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# Seasonal variability of PM<sub>2.5</sub> and PM<sub>10</sub> composition and sources in an urban background site in Southern Italy

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## Highlights

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Composition and sources of PM<sub>2.5</sub> and PM<sub>2.5–10</sub> are investigated in South-eastern Italy.

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Secondary organic and inorganic components were 43% of PM<sub>2.5</sub> with opposite seasonal trends.

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Two forms of nitrate were observed: sodium nitrate and ammonium nitrate (only in winter).

- PMF and mass-closure identified two soil sources accounting for 29% of PM<sub>2.5-10</sub>.

- Biomass burning is an important source at the urban background site even during warm seasons.

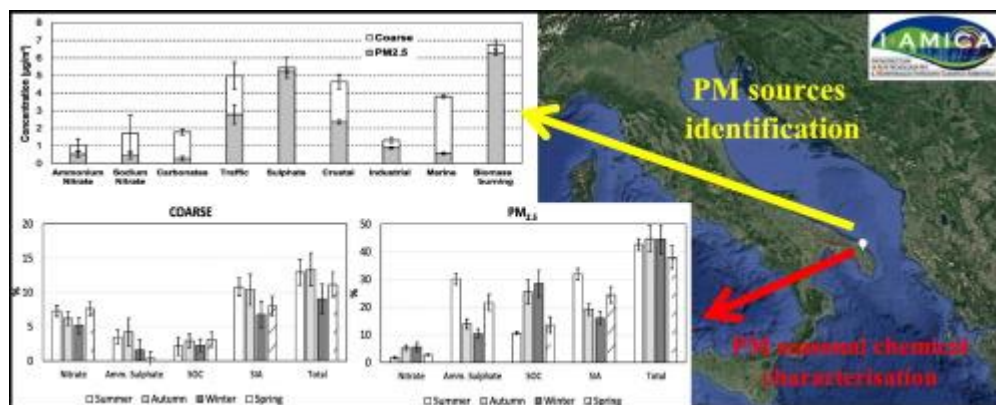
## Abstract

Comparison of fine and coarse fractions in terms of sources and dynamics is scarce in southeast Mediterranean countries; differences are relevant because of the importance of natural sources like sea spray and Saharan dust advection, because most of the monitoring networks are limited to PM<sub>10</sub>. In this work, the main seasonal variabilities of sources and processes involving fine and coarse PM (particulate matter) were studied at the Environmental-Climat Observatory of Lecce (Southern Italy).

Simultaneous PM<sub>2.5</sub> and PM<sub>10</sub> samples were collected between July 2013 and July 2014 and chemically analysed to determine concentrations of several species: OC (organic carbon) and EC (elemental carbon) via thermo-optical analysis, 9 major ions via IC, and 23 metals via ICP-MS. Data was processed through mass closure analysis and Positive Matrix Factorization (PMF) receptor model characterizing seasonal variabilities of nine sources contributions. Organic and inorganic secondary aerosol accounts for 43% of PM<sub>2.5</sub> and 12% of PM<sub>2.5-10</sub> with small seasonal changes. SIA (secondary inorganic aerosol) seasonal pattern is opposite to that of SOC (secondary organic carbon). SOC is larger during the cold period, sulphate (the major contributor to SIA) is larger during summer.

Two forms of nitrate were identified:  $\text{NaNO}_3$ , correlated with chloride depletion and aging of sea-spray, mainly present in  $\text{PM}_{2.5-10}$ ;  $\text{NH}_4\text{NO}_3$  more abundant in  $\text{PM}_{2.5}$ . Biomass burning is a relevant source with larger contribution during autumn and winter because of the influence of domestic heating, however, is not negligible in spring and summer, because of the contributions of fires and agricultural practices. Mass closure analysis and PMF results identify two soil sources: crustal associated to long range transport and carbonates associated to local resuspended dust. Both sources contribute to the coarse fraction and have different dynamics with crustal source contributing mainly in high winds from SE conditions and carbonates during high winds from North direction.

## Graphical abstract



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## Keywords

PM<sub>2.5</sub>PM<sub>10</sub>Source apportionmentSeasonal variabilitiesSecondary aerosolChloride depletion

## 1. Introduction

Particulate matter (PM) is one of the most studied atmospheric pollutant due to its potential effects on local and regional air quality, on visibility, and on global climate (Fuzzi et al., 2015). Moreover, there is a compelling evidence that exposure to PM leads to adverse health effects including respiratory and cardiovascular diseases, allergies, and premature mortality (Pope et al., 2004, Delfino et al., 2005, Dockery and Stone, 2007, Gauderman et al., 2015, Velali et al., 2016). Current studies indicate that PM<sub>2.5</sub> (particles with an aerodynamic diameter smaller than 2.5 µm) was responsible in 2010 of over 3 million premature deaths per year worldwide and 11.5% of these premature deaths are concentrated in Europe (Jerret, 2015, Lelieveld et al., 2015).

Atmospheric PM concentrations in Mediterranean basin are influenced by air masses coming from Europe, Eastern Countries and Africa (Lelieveld et al., 2002). Mediterranean Sea is bordered by 21 Countries accounting for > 400 million inhabitants (in 2011), mostly concentrated near the coasts (Salameh et al., 2015). Being delimited at North by highly industrialised southern Europe Countries and by Africa in the South, PM concentrations are affected by a number of natural and anthropogenic sources such as road traffic, biomass burning, shipping, Saharan dust advection, and sea spray (Viana et al., 2014, Contini et al., 2014a, Salameh et al., 2015, Amato et al., 2016, Merico et al., 2017). Mediterranean region is also characterised by complex meteorology that favours aging of polluted air masses (Artiñano et al., 2001). This plays an important role in formation of secondary particles and in their successive aging with a high degree of oxidation of the organic aerosol (Hildebrandt et al., 2011).

Recent results of the AIRUSE project (Amato et al., 2016) evidenced that the spatial variability and the sources of PM<sub>2.5</sub> in southern Europe are less known with respect to PM<sub>10</sub> because the fine fraction is not widely measured. As a consequence, there is also limited information on spatial and temporal variability of coarse fraction (PM<sub>2.5-10</sub>), often linked to local and natural sources, being an increasing concern for health (Brunekreef and Forsberg, 2005). Therefore, further research efforts are needed to investigate long-term trends of sources of fine and coarse PM fractions in this area for air quality applications, for management of health risks, and for analysis of PM impact to climate change in Mediterranean basin.

This work analyses the first year (between summer 2013 and summer 2014) of simultaneous measurements of PM<sub>2.5</sub> and PM<sub>10</sub> concentrations and chemical compositions collected at the Environmental-Climat Observatory, recently built in South-Est Italy (in Lecce), regional station of the Global Atmosphere Watch (GAW) network. Chemical composition is studied evaluating the concentrations of nine major water-soluble ions, of 23 metals including elements of crustal and anthropogenic origin, and evaluating the carbon content. Carbonaceous species were determined separating elemental carbon (EC) mainly of primary origin from combustion sources, and organic carbon (OC) having a primary and a secondary component. Chemical composition was used for mass closure analysis and for application of Positive Matrix Factorization (PMF) receptor model to investigate seasonal variabilities of the contributions of the main natural and anthropogenic sources to fine (PM<sub>2.5</sub>) and coarse size fractions. Seasonal variabilities of secondary organic and inorganic aerosol concentrations were investigated, including their correlation with local meteorology, to improve the understanding of the main chemical and physical processes governing the dynamics of PM in this area.

## **2. Experimental**

## 2.1. Measurement station and sampling

PM<sub>10</sub> and PM<sub>2.5</sub> daily samples were collected at the Environmental-Climate Observatory of Lecce (Fig. S1), regional station of the GAW-WMO network (Global Atmosphere Watch, see [Cristofanelli et al., 2016](#)). The Observatory is located in south-eastern Italy (40°20'8"N–18°07'28"E) at 37 m a.s.l. inside the University Campus of Lecce. The station could be characterised as urban background because it is not strongly influenced by traffic or industrial emissions ([Chirizzi et al., 2017](#)). In this site, pollution levels are not significantly influenced by local specific sources rather by the integrated contributions of all sources upwind. The Observatory site is influenced by the activities (included traffic) inside the University Campus, and by the diffused emissions of the town of Lecce and of the other small villages located nearby the Campus. Moreover, the area is sometimes downwind of the largest industrial settlements of the Apulia Region: the area of Taranto (about 80 km in the NW direction) and the area of Brindisi (about 30 km in the NNW direction).

