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Sources of PM in an Industrial Area: Comparison between Receptor Model Results and Semiempirical Calculations of Source Contributions

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ABSTRACT

Source apportionment of PM_{10} and $PM_{2.5}$ samples collected in an industrial area of the Po Valley was performed by using the Positive Matrix Factorization (PMF) model and a semiempirical calculation of five macro-source contributions. Samples were collected during four monitoring periods, January–February 2011, June 2012, January–February 2012, May–June 2012, resulting in a total of 720 samples (360 for PM_{10} and 360 for $PM_{2.5}$). PMF variables included major elements, ions, elemental carbon and organic compounds and minor and trace elements. In order to increase the selectivity of minor and trace elements as source tracers, a chemical fractionation methodology based on the elemental solubility was employed; it was thus possible to include the extractable, the residual or both thefractions of the minor and trace elements in the database.

PMF resolved six factors for PM_{10} (crustal matter, marine aerosol, industry, secondary/oil combustion, secondary nitrate/biomass burning/exhaust particles, brake/tyre wear/re-suspended road dust) and seven factors for $PM_{2.5}$ (crustal matter, marine aerosol, industry, secondary nitrate, biomass burning, other secondary components, secondary sulphate/oil combustion). Mixing properties of the lower atmosphere were monitored by using natural radioactivity. The lack in the separation of some sources was shown to be due to their co-variation during periods of high atmospheric stability in the cold months. Seasonal variations of the source contributions were evaluated and discussed.

PMF results were compared with those obtained by a semiempirical calculation method in which analytical results are grouped into five macro-sources (crustal matter, marine aerosol, secondary inorganic compounds, combustion products from vehicular emissions and organics). Although similar trends in the temporal variation of the main PM sources were obtained, the absolute magnitude of the concentrations varied in some cases, especially for crustal matter and marine aerosol sources.

Keywords: Particulate matter; Po valley; Positive matrix factorization; Macro-source calculations; Elemental fractionation.

INTRODUCTION

Particulate matter (PM) is one of the main pollutants exceeding the ambient standards for air quality in Europe (Harrison *et al.*, 2008). Its direct and indirect influences on human health, global climate change and reduced visibility have led to numerous studies focusing upon its complex composition, toxicology and the source attribution (Pope *et al.*, 2002; Hwang *et al.*, 2007).

The Po Valley is a large industrialised and highly populated area located in the north of Italy. It is characterized by highly adverse meteorological conditions, including weak circulation of air masses in the winter period, and alternation of hot-dry and humid days in summer (Bernardoni *et al.*, 2011; Larsen *et al.*, 2012). This leads to the accumulation of pollutants in the local atmosphere and to the consequent frequent exceedance of the European air quality standards, particularly for PM (Marcazzan *et al.*, 2003; Larsen *et al.*, 2012). The further development of abatement strategies in this area is thus essential for the protection of both human health and environment.

One of the most powerful tools for the formulation of abatement policies is particulate matter source apportionment by the combination of chemical and statistical analysis.

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Receptor models have been widely used over the past three decades to apportion ambient concentrations to sources. Among these, the Chemical Mass Balance (CMB), Principal Component Analysis (PCA) and Positive Matrix Factorisation (PMF) methods are the most widely used. CMB can be used if sources and emission profiles of PM are known “a priori” (Viana *et al.*, 2008a; Ducret-Stich *et al.*, 2013). However, a detailed knowledge of sources and emissions is often not available; in these cases it is preferable to use multivariate models like PCA and PMF, which attempt to apportion the sources on the basis of the internal correlations at the receptor site (Viana *et al.*, 2008a). Moreover, some hybrid models combining the features of chemical mass balance models and non-negative factor analysis, such as Multilinear Engine-2 (ME-2) and Constrained Physical Receptor Model (COPREM), can be also used (Paatero, 1999; Wahlin, 2003).

An alternative to the statistical data analyses is given by simpler models based purely on chemical analysis of major PM components. Basically, chemical determinations are individually summed to obtain a mass closure and then grouped in order to determine the macro-sources (MS) of PM (Harrison *et al.*, 2003; Almeida *et al.*, 2006; Perrino *et al.*, 2014).

A number of works in the literature report the source apportionment of PM_{10}, $PM_{2.5}$ and even PM_1 in several cities located in the Po Valley using different receptor models (Marcazzan *et al.*, 2003; Vecchi *et al.*, 2008; Contini *et al.*, 2012). In these cities a significant contribution to PM emissions is given by anthropogenic sources, including traffic and industry. Industrial sources are responsible for a wide range of different elemental emissions, depending upon the characteristics of the plants (e.g., steel mills, power plants, waste incinerators, etc.), but the use of elements as tracers of industrial emissions in source apportionment studies is particularly difficult due to their lack of specificity. Many elements, in fact, are emitted in different proportions from a range of different industrial sources.

To enhance the selectivity of the elements as source tracers, a size fractionation of PM can be performed, as it is well known that fine particles (< 2.5 µm) are mainly emitted from combustion sources and coarse particles (> 2.5 µm) are generated from mechanical-abrasive processes (Allen *et al.*, 2001; Samara *et al.*, 2005). Also, additional improvements can be obtained by performing a chemical fractionation based on elemental solubility. The different solubility of the elements depends on the chemical form in which they are present and can be a useful indicator of their emission source, bio-accessibility and environmental mobility (Smichowsski *et al.*, 2005; Canepari *et al.*, 2006a; Canepari *et al.*, 2010). In this context the combination of a chemical fractionation methodology together with a receptor model could be beneficial in identification of the PM sources within highly polluted areas.

In this study, the PMF model was applied to identify and apportion the main sources of PM_{10} and $PM_{2.5}$ in samples collected within an industrial area close to the city of Ferrara (Emilia Romagna Region, Italy), where the unfavourable meteorological conditions and the many anthropogenic PM sources, as described by Canepari *et al.* (2014) and Perrino *et al.* (2014), lead every year to many exceedences of the PM concentration limits, especially in the cold months.

In order to increase the selectivity of elements as tracers of industrial and traffic related sources, the extractable (soluble) and residual (insoluble) fractions of trace elements, determined by means of chemical fractionation, were used as processing variables (Canepari *et al.*, 2006a,b; 2009a).

The influence of the meteo-climatic conditions on the time variation of source contributions was examined by comparing the source time patterns obtained by the PMF model with the mixing properties of the lower atmosphere traced by natural radioactivity measurement.

PMF results were compared with those obtained by applying a MS calculation in order to examine the potential and the limitations of the two approaches.

METHODS

Sampling Sites and Sample Collection

Samples of PM_{10} and $PM_{2.5}$ were collected in the suburban area of Ferrara, a city with about 132,000 inhabitants located in the eastern Po Valley. 24-hour PM_{10} and $PM_{2.5}$ samples were collected, on a daily basis, during four 1-month intensive monitoring campaigns (January–February 2011, June 2011, January–February 2012 and May–June 2012) at three different sites: an industrial site (A, 44°51′N 11°33′E), a rural site (B 44°49′N 11°32′E) and a residential site (C 44°50′N 11°33′E). The map of the sampling sites is shown in supplementary material (Supp.1). A total of 720 samples were collected. A complete description of the monitored area and of the sampling sites can be found in Perrino *et al.* (2014).

Mass concentration was measured daily at all three sites, by means of dual channel beta attenuation automatic monitors (SWAM 5a Dual Channel Monitor – FAI Instruments, Fonte Nuova, Rome - IT) configured with PM_{10} and $PM_{2.5}$ heads compliant with the EN 12341 (PM_{10}) and EN14907 ($PM_{2.5}$) standards. Samplers were equipped with teflon membrane filters (TEFLON, 47 mm, 2.0 micron pore size, PALL Life Sciences). Three additional dual channel samplers (HYDRA Dual Sampler, FAI Instruments, Fonte Nuova, Rome - IT) were placed at the three sites in order to collect daily PM_{10} and $PM_{2.5}$ samples also on quartz fibre filters (TISSUQUARTZ 2500QAT, 47 mm, PALL Life Sciences).

During the same periods, the mixing properties of the lower atmosphere were evaluated at site C, on a 1-h hour time basis, by using an automated monitor (PBL Mixing Monitor, FAI Instruments, Fonte Nuova, Rome - IT). The instrument measures the natural radioactivity of short-life beta-decay products of Radon. Radon gas is emitted only from the ground, at a rate that can be assumed to be constant on a time and space scale of few weeks and several kilometres, respectively. Therefore, the variability of the measured radioactivity is due to the variability of the mixing properties of the low atmosphere: radon concentration increases when the atmospheric mixing is poor and decreases in situations of advection or of efficient convective mixing. A more detailed description of this approach can be found in Perrino *et al.* (2001) and Perrino *et al.* (2008).

Chemical Analysis

The simultaneous sampling of PM on teflon and quartz filters allowed the chemical determination of several components. The analysis of Organic Carbon (OC) and Elemental Carbon (EC) was performed on quartz filters by means of a thermo-optical analyzer (OCEC Carbon Aerosol Analyzer, Sunset Laboratory, OR-U.S.A; NIOSH-QUARTZ temperature protocol).

