A mass closure and PMF source apportionment study on the sub-micron sized aerosol fraction at urban sites in Italy

R. Vecchi[a],*, M. Chiari[b], A. D'Alessandro[a], P. Fermo[c], F. Lucarelli[d], F. Mazzei[e], S. Nava[b], A. Piazzalunga[c], P. Prati[e], F. Silvani[a], G. Valli[a]

[a]*Institute of Applied General Physics, University of Milan, and INFN, 20133 Milan, Italy*
[b]*National Institute of Nuclear Physics, INFN-Florence, 50019 Florence, Italy*
[c]*Department of Inorganic, Metallorganic and Analytical Chemistry, University of Milan, 20133 Milan, Italy*
[d]*Department of Physics, University of Florence, and INFN, 50019 Florence, Italy*
[e]*Department of Physics, University of Genoa, and INFN, 16146 Genoa, Italy*

Abstract

Sub-micron sized particles are of increasing concern owing to their effects on human health and on the environment. Up to now there are still very few studies on PM1 (i.e. particulate matter with aerodynamic diameter smaller than $1\,\mu m$) chemical characterisation; the sub-micron sized fraction is not under regulations although it is of interest because it is almost exclusively associated to anthropogenic sources. To perform the first large-scale assessment of sub-micron sized aerosol concentrations, composition and sources, two monitoring campaigns at three urban sites in Italy were carried out during the wintertime and summertime of 2004.

Chemical characterisation (elements, soluble ionic fraction, elemental and organic carbon) was carried out on PM1 samples: major contributions were due to organic matter (about 30% in summer and 50% in winter) and ammonium sulphate (about 10% in winter and 40% in summer). During the cold season, nitrates also contributed up to 30% in Milan (lower contributions were registered at the other two urban sites). Chemical mass closure was achieved with an unaccounted mass in the range 14–22%. Positive Matrix Factorisation (PMF) was applied to identify the major sub-micron sized particles' sources.

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1. Introduction

In the last few years, a large interest for aerosol fine particles has increased within the research community. Literature studies suggest that atmospheric particles of small sizes ($<2.5\,\mu m$) are responsible for health effects in urban polluted areas because they act as carriers for toxicants and mutagenic components (Pope and Dockery, 2006 and reference therein).

Elevated particulate matter (PM) concentrations in urban areas originate not only from direct emissions but also from gas-to-particle conversion

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*Corresponding author at: Institute of Applied General Physics, University of Milan, 20133 Milan, Italy.
Tel.: +39 02 50317498; fax: +39 02 50317496.

E-mail address: roberta.vecchi@unimi.it (R. Vecchi).

in the atmosphere and secondary aerosols are mainly in the accumulation mode, i.e. between 0.1 and 1 μm (EPA, 2004). Sub-micron sized particles show the highest atmospheric number concentration at urban locations, typically up to 10^4–10^5 particles cm^{-3}. The PM fine fraction control is a challenging problem, especially in cities where large populations are exposed to high concentrations. To set up effective abatement strategies the knowledge of fine particle physical–chemical properties as well as the identification and quantification of emission sources is mandatory. Many papers in the literature deal with PM10 and/or PM2.5 chemical composition also at the same sites investigated in this paper (Marcazzan et al., 2001; Lucarelli et al., 2004; Ariola et al., 2006). However, there are still few investigations on PM1, although it is almost exclusively associated to anthropogenic sources and has relevance in exposure studies. Moreover, available data on PM1 mass concentration and composition are often limited to short measurement campaigns and/or to a single site (Putaud et al., 2002; Vecchi et al., 2004; Spindler et al., 2004). Preliminary results show that PM1 contributes largely to PM10 and PM2.5; thus, the attainment of the EU limit (EU Directive 99/62) in force for PM10 and the provisional limit for PM2.5 becomes increasingly difficult.

To have a wide outlook on PM1 mass concentration and chemical composition of sub-micron sized aerosol, we performed two measurement campaigns (in winter/summer periods) at three Italian towns with different characteristics. As far as we know, this was the first large-scale investigation on PM1 in Italy and likely in Europe. As a part of this research project, Positive Matrix Factorisation (PMF) was applied to aerosol elemental composition data aiming at the identification of PM1 major sources and at the estimation of their contributions to mass concentrations.

2. Materials and methods

2.1. Sites description

The monitoring campaigns were performed at three major Italian towns (Milan, Genoa, and Florence) with differences in their orography, extension, population and emission sources.

Milan (MI, 45°28′N; 9°13′E) with about 1,500,000 inhabitants is the second largest town in Italy; considering the whole area of the Milan province, the population rises up to about 4 millions. Milan is situated in the Po valley (North-ern Italy), which is heavily industrialised, trafficked and populated; indeed, it is one of the largest pollution hot spots in Europe. It is characterised by a typical continental climate, and very frequent stable atmospheric conditions occur especially during wintertime. Genoa (GE, 44°24′N; 8°55′E) is the most populated (about 600,000 inhabitants) coastal town in the north-west of Italy. In Genoa there is one of the largest harbours in Italy, together with steel factories and power plants. It has a Mediterranean climate with stable atmospheric conditions during summertime. Florence (FL, 43°47′N; 11°17′E) is located in central Italy and it is the smallest among the investigated towns (about 400,000 inhabitants). Commercial and tertiary activities are the most important, due to the huge number of tourists visiting the town. Its location in a closed basin and its continental climate favour atmospheric stability conditions during wintertime.

2.2. PM sampling and mass measurement

Samplings were carried out in parallel in MI, GE, and FL, and the same experimental methodology for sampling and mass determination was applied. The sampling sites were background urban locations, not directly influenced by traffic emissions. Aerosol samples were collected daily during wintertime (December 2003–March 2004) and summertime (June–September 2004) using sequential CEN-equivalent samplers (flow rate: 2.3 m^3 h^{-1}) equipped with PM1 inlets. Twenty-four hour samplings were carried out daily alternating PTFE and pre-fired quartz fibre filters; different filter types were necessary to achieve the chemical characterisation of the samples as for elements, ions, elemental (EC) and organic carbon (OC).

The PM1 mass was gravimetrically determined by the three laboratories involved in the research, using microbalances (sensitivity 1 μg) located in air-controlled weighing rooms ($T = 20 \pm 1\,°C$ and RH $= 50 \pm 5\%$) where the filters were conditioned for 48 h before weighing. Routine calibration procedures checked the microbalance performance. According to our weighing laboratory protocol, both before and after sampling, each filter was weighed three times to obtain one mass measurement result.

