	0.3	0.4	0.3	0.1	2.4	0.1	0.09	0.002	0.6
Na^+	0.3	0.2	0.03	0.8	0.1	0.1	0.03	0.6	0.1	0.1	0.002	0.9	0.2	0.2	0.1	2.4	0.2	0.2	0.01	0.9
ng m^{-3}																				
Ca	145	111	18	401	1092	639	31	4353	110	87	9	461	na	na	na	na	2044	1519	25	6988
Cr	1.3	1.0	0.1	3.9	2.1	1.3	0.2	7.1	na	na	na	na	7	5	1	33	30	18	0.3	106
Fe	155	132	32	490	265	207	36	750	142	124	11	376	357	298	102	1649	908	650	15	2531
K	128	110	16	445	225	201	58	611	100	86	16	382	na	na	na	na	433	213	1	1765
Mg	47	39	6	141	144	130	49	290	36	31	6	107	na	na	na	na	441	274	12	1547
Mn	5	4	1	13	11	9	3	57	4	4	1	26	na	na	na	na	91	72	4	243
Cu	7	6	1	39	17	11	1	100	6	6	1	18	18	14	2	76	84	63	9	346
Ni	3	2	0.4	12	4	4	1	15	7	5	1	26	4	4	2	19	26	16	1	100
Pb	6	5	0.4	17	8	7	2	23	6	5	1	24	12	9	1	77	41	35	11	98
V	6	5	1	30	6	5	1	21	14	11	1	71	7	5	1	18	11	7	0.2	75
Zn	42	28	4	152	24	19	3	73	19	15	1	64	81	77	50	154	77	20	0.3	442

na: not available.

(a) Number of $PM_{2.5}$ samples.

(b) The highest $PM_{2.5}$ mass concentration bolded.

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For on-road vehicle emissions, OC-to-EC ratios range typically from 1.4 to 5 for gasoline catalyst light duty vehicles and from 0.3 to 1 for diesel light and heavy duty vehicles (Fujita et al., 2007; Platt et al., 2013; May et al., 2014; Schauer et al., 1999; Zielinska et al., 2004). In Europe, diesel vehicles represent the major fraction of the vehicular fleet. According to the World Bank database, the diesel fuel consumption represented, in 2011, 81.9% for France (MRS), 81.7% for Spain (BCN), 70.6% for Italy (GEN and VEN) and 41.5% in Greece (THE) of the total fuel consumption per capita (road sector only). For comparison purpose, this percentage is only 26.8% in the US. In MRS, a tunnel study was performed by El Haddad et al. (2009). They observed an OC-to-EC ratio ranging from 0.32 to 0.44 totally in line with the high proportion of diesel vehicles. Thus, an OC-to-EC ratio of about 0.3–1.2 should be expected if primary vehicular exhaust is the prevalent driver of the OC-to-EC ratios in the ambient atmosphere of the cities. This ratio for primary vehicular emission can be slightly modified by the implementation of the new European emission regulation (i.e. EURO5, released in 2009) and by the abundance of scooters in the Mediterranean cities. The new emission regulation significantly decreases the OC-to-EC ratio for gasoline cars (May et al., 2014; Platt et al., 2013) and the implementation of Diesel Particles Filter (DPF) seems to increase this ratio for diesel car (May et al., 2014). However, the drastic decrease of EC and OC emission rates from diesel car equipped with a DPF will not modify the overall OC-to-EC ratio (May et al., 2014). In addition, the percentage of EURO 5 vehicles was only 9% of the total vehicular fleet in France, in 2011. A peculiarity of the Mediterranean area is the abundance of two stroke scooters which have been recently qualified as "asymmetric polluters" by Platt et al. (2014) (i.e. despite they represent a small number of vehicles, they may dominate vehicular pollution). For two stroke scooters the OC-to-EC ratio is very high, ranging from 30 to 300 (May et al., 2014). The influence of two stroke scooters could thus potentially change significantly the OC-to-EC ratio from primary vehicular emissions in the five cities under study. Primary wood combustion aerosol particles, the second most important source of EC in many urban areas, are characterized by an OC-to-EC ratio ranging from 3 to 70 (Fine et al., 2001, 2002, 2004a,b; Schmidl et al., 2008; Sheesley et al., 2007). This ratio is highly dependent of the nature of the fuel burned (hardwood, softwood, presence of leaves, among others) and the combustion conditions (open burning, stove, among others) but is significantly higher than those reported for vehicular emissions, especially in environments highly impacted by diesel emissions.

