

Source apportionment and location by selective wind sampling and Positive Matrix Factorization

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Received: 14 September 2013 / Accepted: 21 December 2013 / Published online: 1 February 2014
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Abstract In order to determine the pollution sources in a suburban area and identify the main direction of their origin, PM_{2.5} was collected with samplers coupled with a wind select sensor and then subjected to Positive Matrix Factorization (PMF) analysis. In each sample, soluble ions, organic carbon, elemental carbon, levoglucosan, metals, and Polycyclic Aromatic Hydrocarbons (PAHs) were determined. PMF results identified six main sources affecting the area: natural gas home appliances, motor vehicles, regional transport, biomass combustion, manufacturing activities, and secondary aerosol. The connection of factor temporal trends with other parameters (i.e., temperature, PM_{2.5} concentration, and photochemical processes) confirms factor attributions. PMF analysis indicated that the main source of PM_{2.5} in the area is secondary aerosol. This should be mainly due to regional contributions, owing to both the secondary nature of the source itself and the higher concentration registered in inland air masses. The motor vehicle emission source contribution is also important. This source likely has a prevalent local origin. The most toxic determined components, i.e., PAHs, Cd, Pb, and Ni, are mainly due to vehicular traffic. Even if this is not the main source in the study area, it is the one of greatest concern. The application of PMF analysis to PM_{2.5} collected with this new

sampling technique made it possible to obtain more detailed results on the sources affecting the area compared to a classical PMF analysis.

Keywords PM_{2.5} · Selective sampling device · Particulate chemical composition · Wind direction · Local and regional sources · Factor analysis

Introduction

In recent years, the mass fraction PM_{2.5} (particulate matter <2.5 μm in aerodynamic diameter) has justifiably attracted scientific interest. Several studies have shown an association between increased PM_{2.5} concentrations and adverse health effects (Pope III and Dockery 2006; Schwartz and Neas 2000), leading the European Parliament to establish legislative regulations regarding this fraction (EC 2008). As these particles may be harmful to humans, the assessment of their level and chemical composition is significant from an environmental health perspective (Alleman et al. 2010). The identification of the various sources and the quantification of their contribution to the ambient concentration of particulate matter are among the main goals of atmospheric research and play a key role in formulating and applying PM_{2.5} abatement strategies (Masiol et al. 2010). In order to identify pollutant sources and quantify their relative contribution, the factor analysis methods may be applied. Among these methods, Positive Matrix Factorization (PMF) is a new approach; it is more powerful and provides quantitative information on source contributions (Qadir et al. 2013; Ramadan et al. 2000; Venturini et al. 2013a). It has several advantages for applications in environmental studies. First of all, measure uncertainties and below detection limit data can be managed. But the most important characteristic is that loading matrix has only positive values and this is a fundamental feature in source

Responsible editor: Constantini Samara

Electronic supplementary material The online version of this article (doi:10.1007/s11356-014-2507-6) contains supplementary material, which is available to authorized users.

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apportionment studies, where each factor should represent a different emission source (Comero et al. 2012; Hopke 2000).

The concentrations of atmospheric fine particulate matter are affected by regional transport of $PM_{2.5}$ as well as local source emissions (Pekney et al. 2006). It is important to locate sources and to examine if they are regional or local in order to develop an effective and efficient strategy for managing air quality (Liu et al. 2003). Airborne concentrations coming from specific sources may display a sharp directional pattern with respect to wind directions. In these cases, concentrations are high when the air flows from certain direction(s), while concentrations associated with other directions are low or nil (Paatero and Hopke 2002). Some studies have assessed the directional dependence of sources. In some of them, the PMF results were coupled with wind direction or back trajectory data to provide reasonable predictions of the locations of emission sources affecting the receptor site (Hellebust et al. 2010; Lee et al. 2002; Lee and Hopke 2006; Polissar et al. 1996; Sun et al. 2011). Trajectory or wind statistic methods have been designed to obtain information about both source locations and preferred transport directions of airborne particles (Zhou et al. 2004). Among these techniques, Conditional Probability Function (CPF) and Potential Source Contribution Function (PSCF) are widely used (Kamae and John 2011; Kim et al. 2003; Kim and Hopke 2004; Lee and Hopke 2006; McGuire et al. 2011; Polissar et al. 1999; Wang et al. 2013). CPF evaluates the influence of a local source on the receptor site by using meteorological data (wind direction and velocity) (Yubero et al. 2011). PSCF combines meteorology in the form of air parcel back trajectories and composition information to provide the likely source areas for materials transported to the site from distant areas (Gildemeister et al. 2007).

In order to locate sources, other approaches are possible: either the PMF analysis can be applied to samples collected from different sites, located in zones affected by different pollutant fallouts (Jia et al. 2010; Lall and Thurston 2006), or wind data can be combined with composition data in PMF modeling (Begum et al. 2005; Chan et al. 2011).

In order to assess the directional dependence of sources, the importance of taking into account wind data for the interpretation of source contribution estimates from PMF has been widely illustrated. However, all these studies consider wind data after having conducted the sampling. In this study, a new approach was followed. Samplers were coupled with a wind direction and speed sensor. This way, it was possible to have a priori samples connected with different wind conditions. This monitoring strategy is still rarely used (Alleman et al. 2010; Martínez et al. 2010; Venturini et al. 2013b). Alleman et al. (2010) applied PMF analysis to samples collected with a selective sampling device in order to better constrain specific sources. In that study, only the elemental composition data of ambient aerosols were taken into account.

The objectives of this study are both to determine the pollution sources affecting the study area and to identify the prevailing origin direction of the input sources, in order to distinguish the pollutant load from local sources compared to long-range and regional transport. To obtain this, an alternate sampling of the $PM_{2.5}$ suspended in the air masses coming from opposite directions and thus influenced by different sources was undertaken. At the same time, another sampler collected $PM_{2.5}$ in calm wind conditions. For each sample, soluble ions, Organic Carbon (OC), Elemental Carbon (EC), levoglucosan (Lvg), some metals, and Polycyclic Aromatic Hydrocarbons (PAHs) were determined. In order to identify and quantify the various sources affecting the area, PMF analysis was applied. This approach should make it possible to determine the sources of fine particulate by using its dependence on meteorological parameters too. This study also aims to evaluate if PMF applied to samples collected with wind select sampling device can provide further insights compared to a classical PMF analysis.

Experimental methods

Sampling strategy

The sampling site, located in the suburban area of the town of Riccione (Fig. 1), is described elsewhere (Vassura et al. 2014). Before starting the sampling campaign, wind conditions (prevalent directions and speed) were examined. The two principal wind directions in the study area are southwest and northeast (land and sea breeze), roughly perpendicular to the coastline (Venturini et al. 2013a; ARPA 2013). Consequently, the site is alternately downwind of the coastal urban area and of the hinterland, which is mainly characterized by the presence of a municipal solid waste incinerator and a motorway. Samplers were coupled with a wind sensor, which allows the turning on and off of the instrument depending on wind direction and speed. Samplers alternately collected PM suspended in the air masses coming from the two principal wind directions and in calm wind conditions. This way, it was possible to have a priori samples connected with different wind conditions; furthermore, samples were not prevalently associated with one direction, but were connected exclusively with one direction.