Elements and inorganic ions were analyzed on teflon filters following the method reported in Canepari *et al.* (2009a). Briefly, macro-elements Al, Fe K, Mg, Ca, Ti, S and Si were analyzed by energy-dispersive X-Ray fluorescence (EPD-XRF, X-Lab 2000, SPECTRO). Then each filter was extracted in an acetate buffer solution using an ultrasonic bath. The solution was divided in two aliquots, one analyzed for anions (Cl^-, NO_3^-, SO_4^{2-}) and cations (Na^+, NH_4^+, Mg^{2+}, Ca^{2+}) using Ion Chromatography (DX 100, DIONEX Co., CA-USA) and the other analyzed for the extractable fraction of the elements (As, Al, Cd, Cu, Fe, Mg, Mn, Ni, Pb, Rb, Sb, S, Si, Sn, Ti, Tl, V, Zn) using inductively coupled plasma (ICP) with optical and mass spectrometer detection (ICP-OES: Vista MPX CCD Simoultaneous, Varian, equipped with an ultrasonic nebulizer U-5000 AT, CETAC; ICP-MS: Bruker 820, equipped with a reaction cell, CRI, and a 400 µL/min MicroMist nebulizer). The residual teflon filter was digested in a mix of HNO_3 and H_2O_2 (2:1) using a microwave oven (Milestone Ethos Touch Control with HPR 1000/6S rotor) and the mineralized fraction was then analyzed by ICP-OES and ICP-MS for its insoluble elemental content. Although it exhibits a poor recovery for Al, Si and Ti, this digestion procedure allows a high data quality for minor and trace elements (Bruno *et al.*, 2000; UNI EN 14902:2005). Anyway, total concentrations of Al and Si were measured by XRF, while Ti recoveries are highly repeatable and ICP measurements are then able to reliably follow the temporal variations of this element (Canepari *et al.*, 2006b; Canepari *et al.* 2009a). The combined use of both ICP-OES and ICP-MS allowed analysis of a larger number of elements. According to the results of our previous studies, we quantified Fe, Cu, Mn and S by ICP-OES and the others elements with ICP-MS.

The overall analytical procedure was previously validated by evaluating recovery percentage and repeatability on both certified material (NIST1648) and real samples (Canepari *et al.*, 2009a). It allows the complete inorganic characterization of PM in a single sample. In addition, the determination of the same element (e.g., Fe, Mg, S) with different analytical techniques makes it possible to check the quality control of the determinations.

PMF Model

PM_{10} and $PM_{2.5}$ sample data were processed using the PMF receptor model developed by Paatero and Tapper (1994). It uses a weighted least squares fit and the weightings are based on the known uncertainties of the elements in the data matrix. Specifically, the mathematical model in matrix form is written as:

$$X = GF + E \tag{1}$$

or in index notation

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij}. \tag{2}$$

where x_{ij} is the concentration of the *j*-th measured species in the *i*-th samples, g_{ik} is the contribution of *k*-th factor to the *i*-th sample, f_{kj} is the concentration of the *j*-th species in the *k*-th factor profile and e_{ij} is the model error of the *j*-th measured species in the *i*-th samples. The goal is to find values for *G*, *F* and *p* that best reproduce *X* (Reff and Eberly, 2007).

In this study EPA PMF3.0 was used for the analysis, which worked under the Multilinear Engine ME-2. Separate data analyses were performed for PM_{10} and $PM_{2.5}$ samples collected at all the three sampling sites (360 samples for PM_{10} and 360 samples for $PM_{2.5}$). For species analyzed by more than one analytical technique (see chemical analysis section) only one value was chosen in order to avoid the double counting of these species (Reff and Eberly, 2007).

The use of an elemental fractionation methodology allows the improvement of the selectivity of most elements as source tracers, by discriminating combustive from mechanical-abrasive sources (Canepari *et al.*, 2008, Canepari *et al.*, 2009b, Canepari *et al.*, 2010). In particular, the processed elements were chosen according to the results reported in Canepari *et al.* (2014), in which the dimensional distributions and solubility of the elements in the monitored area were examined in detail: it was discovered that the extractable fractions of As, Cd, Ni, Pb, Rb, Fe, Sb, Tl, V, Zn are generated by combustion sources in the fine particles, while the residual fraction of Ba, Cu, Fe, Sb, Mn, Ti are released as coarse particles by mechanical-abrasive sources. According to this, twenty-nine species were selected as PMF variables: OC, EC (thermo-optical analysis), Al Si, K (XRF), Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+ (Ion Chromatography), extractable fraction of As, Cd, Mg, Ni, Pb, Rb, Sb, Tl, V, Zn, residual fraction of Ba, Cu, Mn, Ti and both fractions of Fe, Sb. PM mass concentration was included in the input data matrix so that the model apportioned it to each factor; its uncertainty was tripled to avoid a large influence on the solution.

Data and uncertainties were handled in the same way for both PM size ranges. The uncertainties matrix was created using the analytical repeatability of the method, calculated using twenty pairs of equivalent real samples (Canepari *et al.*, 2006b; Canepari *et al.*, 2009a). Missing data were replaced with the species median concentration and their uncertainties were set to four times the median concentration. Data below detection limit were replaced with half of detection limit and their uncertainties were increased to 5/6 the detection limit (Polissar *et al.*, 2008). Species were classified as “strong”, “weak”, and “bad” based on the signal-to-noise ratio, the shape of the distribution of scaled residuals and the “observed/predicted” plots (Reff and Eberly, 2007). All the factors found in the two analyses were independent, indicating the absence of a rotational ambiguity in the solution. As confirmation, PMF solutions with Fpeak value between –1 and 1 were explored. The resulting solutions were similar, giving no further information about the factors' identification.

Mass Closure and Macro-Sources Calculation

Mass closure is the correspondence between the total mass concentration of PM and the sum of the single major components (species which account for more than about 1% of the total PM mass). To perform a mass closure, a correction factor for oxygen had to be applied to the major elements in order to consider them as metal oxides (Marcazzan *et al*., 2001). OC was multiplied by a factor α that takes into account the atoms other than C present in the organic molecules (Turpin and Lim, 2001; Viidanoja *et al*., 2002). The value of α was set to 1.8 for suburban sites A and C and to 2.1 for rural site B. It must be taken into account that these approximations represent one of the most important sources of uncertainty in the mass closure calculation (Terzi *et al*., 2010). Indeed, the value of α is subject to a variability depending on the aerosol composition and thus on the location of the sampling site. When a good correspondence between the sum of the chemical components and the total PM concentration is obtained, a reliable chemical characterization of PM is ensured.

The chemical determinations were then grouped into five macro-sources (MS): crustal matter, marine aerosol, secondary inorganic compounds, combustion products (vehicular emissions) and organics (Perrino *et al*., 2014).

The crustal matter contribution was calculated by adding the concentration of elements generally associated with mineral dust (total Al, Si, Fe, measured by XRF, and the insoluble fractions of Na, K, Mg and Ca, calculated as the difference between the XRF and the Ion Chromatography determinations) and carbonate, calculated from calcium and magnesium determined by Ion Chromatography. As before mentioned, a correction factor for oxygen in metal oxides was applied.

$$\text{Crustal matter} = 1.89\,\text{Al} + 2.14\,\text{Si} + 1.42\,\text{Fe} + 1.35\,\text{Na}_{\text{insoluble}} + 1.2\,\text{K}_{\text{insoluble}} + 1.67\,\text{Mg}_{\text{insoluble}} + 1.4\,\text{Ca}_{\text{insoluble}} + \text{CO}_3^{2-} \quad (3)$$

where:

$$\text{CO}_3^{2-} = 2.5\,\text{Mg}^{2+} + 1.5\,\text{Ca}^{2+} \quad (4)$$

The marine aerosol contribution to PM_{10} was calculated from the sum of the concentrations of soluble sodium and chloride, determined by Ion Chromatography, multiplied by 1.176 in order to take into account of minor sea water components (sulphate, magnesium, calcium, potassium).

Secondary inorganic components were calculated by adding the non-sea-salt sulphate, nitrate and ammonium concentrations.

Combustion products from vehicular emission were calculated by adding elemental carbon to the same amount multiplied by 1.1, in order to take into account organic species that condense in the exhaust gases and coat the surface of elemental carbon particles (Castro *et al*., 1999). A more detailed discussion about the estimation of this contribution can be found in Perrino *et al.* (2014).

$$\text{Combustion products} = \text{EC} + 1.1\,\text{EC} \quad (5)$$

Organics were calculated by multiplying the non-primary organic carbon by the correction factor for non-carbon atoms α (Turpin and Lim, 2001). It includes primary OC coming from biomass combustion and biogenic aerosol and secondary organic compounds.

$$\text{Organics} = \alpha\,\text{OC} - (1.1\,\text{EC}) \quad (6)$$

RESULTS AND DISCUSSION

PMF Source Profiles

The minimum number of factors (p) to be chosen in the PMF analysis was evaluated calculating the maximum individual column mean (IM) and the maximum individual column standard deviation (IS) parameters from the scaled residuals matrix and the Q values, as suggested by Lee *et al.* (1999). These parameters gave information about the quality of the fit and were useful to determine the number of factors (Supp. 2). Results indicated that the number of factors to be studied was greater or equal to 6 for PM_{10} and greater or equal to 5 for $PM_{2.5}$. A p = 6 solution and p = 7 solution were chosen for PM_{10} and $PM_{2.5}$ respectively; in both cases, solutions with higher values of p were rejected as they evidently separated variables belonging to the same source in more than one factor.