Thus, an increase of OC-to-EC ratio may be assigned to several factors: (i) enrichment of OC from biomass burning sources, (ii) additional contribution of secondary OC, for example from biogenic SOA; and (iii) a condensation of semi-volatile organic compounds favored at low temperature and high PM concentrations.

The seasonal variation of the OC-to-EC ratios in the studied sites is presented in Fig. 3 (see appendix C in supplementary data for more details on OC and EC seasonal concentrations). The annual mean OC-to-EC ratios ranged from 2.1 (in GEN) to 5.2 (in THE) and fall within the range reported for UB sites throughout Europe (Querol et al., 2013). Except for BCN, the lowest values of the ratio are observed during summer: 2.5 for MRS, 1.9 for GEN and 3.7 for THE (Fig. 3). In BCN, the average OC-to-EC summer's ratio was 2.7; just slightly above the minimum observed during fall (2.1). In a first approach, these values can be regarded as the combination of the primary vehicular emissions and the maximum contribution of secondary OC in the different cities. The highest value of the OC-to-EC ratio found in THE during summer compared to the other cities can possibly be explained by the higher proportion of gasoline powered vehicles in Greece, or to a higher contribution of biogenic and anthropogenic SOA. It should be noted that the higher OC-to-EC ratio observed in THE compared to the other cities can also be partly explained by the use of the NIOSH method (see Section 2.2). THE, MRS and, in a lesser extent, GEN were characterized by significantly higher OC-to-EC ratio during fall with 7.2, 3.6, and 2 respectively, and in winter with 5.4, 4.5 and 2.5 respectively. As the vehicular emissions can be assumed as constant all along the year, the high values of OC-to-EC observed in these cities in the seasons during which atmospheric oxidation processes are less intense than during summer can be explained by the additional contributions of OC rich sources such as biomass burning.

Previous studies reported that soluble potassium may be a useful chemical marker of biomass burning aerosol due to its release during combustion processes (Andreae, 1983), whereas the combustion of fossil fuel seems to produce very little potassium (Ram and Sarin, 2010). Seasonal concentrations of the non-seasalt potassium (nss-K^+) observed in the five cities are presented in Fig. 3. Furthermore, Pearson correlation coefficients between potassium and OC (TC for VEN) abundances were also determined. A strong correlation between nss-K^+ and OC is observed in MRS during winter and fall ($r = 0.94$–0.96, $p < 0.05$), and in THE ($r = 0.8$, $p < 0.05$) during spring. Likewise, significant and strong correlation between nss-K^+ and TC is observed in VEN during winter, spring and fall ($r = 0.7$-0.9, $p < 0.05$). Finally, BCN showed also a strong relationship between total potassium and OC during winter ($r = 0.95$, $p < 0.05$). These high correlations associated with high levels of potassium indicate that biomass combustion is an important source of OC and contributes to the high ambient OC-to-EC ratios. In Barcelona, previous studies based in AMS and levoglucosan measurements have demonstrated that the contribution of this source is around 20-30% of OC (Minguillón et al., 2011; Reche et al., 2012). Moreover, nss-K^+ concentration was significantly higher in VEN compared to the other cities, especially during fall and winter period, where the seasonal mean concentration reached 640 and 850 ng m^{-3}, respectively (Fig. 3). These higher concentration observed in VEN are related to very stable conditions, associated with persistent thermal inversion at the ground, that are frequent during the cold season not only in the city but also in all the Po Plain (the North Italy basin of the Po river). These meteorological conditions favor the photochemical formation of aerosols and contribute to high levels of ammonium nitrate (see Section 3.3.2) and organic matter, and consequently make the biomass burning pollution more obvious in VEN with respect to the other cities.