Samples were collected daily for a one-year period between 17/07/2013 and 14/07/2014 using a low-volume (2.3 m<sup>3</sup>/h) dual channel (one for PM<sub>2.5</sub> and one for PM<sub>10</sub>) sequential sampler (SWAM, Fai Instruments) with automatic detection of aerosol concentration using  $\beta$ -ray attenuation. Particulate matter was collected on quartz filters (Whatman Q-grade, diameter 47 mm) pre-fired for 2 h at 700 °C. Mass concentration measurements with this instrument were in very good agreement with standard reference gravimetric method and the typical uncertainty on measured mass concentration was 2% on PM<sub>10</sub> and 3% on PM<sub>2.5</sub> ([Dinoi et al., 2017](#)).

Meteorological conditions, specifically wind velocity and direction, temperature, cumulative rain, and relative humidity were obtained from the meteorological station (Vaisala WXT520) of the Observatory.

## 2.2. Chemical analysis

Roughly, one sample every three days was chemically analysed for a total of 226 simultaneous samples (113 for PM<sub>10</sub> and 113 for PM<sub>2.5</sub>). Each filter was divided into four quarters, three of them used for the chemical analysis and one used for quality control: replication of specific analysis.

One quarter of the filter was used to obtain a punch (1 cm<sup>2</sup>) for the determination of OC and EC concentrations via thermo-optical method (Sunset OC/EC Analyser), following the NIOSH 5040 protocol. To ensure the accuracy of the OC and EC analysis, the analyser was calibrated (multipoint) using as external standard a sucrose solution. Blank filters were also analysed to correct measured values, obtaining for OC an average contamination level of 2.1 µg/cm<sup>2</sup> (standard deviation ± 0.9 µg/cm<sup>2</sup>) and negligible contamination for EC (< 0.1 µg/cm<sup>2</sup>).

The second quarter was used for determination of water soluble ions concentrations via High Performance Ion Chromatography (Dionex DX600 IC system composed of an AS40 Autosampler, a GP50 Gradient Pump, an LC25 Chromatography Enclosure, an ED50 Conductivity detector equipped with a temperature compensated conductivity cell) with a 125 µL injection loop. The extraction was done in two steps (20 min each in ultrasonic bath) in 20 mL of ultrapure water (Milli-Q MΩ 18). Anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>) were separated using a Dionex AS4A-4 mm column coupled with IonPac AG14 guard column and 2.7 mM Na<sub>2</sub>CO<sub>3</sub> and 1.0 mM NaHCO<sub>3</sub> as eluent in isocratic mode. Cations (Ca<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Mg<sup>2+</sup>) were separated using a Dionex (CS12A-4 mm) column coupled with IonPac CG12A guard column and 20 mM MSA as eluent in isocratic mode. The self-regenerating suppressors (Dionex ASRS ULTRA and Dionex CSRS ULTRA II for anions and cations, respectively) were used in the electrochemical suppression mode, operating at 50 mA to convert the

eluent solution to weakly conducting water. The external standard calibration was performed using single anions and cations solutions at 1000 mg/L (Inorganic Ventures). The laboratory control sample (LCS) was prepared adding an analytes standard solution to pre-fired filters (and successively analysed) once every 20 samples. The method detection limits (MDLs) were obtained as three times the standard deviation of the signal of blanks pre-fired filter measurements ( $n = 10$ ), divided by the slope of the calibration curve. The MDLs values ( $\mu\text{g/L}$ ) were as follows: 10.2 ( $\text{Na}^+$ ), 6.1 ( $\text{K}^+$ ), 39.9 ( $\text{NH}_4^+$ ), 6.9 ( $\text{Ca}^{2+}$ ), 2.0 ( $\text{Mg}^{2+}$ ), 4.9 ( $\text{Cl}^-$ ), 8.2 ( $\text{NO}_3^-$ ), 140 ( $\text{SO}_4^{2-}$ ), and 10.2 ( $\text{C}_2\text{O}_4^{2-}$ ). Accuracy and precision tests were performed, for  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , using certified material of fly ash (NIST SRM 1648a) and, for the other ions, on pre-fired quartz filters spiked with  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{C}_2\text{O}_4^{2-}$ . The values of relative standard deviation (RSD%) were  $< 8\%$  while the recovery values were between 88% ( $\text{Ca}^{2+}$ ) and 108% ( $\text{C}_2\text{O}_4^{2-}$ ).

The third quarter of filter was used to determine metals concentrations via ICP-MS (Thermo X Series II). Each sample was microwave digested in closed Teflon vessels using a two steps procedure (Aldabe et al., 2013). In the first step the sample was digested in 3 mL HF + 3 mL  $\text{H}_2\text{O}_2$  + 1 mL HCl + 4 mL  $\text{HNO}_3$  with the following temperature program: from room temperature up to 180 °C in 15 min, dwell time of 15 min, up to 210 °C in 15 min and a final dwell time of 15 min. The samples were then cooled overnight and evaporated to dryness for 20 min at 500 W. In the second step after addition of 10 mL of 5%  $\text{H}_3\text{BO}_3$ , temperature was increased up to 120 °C in 20 min followed by a dwell time of 15 min and 30 min cooling. Finally, samples were diluted to 25 mL in volumetric flask using water (Milli-Q M $\Omega$  18). The ICP-MS was tuned using a TUNE A solution (Thermo) at 10  $\mu\text{g/L}$ . The sample (1 mL) was transferred into 15 mL graduate tube, 200  $\mu\text{L}$  of EPA6020ISS solution at 500  $\mu\text{g/L}$  (Inorganic Ventures) and 8800  $\mu\text{L}$  of 2%  $\text{HNO}_3$  solution were added, and was analysed



following US EPA 6020A guidelines. The external calibration was performed for the following elements: Al, As, Ba, Cd, Ce, Co, Cu, Dy, Fe, La, Li, Mn, Nb, Nd, Pb, Rb, Sb, Se, Sr, Th, Ti, V, Zn using EPA6020CAL and single analyte standard solutions (Inorganic Ventures). Quality control checks were performed monitoring the intensities of all internal standards for every sample analysis and analysing the laboratory control sample (LCS), in each sample batch, at a frequency of one LCS every 20 samples. The LCS were prepared by pre-fired quartz filters spiked with analytes of interest before microwave procedure. The MDLs, calculated with the same approach used for anions and cations, were between 0.89 µg/L (Al) and 0.001 µg/L (La). Metal recoveries, calculated using certified material of fly ash (NIST SRM 1648a), ranged from 85% (Pb) to 112% (La) with RSD% < 15%.

Field blanks (20 for PM<sub>2.5</sub> and 20 for PM<sub>10</sub>) were analysed following the same procedure of the exposed samples. Concentrations of the different species were obtained after subtraction of the average level present in the blank samples. The concentration for a specific species and sample was quantified if it was larger than the standard deviation  $\sigma_B$  of the blank filters; otherwise, a threshold value equal to  $\sigma_B/2$  was considered. In cases in which the concentration was below the MDL, or not detectable above the average variability of the field blanks, a concentration value equal to the maximum between the MDL/2 and  $\sigma_B/2$  was assumed. The uncertainty for concentrations < MDL or not distinguishable from blanks were assumed to be 100%, whereas the uncertainty for quantified concentration,  $C_{ij}$ , of the sample  $i$  relative to the species  $j$ , was calculated as in [Cesari et al. \(2014\)](#), using the Eq. (1):

$$\Delta C_{ij} = \sigma_{Bj}/2 + h_j C_{ij}$$

The values of  $h_j$  were calculated taking into account uncertainties associated to chemical analysis and the obtained values were: 2.5% for Na<sup>+</sup>; 6% for NH<sub>4</sub><sup>+</sup>; 2.8% for K<sup>+</sup> and Ca<sup>2+</sup>; 2.5% for Mg<sup>2+</sup>; 4.5% for Cl<sup>-</sup>; 3.1% for NO<sub>3</sub><sup>-</sup>; 3.8% for SO<sub>4</sub><sup>2-</sup>; 3% for C<sub>2</sub>O<sub>4</sub><sup>2-</sup>; 5% for OC and EC; 9% for Al, Ti, Fe,

and Sr; 5% for Sb, La, Pb, and Ce; 6% for Mn, and Rb; 7% for Dy, Cu, Zn, Nb, and Th; 4% for Ba; 8% for Nd; 13% for V and Cd; 15% for Co; 16% for Li; 22% for As; 33% for Se.