2.3. Analytical techniques

Energy-dispersive X-ray fluorescence analysis was performed on aerosol samples collected on PTFE

filters. The concentrations of 16 elements (Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Pb) were detected by the laboratories of the Universities of Milan and Genoa, using two identical XRF spectrometers (ED2000, Oxford Analytical) and the same analytical procedure (Marcazzan et al., 2004).

An inter-comparison between the two laboratories was carried out before the campaign, with results in agreement within 10%. The minimum detection limit was in the range $1–10\,ng\,m^{-3}$ for different elements. Micromatter standard reference samples were used for the quantitative calibration of the systems. A check of the calibration was periodically performed analysing the NIST standard SRM2783. A programme on a personal computer supervised the data acquisition, storage, and reduction; the analysis of X-ray spectra was performed using the Axil code. Experimental overall uncertainties were in the range 10–15%.

The water-soluble inorganic fraction was determined by standard ion chromatography (IC). A quarter of each quartz fibre filter was extracted in MilliQ ultra pure water (three successive extractions of 20 min in an ultrasonic bath, with the renewal of the water at each step, were needed for a complete recovery), and the extracts were analysed by IC for major ionic species, i.e. NO_3^-, SO_4^{2-}, NH_4^+. The overall uncertainty for ionic concentrations was estimated to be 10%.

EC and OC fractions were determined on pre-fired quartz fibre filters by means of a thermal-evolved method using thermo-gravimetric analysis/ Fourier-transformed infrared (TGA–FTIR) spectroscopy. More details on the system set-up and experimental methodology are given in Fermo et al. (2006). The technique detection limit was $0.5\,\mu g\,C\,cm^{-2}$ and the uncertainty was 10%.

Meteorological parameters, gaseous pollutants, PM10, and PM2.5 mass concentrations were given by the regional air quality monitoring networks.

2.4. Statistical analysis

PM1 elemental concentration data sets were analysed by PMF aiming at the identification and quantification of the major sub-micron sized aerosol sources. PMF is an advanced factor analysis technique based on the work of Paatero and Tapper (1994); it uses realistic error estimates to weigh data values and imposes non-negativity constraints in the factor computational process. Briefly, it is a weighted least squares fit, with weights based on the

known standard deviations of the element concentrations in the data matrix. The factor model PMF can be written as $X = GF+E$, where X is the known $n \times m$ matrix of the m measured chemical species in n samples. G is an $n \times p$ matrix of source contributions to the samples (time variations of factors scores). F is a $p \times m$ matrix of source compositions (source profiles). G and F are factor matrices to be determined and E is defined as a residual matrix, i.e. the difference between the measurement X and the model $Y = GF$ as a function of G and F.

The application of PMF depends on uncertainties for each of the measured data values. The uncertainty estimation provides a useful tool to decrease the weight of missing and below detection limits data in the solution; this is a particularly interesting feature when fine fractions with very low elemental concentrations are analysed. In this work, the widely adopted procedure suggested by Polissar et al. (1998) was used for the measurement data and the associated uncertainties as the input data. PMF was run in the robust mode.

3. Results and discussion

3.1. PM1 mass concentration and chemical composition

PM1 mass concentrations (in $\mu g\,m^{-3}$, standardised at 273 K and 101.3 kPa) are reported in Table 1.

During wintertime, a very high PM1 concentration (median: $44.5\,\mu g\,m^{-3}$) was registered in MI, due to the high loading of pollutants and the atmospheric stability typical of the Po valley. Because of this peculiar meteorological condition and the pollutants heavy emission from different sources, the Po valley is one of the most critical areas in Europe in relation to limit values exceedances. Poor atmospheric dilution conditions influenced PM1 values (median: $21.5\,\mu g\,m^{-3}$) in FL during the winter period. A completely different situation was observed in GE, where low PM1 concentration levels (median: $11.0\,\mu g\,m^{-3}$) were due to the wintertime wind regime, which favoured pollutants dispersion.

During summertime, PM1 concentrations significantly decreased both in MI (median: $19.1\,\mu g\,m^{-3}$) and in FL (median: $11.7\,\mu g\,m^{-3}$), because mixing layer heights and average wind speeds were typically higher than during the winter campaign. On the contrary, in GE the PM1 median value for the summer period was $15.6\,\mu g\,m^{-3}$; indeed, the

Table 1
PM1 mass concentration at the three urban sites

	Samples no.	Median	Average	Standard deviation	10th percentile	90th percentile
Milan_winter	90	44.5	48.8	22.9	21.9	78.1
Florence_winter	44	21.5	25.3	17.9	5.6	53.2
Genoa_winter	73	11.0	11.5	5.4	5.3	18.0
Milan_summer	93	19.1	19.4	7.5	9.9	29.8
Florence_summer	84	11.7	11.8	4.2	6.9	18.3
Genoa_summer	89	15.6	17.4	8.1	9.0	30.1

The values in $\mu g\,m^{-3}$ are given as median, mean, 10th and 90th percentile. The standard deviation (in $\mu g\,m^{-3}$) here represents the variability in the data set.

atmosphere was often stable and the dilution was poor so that the pollutants concentration accumulated. In addition, it is important to note that in GE during the summer period (April–September) shipping emissions generally increase due to the larger number of ships in the harbour (roughly $+20\%$ as reported by local authorities). However, considering only data referring to mid-August (the traditional vacation period in Italy), a lowering in mass concentrations was registered in MI (-36%) and FL (-24%) likely due to the strong traffic reduction and the shutdown of a number of industrial and tertiary activities. In contrast, a slight PM1 mass increase ($+15\%$) was observed in GE in agreement with the increase in the number of ships during the month of August (about $+10\%$ in comparison to the summertime average number) and in passenger traffic.

The concern for possible adverse health effects and problems in attaining PM10 and PM2.5 limits is enhanced by PM1 to PM2.5 and PM10 ratios: PM1/PM2.5 = 0.6–0.9 (winter) and 0.5–0.8 (summer) and PM1/PM10 = 0.4–0.6 (winter) and 0.4–0.5 (summer) at the three urban sites. Future pollution control strategies should take into account these evidences for an effective PM10 and PM2.5 abatement strategy.

Average elemental (in $ng\,m^{-3}$), EC, OC and ionic (in $\mu g\,m^{-3}$) concentrations are reported in Table 2. At all locations, elemental S and K gave the highest contributions. S concentrations were very similar in GE and FL during both seasons. In MI sulphur concentrations were much higher (about 1.5 and 2 times in summer and winter, respectively) than in FL and GE, pointing at the impact of local and regional (the Po valley acts often as a single basin) sources. Potassium showed comparable concentrations in MI and FL, while it had much lower values in GE during both seasons. K in the sub-micron

sized particles is unlikely due to the soil source and it has to be ascribed more likely to combustion processes. In FL high K and OC levels were already observed in the aerosol fine fraction ($<2\,\mu m$) by Cachier et al. (2004), who suggested the biomass burning for residential heating as their main source. Although biomass burning would be a possible contributor for OC in Florence, measurements of more specific tracers (i.e. levoglucosan or radiocarbon) are needed to confirm it.