3.3.2. Inorganic aerosol (nss-SO_4^{2-}, NO_3^- and NH_4^+)

On an annual basis, the secondary inorganic fraction accounted for 4.8 µg m^{-3} (26% of $PM_{2.5}$) in BCN; 5.4 µg m^{-3} (27% of $PM_{2.5}$) in MRS; 5.5 µg m^{-3} (39% of $PM_{2.5}$) in GEN; 11 µg m^{-3} (37% of $PM_{2.5}$) in VEN; and 8.4 µg m^{-3} (23% of

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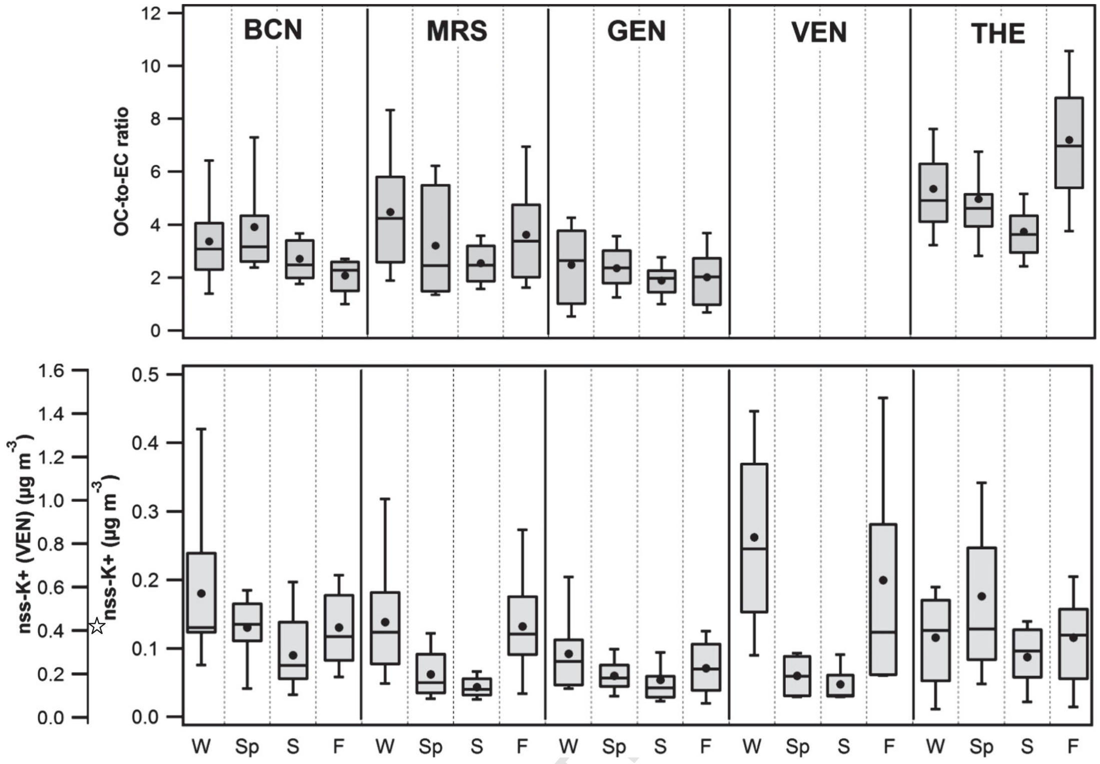

Fig. 3. Seasonal variability of the OC-to-EC ratios (upper panel) and nss-K^+ concentrations (lower panel) at the five sites. The boxes and whiskers denote the 10th, 25th, medians, 75th and 90th percentile; the dots denote the mean value. For BCN nss-K^+ was not measured and was replaced by the total K concentration.