### **2.3. Source apportionment using Positive Matrix Factorization**

The characterisation of particle sources was done using the PMF approach (Paatero and Tapper, 1994). The goal of PMF is to identify the number of factors/sources, their chemical profiles, and the amount of mass, associated with each factor/source, that contributed to measured PM concentrations. In this work, the EPA PMF5 code, based on the application of the Multilinear Engine (ME-2) was used. A single input data set was obtained pooling together fine (PM<sub>2.5</sub>) and coarse (PM<sub>2.5-10</sub>) chemical composition. This approach has been used in other PMF applications pooling together samples belonging to particles of different sizes (Amato et al., 2009, Contini et al., 2014b) or particles collected at different sites (Pandolfi et al., 2011, Contini et al., 2012, Cesari et al., 2016a, Cesari et al., 2016b). The approach has proven to increase the statistical significance of the analysis, although it assumes that the chemical profiles of the sources do not vary for the two size fractions. The input variables were classified using the Signal-to-Noise (S/N) criteria (Paatero and Hopke, 2003), however, the percentage of data above the detection limit was also used as complementary criterion (Amato et al., 2016, Contini et al., 2016). The species Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, OC, EC, Ti, V, Fe, Cu, Rb, Nb, Cd, Sb, and Pb were classified as “strong variables” and used as they are in PMF5; the species C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, Al, Mn, Zn, As, Se, Sr, Ba, La, Ce, Nd, Dy, and Th as “weak variables” and a tripled uncertainty was used for them in PMF5. Li and Co were classified as “bad variable” and eliminated during application of PMF5.

The best solution for the base run was obtained using eight factors. The determination of the optimal number of factors with a reasonable physical meaning was achieved analysing the parameters IM (the maximum individual column mean), and IS (the maximum individual column standard deviation), obtained from the scaled residual matrix, together with Q-values (goodness of fit parameter). In particular, for Q-values, the solution to the system was the point where the slope of the curve showed a marked change. When the number of factors increased to a critical value, IM and IS parameters experienced a marked drop. The eight factors found have a reasonable physical interpretation and the analysis of the scaled residual are symmetrically distributed for almost all variables, meaning that the model is able to reasonably fit each chemical species.

Successively, a constrained run was performed. The constraints used were: set to zero SO<sub>4</sub> in nitrate profile to improve the separation between secondary inorganic components; NO<sub>3</sub><sup>-</sup> pull down maximally and Na<sup>+</sup> pull up maximally in marine profile to improve the separation between fresh and aged sea spray as shown in [Cesari et al. \(2016a\)](#); K<sup>+</sup> pull up maximally in biomass burning profile that gave good results in source apportionment in central Italy ([Contini et al., 2016](#)). The maximum change in Q allowed for each constraint was 5% and the final dQ with respect to base run was 6.4% that is comparable with the dQ used in different PMF applications ([Amato et al., 2016](#), [Cesari et al., 2016a](#), [Contini et al., 2016](#)).

PMF<sub>5</sub> results reconstruct reasonably well measured concentrations for both size fractions. The fractions unexplained by the model (i.e. the average difference between measured and reconstructed concentrations) is 3% for PM<sub>10</sub> and - 3.5% for PM<sub>2.5</sub>. The linear fit of the correlation between PM<sub>10</sub> reconstructed and measured concentrations had a slope of 0.93 (± 0.05) and an intercept of 1.8 (± 1.4) µg/m<sup>3</sup>. The same analysis for PM<sub>2.5</sub> gave a slope of 1.03 (± 0.03) and an intercept of 0.1 (± 0.7) µg/m<sup>3</sup>.

The uncertainties on PMF<sub>5</sub> estimated factor profiles and contributions were evaluated using the bootstrap method (Paatero et al., 2014). The bootstrap of the “constrained solution” (applied with 100 runs with random seed, block size suggested 23, and R = 0.6) gave a good mapping of the PMF<sub>5</sub> solution with unmapped cases limited to 1% (for carbonates and nitrate) and to 2% for crustal with the other five profiles completely mapped. The swap between the profiles was limited to 10% for all profiles with the exclusion of carbonates.

The analysis of G-space plot performed for both the base and the constrained solutions revealed that no edges are evident suggesting that the factors found are linearly independent.

### **3. Discussion of measured concentrations**

#### **3.1. Seasonal variabilities of the different chemical species**

The yearly average PM<sub>2.5</sub> concentration was 18.7 ( $\pm$  11.3 standard deviation)  $\mu\text{g}/\text{m}^3$ ; the yearly average concentration of PM<sub>10</sub> was 29.5 ( $\pm$  19.2 standard deviation)  $\mu\text{g}/\text{m}^3$ .

Average ( $\pm$  standard deviations) of measured concentrations are reported in Table S1, separating the warm (spring and summer) from the cold (autumn and winter) seasons. The statistical test of Wilcoxon-Mann-Whitney has been used to individuate the species that had statistically significant (at  $p < 0.05$  probability level) different median concentrations comparing the cold seasons (with an average temperature 13.8 °C) with the warm seasons (average temperature 21.7 °C). It clearly appears that chemical species in PM<sub>10</sub> and PM<sub>2.5</sub> could be divided into three groups. The first group includes the species EC, OC, K<sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Sb, and Pb that had seasonal variabilities with median concentrations

larger during the cold seasons in both size fractions and species that have median concentrations larger during the cold season only in PM<sub>2.5</sub> (Ni, As, Rb, and Ba). These species are likely associated to combustions sources like traffic, EC, OC, Sb, and Pb (Viana et al., 2006, Pakbin et al., 2011, Pulong et al., 2017) and biomass burning, EC, OC, and K<sup>+</sup> (Almeida et al., 2006, Cesari et al., 2016b), to sea spray (Cl<sup>-</sup>) (Jain et al., 2017), and to secondary nitrate (NO<sub>3</sub><sup>-</sup>). The second group includes the species that presented lower median concentrations during the cold seasons in both size fractions (NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>), only in PM<sub>2.5</sub> (Ti and V) or only in PM<sub>10</sub> (Cr, La, and Ce). These species are associated to secondary sulphate, to crustal/road dust material (Cr, La, Ce, and Ti) (Amato et al., 2014, Landis et al., 2017) and to ship emissions (V) (Sippula et al., 2009). The third group includes species that do not have statistically significant different median concentrations in the two periods: Na, Mg, Ca, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, Li, Al, Mn, Fe, Co, Cu, Zn, Se, Sr, Nb, Cd, Nd, Dy, Th.

Concentrations of measured species represent, on average, 56% ( $\pm$  9% standard deviation) of PM<sub>10</sub> and 61% ( $\pm$  10%) of PM<sub>2.5</sub>. In PM<sub>10</sub>, the average distribution was 2.7% ( $\pm$  2.2%) EC; 19.3% ( $\pm$  16.8%) OC; 18.2% ( $\pm$  11.2%) sum of SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> (species associated with secondary inorganic aerosol, SIA); 11.8% ( $\pm$  9.8%) sum of the other water soluble ions; 2.1% ( $\pm$  2.3%) metals. In PM<sub>2.5</sub>, the average distribution was 3.1% ( $\pm$  2.2%) EC; 26.9% ( $\pm$  25.8%) OC; 22.4% ( $\pm$  16.0%) sum of SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, and NO<sub>3</sub><sup>-</sup>; 6.1% ( $\pm$  3.7%) sum of the other water soluble ions; 1.9% ( $\pm$  1.5%) metals.

### **3.2. Enrichment factors of PM<sub>2.5</sub> and PM<sub>2.5-10</sub>**

The crustal enrichment factors (EFs) furnish information to identify the elements that have mainly a crustal origin (L. Zhang et al., 2008). The EF compares the ratios of the atmospheric concentrations of various elements with the corresponding ratios in geological material (Watson et al., 2002).

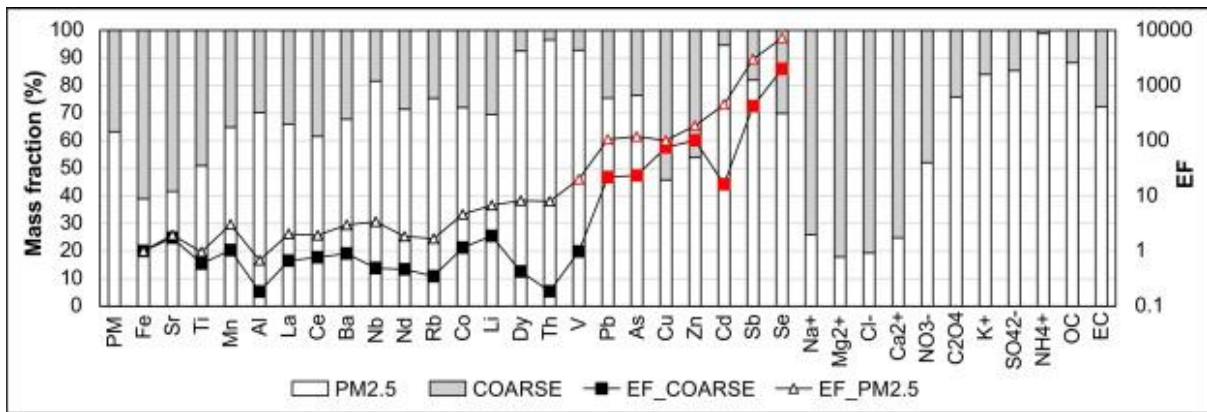
This approach is often used together with source apportionment based on receptor models (Contini et al., 2012, Tositti et al., 2014, Amato et al., 2016, Ledoux et al., 2017) to support assumptions for receptor species and sources for which little information is available (Belis et al., 2013).