The sources of PM_{10} and $PM_{2.5}$ and their chemical composition are shown in Figs. 1 and 2. The "crustal matter" source, accounting for about 20% of the PM mass concentration in both size fractions, was identified by high values of Al and Si. High percentages of OC, EC and SO_4^{2-} were also included in both the profiles (12%, 14%, 36% in PM_{10} and 32%, 25% and 24% in $PM_{2.5}$ respectively). This is quite surprising as the crustal elements are mainly confined in coarse particles, while OC, EC and SO_4^{2-} are mainly contained in fine particles (Perrino *et al*., 2014). Perrone *et al.* (2013) found the latter components mixed with crustal markers in $PM_{2.5}$; they hypothesized that the mineral particles can change their original composition during their ageing in the atmosphere, getting mixed/coated with inorganic ions, organics and black carbon. Although this hypothesis may partly explain the high concentration apportioned to this factor in the PM fine fraction, the crustal source appears to be not clearly separated by the model.

The "marine aerosol" source was identified by the presence of Na^+, Cl^- and Mg in both PM_{10} (5% of PM) and $PM_{2.5}$ (2% of PM).

A factor characterized by the presence of several elements in the soluble fraction (As, Cd, Pb, Fe, Tl, Zn) was found in PM_{10} and $PM_{2.5}$ accounting respectively for 10% and 4% of the PM concentration. These elements are usually associated with different industrial emissions and are emitted by the several plants located in the area under study (Viana *et al*., 2008b; Contini *et al*., 2012). The factor was then

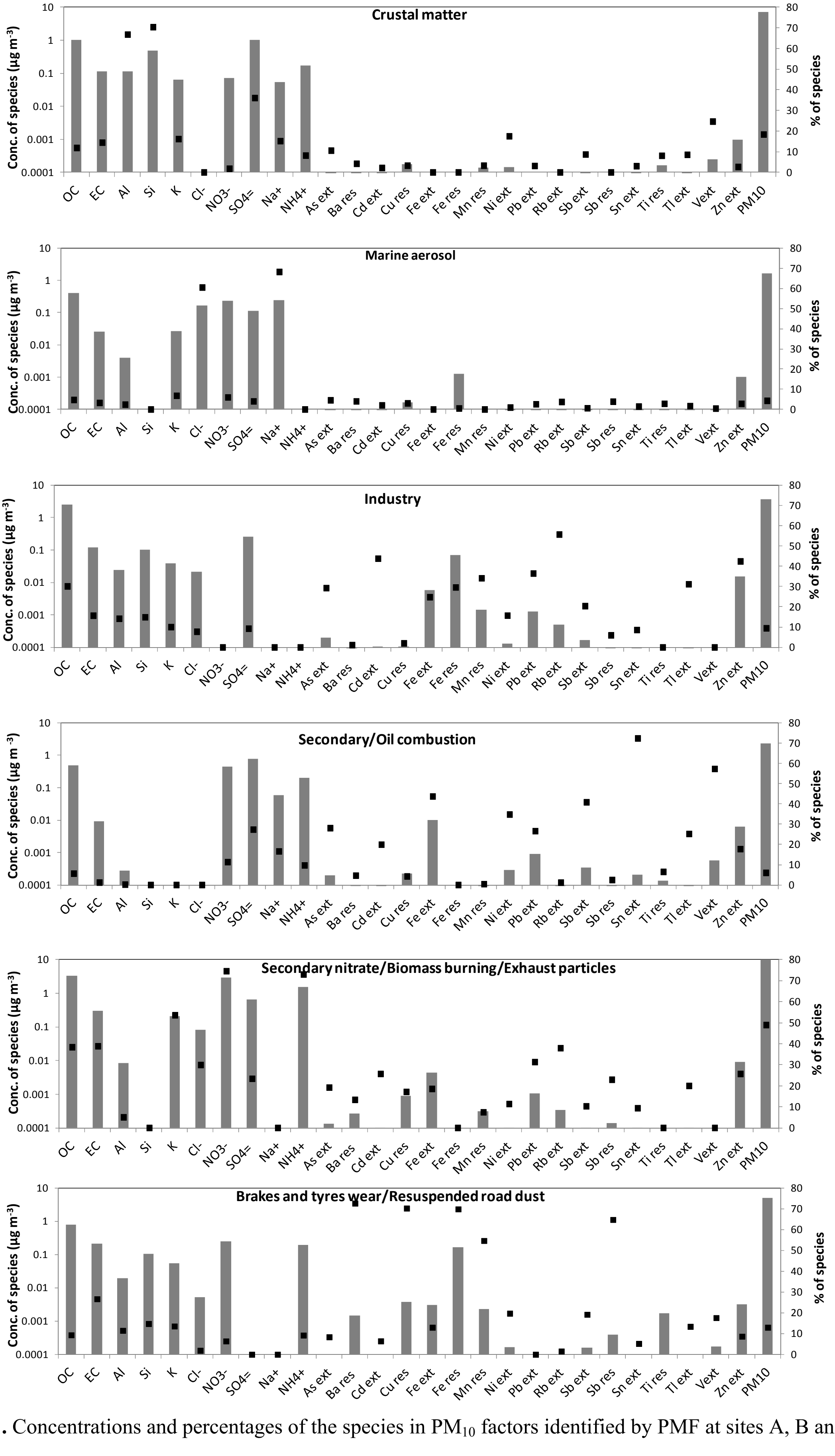

Fig. 1. Concentrations and percentages of the species in PM_{10} factors identified by PMF at sites A, B and C.

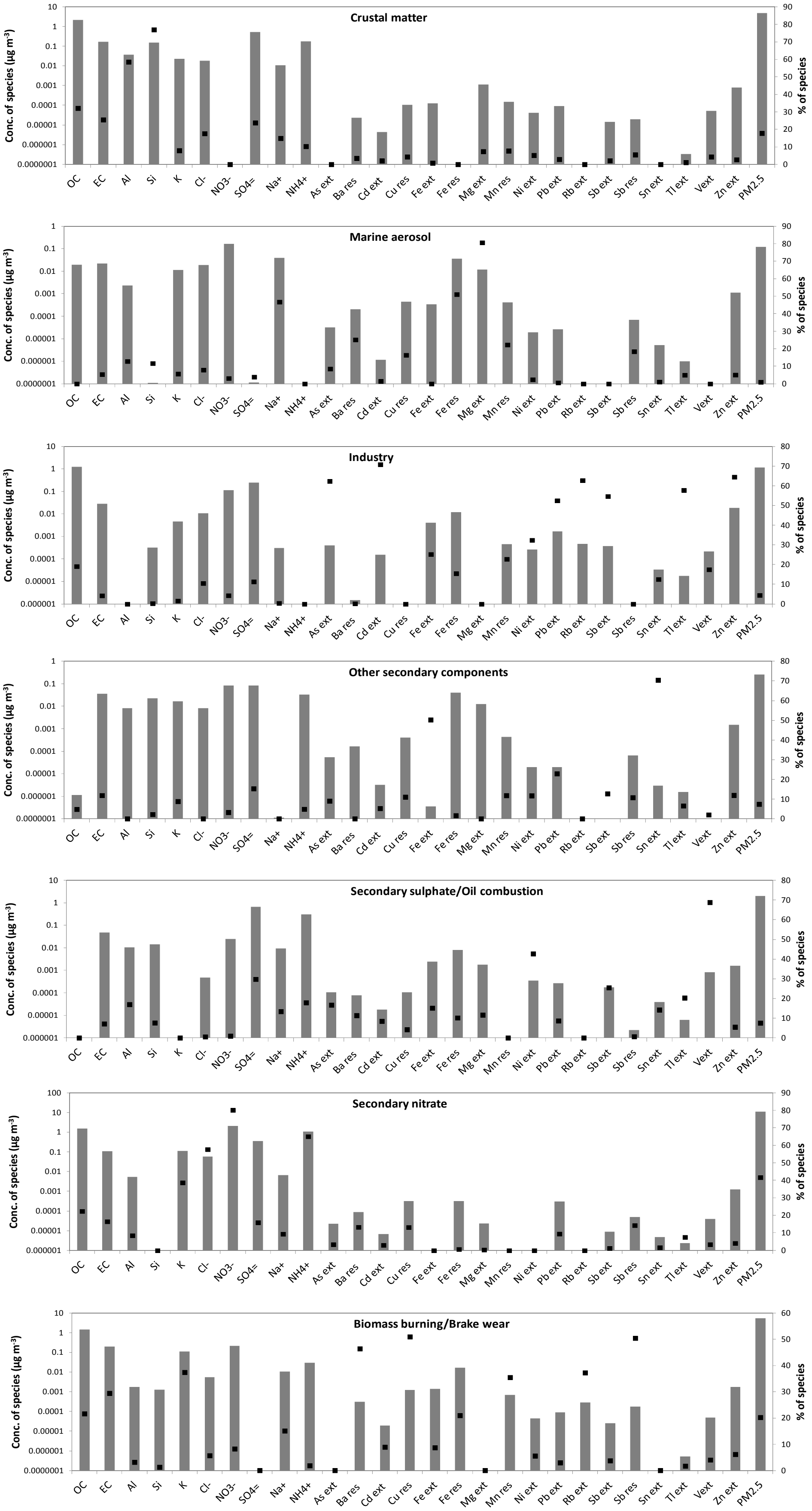

Fig. 2. Concentrations and percentages of the species in $PM_{2.5}$ factors identified by PMF at sites A, B and C.

named “industry”. Chemical analyses of these elements showed that they all were almost wholly present in the fine fraction of PM (Canepari *et al.*, 2014). In this work the greater contribution of these species in the PM_{10} factor was probably due to the presence in the chemical profile of Al, Si and residual Fe and Mn, mainly present in the coarse fraction.