In MI and FL during wintertime a not negligible contributor was Cl (440 and 190 $ng\,m^{-3}$, respectively), while in the coastal town chlorine was detected only in 50% of the measured data. This result suggested that sea-spray did not likely contribute to sub-micron sized aerosol. Previous studies carried out in GE and surroundings by the authors (Mazzei et al., in press) evidenced that sea-spray contribution on a yearly basis was about 10% in PM10 and 8% in PM2.5, while the sea-spray presence was only rarely detected in PM1 (accounting for about 5% of the total mass). During the summer at all sites Cl concentrations were below minimum detection limits because of its volatile nature.

With regard to the water-soluble ions results (see Table 2), during wintertime in MI and FL the major contributor to PM1 mass was nitrate, while in GE, sulphate had concentrations slightly higher than nitrate ones. During the summer at all sites, the sulphate level was the highest in the water-soluble fraction, accounting for about 3–4 $\mu g\,m^{-3}$. The strong reduction in the nitrate concentration can be explained by the summertime temperatures (on average 25 °C), which favoured the gas phase more than the particulate one; moreover, possible negative sampling artefacts cannot be completely excluded.

OC was the most abundant species at the three sites, accounting, on average, for 4.8–14.8 $\mu g\,m^{-3}$ of

Table 2
Average elemental values (in $ng\,m^{-3}$)

	Milan		Florence		Genoa	
	Winter	Summer	Winter	Summer	Winter	Summer
Al	16	11	12	19	14	16
Si	37	40	24	32	27	45
S	1200	1500	560	1100	550	1000
Cl	440	<15	190	<15	31	<15
K	300	98	270	94	91	59
Ca	27	22	28	34	18	56
Ti	4	4	4	4	4	4
V	4	4	3	4	4	15
Cr	3	2	1	1	1	1
Mn	9	5	2	2	1	3
Fe	86	42	41	26	24	37
Ni	6	2	6	2	3	5
Cu	7	4	4	4	2	7
Zn	59	34	20	9	13	9
Br	9	5	4	2	3	2
Pb	31	11	12	4	6	4
EC	1.8 (0.5–4.3)	1.1 (0.4–2.4)	0.9 (0.4–1.9)	0.6 (0.3–1.4)	0.9 (0.3–1.8)	0.9 (0.2–1.6)
OC	14.8 (2.2–33.0)	4.8 (1.8–12.7)	12.0 (3.1–29.6)	2.7 (1.3–5.3)	5.0 (2.4–9.8)	3.4 (1.3–7.3)
SO_4^{2-}	4.7 (2.1–7.6)	3.9 (1.2–8.5)	1.7 (0.5–3.3)	3.2 (0.4–8.8)	1.7 (0.7–3.5)	3.8 (1.3–13.1)
NO_3^-	13.6 (4.0–30.5)	0.9 (0.1–5.5)	3.2 (0.4–9.8)	0.1 (0.04–0.2)	1.1 (0.4–2.8)	0.2 (0.1–0.7)
NH_4^+	4.2 (2.1–6.9)	1.8 (0.6–3.2)	1.6 (0.2–3.6)	1.3 (0.1–3.0)	1.0 (0.5–1.8)	1.4 (0.5–4.4)

Ions, elemental carbon and organic carbon are given in $\mu g\,m^{-3}$ and minima and maxima values are also reported in brackets.

the PM1 mass in MI, 3.4–5.0 $\mu g\,m^{-3}$ in GE, and 2.7–12.0 $\mu g\,m^{-3}$ in FL during summertime and wintertime, respectively. The EC contribution was 1.1–1.8 $\mu g\,m^{-3}$ in MI, 0.9–0.9 $\mu g\,m^{-3}$ in GE, 0.6–0.9 $\mu g\,m^{-3}$ in FL during summer–winter, respectively. As already mentioned before, high OC values and the corresponding quite low EC levels detected in FL might be explained more by biomass burning contributions than by traffic.

Literature data (Turpin and Huntzinker, 1995) report that OC/EC ratios higher than 2–2.5 are indicators for secondary organic aerosol formation. Indeed, at the monitored sites high OC/EC ratios were observed in MI (4.5–8.2), GE (4.0–5.6) and FL (4.3–13.4), with higher values typically measured in winter. The abundance of organic carbon during the winter period was likely due to lower temperatures, which favoured the aerosol particle phase of organic compounds, and due to low mixing layer heights, which allowed the accumulation of gaseous precursors and the acceleration of secondary organic aerosol formation.

The chemical mass closure obtained at the three urban locations is shown in Fig. 1. Mineral and heavy metal oxides have been calculated from XRF