Two medium volume samplers (Skypost PM, TCR TECORA), equipped with a $PM_{2.5}$ sampling head were used. Each sampler operated at the flow rate of 38.33 l/min. The characteristics of these samplers fulfill European Method 12341 and US EPA law 40 CFR Part 50 (CEN EN 1998; EPA 2006). In addition to these, a third sampler (ECHO HiVol, TCR TECORA) equipped with a $PM_{2.5}$ sampling head and operating at the flow rate of 200 l/min was used. Thanks to the wind direction and speed sensor, samplers switched on

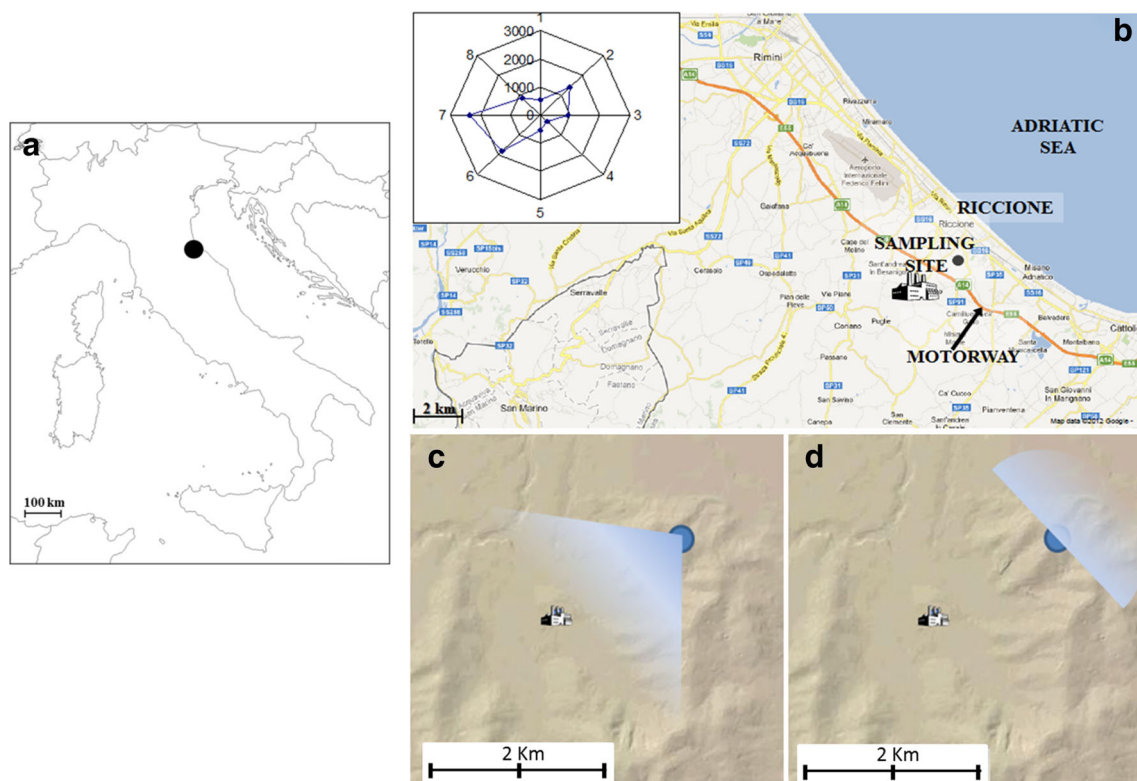


Fig. 1 Studied area and monitoring site **a** on a large-scale map and **b** a local map (from © 2011 Google Images © 2011 [ena]-modified) with principal wind direction in the area and alternate sampling conditions for

either when they were downwind of the inland $\pm 60^\circ$ (120° window) (Fig. 1c) or when they were downwind of the coast $\pm 90^\circ$ (180° window) (Fig. 1d). In the first case, they collected $PM_{2.5}$ coming from the inland and influenced by both the incinerator and the motorway, while in the second case, samplers collected $PM_{2.5}$ coming from the coast and samples were thus influenced by the urban area. The medium volume samplers collected simultaneously $PM_{2.5}$ in the air masses coming from the same direction. At the same time, the high volume sampler collected $PM_{2.5}$ in calm conditions, i.e., when wind speed was lower than 0.5 m/s.

The sampling campaign started on November 29, 2011 and ended on April 28, 2012. This period was chosen because $PM_{2.5}$ mass concentrations are much higher in winter. This is due to low vertical atmospheric mixing in the Po valley region during the winter (Minguillón et al. 2013; Perrino et al. 2013; Province of Rimini and ARPA Emilia Romagna 2011; Squizzato et al. 2012). This is thus the most critical period that involves the greatest concern for PM air pollution. Overall, 60 samples were collected: 31 for calm conditions, 15 influenced by air masses coming from the inland, and 14 influenced by air masses coming from the coast. The input time for each sampling was 48 h. In fact, during this time interval, the samplers collected $PM_{2.5}$ only in the above-mentioned wind conditions. This sampling approach is strongly influenced by wind conditions and on some days it was not possible to collect a

medium volume samplers: **c** sampling window when the samplers collected air masses downwind of the incinerator and **d** sampling window when the samplers collected air masses upwind of the incinerator

sufficient amount of PM for the required analysis. Therefore the filter was left in the sampler and PM continued to be collected for a longer time. More details on the sampling campaign are reported in Supplementary Material (Table S1: Sampling dates, wind conditions, and sampling spans).

Analytical determinations

$PM_{2.5}$ samples were collected on quartz fiber filters (MUNKTELL); the samples influenced by wind direction had a 47-mm filter diameter while calm wind samples had a 102-mm filter diameter.

To determine the ambient concentration of $PM_{2.5}$, the European Standard 14907 was the reference method (CEN EN 2005). After PM quantification, filters were split into parts for the different chemical specie determination. Medium volume samplers simultaneously collected $PM_{2.5}$ coming from the same direction. The sampled filters were considered as a unique sample and each one was used for different chemical specie determination. Filter splits are shown in Table 1.

The subsample dimensions were chosen on the basis of expected air concentration of the different chemical species and of the quantification limits of the methods.

Inorganic ions (SO_4^{2-} , NO_3^- , Cl^- , Ca^{2+} , Na^+ , NH_4^+ , Mg^{2+} , and K^+) were determined by ionic chromatography after filter aqueous extraction (10 ml).