A factor identified by high concentration of OC, NO_3^-, SO_4^{2-} and NH_4^+ and a large contribution to extractable V and Ni occurred in PM_{10} (6%). These are indicators of secondary particles and of oil combustion (Vecchi *et al.* 2008). The same components were separated into two factors in $PM_{2.5}$, (Other secondary components; Secondary sulphate/Oil combustion) each one accounting for 7%.

A factor associated with three different sources was found in PM_{10} (50% of the mass concentration). The main species were NH_4^+ and NO_3^-, which identified a “secondary nitrate” source. In the same factor we found EC, OC, K and Rb, which are identified in literature as tracers of biomass burning (Gianini *et al.* 2012; Ducret- Stich *et al.*, 2013). This factor also includes Zn together with EC, considered as tracers of traffic exhaust emissions (Viana *et al.*, 2008a; Weckwerth, 2001). This factor was then named “secondary nitrate/biomass burning/exhaust particles”.

In $PM_{2.5}$ the “secondary nitrate” source was resolved in a single factor, accounting for more than 40% of the mass concentration, while the biomass burning source, showing a high loading on K, OC and EC, was resolved in a factor unexpectedly including also Ba, Cu, Fe, Mn, Sb in the residual fraction (20% of PM concentration). These particles in their coarse fraction are mainly generated from mechanical-abrasive processes (brake wear) and can serve as indicators of non-exhaust traffic emissions (Harrison *et al.*, 2004; Canepari *et al.*, 2008; Gietl *et al*, 2010). The size distribution of brake wear extends into the fine fraction of PM, and it seems likely that PMF has failed to separate the biomass burning and brake wear signatures in $PM_{2.5}$.

The last factor, found only in PM_{10} and accounting for 13%, contributed substantially to Ba, Cu, Fe, Mn, Sb and Ti, all in the residual fraction. These elements are associated with brake and tyre wear, and the small percentages of Al and Si in the factor indicate a probable contribution from re-suspended road dust, in which soil is one of the components (Harrison *et al.*, 2003; Viana *et al.*, 2008a; Amato *et al.*, 2011). It was called “brake and tyre wear/resuspended road dust” as it was clearly related to particles emitted by the non-exhaust traffic source.

The application of a chemical fractionation methodology was useful to identify some PM_{10} sources that have similar composition in terms of total elemental concentration, as the extractable and the residual fractions of some elements individually correlate in different factors (e.g., natural crustal matter and re-suspended road dust, traffic exhaust and brake and tyre wear).

Sources contributing to PM_{10} and $PM_{2.5}$ were very similar, although better separated in $PM_{2.5}$, and on the whole they are in agreement with the results of other studies performed at urban sites in the Po Valley (Marcazzan *et al.*, 2003; Vecchi *et al.*, 2008; Bernardoni *et al.*, 2011, Tositti *et al.*, 2014). However, PMF is unable to give a complete separation of different source signatures in the studied industrial area, probably because the main sources are widespread at ground level and consequently their emissions are dispersed in a similar way.

Spatial and Temporal Variation of the Sources Identified by PMF

The seasonal patterns and the differences among the sampling sites have been evaluated for each factor identified by the PMF model. Fig. 3 shows the time evolution of crustal matter and marine aerosol sources in daily PM_{10} and $PM_{2.5}$ samples obtained in winter 2011 and summer 2012 at sampling sites A, B and C.

Source contributions at the three sites did not show very significant differences, confirming the homogeneity of the air masses in the area under study and the robustness of the chemical analysis (Canepari *et al.*, 2014; Perrino *et al.*, 2014). The crustal matter source was higher in summer, consistently with the dryness of the soil in this season. During summer 2012, the higher contribution of the crustal matter registered during the days of 19–22 June at all the sites was attributable to transport of mineral dust from the desert regions of North Africa towards Northern Italy. This episode was detected by the model BSC-DREAM8b (Dust REgional Atmospheric Model, Basart *et al.*, 2012). Marine aerosol contributions were higher in PM_{10}, as expected. A seasonal pattern was not clearly defined, as some intense advection phenomena that carried the sea-spray towards inland areas, resulting in higher values of this contribution, occurred in both winter and summer periods (January 21–29, February 4–10, June 8–13 and June 26th).

Spatial and temporal variability of the other sources was difficult to interpret on the basis of time series only, because some factors resolved by PMF, particularly in PM_{10}, were associated with a mixing of different sources. It is well known that one of the limitations of this model is the inability to separate sources which co-vary in time (Viana *et al.*, 2008b).

Covariation of the sources was mainly due to the particular meteorological conditions encountered during the cold months within the studied area, where the weak circulation of the air masses associated with high atmospheric stability led to the homogenous accumulation of pollutants. This was confirmed by comparing the source contributions with the natural radioactivity time pattern. As an example, Fig. 4 shows the time pattern of the PM_{10} secondary nitrate/biomass burning/exhaust traffic source at the three sites compared with the natural radioactivity pattern during winter 2011 (upper panel) and the time pattern of PM_{10} brake and tyre wear/re-suspended road dust sources compared with natural radioactivity during summer 2012 (lower panel).

In winter, weak atmospheric mixing during both night and day corresponds to constantly high radioactivity values for many subsequent days. The upper graph shows a very close agreement between the temporal pattern of concentrations and natural radioactivity, confirming the modulation of these sources by the action of atmospheric stability. It has to be noted that during the first days of the winter 2011 an intense fog event occurred in Ferrara. This led to an increase in the average diameter of the particles (> 10 μm) that were thus excluded from the sampling head. For this reason, contributions were lower than expected on the basis of the natural radioactivity pattern (Canepari *et al.*, 2014). These ground-level sources, constant in time and homogeneously distributed in the monitored area, result to

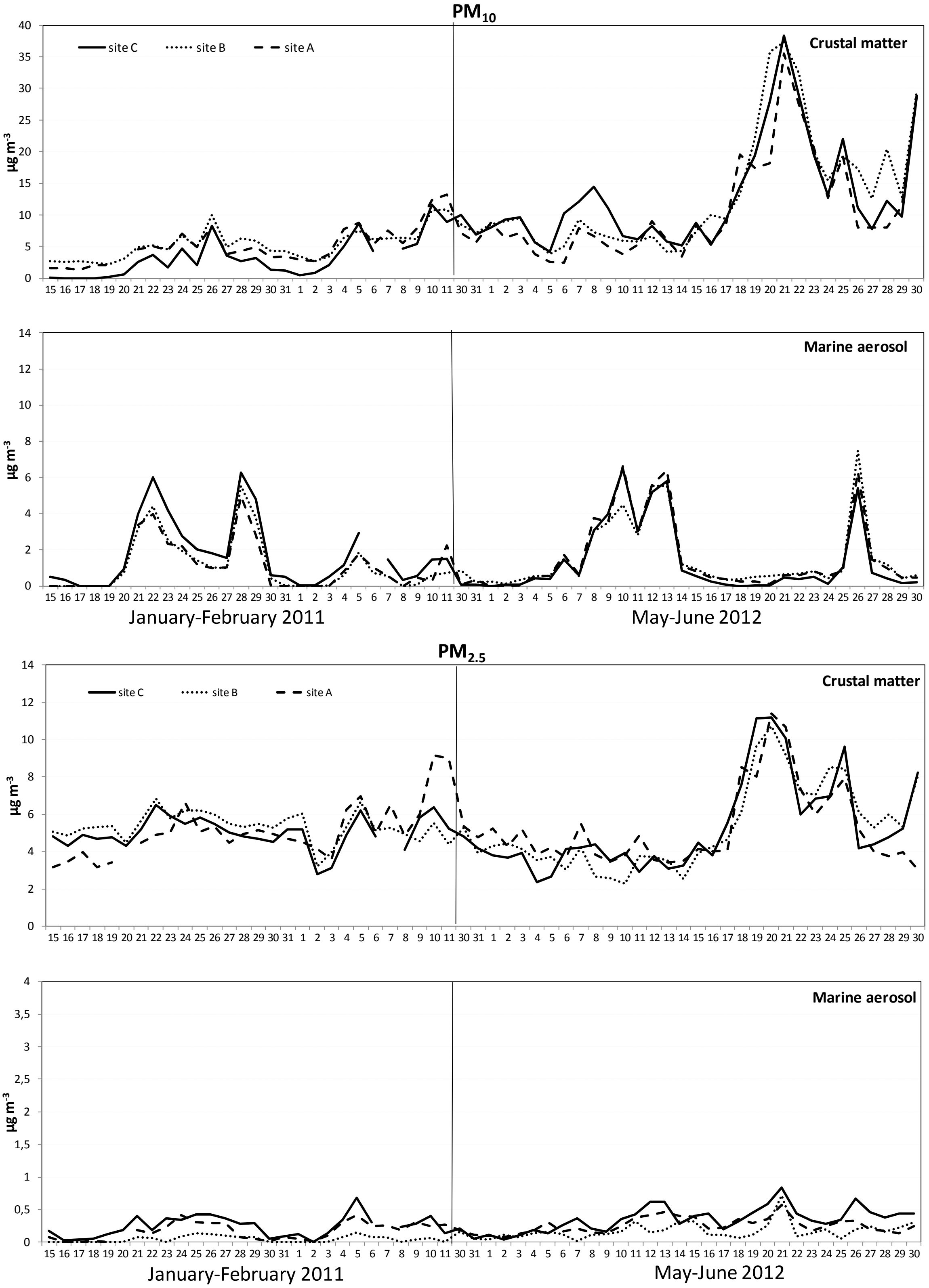

Fig. 3. Spatial and temporal variability of PM_{10} and $PM_{2.5}$ crustal matter and marine aerosol sources in winter 2011 and summer 2012 at sites A, B and C.