data using the sum of oxides algorithm (Marcazzan et al., 2001). These two components explained a little part of the PM1 mass: a percentage of 0.3–0.6% for heavy metal oxides and 0.7–2.3% for mineral oxides. Ammonium sulphate and nitrate were obtained by IC analyses as previously described. At all sites, $(NH_4)_2SO_4$ accounted for 10–12% in winter and 34–45% in summer. NH_4NO_3 percentages were in the range 0.5–5% in summer and 9–29% in winter. The organic carbon concentrations were converted in organic matter (OM) concentrations using an average mean molecular-to-carbon ratio of 1.6 as proposed by Turpin and Lim (2001) for urban aerosol. Nevertheless, this ratio varies significantly with location, season, time of the day and aerosol ageing as the mix of organic compounds in the aerosol changes and generally it is higher where a large fraction of the aerosol is organic (as in our monitoring locations). OM was the major contributor during both seasons, accounting for a large part of PM1 mass (about 40% on average); EC percentages were comparable at all sites during both seasons (about 4%). The unaccounted mass fraction (14–22%) given by the chemical mass balance resulted from aerosol-bound
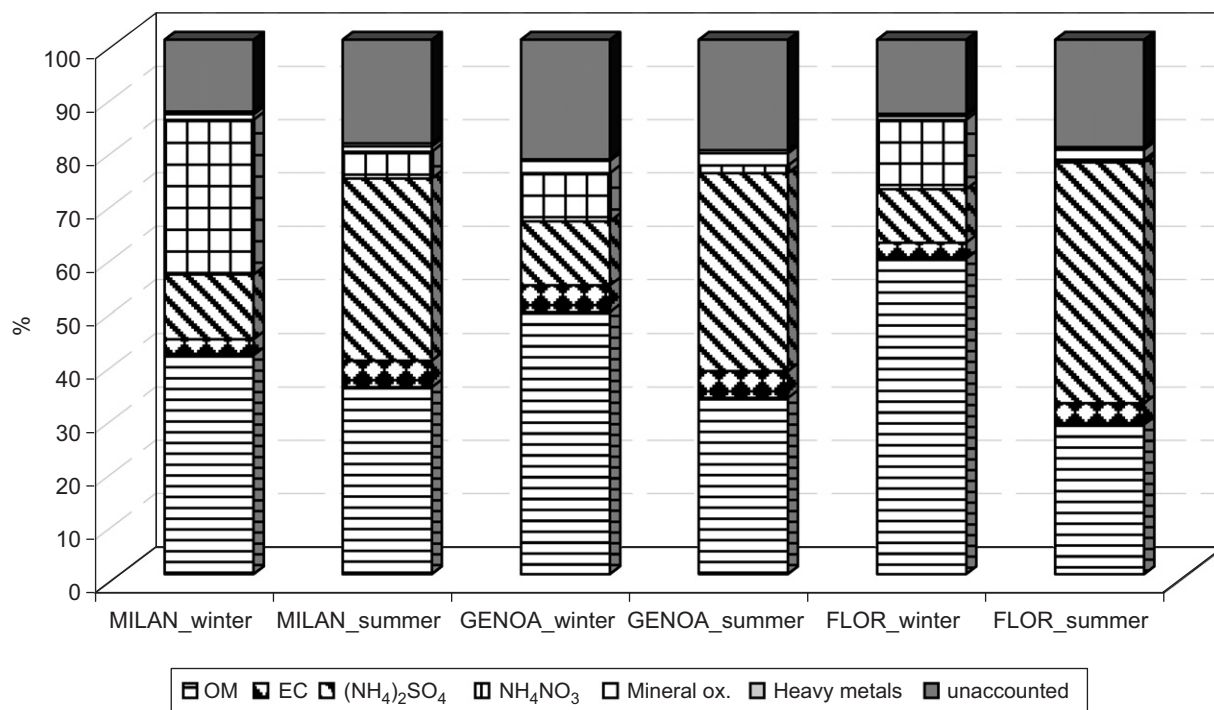
Fig. 1. Chemical mass closure for summer and winter at Milan, Florence and Genoa.

water, minor components, and measurement errors evaluated in 10% following Rees et al. (2004).

3.2. PMF data analysis

In this paper, the chemical speciation of samples used in the factor analysis refers only to elements (ionic components and EC/OC data are not contemporary), which covered a small portion of PM1 mass; thus, PM1 mass concentration was included as an independent variable in the PMF modelling to provide direct mass apportionment. As suggested by the literature (Kim and Hopke, 2007), the uncertainties on PM mass were substantially increased (5 times) to ensure that it did not affect the PMF solutions.

The availability of elements only was an additional difficulty in the source interpretation as major PM components (EC and OC, ammonium and nitrate) and relevant source tracers (e.g. EC for traffic) are missing. In addition to the critical choice of the number of factors, which is common to all PMF users, a problem in dealing with PM1 source apportionment is that no source emission profiles are available for sub-micron sized particles in the investigated areas and, in general, in the literature. Source identification was carried out using available literature source profiles for PM fine fractions,

looking at source contributions time series and taking into consideration explained variation values (EV). The availability of a PM1 complete chemical characterisation for a statistically significant number of samples could partially reduce difficulties in source identification.

PMF results can be greatly influenced by species with a high proportion of data lower than the minimum detection limits; thus, in this work 'weak' variables (i.e. Ti in Milan; Cl, Ti, Cr, and Mn in Genoa; Ti and Cr in Florence data sets) according to signal-to-noise (S/N) ratio criterion (Paatero and Hopke, 2003) were not included in the analysis. Cl data in MI and FL data sets were also excluded because, although defined 'normal' by the S/N criterion, they were detected exclusively during the winter period and had 46% (MI) and 75% (FL) of the data below minimum detection limit.

Rotational ambiguity is always a problem in factor analysis (Paatero et al., 2002) because of the free rotation of matrices. In this work PMF solutions for multiple values of FPEAK values were systematically explored (FPEAK values between -1 and $+1$, in steps of 0.2) and the resulting IM, IS, Q values, F and G matrices as well as scaled residuals were examined to find out the most reasonable solution. To exclude the existence of

local minima in addition to the global minimum, PMF was run 10 times for each FPEAK value, starting the analysis from different initial values.

It should be remembered that in PMF the choice of factors is always a compromise because PMF is a descriptive model and there is no objective criterion to choose the ideal solution. Indeed by using too few factors sources of different nature are combined together, while using too many factors a real factor is likely split into two or more unreal or not easily interpretable sources.

The IM and IS parameters taken from the scaled residual matrix can help in the identification of the number of factors; in fact, when the number of factors increases to a critical value IM and IS will experience a drastic drop (Lee et al., 1999). In this work IM and IS values showed significant drops in correspondence of 4 and 7 factors in the MI data set, 4 and 10 factors in GE and 7 factors in FL. IM and IS for each analysed database and for a number of possible rotations showed only little variations.

It is noteworthy that the comparison of the possible solutions singled out that three factors were common for all sites, although some differences in the source profiles may occur because the source composition can be slightly different for each individual source.

Results obtained for the 5-factorial solution will be presented and discussed here. Figs. 2–8 show the resolved factor chemical composition profiles for PM1 and the error bars represent the computed error estimates. As mentioned before, all solutions were systematically explored for multiple FPEAK values in the range between −1 and +1; in this way, we gathered additional information on the stability of the solution. This is an important point when, as in our case, there is a lack in the knowledge of emission profiles for PM1. In this work, FPEAK values of −0.4 in MI, 0 in GE and +0.4 in FL were chosen with motivations that will be clarified in the following; all the source apportionments here reported referred to solutions corresponding to these FPEAK values.