$PM_{2.5}$) in THE. The nss-SO_4^{2-} was the prevailing anion, contributing between 10% (in THE) to 26% (in GEN) of the $PM_{2.5}$ mass, except in VEN where NO_3^- was the dominant anion (5.4 µg m^{-3} contributing to 18% of $PM_{2.5}$ mass). Compared with other studies, the relative contribution of the secondary inorganic aerosol to the $PM_{2.5}$ mass were in agreement with those observed at different urban sites throughout Europe (Putaud et al., 2010; Querol et al., 2004b). Although, it is worthy to note that the annual mean concentration of sulfate in GEN was higher than that measured in BCN, MRS, VEN, and comparable to THE. These results were consistent with the high levels of SO_2 measured in GEN (10.5 µg m^{-3}) and discussed previously (see Fig. 1 and Section 3.1). Therefore, compared to the other cities, the relative contribution of the nss-SO_4^{2-} to the $PM_{2.5}$ mass in GEN was accounting for 26% on annual average with much higher contribution mainly during the summer period.

The analysis of the seasonal variation (Fig. 4) of the secondary inorganic fraction revealed that the nss-SO_4^{2-} relative contribution to the $PM_{2.5}$ mass was, as expected, higher during summer at all sites (except for MRS in spring), and is the major component of $PM_{2.5}$ in GEN (4.2 µg m^{-3} – 32%). This maximum summer sulfate might be due to: (a) an enhanced photochemical activity, which increase the oxidation of SO_2 and its conversion rate to sulfate (Khoder, 2002; Mihalopoulos et al., 2007); (b) an increased shipping emissions at these coastal cities due to the large number of tourist ships at the harbors during the holiday period (Vecchi et al., 2008); and (c) the stagnation of air masses over the Mediterranean Basin (Rodríguez et al., 2004).

Conversely, nitrate aerosols are more sensitive to temperature and the shift in equilibrium from gas-phase ammonia and nitric acid to particulate phase ammonium nitrate is favored at lower temperatures. At all sites, the relative contribution of nitrate to the total $PM_{2.5}$ mass peaked mainly during the winter period with the highest contribution observed in VEN (11.3 µg m^{-3}, 21%). The larger availability of NO_x gaseous precursor (e.g. NO_x in VEN, 75 µg m^{-3}; Fig. 1) released from combustion processes (Khare and Baruah, 2010; Prodi et al., 2009) during the cold season can also play a role.

3.3.3. Sea-salt

Sea-salt contribution to aerosol mass is highly dependent on the distance of the sampling site to the sea. It is a major contributor to the coarse fraction (Pérez et al., 2008). In our study, it contributed marginally to the $PM_{2.5}$ mass. Annual relative contribution was relatively higher in BCN (4.7%) and in GEN (3.5%) and smaller at the remaining sites (e.g. 2.4% in VEN, 2.3% in MRS and 1.9% in THE).

3.3.4. Mineral dust

Despite the fact that mineral matter is mainly in the coarse mode (Pérez et al., 2008), $PM_{2.5}$ is also influenced by this PM component, especially in THE and MRS. On an annual basis, the relative contribution of dust matter to $PM_{2.5}$ mass ranged from 5 to 32% in the following order: THE (32%) > MRS (19%) > VEN