Table 1 Filter splits for the different analyses and filtered air volume range for each subsample

	PAH	OC and EC	Ions	Lvg	Metals
Sample influenced by wind direction (medium volume filter)	Filter 1 (24.1–105 m ³)	1 cm ² punch of filter 2 (2.67–10.5 m ³)	1.6 cm diameter punch of filter 2 (5.36–21.1 m ³)	0.6 cm diameter punch of filter 2 (1.34–5.27 m ³)	Remaining part of filter 2 (19.8–72.5 m ³)
Calm wind condition sample (high volume filter)	Around 1/4 filter (32.1–102 m ³)	1 cm ² filter punch (1.46–9.20 m ³)	1 or more filter punches of 1.6 cm diameter (7.65–18.5 m ³)	1.6 cm diameter filter punch (2.93–18.5 m ³)	Around 1/4 filter (28.2–108 m ³)

The thermal–optical transmittance technique by the Sunset Carbon Analyzer Instrument was used to determine EC and OC mass concentrations by using high-temperature protocol (Piazzalunga et al. 2011).

Four-, five-, and six-ring compounds of US EPA PAHs priority pollutant list (fluoranthene, Flu; pyrene, Pyr; benz[a]anthracene, B(a)A; chrysene, Cri; benzo[b]fluoranthene, B(b)F; benzo[k]fluoranthene, B(k)F; benzo[a]pyrene, B(a)P; dibenz[a,h]anthracene, D(a,h)A; benzo[ghi]perylene, B(g,h,i)P; indeno[1,2,3-cd]pyrene, I(1,2,3)P) were determined by HPLC with a fluorimetric detector.

The Lvg extraction procedure was based on the method suggested by Fabbri et al. (2008). Extracts were analyzed by GC-MS.

Metals (Cd, Cu, Ni, Pb, Fe, and Zn) were determined after the mineralization of filters and the analysis by an atomic absorption spectrometer.

Details of the techniques and of PM determination are reported in the supplementary material provided by Vassura et al. (2014). Information on quality control procedures are offered in the Supplementary Material (SM).

Statistical analysis

Positive Matrix Factorization

The two-dimensional Positive Matrix Factorization model (PMF2) for source apportionment assumes that the measured concentrations are linear sums of constant profiles from all of the contributing sources (Ogulei et al. 2006a). Mathematically, the model is (Paatero 2007)

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

where X(*n*×*m*) is the data matrix; *n* and *m* are the number of samples and species, respectively. G(*n*×*p*) is the contribution matrix where *p* is the number of source factors extracted. F(*p*×*m*) is the factor score matrix. E(*n*×*m*) is the unexplained part of X. The elements in G and F are constrained to non-negative values only. Then, the task of PMF2 is to minimize the residual sum of squares, *Q*, given by:

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left(\frac{e_{ij}}{s_{ij}} \right)^2 = \sum_{i=1}^n \sum_{j=1}^m (r_{ij})^2 \tag{2}$$

where *e_{ij}* are the elements in E and *s_{ij}* are the estimated standard deviations of the measured concentrations. The ratio between *e_{ij}* and *s_{ij}* (i.e., *r_{ij}*) represents the scaled residuals.

Details of this method appear in the supplementary material provided by Venturini et al. (2013a) and in the SM of this article.

Information about the input concentration matrix for PMF analysis (chemical species included in the PMF analysis, missing values, values under detection limit) is reported in Table 2. One of the advantages of PMF, when compared to other factorial analysis, is that measure uncertainties and below detection limit data can be managed. In general, more of the data can be retained in the analysis than is possible with eigenvector-based approaches where such a high level of “missing” data would have resulted in badly distorted results (Hopke 2000). For this reason, all the determined species were included in the analysis. The optional parameter “BDLneg r1 r2” was used. Std-dev *s_{ij}* of missing or BDL values was dynamic weighted in order to achieve correct BDL and missing values handling.

The appropriate number of factors extracted and the value of C3—a constant of the equation used to calculate standard deviations (see SM)—were determined based on satisfying most of the following criteria (the first four criteria were based on Lee et al. (1999) and Venturini et al. (2013a))

- Value of *Q* close to *n*×*m*−*p*×*m*−*p*×*n* (i.e., the degree of freedom of the analysis).
- R90 (the 90 percentile of the scaled residuals, *r_{ij}*) is within ±2. That is, most of the residuals are within 2.
- A sharp drop in IM (the maximum of the mean values of *r_{ij}* of each species) and/or IS (the maximum of the S.D. of *r_{ij}* of each species).
- A significant increase in the largest rotmat element
- Reasonable estimated source profiles.

Three to 12 different factors and different values for C3 were tested, but only six factors and C3=0.09 were found to comply with all the required constraints and resulted in physically meaningful solution. The optimal *Q* value obtained with this model was 1,222, which compares reasonably well with the theoretical value of 1,098 for the six-factor model. R90 was within ±2. Specifically, 97 % of the residuals were within

Table 2 Number of data Below Detection Limits (BDL) and missing for PMF analysis, air concentration Geometric Means (GM) and Geometric Standard Deviations (GSD) of PM_{2.5} and its determined components for air masses coming from inland, from the coast, and sampled in calm conditions

	Number of BDL values (%)	Missing values	Mean yearly limit value (ng/m ³)	GM coast (ng/m ³) ^a	GSD coast	GM calm (ng/m ³) ^a	GSD calm	GM inland (ng/m ³) ^a	GSD inland
PM _{2.5}	NA	NA	25,000	24,227	1.58	29,221	1.53	27,400	1.79
Na ⁺	0 (0.0)	2		126	1.89	74.2	1.60	101	1.43
NH ₄ ⁺	0 (0.0)	2		1,299	1.98	1,666	2.15	1,869	2.34
K ⁺	11 (19.0)	2		126	2.83	113	3.51	144	2.39
Ca ²⁺	4 (6.9)	2		116	1.47	103	1.64	115	1.43
Mg ²⁺	50 (86.2)	2		37.7	1.62	20.0	1.32	25.8	1.69
Cl ⁻	6 (10.3)	2		257	2.44	200	3.05	217	2.12
NO ₃ ⁻	0 (0.0)	2		2,254	2.64	4,547	2.44	4,523	2.59
SO ₄ ²⁻	0 (0.0)	2		1,831	1.96	1,653	1.77	1,679	1.76
OC	0 (0.0)	2		6,373	1.54	6,740	1.59	4,756	1.98
EC	0 (0.0)	2		628	1.95	970	1.42	1,040	3.04
LVG	0 (0.0)	2		216	2.80	201	2.25	208	2.55
Cd	4 (6.9)	2	5	0.17	1.61	0.09	2.10	0.12	1.43
Pb	0 (0.0)	2	500	9.11	1.72	5.82	2.13	8.12	1.69
Cu	0 (0.0)	2		7.31	1.65	3.55	1.63	5.42	1.33
Ni	0 (0.0)	2	20	3.10	1.41	1.92	1.51	2.05	1.37
Fe	8 (13.8)	2		101	1.81	92.2	1.52	112	1.92
Zn	39 (67.2)	2		35.4	1.98	10.5	1.79	22.9	2.74
Flu	11 (19.0)	2		0.21	3.67	0.18	3.02	0.15	2.72
Pyr	17 (29.3)	2		0.26	3.30	0.24	2.63	0.19	2.71
B(a)A	6 (10.3)	2		0.12	4.68	0.13	2.64	0.10	2.13
Cri	2 (3.4)	2		0.23	3.48	0.26	2.41	0.21	1.94
B(b)F	0 (0.0)	2		0.37	3.35	0.41	2.19	0.37	1.63
B(k)F	2 (3.4)	2		0.13	3.08	0.14	2.19	0.13	1.73
B(a)P	1 (1.7)	2	1	0.18	3.28	0.21	2.72	0.18	2.16
D(a,h)A	10 (17.2)	2		0.08	2.74	0.08	2.57	0.07	1.44
B(g,h,i)P	1 (1.7)	2		0.27	2.76	0.32	2.14	0.29	1.65
I(1,2,3)P	5 (8.6)	2		0.23	3.81	0.24	2.81	0.22	1.73