The element chosen for reference is Fe to allow comparison with a previous work in this area (Contini et al., 2010) and the upper-crust composition in Wedepohl (1995) was used as geological reference. Enrichment factors calculations were also performed using Al as reference element, leading to the same conclusions regarding the elements having mainly crustal or anthropogenic origin. The EFs were analysed following the two-threshold method defined in Cesari et al. (2012) in which  $EF < 10$  indicates an element with relevant crustal contribution;  $EF > 20$  indicates a likely anthropogenic origin;  $10 < EF < 20$  indicates a mixed origin with important contribution from both natural and anthropogenic sources.

Results are reported in Fig. 1 for both the fine and the coarse fraction, also including the relative abundances of the different chemical species in each fraction. The species Fe, Sr, and Ti, generally of crustal origin present a low EF and are mainly (> 50%) contained in the coarse fraction (PM<sub>2.5-10</sub>). For these elements, the EFs are similar in the fine and coarse fraction; for all other elements the EFs of the coarse fraction is lower than those of the fine fraction. The elements Mn, Al, La, Ce, Ba, Nb, Nd, Rb, Co, Li, Dy and Ti have low EFs being mainly of crustal origin in both size fractions.

Lanthanides occur in the order of abundance  $Ce > La > Nd$  in both size fractions as it happens in natural crustal dust (Hsu et al., 2016). There is a strong correlation (Spearman coefficient 0.75,  $p < 0.05$ ) between Ce, La, and Nd (in both size fractions PM<sub>2.5</sub> and PM<sub>10</sub>). The average ratio Ce/La is 2.3 ( $\pm 0.2$ ), for both size fractions, comparable with the typical ratio (about 2) observed in crustal dust (Amato et al., 2016) confirming the mineral crustal origin of these species. V is essentially crustal in the coarse fraction

but has a relevant anthropogenic contribution in PM<sub>2.5</sub> (EF > 10). The anthropogenic influence on V could originate by heavy oil burning, including shipping, that was relevant in the area near the coast, especially in PM<sub>2.5</sub> (Viana et al., 2009, Gregoris et al., 2016, Merico et al., 2017). The elements Pb, As, Cu, Zn, Cd, Sb, and Se are enriched and likely mainly of anthropogenic origin in both size fractions. The ratio La/V in crustal particles is variable between 0.25 and 0.5 (Kamber et al., 2004). The La/V ratios observed are 0.12 (± 0.02) in both size fractions confirming a possible influence of industrial emissions of V due to heavy oil combustion (Kamber et al., 2004, Hsu et al., 2016).



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Fig. 1

### 3.3. Secondary organic and inorganic aerosol

Regarding carbonaceous species, while soot has a primary origin, OC can be both primarily emitted but also formed in the atmosphere through condensation to the aerosol phase of low vapour pressure compounds emitted as primary pollutants or formed in the atmosphere (Robinson et

al., 2007, Gentner et al., 2012). Because of this, the ratio OC/EC in aerosol fractions differs widely, both in space and seasonally, and is a useful diagnostic ratio that could give information regarding the typology of the sampling sites and emission sources, and also regarding the processes happening in atmosphere which can lead to the formation of secondary organic compounds. In this study, the average OC/EC ratio was 7.8 ( $\pm$  3.9) in PM<sub>10</sub> and 8.8 ( $\pm$  4.9) in PM<sub>2.5</sub>, in reasonable agreement with typical ratios observed at other sites of the same typology in Italy (Sandrini et al., 2014) and in Europe (Escudero et al., 2015). However, OC/EC has a seasonal variability with a minimum value in summer of 7.7 ( $\pm$  0.5) and a maximum of 11.9 ( $\pm$  1.4) in winter in PM<sub>2.5</sub>. The OC/EC ratio depends on both the proximity of the emissions and the relative weight of road traffic and biomass burning. The OC/EC ratio of road traffic emissions varies between 1.4 and 5 for gasoline catalyst vehicles and from 0.3 to 1 for diesel vehicles (Salameh et al., 2015, Amato et al., 2016). Larger values (between 5 and 12) of this ratio are generally found for biomass burning emissions (Szidat et al., 2006). The values observed at this site are larger than those associated to fossil fuel combustion and they are compatible with an urban background site located at distance from the road traffic hotspots and influenced by biomass burning especially in the cold period.

Andreae and Merlet (2001) reported values of nss-K<sup>+</sup>/EC between 0.2 and 1.1 as typical for biomass burning and nss-K<sup>+</sup>/EC approaching zero for fossil fuel emissions where nss-K<sup>+</sup> = K<sup>+</sup> - 0.129Na<sup>+</sup> indicates the non-sea-salt water soluble potassium. Measured nss-K<sup>+</sup>/EC ratios in this study are significantly larger than zero: 0.14 ( $\pm$  0.05) during the warm seasons and 0.29 ( $\pm$  0.05) during the cold seasons, suggesting a contribution of biomass burning to EC especially during the cold seasons.

The correlation of OC with K<sup>+</sup> (Spearman coefficient 0.79 ( $p$  < 0.05) in PM<sub>2.5</sub> and 0.75 ( $p$  < 0.05) in PM<sub>10</sub>) is comparable with that between OC



and EC (Spearman coefficient 0.79 ( $p < 0.05$ ) in  $PM_{2.5}$  and 0.82 ( $p < 0.05$ ) in  $PM_{10}$ ). EC is a tracer of road traffic emissions (Amato et al., 2016) while  $K_+$  is a tracer of biomass burning emissions (Almeida et al., 2006). The correlations found suggest that both of these sources contribute to measured concentrations.

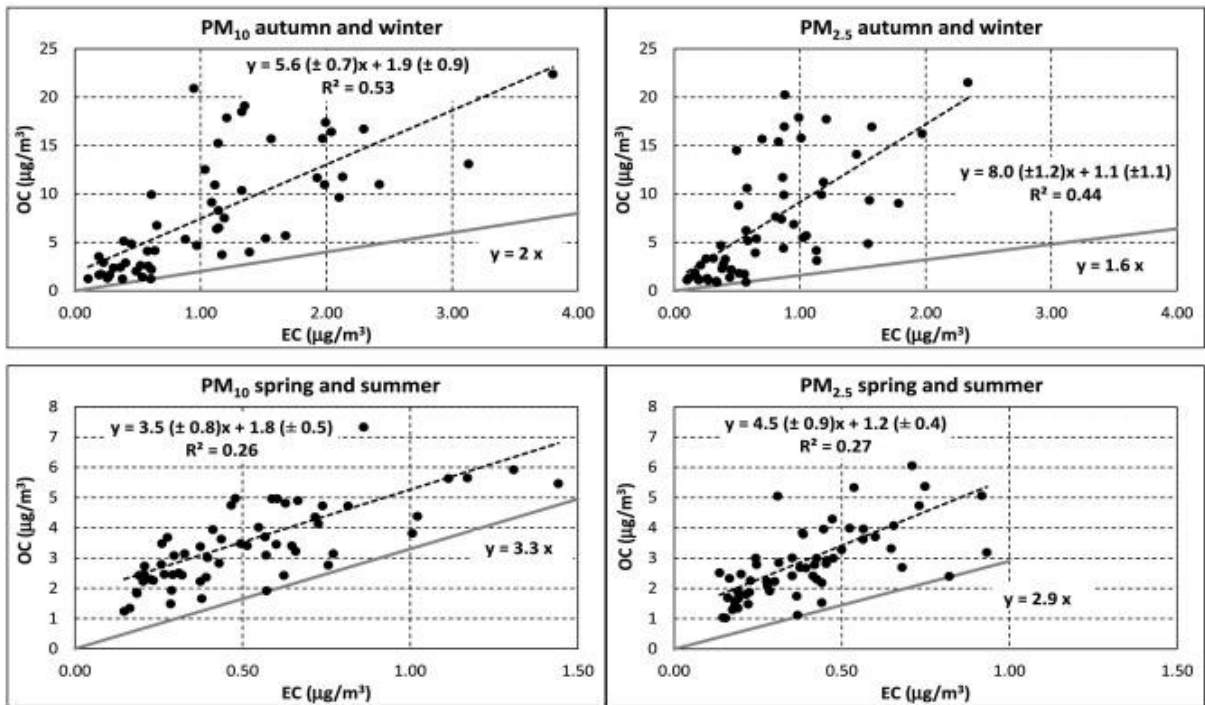
Organic matter (OM) could be evaluated as  $OM = 1.6OC$  where the factor 1.6 accounts for the non-C atoms in organic matter mass concentration (Sandrini et al., 2014). OM accounted for 31% of  $PM_{10}$  and 43% of  $PM_{2.5}$ . The OC/EC minimum ratio method was used to estimate the secondary organic carbon SOC concentrations (Pio et al., 2011) applying the equation:

$$SOC = OC - OCEC_{min}EC$$

The

$OCEC_{min}$

ratios were determined separately for the warm and the cold periods looking at the minimum slopes (Fig. 2). The ratios for  $PM_{2.5}$  were 1.6 (cold season) and 2.9 (warm season). The ratios for  $PM_{10}$  were 2.0 (cold season) and 3.3 (warm season). The differences observed between the warm and the cold seasons were likely related to the different influence of biomass burning compared to road traffic during the cold and warm seasons. This is consistent with results obtained by other studies (Shubhankar and Ambade, 2016, Blanchard et al., 2016, Zeng and Wang, 2011). SOC was mainly present in the  $PM_{2.5}$  fraction, representing on average, 76% of total OC in  $PM_{2.5}$  and 66% of total OC in  $PM_{10}$ . The relative share of primary (POC = OC-SOC) and secondary organic carbon in  $PM_{2.5}$  has a clear seasonal variability (Fig. 3). Autumn and winter seasons have a SOC/OC ratio in  $PM_{2.5}$  between 0.80 ( $\pm 0.04$ ) and 0.86 ( $\pm 0.02$ ) larger than the values observed during spring and summer (around  $0.60 \pm 0.04$ ).



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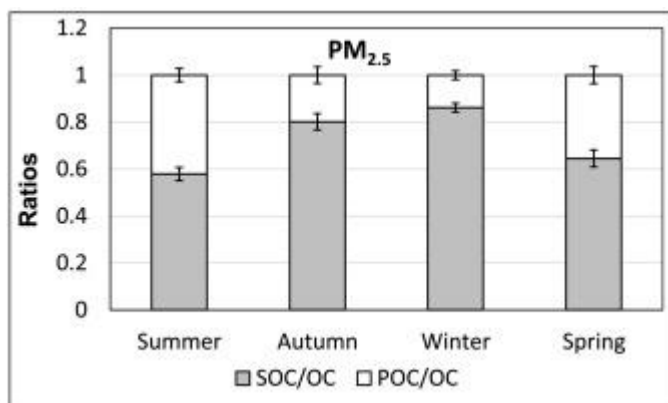


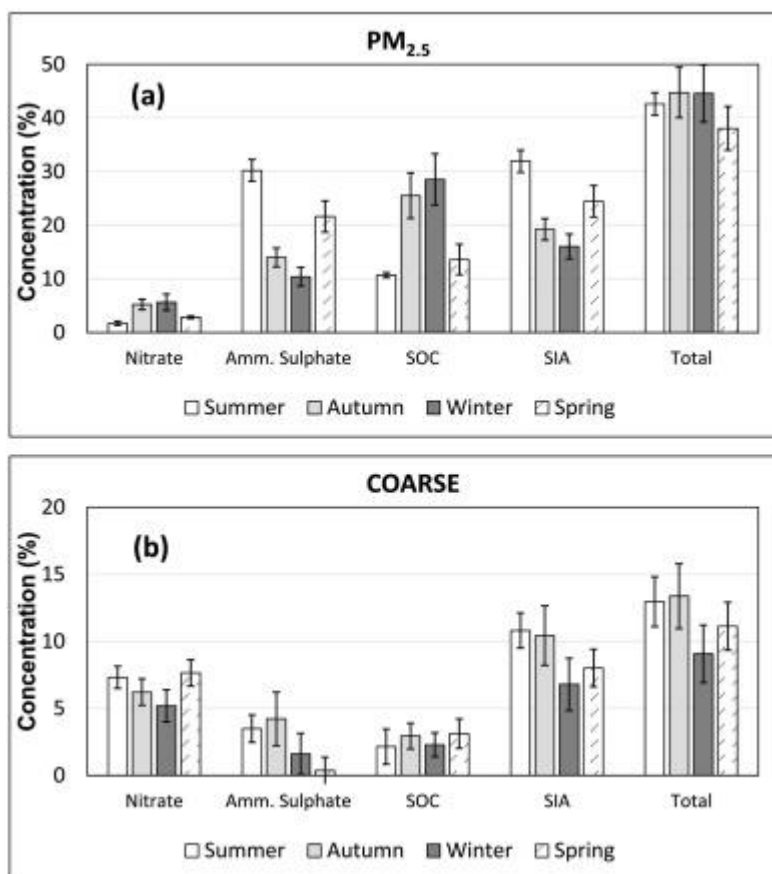
Fig. 2

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Fig. 3

The non-sea-salt sulphate was evaluated as  $nss-SO_{42-} = SO_{42-} - 0.25Na+$ , it represented 91.9% of total sulphate in  $PM_{10}$  and 97.6% in  $PM_{2.5}$ . There is a strong correlation (Spearman coefficient 0.88 ( $p < 0.05$ ) in  $PM_{2.5}$  and 0.74 ( $p < 0.05$ ) in  $PM_{10}$ ) between  $SO_{42-}$  and  $NH_{4+}$  indicating that, on average, secondary sulphate is present as a mixture of ammonium sulphate and bisulphate. Its concentration ( $nss-SO_{42-} + NH_{4+}$ ) is, on average,  $3.4 \mu g/m^3$  in  $PM_{2.5}$  and  $3.7 \mu g/m^3$  in  $PM_{10}$ . The ratio  $nss-SO_{42-}/NH_{4+}$  in  $PM_{2.5}$  is 2.9 near the stoichiometric ratio (2.66) expected for  $(NH_4)_2SO_4$  indicating that the dominant form of secondary sulphate is, on average, ammonium sulphate.

In [Fig. 4](#) the seasonal variability of secondary inorganic species (SIA indicates the sum of nitrate and ammonium sulphate) and SOC in fine and coarse fractions are reported. Results shows that nitrate contribution is larger on coarse fraction compared to  $PM_{2.5}$ , instead ammonium sulphate and SOC contribute mainly to  $PM_{2.5}$ . Looking at  $PM_{2.5}$  fraction, there is a decrease of nitrate contribution during the warm seasons (spring and summer) because of its thermal instability ([Querol et al., 2008](#), [Pey et al., 2009](#)) and likely for the lower NOx emissions of traffic and biomass burning during the warm period in this area ([Cesari et al., 2016b](#)). Secondary ammonium sulphate has a larger contribution during the warm seasons (spring and summer) compared to the cold seasons (autumn and winter) because the formation of ammonium sulphate is favoured at high temperatures ([Querol et al., 2008](#), [Ripoll et al., 2015](#)). The seasonal variability of SIA follows that of ammonium sulphate which is most abundant than nitrate. In coarse fraction, nitrate contribution is similar in the different seasons and the same happens for SOC, however, ammonium sulphate is lower during winter and spring. Therefore, the total secondary contribution to the coarse fraction is relatively limited and variable between 9% (in winter) and 13% (in autumn).



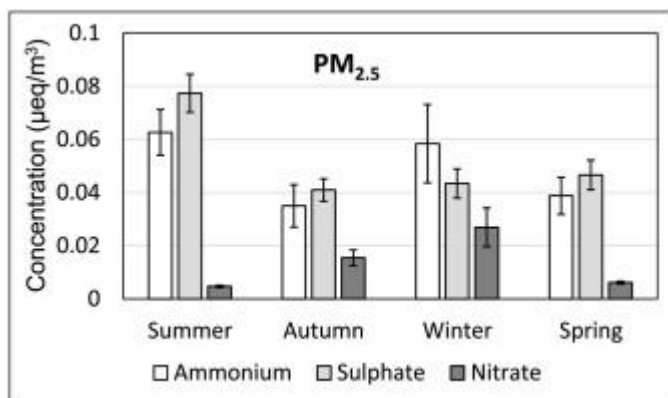
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Fig. 4

SOC has a seasonal variability opposite to that of SIA with larger concentrations during the cold period, similarly to what has been observed for OC. Low temperature favours the formation of SOC via gas-to-particle conversion of oxidized products of volatile organic compounds present in the atmosphere (Sahu et al., 2011). The opposite variabilities of SIA and SOC bring limited seasonal changes of the total secondary fraction of PM<sub>2.5</sub> variable between 38% during spring and 45% during autumn/winter. Using the same factor (1.6) to account for non-C atoms in secondary organic

matter (SOM = 1.6SOC) the total secondary mass (SIA + SOM) is variable from 33% to 43% of PM<sub>10</sub> and from 46% to 62% of PM<sub>2.5</sub>. These percentages are comparable with those observed in Barcelona (Spain) and lower than those observed in Northern and Central Italy (Amato et al., 2016).