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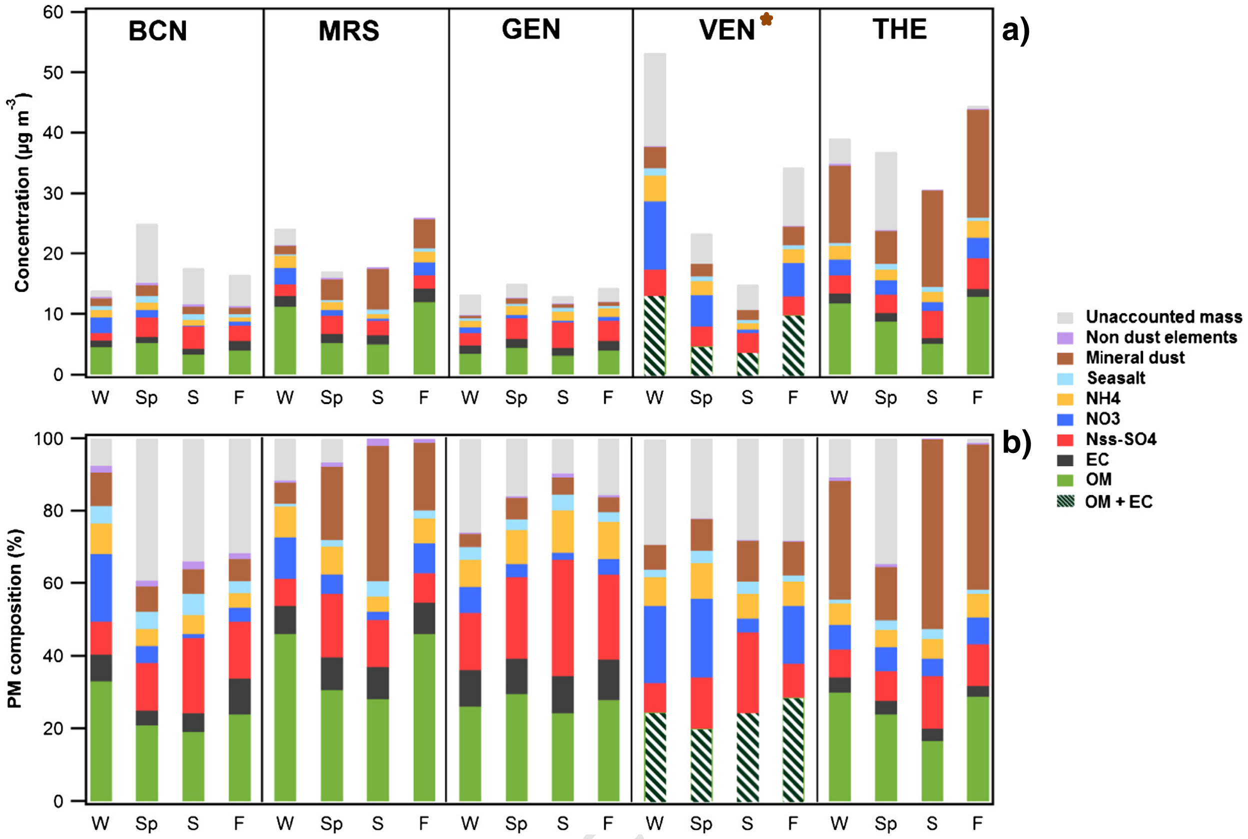

Fig. 4. Mean mass concentrations (in μg m^{-3}) (a), and relative contributions (in %) (b) of $PM_{2.5}$ chemical components at the five sampling sites.

(8%) > BCN (7%) > GEN (5%), and was the predominant constituent of $PM_{2.5}$ in THE (12 μg m^{-3}).

Moreover, mineral dust concentration exhibited strong seasonal variability in THE and MRS, whereas a slight variation is observed at the remaining sites (Fig. 4). A relatively clear maximum contribution of the dust matter is observed in THE during summer and fall (52% and 40% of the $PM_{2.5}$ mass, respectively), and in MRS largely during summer (37% of the $PM_{2.5}$ mass). Crustal PM contributions might derive from both external (e.g. African dust outbreaks) and local sources (e.g. road dust resuspension, construction activities) (Rodríguez et al., 2004). However, during the sampling period, the occurrence of African dust outbreaks over THE should not be enough to explain the extremely high concentrations (Pey et al., 2013b). This means that most of mineral matter is mainly related to nearby sources, e.g. metro construction activities. Likewise, the abundance of dust particles in MRS city was mostly due to mineral matter released from the large renovation and development activities implemented during the long monitoring campaign, to develop the city elected the "European Capital of Culture for 2013". The comparison of MRS data with a previous study (El Haddad et al., 2011a) carried out at the same sampling site in summer, shows that the concentrations of mineral dust in our study are between one and two order of magnitude higher than those reported in the abovementioned study (e.g. Ca 1843 ng m^{-3} vs. 62 ng m^{-3} and Fe 331 ng m^{-3} vs. 53 ng m^{-3}). These observations highlight the singularity of the study year and the impact of construction activities on PM levels over the whole city.