NA not applied, i.e., not insert in PMF analysis

^a When the component concentration was below the limit of quantification, air concentration was calculated using ½ DL, as suggested by the Italian National Institute of Health (ISS) (Menichini et al. 2004)

±2. Six factors explained >75 % of the variations in most species. The rotational state of the result was controlled by the “peaking parameter” FPEAK. The solution with FPEAK=0 (no rotation) resulted in the most physically meaningful solution.

Multi-Linear Regression

In order to quantitatively estimate the mass contributions of the six resolved sources, the fine PM mass was regressed against factor scores by using Multi-Linear Regression (MLR). The linear regression constant was assumed to be zero. This regression process also provided an additional test for the PMF model as well as the appropriate number of factors that

had been chosen for the analysis. An unrealistic number of factors for the PMF model very often resulted in negative values for the MLR coefficients (Ramadan et al. 2000). For the six-factor solution, the regression coefficients obtained were all positive values. *p* values lower than 0.05 for four of the six factors, such as *R*-squared value (0.950), statistically indicate that the observed PM mass concentrations were represented quite well by the resolved six factors (Table S3: Multiple regression analysis of fine particles parameters. Reported in Supplementary Material). The third factor shows a high standard deviation value of the MLR coefficient (*p* value=0.451); therefore, the results for this factor should be misleading. A summary of regression results is in Table S3.

Results and discussion

Pollutant air concentrations

Geometric means for PM_{2.5} and its determined components are shown in Table 2, while a complete overview of the results obtained is given in Supplementary Material (Table S4: Air concentrations of PM_{2.5} and its components). Samples have been split in order to compare air masses coming from the inland, from the coast, and connected with calm conditions. PM_{2.5} mean concentrations are 29 µg/m³ for coast samples, 32 µg/m³ for inland samples, and 32 µg/m³ for calm wind samples. These values are above the European law limit of 25 µg/m³ (yearly mean) that will become mandatory in 2015 (EC 2008). Samples were mainly collected in cold months and, therefore, do not represent a yearly mean, where the summer months contribute to reducing the mean PM_{2.5} concentration. Nevertheless, the registered values are quite high and the study area proves to be subject to a significant pollutant load and worth monitoring. As for other regulated pollutants, i.e., Cd, Pb, Ni, and B(a)P, they are well below legislation limits.

Main PM components are nitrates, ammonium, and sulfates, connected with secondary particulate matter, and OC. EC contribution is also important. Generally, contaminant concentrations are similar to what is found in other suburban sites and markedly lower than urban concentrations (Akyüz nad Çabuk 2008; Bourotte et al. 2005; Canepari et al. 2009; Fabbri et al. 2008; Hueglin et al. 2005; Lonati et al. 2005; Marcazzan et al. 2003; Na and Cocker III 2009; Pashynska et al. 2002; Perrone et al. 2011; Yin et al. 2005). Among the components determined, OC is the only one that shows a concentration which can be considered quite high in comparison with what is generally found in other sites (Alolayan et al. 2013; Hueglin et al. 2005; Niu et al. 2013; Perrone et al. 2011; Pey et al. 2009; Qadir et al. 2013; Zhang et al. 2013). The highest concentrations are registered during the first samplings, i.e., in November and December. In 2012, concentrations decreased; nevertheless, they continue to be particularly high (Table S4, reported in Supplementary Material).

As expected, PM_{2.5} concentration is higher in calm condition samples (Squizzato et al. 2012). Winds generally lead to a greater atmospheric mixing, which tends to disperse pollutants, and therefore decrease their air concentration. OC and PAHs show the same trend.

Ammonium, EC, potassium, and iron concentrations are higher in air masses coming from inland and may thus be somehow connected with the incinerator or motorway activity.

Nevertheless, the variability is very high and it is difficult to arrive at definitive, proven conclusions. Therefore, a deeper data analysis is essential for obtaining information on the effect of the sources impacting the area.

Source apportionment

Source profile

The overall mass concentration profiles of the six factors are shown in Fig. 2. The first factor consists mainly of OC and sulfate: 41 and 31 %, respectively. Sulfate formation and transport are of a regional nature; therefore, this factor can be identified as regional transport (Liu et al. 2005; Saarikoski et al. 2008). Sulfate is a secondary material, since it is due to the oxidation of SO₂, and it is usually associated with other secondary materials, such as OC (Pekney et al. 2006). By considering the molar ratio NH₄⁺/SO₄²⁻, sulfate is in strong excess. This may be due either to the evaporation of ammonium during sample analysis (Liu et al. 2005) or to other sources of sulfate, e.g., marine spray. Indeed, this factor is also made up of sodium (4 %), magnesium (2 %), calcium (4 %), chloride (3 %), and iron (3 %). This suggests that, in addition to secondary materials, the regional transport aerosol was also made up of marine spray and resuspended soil (Saarikoski et al. 2008). Sodium origin is usually connected with sea contribution, while calcium is one of the main constituents of soil.

The second factor may be associated with secondary aerosol factor. This factor consists of high concentrations of nitrate and ammonium: 82 % for the former and 54 % for the latter were loaded in this factor. Sulfate (53 %) and potassium (40 %) and a small amount of chloride (17 %) and OC (20 %) were also associated with this factor. This may also be explained by the secondary aerosol formation process, as previously mentioned. Nitrate is due to the conversion of NO_x, emitted both by vehicular traffic and by other combustion processes. The presence of potassium, a marker of biomass combustion, suggests that NO_x is also emitted from this source. PMF results reported in other studies show a similar behavior, with the presence of potassium in secondary aerosol factor (Liu et al. 2005; Tao et al. 2013).