In Figs. 2, 4 and 6 the chemical profiles for three common factors are represented for each FPEAK value considered and in Figs. 3, 5 and 7 the profile corresponding to the chosen solution is given.
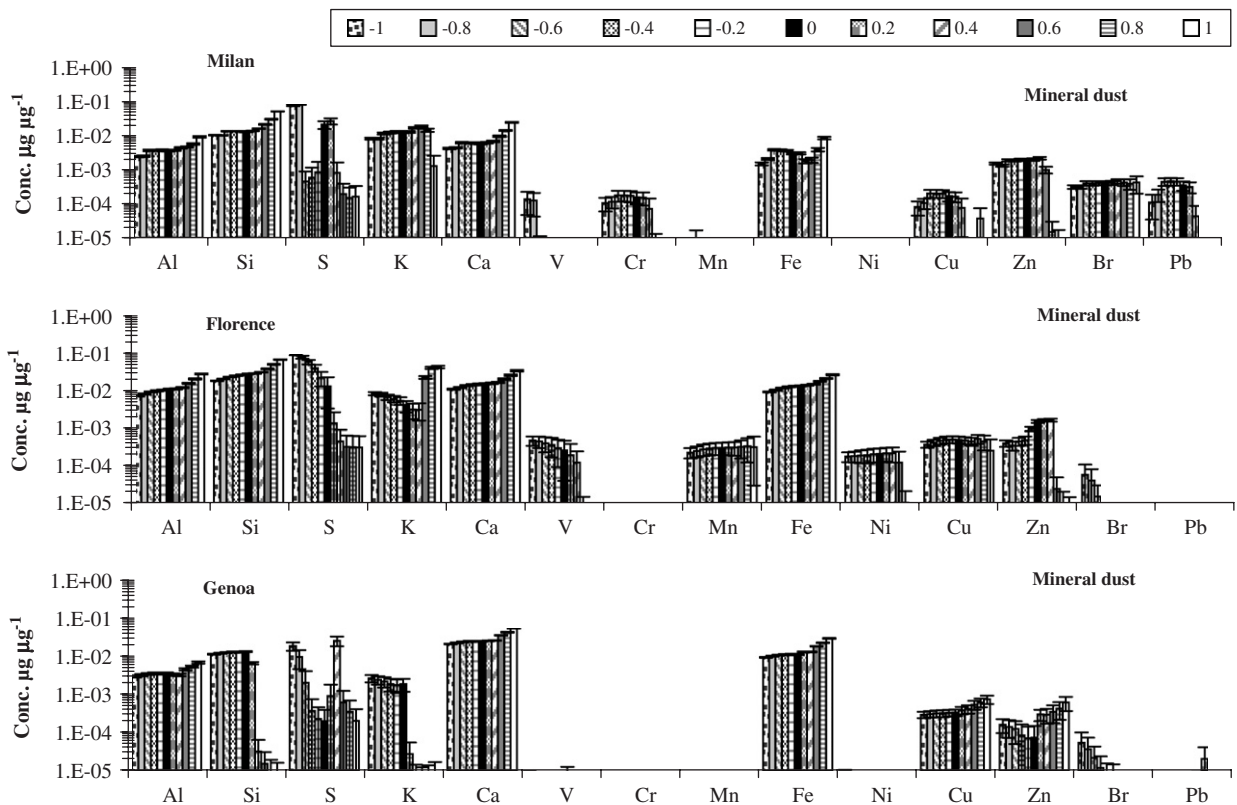

Fig. 2. 'Mineral dust' source profiles resolved at Milan, Florence and Genoa. Results are given for the different FPEAK values from −1 (first value on the left) to +1 (last value on the right).
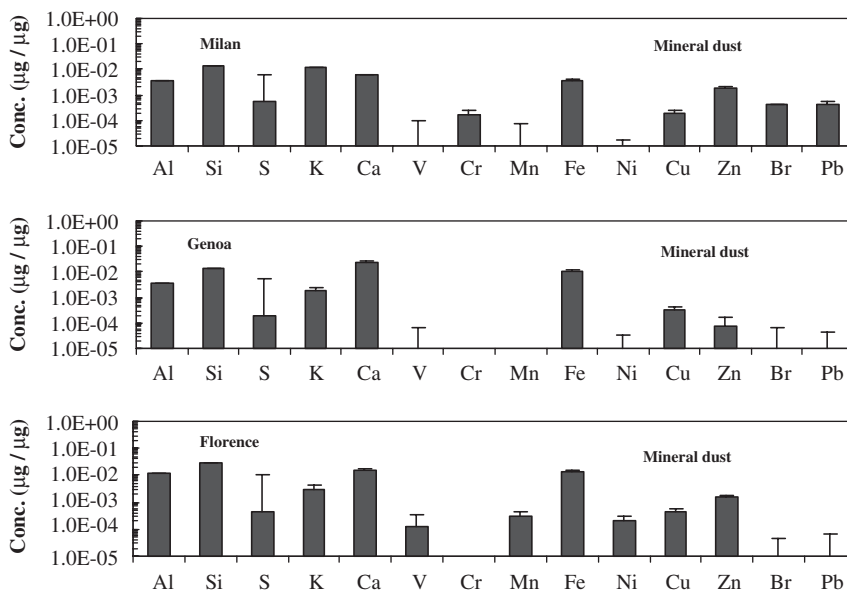
Fig. 3. 'Mineral dust' source profiles resolved at Milan, Florence and Genoa. Results are given for FPEAK $= -0.4/0/+0.4$ in MI/GE/FL.
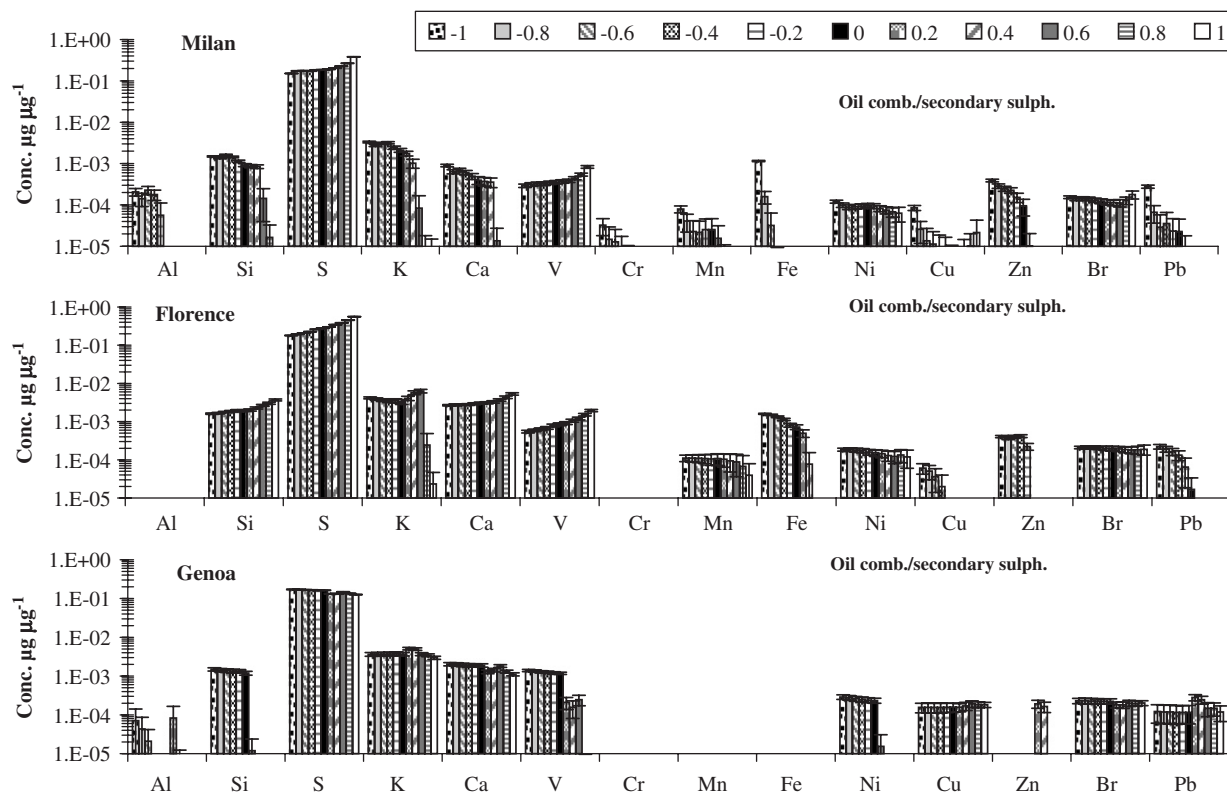