In order to better understand the seasonal variability of SIA, the equivalent concentrations of NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup> in PM<sub>2.5</sub> are reported in Fig. 5. In spring, autumn and summer, ammonium concentrations are lower than what is necessary to completely neutralize sulphate, however, in winter there is an excess of ammonium with respect to sulphate suggesting the possibility of ammonium nitrate formation. Considering also the relatively low chloride depletion (discussed in Section 3.4) in sea-spray observed in winter, it is likely that the two forms of nitrate (sodium and ammonium nitrate) coexist mainly during winter.

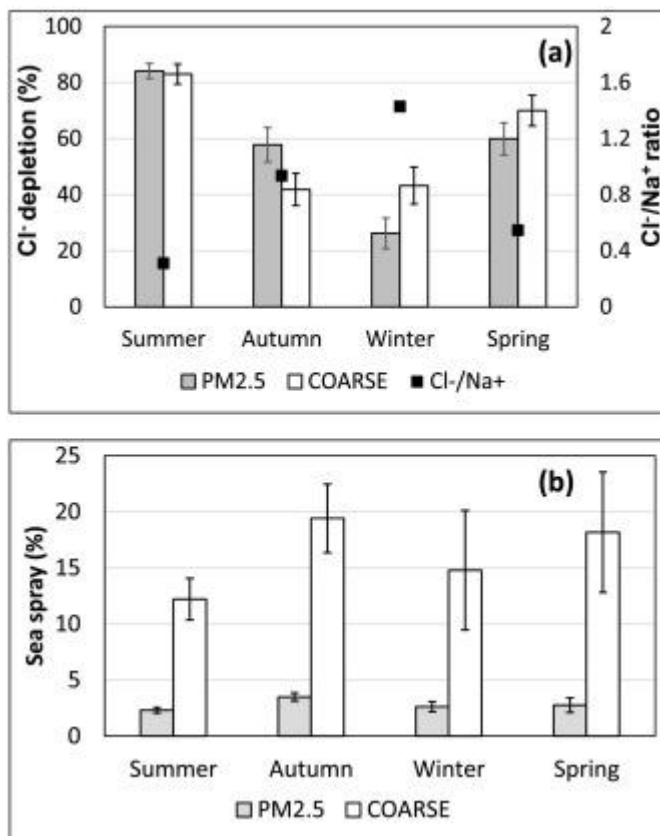


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Fig. 5

### 3.4. Sea-spray and crustal sources

The correlations observed between  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{Mg}^{2+}$  indicates that the site is influenced by sea-spray (Querol et al., 2001a). The yearly averages of  $\text{Cl}^-/\text{Na}^+$  ratios were 0.76 ( $\pm 0.06$ ) in  $\text{PM}_{10}$  and 0.94 ( $\pm 0.11$ ) in  $\text{PM}_{2.5}$ , significantly lower than the expected value (1.81) in sea water (Prodi et al., 2009). This indicates that, on average, sea-spray reaching the site is relatively aged as consequence of chemical reactions involving NaCl and nitric acid which lead to the formation of  $\text{NaNO}_3$  and gaseous HCl (McInnes et al., 1994, Pio et al., 1996, Zhao and Gao, 2008). This explains the chloride depletion and, in turn, the low  $\text{Cl}^-/\text{Na}^+$  that was observed also in previous studies in the same area (Contini et al., 2014b, Guascito et al., 2015). The yearly average percentages of depleted  $\text{Cl}^-$  are 60% ( $\pm 3\%$ ) in both size fractions. The sea spray contribution, evaluated as  $\text{Cl}^- + 1.4468 * \text{Na}^+$  (Marenco et al., 2006), is reported in Table S1. The percentages of depleted  $\text{Cl}^-$  are comparable in fine and coarse fractions and are maximum during the warm seasons as shown in Fig. 6a. Consequently, the  $\text{Cl}^-/\text{Na}^+$  ratio is lower during warm seasons with respect to cold seasons. The sea spray contributions to  $\text{PM}_{2.5}$  and to coarse fraction, for the different seasons, are compared in Fig. 6b. Sea spray ranges from 2.3% to 3.5% in  $\text{PM}_{2.5}$  and from 12.2% to 19.4% in the coarse fraction. Thereby, as expected, this source influences mainly large particles. The minimum contribution to measured concentrations is observed during summer.



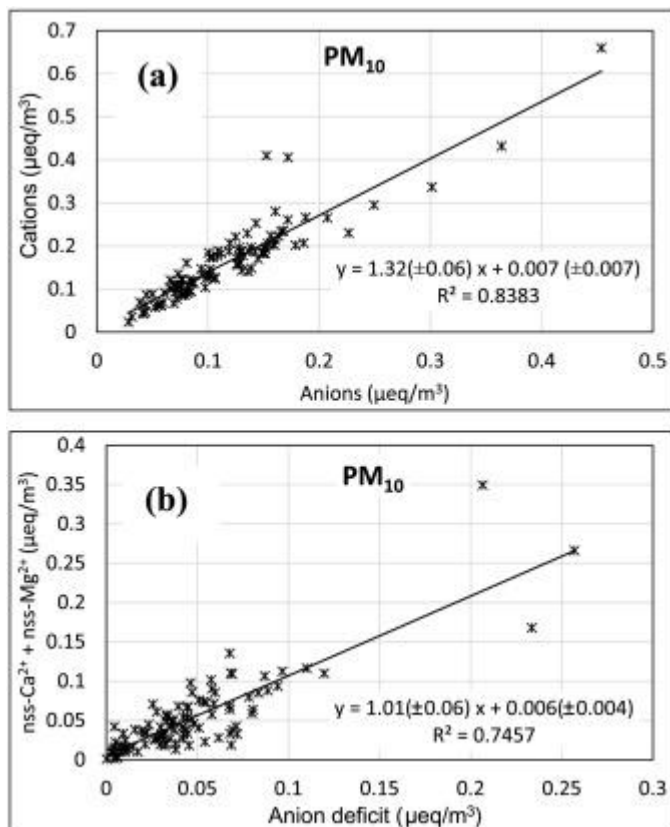
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Fig. 6

Crustal contribution can be calculated summing the concentration of elements (as metal oxides) generally associated with mineral dust: Al, Si, and Fe plus the insoluble fraction of K and Ca (indicated with an asterisk) as  $1.15 (1.89 \text{ Al} + 2.14 \text{ Si} + 1.67 \text{ Ti} + 1.4 \text{ Ca}^* + 1.2 \text{ K}^* + 1.36 \text{ Fe})$  and carbonates calculated from non-sea-salt calcium and magnesium as  $1.5 \text{ nss-Ca}_2 + + 2.5 \text{ nss-Mg}_2 +$  (Perrino et al., 2014, Cesari et al., 2016c). The factor 1.15 takes into account sodium and magnesium oxides (Marcazzan et al., 2001). The Si concentrations, not measured, were estimated considering that  $3\text{Al}_2\text{O}_3 = \text{SiO}_2$  thereby giving  $\text{Si} = 2.65 \text{ Al}$  (Querol et al.,

2001b). The typical ratio between water soluble and total concentration of Ca and K, measured in the Apulia (SE Italy) region (Contini et al., 2010) were used. The non-sea-salt component of  $\text{Ca}^{2+}$  was evaluated as  $\text{nss-Ca}^{2+} = \text{Ca}^{2+} - 0.038 \text{ Na}^+$  and that of  $\text{Mg}^{2+}$  as  $\text{nss-Mg}^{2+} = \text{Mg}^{2+} - 0.129 \text{ Na}^+$ . The ionic balance indicates a good correlation between total anions and total cations concentrations in  $\text{PM}_{10}$  (Fig. 7a). However, there was an anion deficit (deficit in negative charges). The same apply for  $\text{PM}_{2.5}$  (not shown) even if the deficit was lower in relative terms about 7.1% (in terms of charges) in  $\text{PM}_{2.5}$  compared to 27.7% in  $\text{PM}_{10}$ . Organic ions, such as formate and acetate, could contribute to the ionic balance; however, the presence of an anion deficit was used, in several sites, to infer the presence and to estimate the concentration of carbonates ( $\text{CO}_3^{2-}/\text{HCO}_3^-$ ) in aerosols (Nicolás et al., 2009, Arsene et al., 2011, Shen et al., 2011, Contini et al., 2014b). Fig. 7b shows that the observed anion deficit is well correlated with the sum of  $\text{nss-Ca}^{2+}$  and  $\text{nss-Mg}^{2+}$ . This suggests the presence of a contribution of calcium and magnesium carbonates due to resuspended local soil that is mainly limestone thereby having relevant Ca content (Cesari et al., 2012).