The third factor is biomass burning, mainly characterized by levoglucosan: nearly all (85 %) of the latter was loaded into this factor. This is probably related to local residential and commercial biomass burning and local agricultural burning. Other major contributors in the chemical profile are NO₃⁻, OC, and EC. The presence of a large fraction (31 %) of potassium (another tracer for biomass combustion) and chlorine (64 %) in the factor profile confirms the attribution of the biomass burning source to this factor (Bernardoni et al. 2011). Pb and PAHs, especially the heaviest, can also be markers of wood smoke, as demonstrated in Vassura et al. (2014). Twenty-one percent of lead was associated with this factor, while between 35 and 55 % of PAHs were represented by this factor. Because of the high contribution due to secondary components (e.g.,

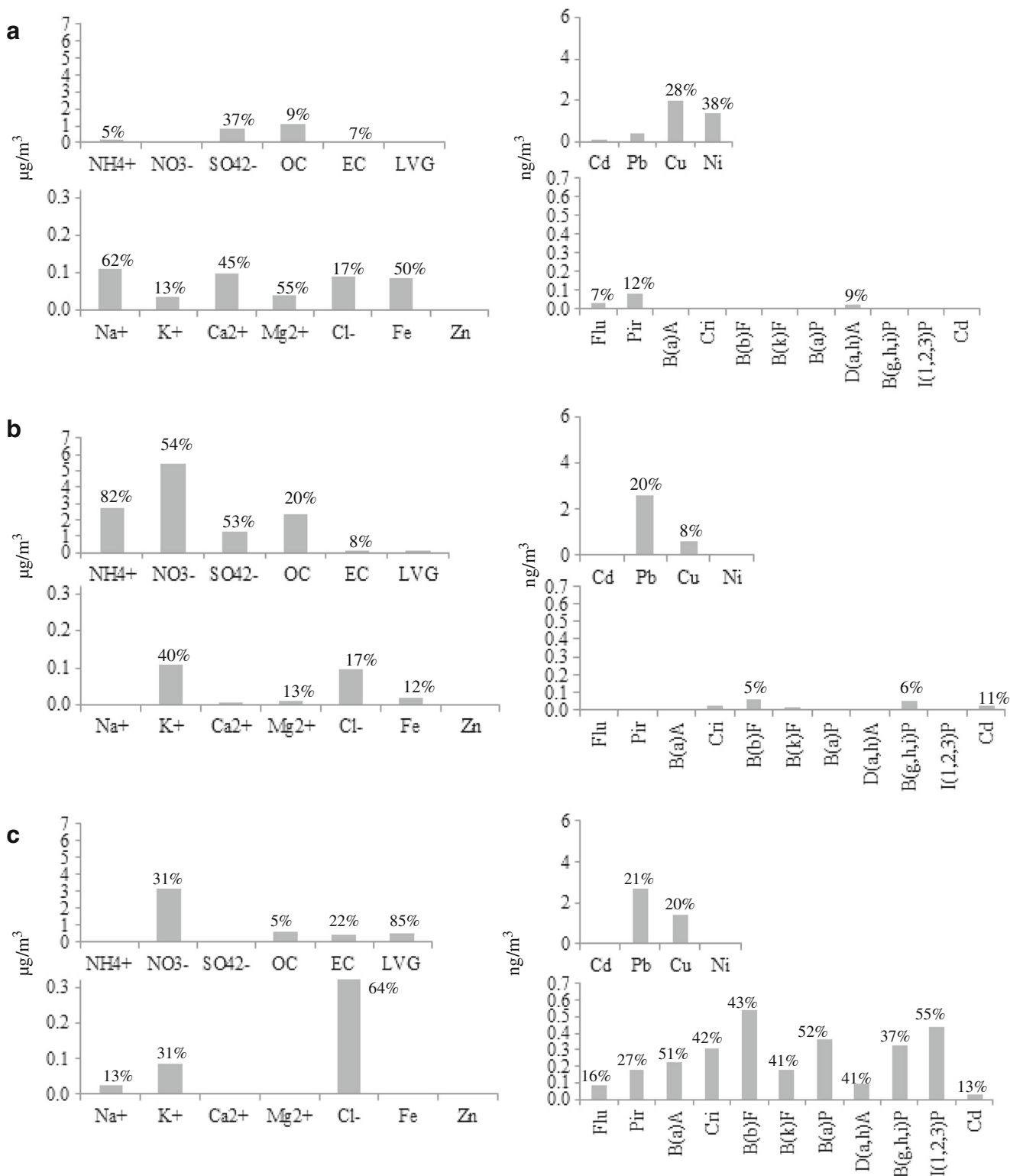


Fig. 2 Source profiles in mass concentration for factor 1 (a), factor 2 (b), factor 3 (c), factor 4 (d), factor 5 (e), and factor 6 (f). The components determined are shown in four charts, depending on their concentration.

The percentage contribution of the factor to each chemical component is also reported

NO_3^-), the factor represents both primary and secondary emissions of the biomass burning (Bernardoni et al. 2011). PAHs diagnostic ratios are frequently used to

identify the origin of PAHs in ambient air (Manoli et al. 2004; Mantis et al. 2005). Many studies (Akyüz and Çabuk 2008; Amador-Muñoz et al. 2013; Manoli