Fig. 4. 'Oil combustion/secondary sulphates' source profiles resolved at Milan, Florence and Genoa. Results are given for different FPEAK values from -1 (first value on the left) to $+1$ (last value on the right).

The 'mineral dust' source was identified by high EV for Al, Si, Ca and Fe; these elements of mineral origin were also the most abundant in the source profile (Figs. 2 and 3). The largest variability in relation to different FPEAK values was observed in S concentration in the profile. Sulphur should not
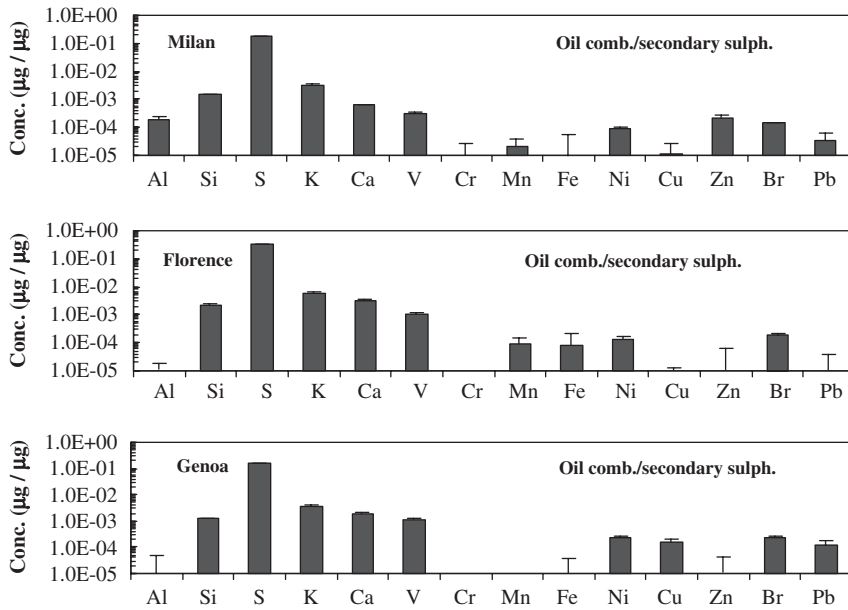
Fig. 5. 'Oil combustion/secondary sulphates' source profiles resolved at Milan, Florence and Genoa. Results are given for FPEAK = −0.4/0/+0.4 in MI/GE/FL.
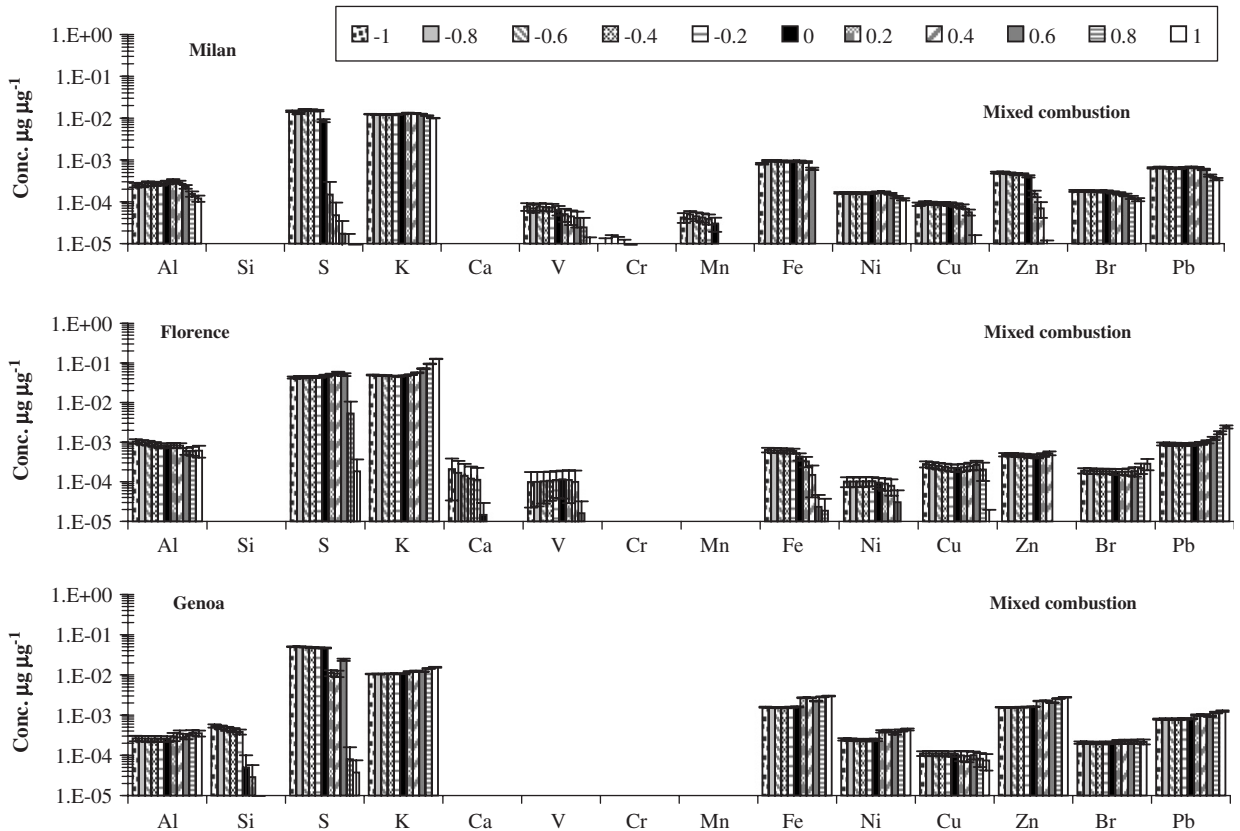