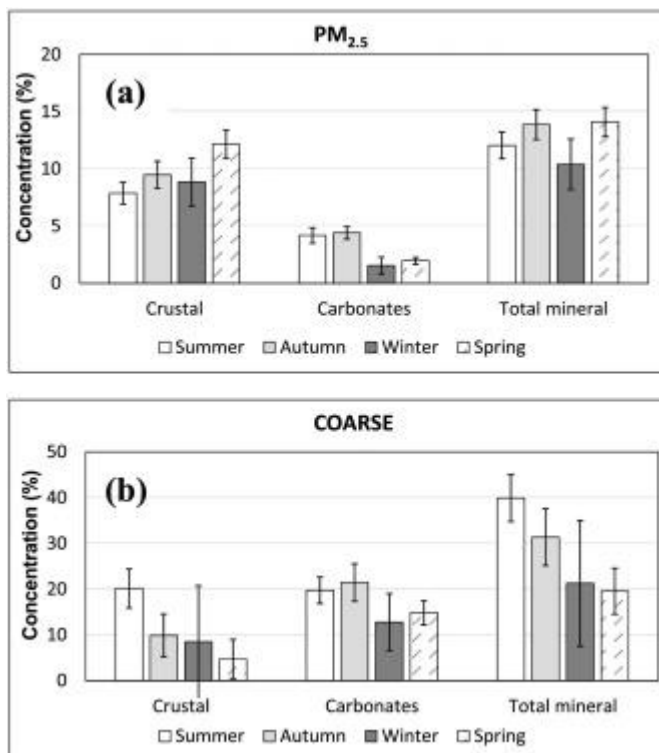


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Fig. 7

The crustal and carbonates contributions to PM<sub>2.5</sub> and to the coarse fraction are reported, for the different seasons, in [Fig. 8](#), including the total mineral contribution calculated as the sum of crustal and carbonates contributions. Results show that both crustal and carbonates components have larger concentrations in the coarse particles, however, their contributions to fine particles are not negligible. This was observed also in other studies, for example, crustal and carbonates were observed in PM<sub>2.5</sub> in several sites ([Ho et al., 2011](#), [Arsene et al., 2011](#), [Cesari et al., 2014](#), [Cesari et al., 2016b](#)). Carbonates contributions present a clear seasonal variability

with a decrease in winter and spring on both size fractions. Crustal contributions have similar contributions to PM<sub>2.5</sub> for the different seasons instead a clear variability is observed in the coarse fraction with contributions in winter and spring lower than those in summer and autumn. This difference among the two size fractions is observed also for the total mineral contribution that is similar during the four seasons for PM<sub>2.5</sub> but the coarse fraction decreases passing from the warm to the cold seasons. The decrease of total mineral contribution in coarse fraction is correlated with precipitations. The percentages of sampling days with precipitations (> 1 mm H<sub>2</sub>O/day) are 6.5% (summer), 17.6% (autumn), 35% (winter), and 39.3% (spring). This suggests that local dust due to resuspension decreases when soil humidity increases and that wet scavenging remove more efficiently coarse particles.



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Fig. 8

## 4. Results of PMF<sub>5</sub> source apportionment

### 4.1. Source profiles

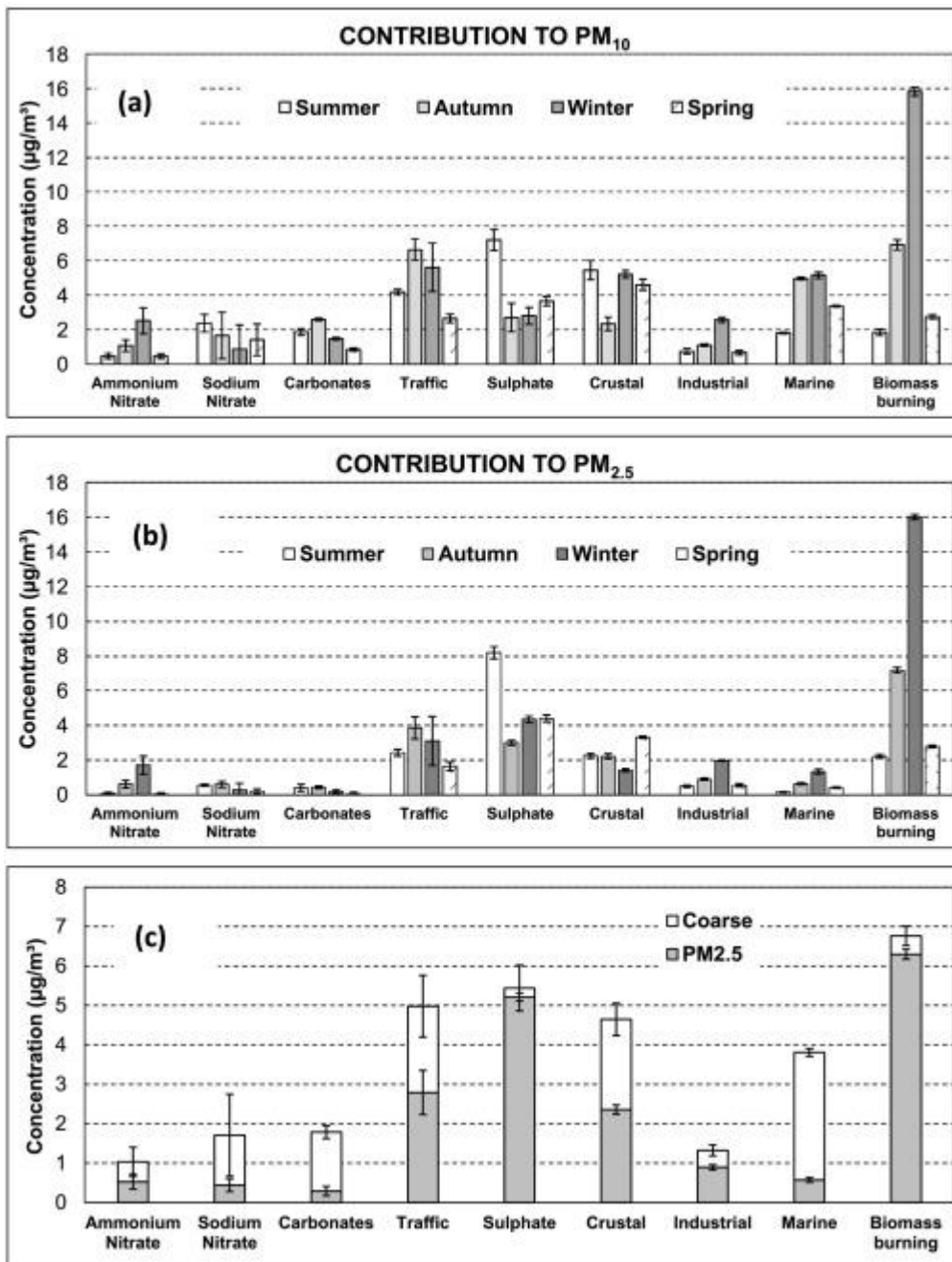
The profiles of the different factors, with the corresponding uncertainties, are shown in Fig. S2. The first factor was associated to marine contribution being loaded with Na<sup>+</sup> and Cl<sup>-</sup>. The second factor was characterised by K<sup>+</sup> and, to a lower degree by OC and EC suggesting its association with biomass burning and fires (Almeida et al., 2006, Zhang et al., 2008b). The third factor represents likely an industrial contribution characterised mainly by Pb. The fourth factor was loaded with EC, OC, Cu, Zn, Mn, and Sb and it represented the contribution of road traffic. The fifth factor was characterised by Al, Ti, V, Fe, Sr, Nb, La, and Ce that are elements generally associated to crustal minerals as it was confirmed by the analysis of the crustal enrichment factors (Section 3.2). The sixth factor was loaded with Ca<sup>2+</sup> and Mg<sup>2+</sup> and it represented resuspended dust contribution. This contribution includes carbonate/bicarbonate (likely calcium and magnesium carbonate), often observed in coarse aerosol, that could originate from local crustal material (Contini et al., 2014b). The presence of carbonates/bicarbonates was also inferred by the analysis of the ionic balance showing an anion deficit (Fig. 7) associated to the CO<sub>3</sub><sup>2-</sup>/HCO<sub>3</sub><sup>-</sup> ions not quantified by ion chromatography. It is interesting to observe that the ability of PMF<sub>5</sub> to separate these contributions is likely due to the different dynamics of crustal and carbonates materials. This was observed also in other works in Southern (Cesari et al., 2016b) and Central Italy (Amato et al., 2016, Contini et al., 2016). Crustal material is associated to long-range transport (including advection of Saharan dust) instead carbonates are associated to local resuspension. The seventh and eighth factors represent secondary nitrate and sulphate respectively.