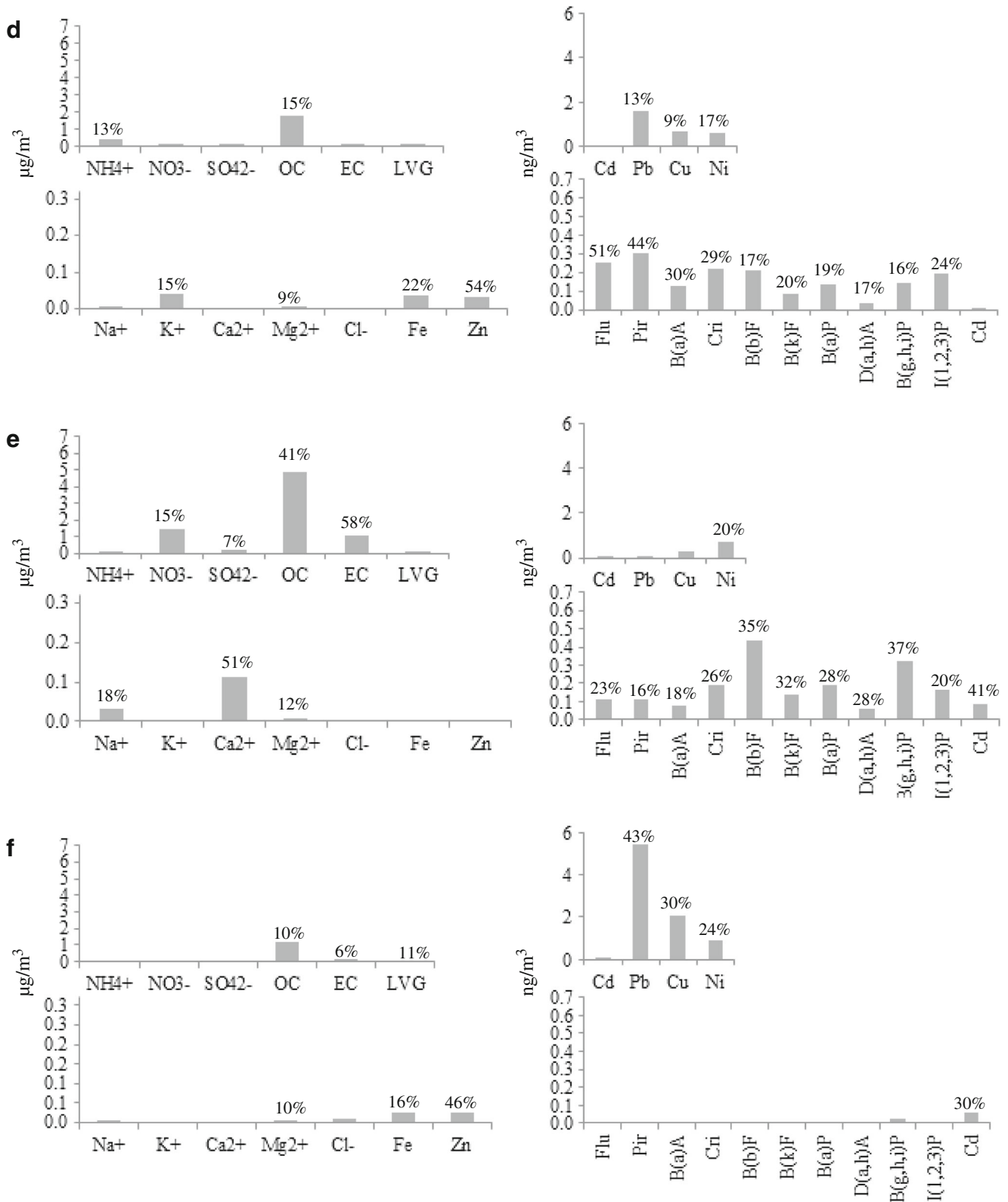


Fig. 2 (continued)

et al. 2004; Mantis et al. 2005) have agreed on two wood combustion diagnostic ratios: $I(1,2,3)P / (I(1,2,3)P + B(g,h,i)P) = 0.62$ and $B(a)A / (B(a)A + Cr) =$

0.43. The values of ratios in this factor are 0.57 for the former and 0.42 for the latter. These results confirm the above-established attribution to biomass combustion

and suggest a connection specifically with wood combustion.

Fifty-one percent of Flu, 44 % of Pyr, 54 % of Zn, and 22 % of Fe were associated with the fourth factor. Flu and Pyr are markers of several emission sources: diesel emission, wood combustion, coal combustion, natural gas, incineration process, oil burning, and gasoline-powered vehicles (Besombes et al. 2001; Bourotte et al. 2005; Fang et al. 2004; Lakhani 2012; Ravindra et al. 2006; Rogge et al. 1993). Nevertheless, diesel emission is also characterized by other markers, such as EC, B(b)F, and B(k)F, which are not well represented by this factor (Bourotte et al. 2005; Ravindra et al. 2006). Wood combustion should have a higher contribution of B(a)P (Bourotte et al. 2005). In addition to this, our previous study (Vassura et al. 2014) demonstrated that Flu and Pyr are the less abundant PAHs during a bonfire event. Lastly, Lvg is not represented by this factor. This factor is unlikely to represent gasoline vehicles, since B(g,h,i)P is the best marker for this source (Ravindra et al. 2006), but it is represented only 16 % by this factor. By considering the source profile, coal and natural gas combustion should be good candidates, due to the high contribution of B(a)A and Cri also (Bourotte et al. 2005; Lakhani 2012; Ravindra et al. 2006; Simcik et al. 1999). Coal combustion sources are not present in the study area, while natural gas is the most widespread fuel used for domestic heating. Considering the emission inventories for the area, the emissions of non-industrial sources (i.e., hot water heating, gas and oil heaters, fireplace, and cookers) account for about 70 % of the total PAHs emissions (ISPRA 2010); this factor may thus be attributed to emissions from natural gas home appliances (Masiol et al. 2012), even if there is no evidence that correlates Zn, which as mentioned above is represented 54 % by this factor, with this emission source. Incinerator emissions might also be a good candidate for this factor. Fe and Zn in PM_{2.5} are good markers of the incineration process (Azimi et al. 2005; Gratz and Keeler 2011; Ogulei et al. 2006b), even if they could also be emitted by vehicle exhaust (Lough et al. 2005; Sternbeck et al. 2002). Probably more sources contribute to this factor. Factor scores could help in the attribution of this factor, which seems to be mainly ascribable to natural gas combustion or incinerator.

Most of OC (41 %) and EC (58 %) are loaded in the fifth factor. EC is a well-known marker of vehicular traffic and the primary organic aerosol is formed during combustion processes; therefore, it is present in vehicular exhausts. Fifty-one percent Ca²⁺, the main road dust component determined, 41 % Cd, and 20 % Ni, elements that can be ascribed to fossil fuel combustion (Betha and Balasubramanian 2011; Horemans et al. 2011; Karar and Gupta 2007; Pulles et al. 2012; Wang et al. 2003), are loaded in the fifth factor. This confirms the attribution to motor vehicle emissions (Liu et al. 2005; Tao et al. 2013). This factor is composed of 63 % OC, 19 % NO₃⁻, and 14 % EC. The strong excess of OC compared to EC and the presence of nitrates indicate that this factor also represents secondary traffic

emissions (Bernardoni et al. 2011). PAHs are also well represented by this factor; among them, B(b)F (35 %), B(k)F (32 %), and B(g,h,i)P (37 %) show the greatest loadings. B(b)F and B(g,h,i)P are components of fossil fuels and a portion of them is associated with their combustion (Yang et al. 2013).

The bulk of the sixth factor (77 %) is composed of OC, but its peculiar characteristic is that most of the Cd, Pb, Cu, Ni, Fe, and Zn masses are attributed to this factor (30, 43, 30, 24, 16, and 46 %, respectively). These elements are quite common in a number of source categories, including motor vehicles, waste incinerators, soil dust, etc. This factor explains most of the Zn and Pb, which are incinerator markers (Gratz and Keeler 2011; Olmez et al. 1988; Pacyna and Pacyna 2001; Polissar and Hopke 2001); furthermore, the total factor profile is similar to what is reported in Ogulei et al. (2006b) and defined as waste incinerator source. The Zn/Pb ratio was equal to 4.9 for this factor, which is about half of the 11 ratio for the fuel gases of the waste incinerator close to the sampling site. In general, a factor with high mass fractions of Zn, Fe, and Pb likely represents a general industrial source (Liu et al. 2005). The study area is not characterized by major industries. Nevertheless, several manufacturing activities (metalworking, harbor areas) are present. These kinds of activities are likely characterized by the same markers.