Fig. 6. 'Mixed combustion' source profiles resolved at Milan, Florence and Genoa. Results are given for different FPEAK values from −1 (first value on the left) to +1 (last value on the right).
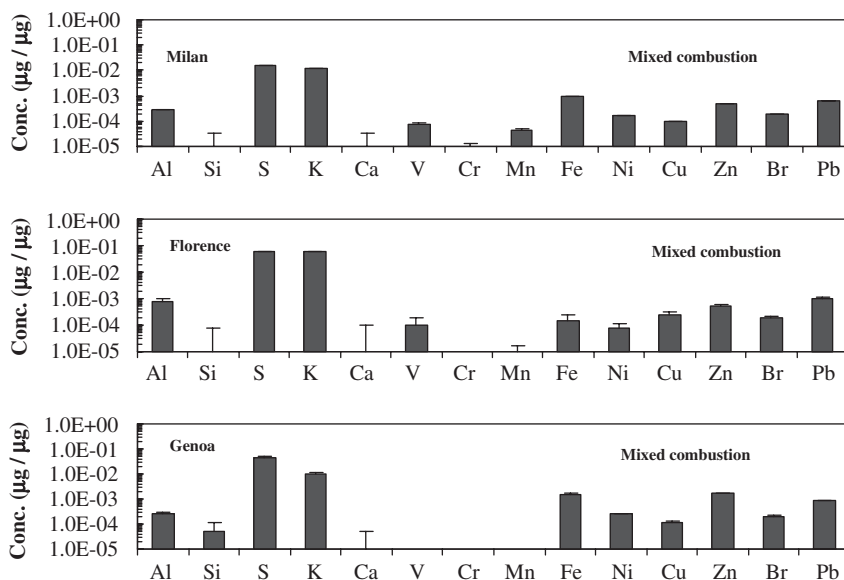
Fig. 7. 'Mixed combustion' source profiles resolved at Milan, Florence and Genoa. Results are given for FPEAK = $-0.4/0/+0.4$ in MI/GE/FL.

be one of the most abundant elements in the 'mineral dust' profile; thus, the best rotated solution might be chosen among those giving the lowest S contribution. It is noteworthy that the Al/Si ratios calculated by the source profile were about 0.3, a value comparable to the one given for the average Earth crust. This source, on average, accounted for 8%, 7% and 5% in GE, MI and FL, respectively, and had a seasonal pattern with higher values in summer. The presence of anthropogenic elements in the source profile was likely due to contaminations of soil dust by deposition of particles emitted by other sources (e.g. traffic).

The 'oil combustion/secondary sulphates' factor was characterised by high EV for S, V and Ni and, as shown in Figs. 4 and 5, in its profile S, V and Ni were present in significant concentrations. Solutions for different FPEAK values were quite comparable and stable in MI and FL data sets. In GE, sulphur concentration in the profile did not vary very much with multiple FPEAK values, while V and Ni contributions significantly decreased for positive FPEAK values suggesting that these should be not the most appropriate values. This source accounted for (winter–summer percentages): 8–29% in FL, 14–41% in MI and 16–48% in GE. It is likely that the large contribution of sulphur found in this factor caused the observed seasonality because as well known, secondary sulphates are formed mainly by photochemical reactions especially during summertime.

In Figs. 6 and 7 the factor with strong signals of S and K, and to a less extent of Fe–Zn–Pb–Al in the source profile, was probably due to a mixing of combustion sources where wood smoke, biomass/ biofuel burning as well as coal combustion were likely the major contributors. S showed the largest difference in the profile especially in MI data set. The solutions corresponding to FPEAK values in the range from $+0.2$ to $+1$ showed very low S values and large errors suggesting that the best rotated solution should be found out in the FPEAK range from -1 to 0. Source profiles obtained in FL and GE were very similar. Moreover, a good agreement with MI results was obtained when negative FPEAK values (i.e. -0.6 or -0.4) were selected. This profile, tentatively called 'mixed combustion', is in fair agreement with the ones found by Han et al. (2006) in sub-micron sized aerosol. This source accounted for 32% of PM1 mass in MI, 12% in FL, and 49% in GE; it presented a seasonal trend, with much higher (about three times) values in winter. According to the INEMAR emission inventory for the Lombardy region (Arpa Lombardia, 2005), where MI is situated, the emissions due to wood/biomass burning account for 25% to PM2.5. Although the source apportionment reported in this paper is only preliminary, it is interesting to note the good agreement with the INEMAR estimate.