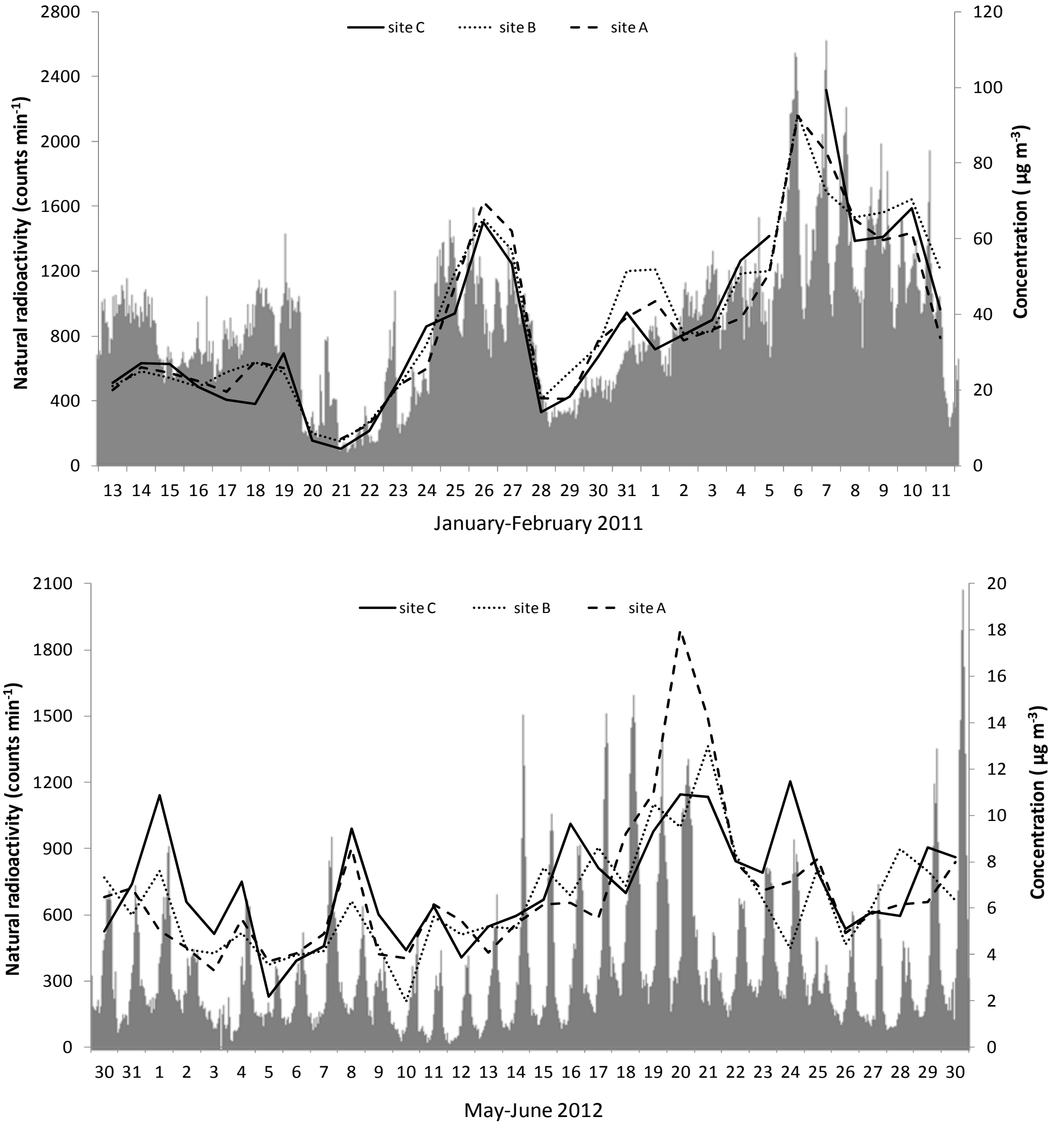

Fig. 4. Upper panel: Comparison between natural radioactivity (histogram) and PM_{10} secondary nitrate/biomass burning/ exhaust particles source at sites A, B and C during winter 2011 (lines). Lower panel: Comparison between natural radioactivity (histogram) and PM_{10} brakes and tyres wear/resuspended road dust at sites A, B and C during summer 2012 (lines).

be the main contributors to the high PM concentrations registered in the winter period. Other sources, like brake and tyre wear/re-suspended road dust sources in PM_{10}, were as much influenced by the mixing properties of the lower atmosphere but their time pattern was also dependent on the variability of the source emission rates.

In summer, the natural radioactivity pattern showed strong daily trends rather than long periods of atmospheric stability so there was no clear relationship of these sources to the radioactivity pattern (Fig. 4 lower panel) and the contributions of brake and tyre wear/re-suspended road dust were attributable mainly to traffic intensity. This contribution is higher during summer due to dryness conditions. Contributions of the secondary nitrate and biomass burning sources were instead lower, due to the higher temperatures enabling the volatilization of the secondary compounds, and the absence of domestic heating.

As regards $PM_{2.5}$ sources, PMF was able to better separate them and also in this case the winter time patterns showed a good agreement with the natural radioactivity for secondary nitrate, biomass burning, industry and secondary sources.

The spatial and temporal variability of $PM_{2.5}$ industry, other secondary components and secondary sulphate/oil combustion sources for winter 2011 and summer 2012 at the three sites appears in Fig. 5. Values at the three sites were fairly similar confirming the low contribution of local point sources, despite the closeness of the industrial area, and their limited influence on the high concentrations of PM recorded in this area (Canepari *et al.*, 2014; Perrino *et al.*, 2014). Industry (upper graph) showed higher contributions in winter, contributing to the worse air quality observed in the area of Ferrara during the cold months. Seasonal variability of

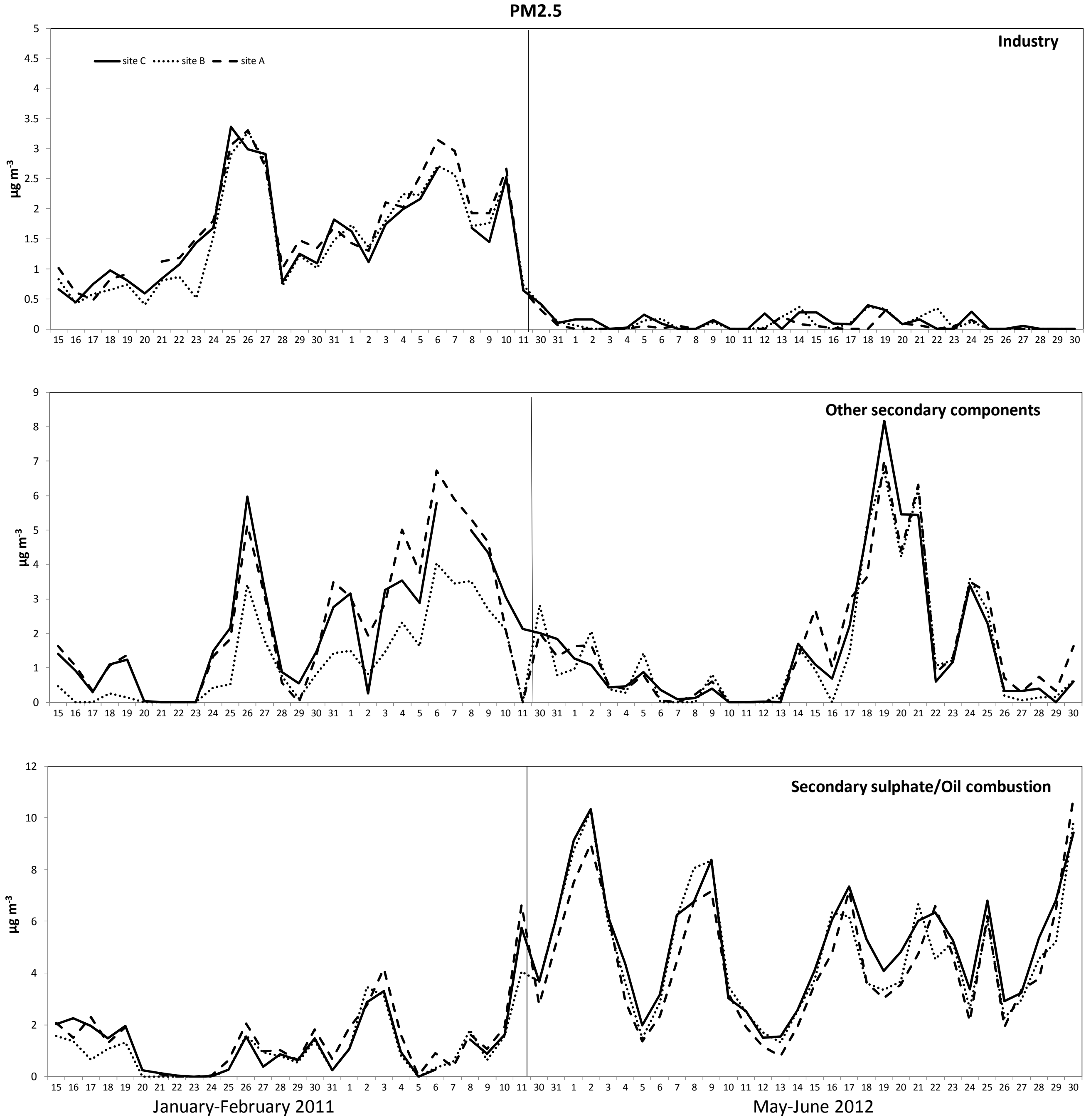

Fig. 5. Spatial and temporal variability of $PM_{2.5}$ industry, other secondary components and secondary sulphate/oil combustion in winter 2011 and summer 2012 at sites A, B and C.