3.4. Speciation of $PM_{2.5}$ during exceedances of the WHO daily AQ guideline

As mentioned previously, frequent exceedances of the WHO daily AQ guideline of 25 μg m^{-3} are observed, especially in THE and VEN. However, a thorough knowledge of $PM_{2.5}$ chemical composition during exceedance days is relevant. This investigation could highlight the components (or sources) that might play a key role in the occurrence of PM air pollution episodes. In Fig. 5, we reported the relative mean composition (in %) of $PM_{2.5}$ during the pollution episodes ($PM_{2.5} > 25$ μg m^{-3}) compared to the non-exceedance periods ($PM_{2.5} < 25$ μg m^{-3}). As shown in Fig. 5, during the pollution episodes, MRS, VEN and THE showed a relatively higher contribution of secondary inorganic ions. The secondary inorganic fraction accounted for 30% in MRS, 38% in VEN, and 22% in THE to the $PM_{2.5}$ during the pollution episodes, while it contributed with 23% in MRS, 32% in VEN, and 19% in THE to the $PM_{2.5}$ during the non-exceedance periods, on a yearly average. However, the increased concentration of secondary inorganic ions during pollution episodes is mainly associated with an enhancement of NO_3^- concentrations. This phenomenon has been described in detail for the Barcelona region (Pey et al., 2010), with ammonium nitrate pollution episodes occurring from November to March under stagnant

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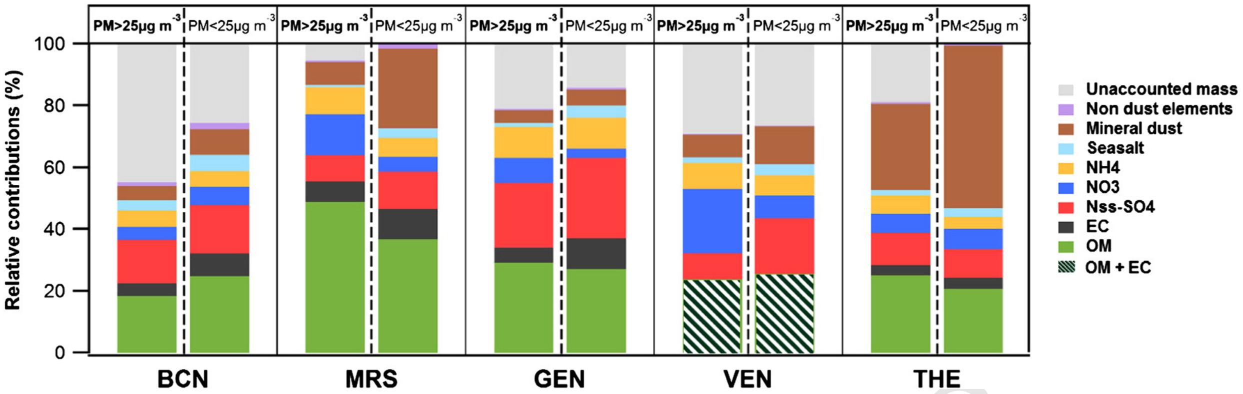

Fig. 5. $PM_{2.5}$ relative mean composition (in %) at each site, both in the case of pollution episodes ($PM_{2.5} > 25$ µg m^{-3}) and for the non-exceedances periods ($PM_{2.5} < 25$ µg m^{-3}).

conditions affecting not only the urban centers but also mountainous areas located in the vicinity.

Moreover, OM represents also a significant fraction of $PM_{2.5}$ during the exceedance days, especially in MRS (49%), THE (25%) and GEN (29%). The highest relative contribution of OM observed in MRS, emphasizes once again the specificity of this environment among the cities under study. It should also be noted the greater relative contribution of dust during the non-exceedance periods. This can be due to the higher mineral load occurring during summer, characterized by lower $PM_{2.5}$ concentrations and scarce precipitation (e.g. resuspension of soil and road dust).