The PMF<sub>5</sub> run, applied with the constraints mentioned in [Section 2.3](#), identifies a secondary nitrate component of sodium nitrate due to the interaction of nitric acid with marine aerosol. However, the balance between ammonium, nitrate and sulphate ([Fig. 4](#)) suggested the presence of ammonium nitrate during winter at low temperature. As a consequence, nitrate during winter period was underestimated by the PMF<sub>5</sub> reconstruction. Therefore, a new PMF<sub>5</sub> run was performed with explicit constraints to increase nitrate contribution limited to the winter period. This allowed finding an ammonium nitrate profile shown in [Fig. S2](#). The contribution to measured concentration of both forms of nitrate was calculated from this PMF<sub>5</sub> solution.

## **4.2. Seasonal variabilities of source contributions and their correlation with meteorology**

The seasonal variabilities of source contributions to PM<sub>2.5</sub> and to PM<sub>10</sub> obtained using PMF<sub>5</sub> are reported in [Fig. 9](#). The yearly average contributions for PM<sub>2.5</sub> and coarse fractions are compared in [Fig. 9c](#). Marine, crustal, and carbonates sources are mainly present in the coarse fraction with seasonal variabilities in reasonable agreement with the behaviours inferred by the mass closure analysis ([Section 3.4](#)). Ammonium nitrate and sulphate are larger in PM<sub>2.5</sub> fraction with respect to the coarse fraction and present an opposite variability with ammonium sulphate reaching maximum concentration in summer and ammonium nitrate in winter. The comparison with mass closure analysis showed that PMF slightly overestimated sulphate. Industrial contributions are larger on PM<sub>2.5</sub> with respect to the coarse fraction and limited to 4–5% of mass concentration. Traffic is an important source in both size fractions with a clear seasonal variability with larger concentrations in autumn and winter, likely because of the increased vehicular traffic at the University Campus during the cold period. Biomass burning is one of the most important source at the site

studied. It is mainly associated to the fine fraction and it has the obvious seasonal variability with larger contributions during autumn and winter, however, its weight is not negligible in spring and summer even if domestic heating are not present. This was observed also in other areas in southern Italy ([Cesari et al., 2014](#)) and it is likely due to a contribution from fires and agricultural practices. This is in agreement with [Cristofanelli et al. \(2017\)](#) who reported very high CO values (a “golden” tracer for combustion emissions) during winter 2015 but still high values during spring-summer for this area.



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Fig. 9

Seasonal variabilities put in evidence a correlation of composition and sources with temperature. To better analyse the correlation with meteorology, an average wind velocity and a prevalent wind direction was calculated for each measurement day. These values were used to produce pollution roses for the different sources dominant in PM<sub>10</sub> (Fig. S3) and in PM<sub>2.5</sub> (Fig. S4). In Figs. S3 and S4 the average contribution of each source is reported as a colour scale, the distance from the centre is proportional to the wind velocity and the angular position represents the wind direction. Fig. S3 shows that larger crustal contributions are associated to relatively high wind velocities from SE direction, similar to the pattern observed for marine contributions. Instead, carbonates are mainly associated to high wind velocity from the North direction. This difference in the dynamics of carbonates and crustal dust is likely one of the reasons that allowed a clear separation of these sources in PMF results. Fig. S4 shows a pollution rose for PM<sub>2.5</sub> different from that of PM<sub>10</sub> because large PM<sub>2.5</sub> concentrations do not have a specific directionality and happens at low wind velocity. A similar pattern is observed also for biomass burning, traffic and ammonium nitrate contributions. Instead, sulphate and industrial contributions have a different pattern with larger values associated to high winds from North. The similarity of the sulphate and industrial pollution roses suggests that secondary sulphate originates at larger distances from the site where industrial emissions of SO<sub>2</sub> are present and could be partly converted in sulphate.

A back-trajectories analysis has been performed in order to infer potential locations of distant sources using Concentration Weighted Trajectory (CWT) analysis (Stohl, 1998, Hsu et al., 2003, Squizzato and Masiol, 2015). Here, the CWT approach (Seibert et al., 1994, Hsu et al., 2003) was chosen since it is suitable to quantify long-range transported aerosol (Jeong et al., 2011). Details of the method used and CWT results are summarized in Supplementary material. Back-trajectories were computed by the Hybrid

Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model (Stein et al., 2015, Rolph, 2016) using the Global NOAA-NCEP/NCAR Reanalysis meteorological data. The HYSPLIT parameters were set as: total run time 72 h, start time at midnight, starting height of 100 m above ground level (agl) at the measurement site. This height allowed an effective transport within the mixing layer, as suggested elsewhere (Begum et al., 2005, Jeong et al., 2011, Westgate and Wania, 2011). Calculations were also performed starting at 50 m (agl) and no significant differences were observed (not shown). Assuming that the use of multiple trajectory-based models over long period may yield more robust results than using individual trajectories (Squizzato and Masiol, 2015), multiple back-trajectories were simulated starting every 3 h.

In Fig. S5 CWT results for biomass burning, industrial, ammonium nitrate, sulphate and traffic contributions are shown for the PM<sub>2.5</sub> fraction. The analysis shows for biomass burning probable source areas over the countries of Albania, Macedonia and North of Greece. This evidence confirms previous investigations carried out in Greece (Saffari et al., 2013) indicating a growing impact of biomass burning due to the switch from heating oil to cheaper material, such as wood, as burning material in residential heating for economic crisis. Industrial and secondary ammonium nitrate contributions present similar source areas (mainly over central and northern Italy) indicating a probable common origin. Conversely, the secondary sulphate seems to be associated to a more extended source area, reflecting different effects due to multiple sources i.e. industrial and/or ship traffic in the Adriatic Sea (Merico et al., 2017) or the effect of different meteorological conditions. Finally, it is quite interesting to note that traffic source does not show a long-range source area, highlighting the local nature of this source.



In Fig. S6 CWT results for carbonate, crustal, marine and sodium nitrate are shown for the PM<sub>10</sub> fraction. The analysis showed a main local source area for carbonate and crustal contributions also highlighting the presence of a source area in North Africa, confirming that the Mediterranean area is influenced by crustal matter long-range transport events. As expected, the source area of the marine contribution is represented by the Ionian and Libyan Sea. More interesting is the area reported for sodium nitrate, indicating the contribution coming from both the sea and lands of south Italy and south Est Europe. This is probably due to interaction between fresh sea spray and polluted air with consequent formation of aged sea salt (sodium nitrate).

## 5. Conclusions

An analysis of seasonal variabilities of fine (PM<sub>2.5</sub>) and coarse (PM<sub>2.5-10</sub>) particulate matter concentrations and composition was performed at an urban background station in Southern Italy. The seasonal variability of the contributions of nine sources (marine, sulphate, sodium nitrate, ammonium nitrate, biomass burning, traffic, industrial, crustal, and carbonates) was investigated using both mass closure and PMF5 receptor models.

Results show that marine contributions, dominant in the coarse fraction, are mainly associated with high winds from SE direction and they are larger during the cold period (autumn and winter) with respect to the warm period (spring and summer). Chloride depletion is relevant in both size fractions with a clear seasonal variability reaching a minimum of 26% (in PM<sub>2.5</sub>) and 43% (in PM<sub>2.5-10</sub>) during winter. This depletion is correlated with the formation of sodium nitrate in the coarse fraction.

Organic and inorganic secondary aerosol accounts for 43% of PM<sub>2.5</sub> and 12% of PM<sub>2.5-10</sub> with small seasonal changes. However, seasonal pattern of

SIA is opposite to that of SOC. SOC is larger during the cold period and sulphate (the major contributor to SIA) is larger during summer. Two forms of nitrate were identified: sodium and ammonium nitrate.  $\text{NaNO}_3$  is mainly present in the coarse fraction during spring, autumn and summer while  $\text{NH}_4\text{NO}_3$  is present only during winter and it is more abundant in the fine fraction like sulphate.

Mass closure analysis and PMF results identify two soil sources: crustal associated mainly to long range transport and carbonates associated to local resuspended dust. Both sources contribute mainly to the coarse fraction and have different dynamics with crustal source contributing mainly in high winds from SE conditions and carbonates during high winds from North direction. Total mineral contribution does not present a seasonal variability in  $\text{PM}_{2.5}$  but, in the coarse fraction, it decreases during the cold seasons, likely because of the scavenging effect of precipitations.

Biomass burning is a relevant source for this area with larger contribution during autumn and winter because of the influence of domestic heating, however, this source is not negligible in spring and summer, likely because of the contributions of fires and agricultural practices.

Industrial contribution is mainly in  $\text{PM}_{2.5}$  contributing for about 4–5% of  $\text{PM}_{2.5}$  and it is correlated with wind velocities and directions similarly to secondary sulphate suggesting a common origin.

Traffic is a source contributing to both size fractions ( $\text{PM}_{2.5}$  and  $\text{PM}_{2.5-10}$ ). Its weight on PM mass concentrations increases during autumn and winter. Traffic contribution has not a specific directionality and it is larger at low wind velocities with limited ventilation.

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## Appendix A. Supplementary data

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Supplementary material

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