the 'other secondary components' factor (middle graph) was not clearly defined, as high contributions were found in both winter and summer period. Secondary sulphate/oil combustion (lower graph) showed higher values in summer. The correlation among Ni, V and SO_4^{2-} suggests that secondary sulphate originated from the oxidation of SO_2 emitted primarily by the industry/power plants located in the monitored area, in particular by the petrochemical plants. Secondary sulphates are formed mainly in summertime because of the higher photochemical activity in the Mediterranean basin (Vecchi *et al.*, 2008). If the source is relatively local, it may be emitting above the mixed layer top in winter and hence not affecting local ground-level concentrations.

Comparison between PMF and Mass Closure/Macro-Sources Results

Results obtained by PMF were compared to those arising from mass closure. Both the approaches, which are among the most widely used for studying the PM sources, allow the reconstruction of the sampled PM mass; in Fig. 6 we compare PM concentration as modelled by PMF and as reconstructed by the sum of the chemical analyses (mass closure) vs. the daily measured concentrations of PM_{10} and $PM_{2.5}$. In the case of PM_{10} we obtained a very similar agreement between the two approaches ($R^2 = 0.94$ for PMF, $R^2 = 0.93$ for mass closure), while for $PM_{2.5}$ the PMF provided a higher correlation between measured and calculated data ($R^2 = 0.93$) than mass closure ($R^2 = 0.90$). Slopes of the curves were very close to 1 in PMF and around 0.7 in mass closure, whereas the intercept values were lower in PMF than in mass closure both for PM_{10} and $PM_{2.5}$. The lower values of the slope obtained in mass closure were most likely due to the presence of significant amounts of water in PM (Canepari *et al.*, 2013; Perrino *et al.*, 2013). By including the water determination in the mass closure the slope value becomes closer to 1. Separate measurements of water in samples rich in Saharan dust or secondary constituents showed a water content up to 10% (paper in preparation). The PM mass reconstruction by PMF was not affected by this missing species and water was indirectly included in the source contributions.

A further comparison between the two approaches regarded the time pattern of the main sources. From the determination of the major components used for the mass closure only five macro-sources (MS) were calculated, while PMF did not have any limitations in the number of factors that could have been found and included in the analysis also trace elements. This resulted in different sources identified with the two approaches, which impair a rigorous comparison. Anyway, for some common sources, the analogies and differences of the two approaches can be discussed.

As an example, in Fig. 7 the daily variation of PM_{10} marine aerosol (upper graphs) and crustal matter (middle graphs) sources at site C during winter 2011 and summer 2012 are shown. The same comparison for $PM_{2.5}$ is reported in Supp. 3. The time pattern yielded by the two approaches were very similar for both sources, in winter and in summertime. However, PMF contributions were generally higher than those obtained by MS calculation. For marine aerosol (MA) the average of the ratio MA_{PMF}/MA_{MS} was 1.7 in winter and 1.2 in summer, while for crustal matter (CM) the average of the ratio CM_{PMF}/CM_{MS} was 0.7 in winter and 1.8 in summer although the two series of data were well correlated ($R^2 = 0.7$ for MA and CM in winter and $R^2 = 0.9$ for MA and CM in summer). Similar results were obtained at sites A and B.

Large differences in the comparison between the results for marine aerosol obtained performing PCA and Mass Balance Analyses were found also by Almeida *et al.* (2006). They suggested that the discrepancy observed for the marine aerosol source was attributable to a poor mass closure that did not include all the components associated with sea spray, and to the reactions of NaCl with inorganic acids (HNO_3, H_2SO_4) that caused the loss of HCl, so that Cl^- was not totally present in particulate form at the sampling site. Nonetheless, the differences in our observations were too high to be explained only by these reasons and we suppose PMF overestimated the contribution of this source during severe sea salts events.

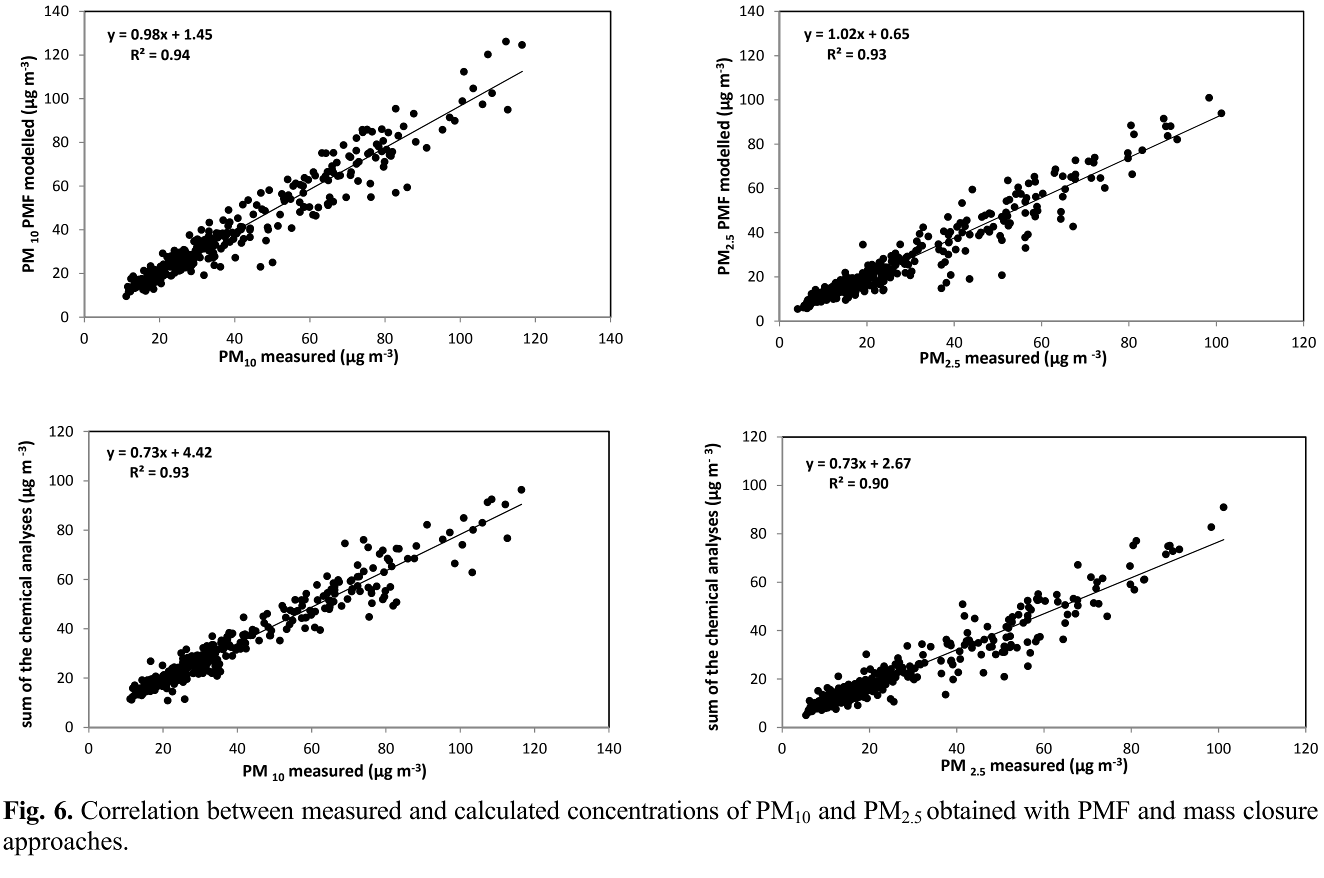

Fig. 6. Correlation between measured and calculated concentrations of PM_{10} and $PM_{2.5}$ obtained with PMF and mass closure approaches.