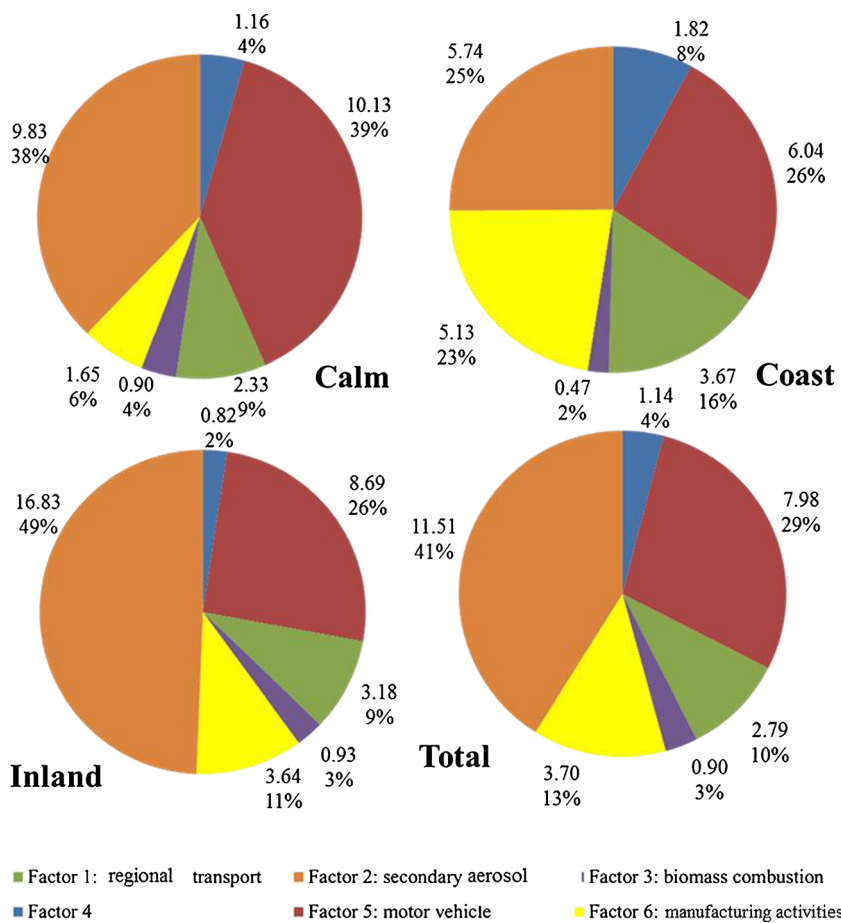
Factor contribution and comparison among air masses

The contribution due to calm conditions, to air masses coming from the coast and from the inland, and the total pollutant load was assessed. By considering the input and the effective sampling span, it was possible to determine the time percentage in the entire period when each of the three conditions is present in the area. Thirty percent of the total time was characterized by calm conditions, 42 % by air masses coming from the inland, and 28 % by air masses coming from the coast.

To quantitatively estimate the mass contribution of the six resolved sources, the fine PM mass was regressed against the factor scores by using MLR. Then, the median contribution of the six sources to the total pollutant amount was considered, by giving a different load to the three conditions on the basis of the temporal percentage contribution reported above. The median contribution of the six sources to calm conditions, to the air masses coming from the coast, and to the air masses coming from the inland was also assessed (Fig. 3). This procedure should help in the identification of local and regional sources. Regional sources contribution should be higher when wind speed is higher (i.e., not in calm wind conditions), since the inefficient atmospheric mixing of calm wind conditions should avoid that regional air masses affect the sampling area.

The main source of PM_{2.5} in the area is secondary aerosol; its contribution to the total PM_{2.5} was 41 %. The greatest contribution is due to the air masses coming from the inland: the median value of the source contribution to these air masses is almost three times higher than in coastal air masses, where

Fig. 3 Median contribution (percentage and concentration in microgram per cubic meter) of each factor to PM for calm conditions, inland air masses, coastal air masses, and total



secondary aerosol is not even the main source. This behavior might suggest that this source is somehow correlated with the incinerator. However, secondary aerosol is not a primary source and the distance between the sampling site and the incinerator is too short to justify the conversion of NO_x and SO_x to nitrates and sulfates. Therefore, this source should have a more distant origin and be due to regional contributions.

The motor vehicle emission source contributes for 29%. In this case, the greatest contribution is due to calm conditions. In these air masses, as in coastal ones, the contribution of both this factor and the secondary aerosol factor is almost the same. Only in inland air masses is secondary aerosol contribution markedly higher, and this supports an inland origin for this source. Since the highest contribution for motor vehicle emission is due to calm conditions, this source likely has a prevalent local origin.

The manufacturing activity source contributes for 13%. The greatest contribution comes from the air masses coming from the coast. This result confirms the attribution of this factor to manufacturing activity source rather than to the incinerator, since the above-mentioned manufacturing activities are mainly localized in the coastal area. Due to the low contribution to calm condition air masses, this source is not likely strictly local. These results made it possible to confirm, as reported in Venturini et al. (2013a), Venturini et al. (2013b) and Vassura

et al. (2011), that even though the incinerator is an emission source—one which commonly creates concern in public opinion—its relative contribution to the total pollutant load seems negligible compared to other sources affecting this area.

Regional transport accounts for 10%. As expected, the contribution of calm conditions (i.e., of local sources) is the lowest, while the main contribution is from coastal air masses, since this factor is also made of marine spray.

On the basis of source profile, more sources seem to contribute to the fourth factor; the source that probably contribute the most to the factor is incinerator emissions or natural gas home appliances. This factor accounts for 4% to the total PM_{2.5}. The main contribution is due to coastal air masses, while inland air mass contribution is the lowest. Therefore, the incinerator unlikely contributes to this factor, but more likely, natural gas home appliances are the main responsible of this factor. This is confirmed also by the significant inverse correlation ($R=-0.70$, p value <0.001) between temperature and the factor. Certainly, other sources contribute, and the high concentration of Zn is ascribable to them. Even if the factor cannot be solely linked to this source, to simplify further discussion, it will be called natural gas home appliances.

Biomass combustion is the factor which presents less significant MLR results, due to the high p value (see MLR