From the above reported considerations the choice of FPEAK = -0.4, 0, and $+0.4$ in FL,
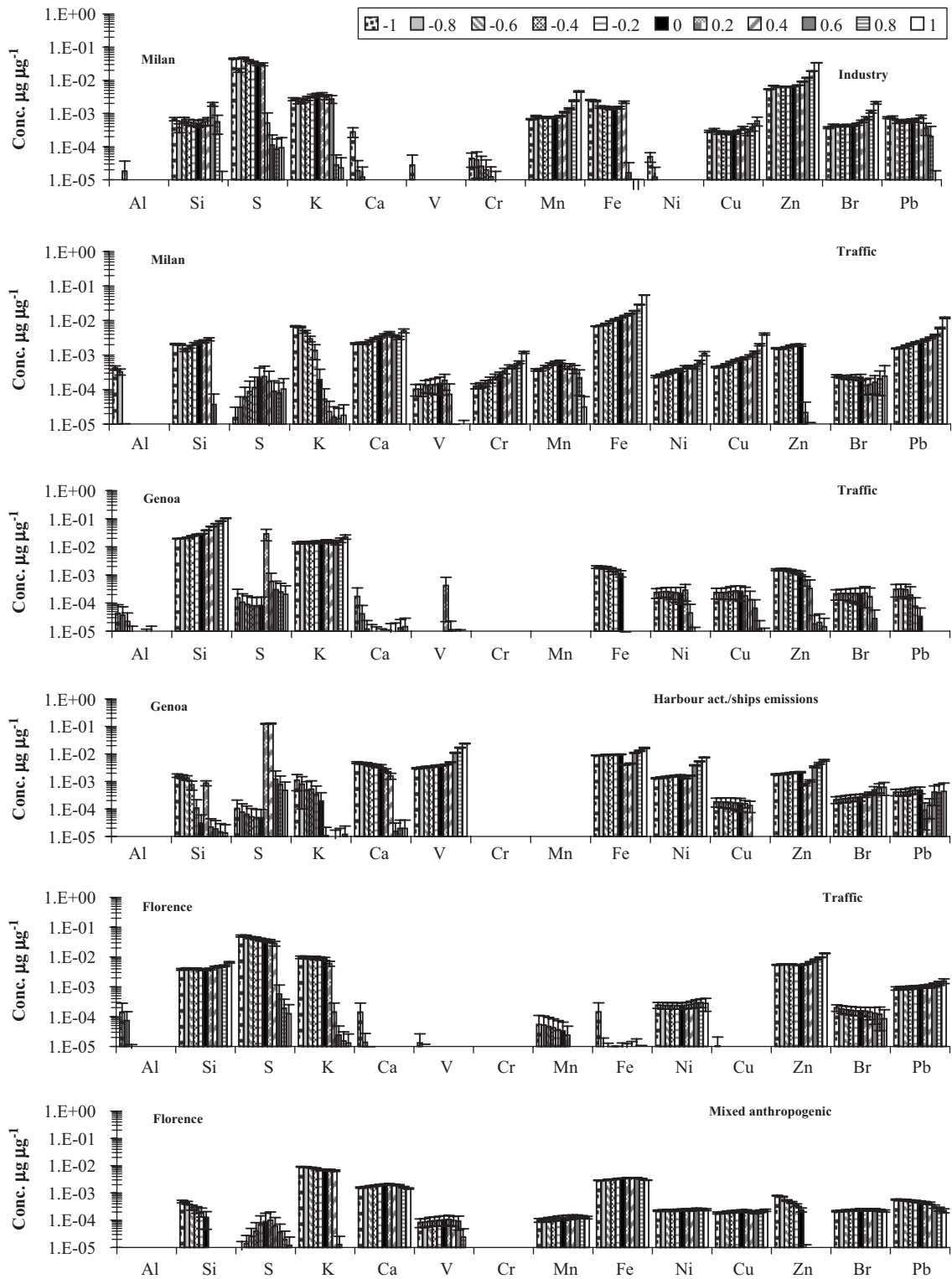
Fig. 8. Different source profiles resolved at the three locations. Results are given for different FPEAK values from −1 (first value on the left) to +1 (last value on the right).

GE, and Mi, respectively, seems to be reasonable especially considering the similarities in the chemical profiles. In contrast, the identification of sources reported in Fig. 8 (which were different at the three locations) was carried out with many difficulties because no common patterns were recognised.

In MI the factor named 'industry' (Fig. 8) is characterised by high EV values of Zn and Mn, which were recognised as markers for generic industrial activities at this location after previous studies performed on high-time-resolved PM2.5 samples (D'Alessandro et al., 2003). This source accounted for 16% of the mass and its temporal pattern had no seasonal modulation but a sharp decrease in concentrations during the Christmas holidays and mid-August appeared. The factor 'traffic' (Fig. 8) in the MI data set showed high EV for Fe, Cu, Cr and Pb which were already identified as traffic markers at the same location (Vecchi et al., 2007); it explained 16% of the sub-micron-sized aerosol mass. In addition, in GE one factor was named 'traffic' (Fig. 8), it has similarities with the same profile found in MI and it explained 7% of the mass. In FL (Fig. 8) the factor identified as 'traffic' accounted for 12% and its profile had similarities with different traffic emissions. In fact, Si, S and K can be considered markers for diesel emissions and the high loading found for Zn points at emissions by two stroke engines as it is used as an additive in their lubricating oil (Salvador et al., 2007). The 'traffic' source at all locations did not show any seasonal pattern. In GE the oil combustion markers (V–Ni) were also found in significant amounts in a separate factor (named 'harbour activities/ships emissions') probably due to the presence of the large harbour and connected activities; this source explained 9% of the PM1 mass with a larger contribution in summer (13%). The last factor singled out in FL was generically called 'mixed anthropogenic' as a clear source cannot be identified from marker elements; it largely contributed to PM1 mass (50%, slightly higher during the winter) but further and more detailed chemical speciation is needed to resolve different contributing sources.

Other possible solutions with 6 and 7 factors were also analysed but they resolved sources not easily explainable without additional markers or emission profiles (not available at the moment). It is important to note that when the sixth and seventh factors were taken into account, the first 5 factors discussed so far did not change much in terms of the chemical source profile or explained variation at all sites. In MI the chemical profiles related to other solutions showed significant contributions (i.e. larger than $10^{-3}\,\mu\mathrm{g}\,\mu\mathrm{g}^{-1}$) for K–Pb–Si–Ca–Zn in the 6-factors case and S–Fe–Zn in the 7-factors one. In GE the 6-factors profile was very similar to the one called 'mixed combustion' in the 5-factorial solution with the only difference that Al was present in the 6-factors profile. The 7th factor profile was characterised by S and Fe, which might be ascribed to emissions from the large steel smelter operating nearby. In FL, the 6-factorial solution showed Ca–K–Fe–Si in significant concentrations and the 7th factor had contributions from S–Fe–Cu.

4. Conclusions

In this work, mass concentrations and composition are given for sub-micron sized particulate matter (PM) at three urban sites in Italy. Experimental results show that PM1 has some common features at the three investigated urban sites; nevertheless, significant differences are evident in mass concentrations, elemental composition and seasonal patterns as each site is also characterised by local emissions and peculiarities in topographical and meteoclimatic conditions.

An interesting result obtained in this study is the PM1 mass closure obtained at different urban sites in winter and summer; it shows that compounds mainly of secondary origin like ammonium sulphates and organics account for the largest part of PM1 mass.

PM1 data reported in this study enhance the concern for possible health effects because of the high mass concentration measured. Moreover, PM1 is about 40–60% of PM10 at the investigated urban sites during both seasons, this result highlights difficulties in attaining the PM10 and the proposed PM2.5 EU-limits. Future PM control strategies should take into account these indications and, in particular, the fact that aerosol of secondary origin dominates the PM1 mass.

An attempt to identify PM1 sources has been also done with the application of Positive Matrix Factorisation to the complete elemental data set for each town. The identification of the factors was particularly difficult due to the lack of chemical profiles for the sub-micron sized particles emissions in the investigated locations and the sole

use of elemental data so that, now, it should be considered only preliminary. To support the results, a systematic study of PMF solutions varying FPEAK values was performed. PMF identified 5 source-related factors contributing to PM1 mass at the 3 urban sites; 3 were common for all locations (named 'mineral dust', 'oil combustion/secondary sulphate' and 'mixed combustion') while the other two factors, more clearly identified in MI and GE, showed differences in the chemical profiles connected to local characteristics.

Acknowledgements

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