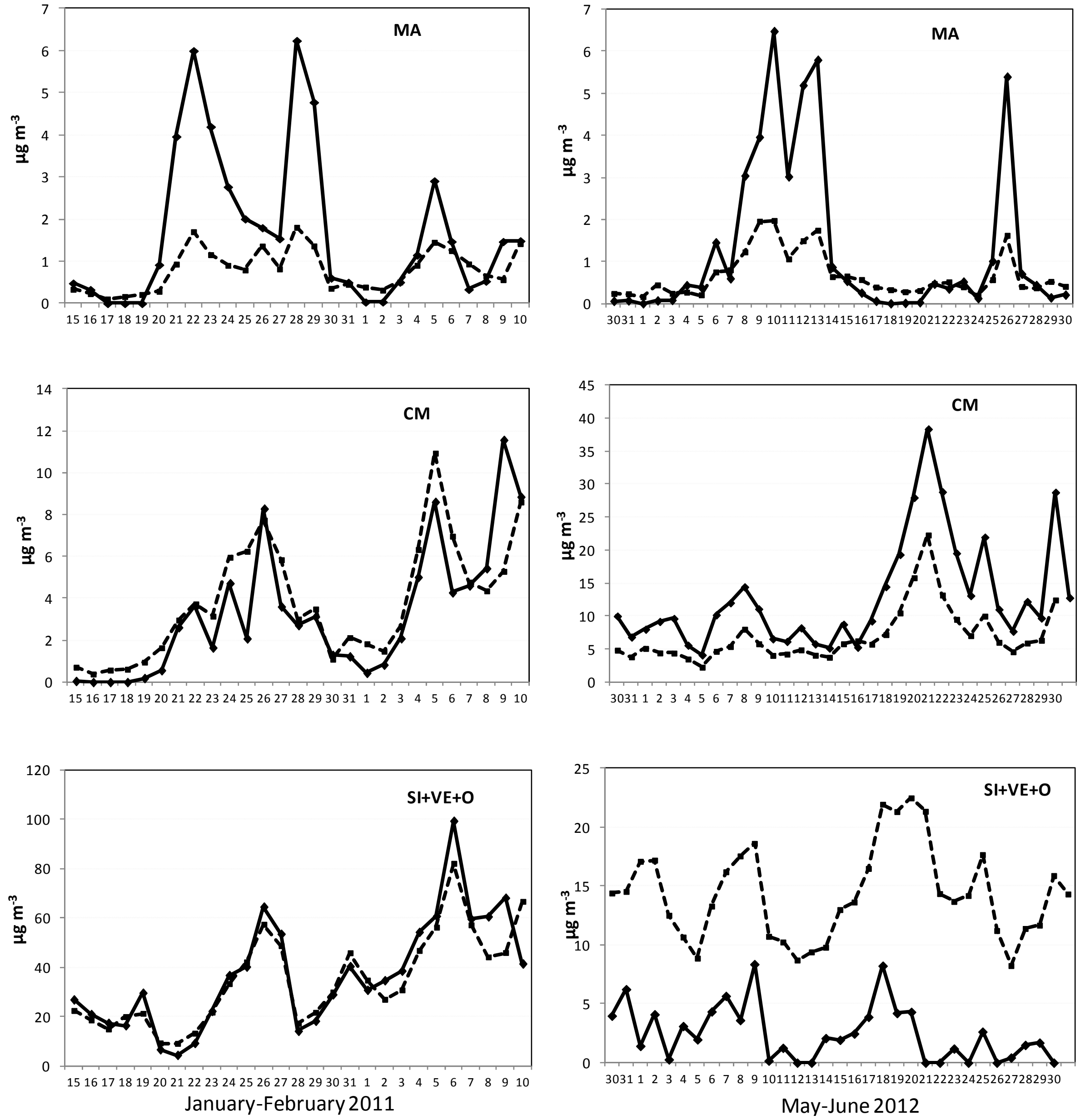

Fig. 7. Daily variation of PM_{10} marine aerosol (MA, upper panel), crustal matter (CM, middle panel) and secondary inorganics + vehicular emission + organics (SI + VE + O, lower panel) sources at site C during winter 2011 and summer 2012. Solid line refers to PMF and dashed line refers to macro-sources (MS) calculation approach.

Also for the crustal matter source the discrepancy observed, particularly evident during summer, may be only in small part explained by the assumption made in the MS approach that all the elements were present as oxides. A further contribution to the PMF factor could have been due to water and to other organic and inorganic species adsorbed on the surface of crustal particles, particularly during Saharan transport events (Canepari *et al.*, 2013; Perrone *et al.*, 2013). However, even in this case, PMF seems to overestimate this source contribution.

The MS approach included separate sources for secondary inorganic compounds, vehicular emission and organics, while PMF showed a mixed source comprising secondary nitrate/biomass burning/exhaust particles and did not show a single factor associated with organic compounds. Some previous studies have highlighted the difficulty of receptor models to detect and interpret sources of organics in the absence of speciated data on the organic matter (Viana *et al.*, 2008a). The contribution of the organic compounds in PMF was assumed to be split among different factors and the main part was included in the nitrate/biomass burning/exhaust particles (see the factor profiles composition). Consequently, secondary inorganic compounds (SI), vehicular emission (VE) and organics macro-sources (O) were summed in order to compare them with the only source present in PMF (SI + VE + O in Fig. 7, lower panel). In winter a very good agreement between the two series of data was observed, the average of the ratio $(SI + VE + O)_{PMF}/(SI + VE + O)_{MS}$

was 1. Conversely, in summer the SI + VE + O was higher in the MS calculation: the average $(SI + VE + O)_{PMF}/(SI + VE + O)_{MS}$ was 0.2. The good correlation in winter indicated that almost all the organics macro-source was constituted by the biomass burning products. The poorer relationship in summer was probably due to the low contribution of the biomass burning organics and to the presence in the organic macro-source of a relevant amount of secondary (originated by photochemical oxidation) and biogenic compounds, which were not included in the considered PMF factor.

CONCLUSIONS

Source apportionment carried out by the PMF model showed very similar sources for both PM_{10} and $PM_{2.5}$ although source separation was better in $PM_{2.5}$ samples. During the winter, the main sources of PM in the area of Ferrara were identified as secondary nitrate and biomass burning, accounting for about 40% and 20% of the $PM_{2.5}$ concentration respectively. In PM_{10} these sources were included in the same factor together with the exhaust particles, accounting, all together, for more than 50% of the total PM_{10} concentration. They were confirmed to be the main components responsible for the several exceedences of the PM_{10} daily limit value registered during the winter period in the area of Ferrara. Traffic and industry showed low contributions, despite the intensive industrial and urban activities around the monitored area. There were no significant differences of the sources among the three sampling sites, confirming the spatial homogeneity of PM despite the close proximity of the sampling points to the industrial area.

The poor separation of co-varying sources was the main weakness of PMF. We could explain the co-variation of some sources, especially in PM_{10}, by comparing the daily trend of the source with the pattern of the natural radioactivity. In the winter months, a very good agreement was observed among homogeneously distributed sources (biomass burning, secondary nitrate, exhaust), whose temporal variations were modulated by the mixing properties of the lower atmosphere. In summer there was no clear correlation between the time pattern of the sources and the natural radioactivity, probably due to the more efficient convective atmospheric mixing during the daytime.

The comparison between PMF source contributions and macro-sources calculation showed that both approaches provided similar spatial and temporal variability of the main PM sources in the monitored area. However, some important discrepancies were found in comparing quantitative estimates of the individual sources. In particular, the PMF model tended to overestimate the source contributions of crustal matter and marine aerosol, above all when transport events occurred, with differences that could not have been explained even when considering the uncertainties in the calculation of the unmeasured species. While the PMF overestimation of the sea spray seemed to be substantially due to an artifact, the differences in crustal matter seemed to be due to a poor separation of this source profile and, at least to some extent, to the adsorption of significant amount of water and other species (secondary inorganic ions, OC) on the crustal particles.