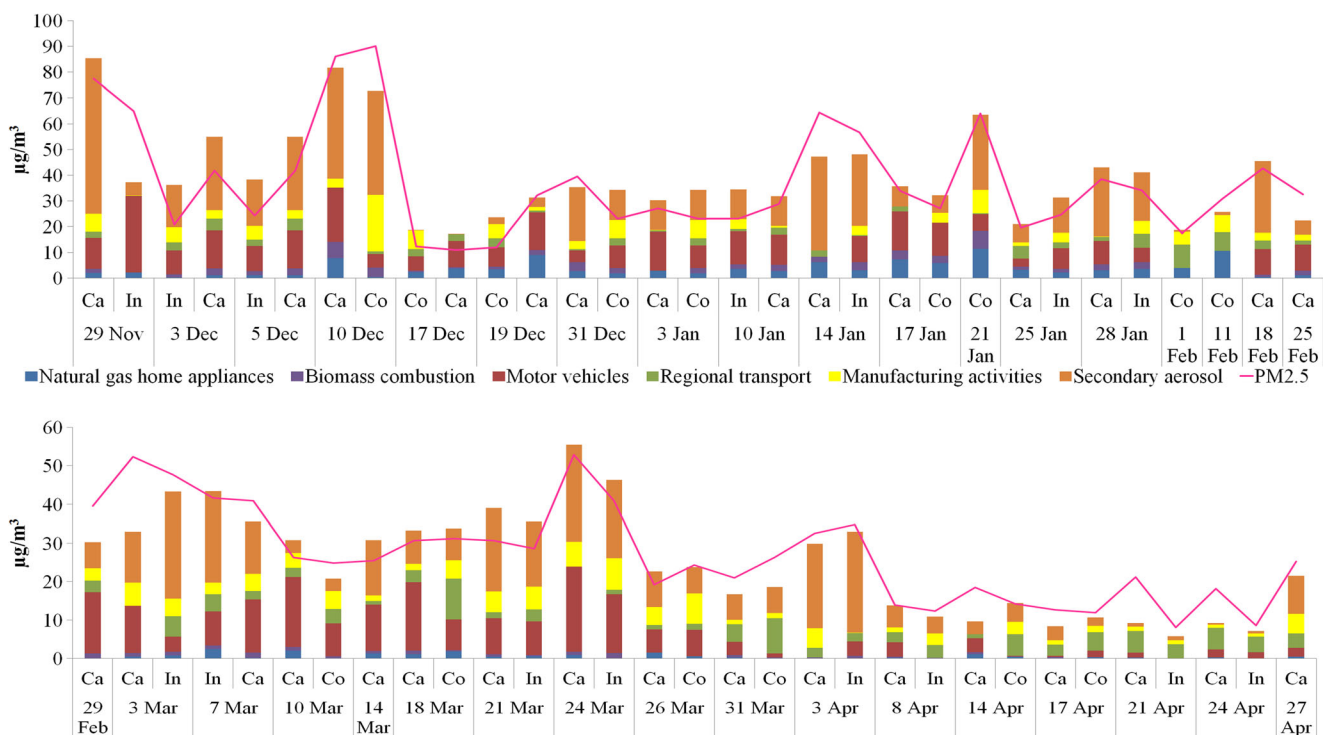


Fig. 4 Temporal trend of factor contribution to PM_{2.5} and of PM_{2.5}. *Ca* calm; *Co* coast; *In* inland. The reported data refers to the start of the sampling

paragraph). Nevertheless, its contribution to the total PM_{2.5} is very low (2 %) and these data affect little the overall results. The main contribution is made by calm conditions and inland air masses. Therefore, the source origin should be local and stronger from inland. This kind of combustion, which is also used for domestic heating, should be more widespread in rural areas than in town. The connection of this source to domestic heating is confirmed by the significant inverse correlation ($R=-0.48$, p value <0.001) between temperature and the factor.

In Fig. 4, the temporal trends of the source contribution and of PM_{2.5} are reported. As expected, the contribution of sources related to domestic heating, e.g., natural gas home appliances and biomass combustion, is higher in winter and decreases at the approach of spring. The secondary aerosol contribution is similar throughout the whole sampling period; only April

samples show a lower contribution. This is consistent with PM_{2.5} concentration, which decreases in April. The motor vehicle emission factor concentration in April is also lower, while regional transport factor concentration increases as spring approaches; this is due to the increase in photochemistry, due to an increase in solar intensity that favors the formation of particulate sulfate (Pekney et al. 2006). Its percentage contribution to PM is particularly high during the last sampling days and during samplings characterized by snowfall (1–2 February and 11–12 February). These last samplings were characterized by high speed winds. Calm conditions were never present (in fact, the calm condition sampler did not collect PM on these days), the minimum wind speed values registered were 1.4 and 3.5 m/s, respectively. Regional transport factor contribution is thus higher when

Table 3 Median percentage contribution of each factor to metals and PAHs in PM_{2.5}

Percent	Natural gas home appliances	Motor vehicles	Regional transport	Biomass combustion	Manufacturing activities	Secondary aerosol
PAHs	9	68	2	11	1	10
Cadmium	0	55	2	2	19	22
Lead	3	0	2	4	36	54
Copper	3	9	23	5	32	28
Nickel	5	41	27	0	23	3
Iron	7	0	38	0	16	38
Zinc	26	0	0	0	73	0

wind speed is higher, consistent with the nature of the source itself. Manufacturing activity emissions is the only source that shows a different temporal trend between calm condition air masses and the coastal and inland ones. While in calm condition air masses the contribution is similar throughout the entire period, in inland and coastal air masses the contribution is lower in April.

Other Pearson correlation results can be found in Supporting Material (Table S5: Pearson correlation coefficients among the factors, PM_{2.5} concentration and temperature. Significant correlations ($p=0.001$) are reported in bold).

Among the components analyzed, heavy metals and PAHs are those which cause the greatest concern, due to their toxicity; metals are also persistent in the environment. Therefore, it is important to assess the main sources of these constituents in the area (Table 3). This was achieved through the analysis of factor scores multiplied by the concentration of the constituent in the factor.

The main PAH source in the area is vehicular traffic. Up to 67 % PAHs is due to this source. This high contribution can be found in all the air masses, and a minimum of 64 % PAHs is ascribable to this source. Other appreciable PAH sources are natural gas home appliances, biomass combustion, and secondary aerosol, which contribute for about 10 % each.

As far as metals are concerned, vehicular traffic is also the main source of Cd and Ni, consistent with their principal source, i.e., fossil fuel combustion. Manufacturing activities are an important source of metals in the area, and the main one for zinc and copper. Secondary aerosol is also an important source of metals. Even if metal concentration in the source profile is very low, the high impact the source has on the area justifies the result. Secondary particulate can form after condensation on preexisting particulate which may contain these metals.

Conclusion

In order to develop an effective and efficient strategy to manage air quality, it is important not only to identify the various sources and to quantify their contribution to the ambient concentration of particulate matter but also to locate them and to examine if they are regional or local. For this purpose, PMF analysis was applied to PM_{2.5} collected with samplers coupled with a wind select sensor. This new approach made it possible for us to obtain more detailed results on the sources affecting the area, compared to a classical PMF analysis. This is mainly due to the greater environmental information that samples collected with this new sampling technique have. Not only were the main PM_{2.5} sources affecting the area resolved, as is the case with every PMF analysis, but the main origin direction of the sources was also determined, thus making it possible to obtain a more correct factor

interpretation. By assessing the directional contribution of the different air masses to the factors and knowing the study area, attribution of factors to sources can be more appropriate.

Furthermore, local and regional contributions to the main sources affecting the area were determined: most probably, sources related to domestic heating and vehicular traffic have a local origin, while secondary sources are mainly due to regional contributions.

Since several studies have shown an association between increased PM_{2.5} concentrations and adverse health effects, an evaluation of the toxicological load of the resolved sources was carried out. The most toxic components determined, i.e., PAHs, Cd, Pb, and Ni, are mainly due to vehicular traffic. Even if vehicular traffic is not the main source in the study area, its prevalent local origin and its contribution of toxic components make it the source of greatest concern for the area and thus the one it is worthy to operate on the most, at least in an attempt to reduce metal and PAHs concentration.

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