In order to go further and to limit the impact of external factors, such as the temperature, the relative enrichment factors (in %) for each component and season have been calculated and reported in Fig. 6. These enrichment factors reflect the change of the relative composition of $PM_{2.5}$ during pollution episodes compared with the average chemical composition of $PM_{2.5}$ during non-exceedance days for each season. From Fig. 6, we observed that (i) nitrate is the most heavily enriched component (up to 182%) with no clear seasonal patterns; (ii) sulfate is the second enriched component and exhibits higher enrichments in MRS during winter (53%) and in THE during winter (55%) and summer (15%); (iii) OM is also significantly enriched in MRS during fall (56%), most probably due to biomass burning influences; (iv) EC is enriched only in MRS during spring (19%); and finally (v) the dust matter is also enriched in THE (19%) during spring. For ammonium, the enrichments reflected its association with sulfate and nitrate. This presentation of results highlights the predominant role of the secondary ions, which appears as the main factor influencing the exceedances of the daily $PM_{2.5}$ WHO air quality guideline. By extension, it shows the influence of photochemical processes on $PM_{2.5}$ pollution episodes even in large cities heavily impacted by fresh primary emissions. These results also point out that most abundant fractions of the $PM_{2.5}$ (i.e., OM in MRS, dust in THE or sulfate in GEN) seem not to play a preponderant role in terms of occurrences of daily guideline exceedances. Thus, a decrease of NO_x emissions appears as an efficient way for reducing the number of $PM_{2.5}$ pollution episodes. Furthermore, significant attention should be paid to the sources of OM and EC, especially in MRS or its surroundings. OM and EC could derive both from biomass burning (e.g. residential wood combustion, green waste burning) and traffic emissions; and or secondary organics from biogenic VOCs in the case of OM.

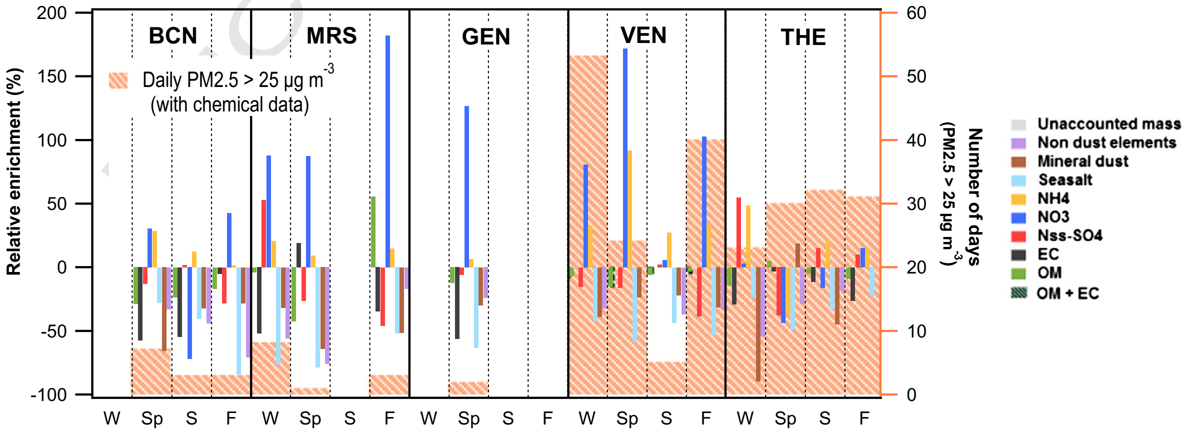

Fig. 6. Seasonal enrichment (in %) of $PM_{2.5}$ relative mean composition (left y-axis) during pollution episodes ($PM_{2.5} > 25$ µg m^{-3}). The number of days whose daily $PM_{2.5}$ concentrations measured is above 25 µg m^{-3} for the collected samples for which we have chemical data is also shown with dashed bars. The relative enrichment factor (in %) is calculated as follows: $\frac{[(\%)i_{(PM2.5>25)} - (\%)i_{(PM2.5<25)}]}{(\%)i_{(PM2.5<25)}}$ x100; *i element*.