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SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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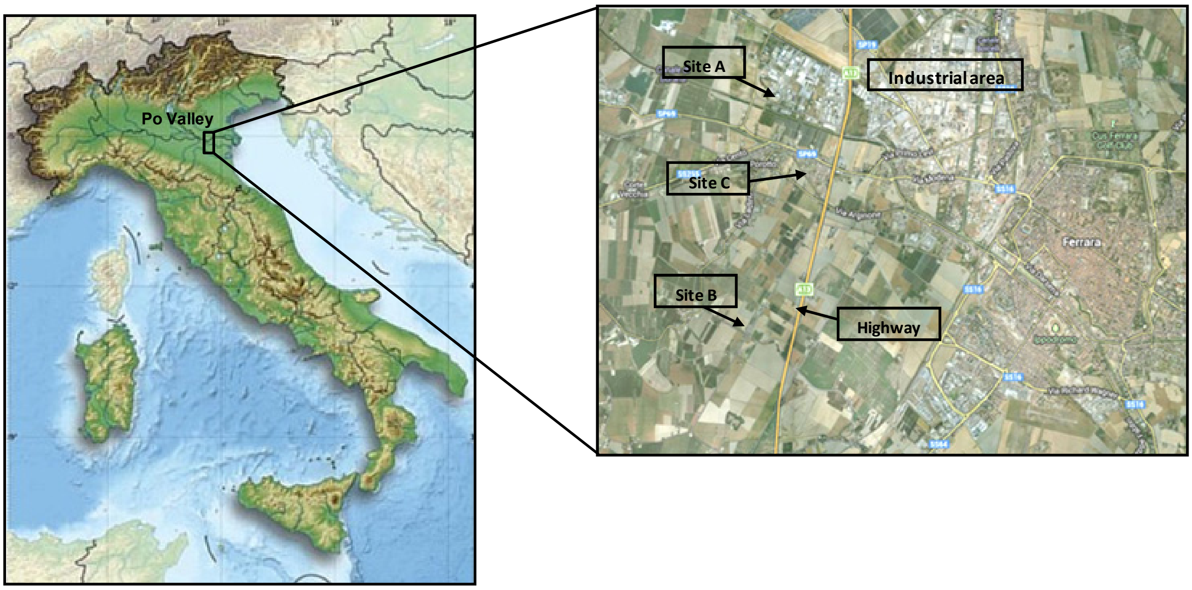
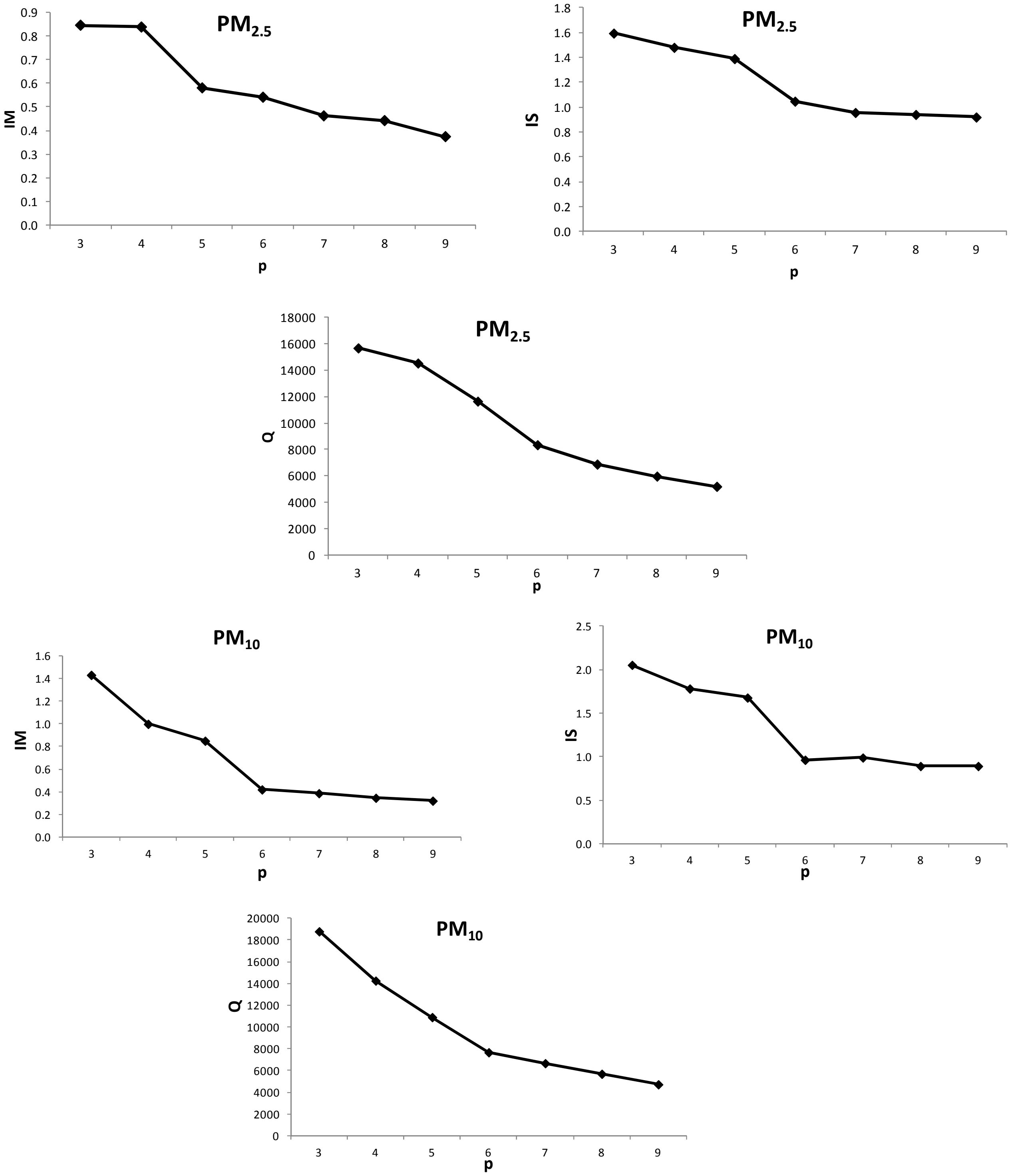
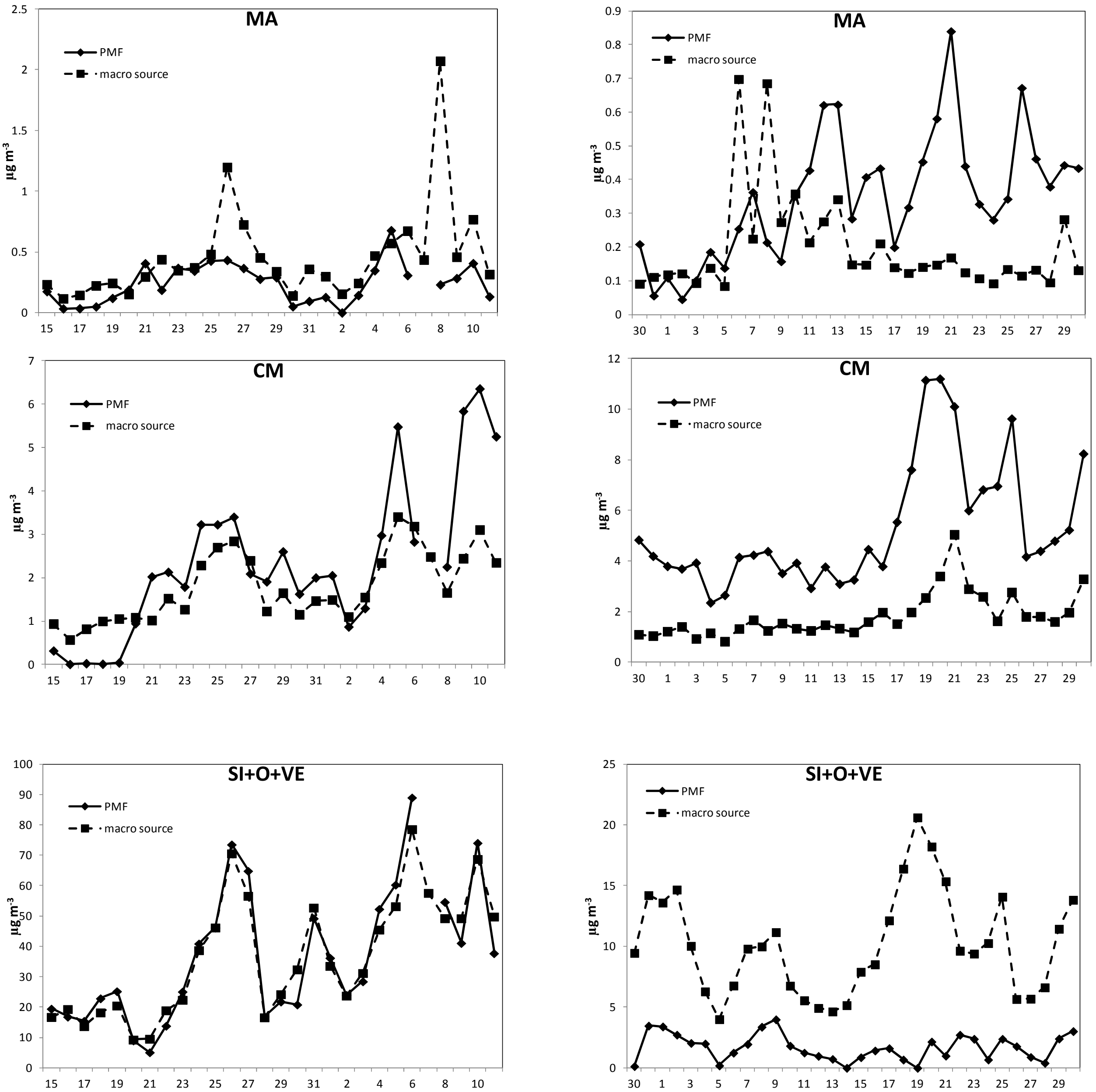
SUPPLEMENTARY MATERIALS



Supp. 1: Map of the monitored area and location of the sampling sites: industrial (site A), rural (site B), residential (site C).



Supp. 2: Maximum individual column mean (IM), maximum individual standard deviation (IS) and Q values vs. number of factor (p) for PM$_{2.5}$ (upper panels) and PM$_{10}$ (lower panels). According to Lee *et al.* (1999), these graphs can be used to establish the minimum number of factor for which the PMF model gives results free from any lack of fit. IM and IS values are calculated from the matrix of the scaled residuals (given by the PMF), while Q is one of the parameter showed among the model results. The minimum number of factor corresponds to the p value for which IM and IS parameters show a drastic decrease and Q curve changes its slope.



January-February 2011

May-June 2012

Supp. 3: Daily variation of $PM_{2.5}$ marine aerosol (MA, upper panel), crustal matter (CM, middle panel) and secondary inorganics + vehicular emission + organics (SI + VE + O, lower panel) sources at site C during winter 2011 and summer 2012. Solid line refers to PMF and dashed line refers to macro-sources (MS) calculation approach.