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Finally, as observed in Fig. 6, the non-dust trace elements fraction (i.e. the sum of all trace elements measured other than geological) did not contribute directly to the WHO AQG exceedances. However, since this study is performed in Mediterranean cities with important harbor activities, shipping emissions can play an important role in terms of NO_x or SO_2 emissions. Around 15% of global NO_x and 5–8% of global SO_x emissions are attributable to oceangoing ships (Corbett et al., 2007; Eyring et al., 2005). Vanadium and Nickel are widely-used tracers of shipping emissions. According to Pandolfi et al. (2011), V/Ni ratio around 3 is typical for shipping emissions. Thus, in order to define the impact of the ships during the year, a V/Ni ratio lying between 2.5 and 3.5 was considered, and an evaluation of the ambient V/Ni ratios in the five cities was performed (Mazzei et al., 2008). The results revealed that a significant number of samples fall within this range, i.e., MRS 24%, GEN 21%, VEN 19%, BCN 17%, and THE 2%, highlighting the influence of shipping emissions on the local air quality during the measurement period. However, these samples do not coincide with the observed $PM_{2.5}$ pollution episode days except in the case of BCN where five days with $PM_{2.5} > 25$ μg m^{-3} presented a V/Ni ratio characteristic of shipping emissions (2.5–3.5). Consequently, despite the impact of ship emissions on air quality, this study shows that shipping emissions are not the main trigger of PM pollution episodes encountered in the Mediterranean basin. Nevertheless, regarding the relative enrichment of Ni and V, it is worthy to note that Ni is highly enriched in GEN (73%) during spring, in THE (60%) during winter, and in MRS (25%) during spring. Nevertheless, V presented relatively higher enrichment values in GEN (45%) and THE (10%) during spring and in VEN during summer (18%) and winter (9%). These findings suggest additional potential sources for these two elements.

4. Conclusions

The present paper aims to evaluate the state of particulate air pollution in five European Mediterranean cities (Barcelona: BCN; Marseille: MRS; Genoa: GEN; Venice: VEN; and Thessaloniki: THE) over a 1-year period (2011-2012). Our results highlight the complexity of the aerosol phenomenology in the Mediterranean region, in which several atmospheric pollution sources coexist and in which atmospheric dynamics play essential roles. Seasonal and spatial characteristics of $PM_{2.5}$ concentrations as well as similarities/differences in their chemical composition between the above-mentioned cities were investigated, with a special focus on $PM_{2.5}$ mass and composition during pollution episodes ($PM_{2.5} > 25$ μg m^{-3}). PM_{10} and $PM_{2.5}$ levels measured during the year under study were the highest in Thessaloniki and Venice. Both cities showed also frequent daily exceedances of the EU daily limit value for PM_{10} and the WHO AQ guideline for $PM_{2.5}$. ANOVA statistical test performed on $PM_{2.5}$ concentrations shows significant seasonal variability with higher winter concentration in VEN (53 μg m^{-3}) and in MRS (24 μg m^{-3}). This maximum was shifted to fall in THE (45 μg m^{-3}) and to spring in BCN (25 μg m^{-3}). These seasonal differences in $PM_{2.5}$ levels were assigned mainly to the variability of local source strengths in combination with the influence of the prevailing meteorological conditions. $PM_{2.5}$ chemical composition was quite different even for similar levels and showed both intra- and inter-variability across cities. On annual average, OM predominates $PM_{2.5}$ mass with a higher contribution observed in MRS (42%), except in THE, where mineral matter was the predominant constituent (32% of the $PM_{2.5}$ mass), and is mainly linked to the contribution from local sources. Moreover, the evaluation of the seasonal OC-to-EC ratios highlights the contribution of three main sources: vehicular emissions (assumed constant along the year), secondary OC (mainly during summer), and biomass burning. The contribution of biomass combustion is also supported by the strong correlations observed between OC and K, except for Genoa. However, a detailed chemical speciation of organic markers is necessary to validate this observation. During pollution episodes, $PM_{2.5}$ relative mean composition presented a relatively higher contribution of secondary inorganic ions, where NO_3^- was the most heavily enriched component followed by sulfate. This result highlights the influence of photochemical processes on the occurrence of $PM_{2.5}$ pollution episodes and outlines the role of NO_3^- as the main driver of $PM_{2.5}$ daily WHO AQ guideline exceedances.

Conflict of interest

The authors declare that they do not have any actual or potential financial and personal conflict of interests with other people or organizations.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.atmosres.2014.12.001.

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