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4-hours resolution data to study PM10 in a "hot spot" area in Europe

Roberta Vecchi · Vera Bernardoni · Paola Fermo · Franco Lucarelli · Federico Mazzei · Silvia Nava · Paolo Prati · Andrea Piazzalunga · Gianluigi Valli

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Abstract Nowadays, high-time resolved aerosol studies are mandatory to better understand atmospheric processes, such as formation, removal, transport, deposition or chemical reactions. This work focuses on PM10 physical and chemical characterisation with high-time resolution: elements (from Na to Pb), ions and OC/EC fractions concentration were determined during two weeks in summer and two in winter 2006 with 4-hours resolution. Further measurements aimed at hourly elemental characterisation of fine and coarse fractions and at the determination of particles number concentration in the 0.25–32 μm size range in 31 bins. The chemical mass closure was carried out in both seasons, enhancing intra-day differences in PM10 composition. In Milan, the highest contribution came from organic matter (34% and 33% in summer and winter, respectively); other important contributors were secondary inorganic compounds (16% and 24% in summer and winter, respectively) and, in summer, crustal matter (14%). Temporal trends showed strong variations in PM10 composition during contiguous time-slots and diurnal variations in different components contribution were identified. Moreover, peculiar phenomena, which would have hardly been detected with 24-hours samplings, were evidenced. Particles removal due to precipitations, aerosol local production and long range transport were studied in detail.

Keywords High-time resolution · Chemical composition · Number size distribution

R. Vecchi (✉) · V. Bernardoni · G. Valli
Institute of Applied General Physics, University of Milan, and INFN-Milan, 20133 Milan, Italy
e-mail: roberta.vecchi@unimi.it

P. Fermo · A. Piazzalunga
Department of Inorganic, Metallorganic and Analytical Chemistry, University of Milan, 20133 Milan, Italy

F. Lucarelli
Department of Physics, University of Florence, and INFN-Florence, 50019 Florence, Italy

S. Nava
National Inst. of Nuclear Physics-Florence, Sesto Fiorentino, 50019 Florence, Italy

F. Mazzei · P. Prati
Department of Physics, University of Genoa, and INFN-Genoa, 16146 Genoa, Italy

Introduction

Aerosols are of great concern because they can have negative effects both on environment and on

human health. Up to now, many studies (for example in Europe: Artiñano et al. 2001; Marcazzan et al. 2001; Hoek et al. 2002; Putaud et al. 2004; Vecchi et al. 2004, among others) have been devoted to particulate matter characterisation using 24-hours resolved samplings. However, it should be noted that within a 24-hours time-interval, PM concentration and composition at a given location could vary significantly. In fact, during 24-hours time-interval, many sources and physical-chemical processes may contribute to a different extent to the measured concentrations and they can be hardly singled out with 24-hours samplings.

Thus, high-time resolved detailed characterisation is mandatory for a better insight on processes such as formation, transport, removal, deposition and chemical reactions in the atmosphere. Moreover, high-time resolution allows a direct comparison with gaseous pollutants and meteorological parameters, which are generally monitored on hourly basis. High-time resolved samplings can also give further information about source emissions: these can heavily impact on air quality with very high emission loadings of toxic (or potentially toxic) elements or compounds during a few hours in a day, and the knowledge about the timing and intensity of specific episodes may be important to assess human exposure.

In this work a physical-chemical characterisation of PM10 with high temporal resolution was performed. The aim was twofold:

- to develop a methodological approach to gather a deeper knowledge on processes influencing PM10 levels and patterns in a "hot spot" pollution area;
- to single out processes occurring on few-hours time intervals.

Experimental

Site and sampling

Milan (45°28′ N; 9°13′ E), with about 1 500 000 inhabitants, is the second largest town in Italy, after Rome; in the whole area of the Milan province the population rises up to about 4 millions inhabitants. Milan is situated in the Po valley (Northern Italy) which is heavily industrialised, trafficked and populated and it is considered one of the largest pollution "hot spots" in Europe.

The samplings were carried out on the roof of the Institute of Physics, at a height of about 10 m a.g.l., at the University campus in Milan. It is an urban background site, generally not directly influenced by local source emissions and it is quite representative of the average air pollution in the city. However, many construction works were carried out both in the garden of the Institute and in the whole University campus area during the sampling periods. Therefore, some episodes with higher particulate matter concentration due to locally resuspended dust were registered and identified by sudden and short-lasting increases in the coarse fraction particles number.

PM10 was sampled with 4-hours resolution in 2006 during two field campaigns, starting at 12 A.M., local time, from 27 June to 11 July during summertime and from 21 November to 6 December during wintertime; six PM samples were collected every day. Samplings were carried out in parallel on PTFE and quartz fibre filters (pre-fired at 700°C for 1 hour) using CEN-equivalent samplers operating at a flow rate of 2.3 m^3 h^{-1}. In total 180 quartz fibre filters and 174 PTFE filters were collected.

During two weeks (4–11 July and 21–26 November), fine ($d_{ae} < 2.5$ μm) and coarse (2.5 μm $< d_{ae} <$ 10 μm) PM fractions were also collected with hourly resolution, using a streaker sampler. The streaker sampler separates particles in two different stages using a pre-impactor (which removes particles with aerodynamic diameter $d_{ae} > 10$ μm) and an impactor. The impactor is a Kapton foil on which coarse particles are deposited. The fine fraction is then collected on a Nuclepore filter (0.4 μm pore diameter). The Kapton foil and Nuclepore filter are paired in a cartridge rotating at constant angular speed (1.8° h^{-1}). This produces a circular continuous deposition on both stages. Further details on the sampler, its cut-off diameters, and its control unit can be found elsewhere (Prati et al. 1998); it should be noticed that mass concentration in streaker samples is not available.

Laboratory analyses

Before and after the samplings, the filters were exposed for 48 hours on open but dust-protected sieve-trays in an air-conditioned weighing room (T = 20 ± 1°C and R.H. = 50 ± 5%) and then weighed using an analytical microbalance (precision 1 μg), which was installed and operated in the weighing room (the weighing protocol is described in Vecchi et al. 2004). Calibration procedures checked the microbalance performance.

Analyses by Energy-Dispersive X-Ray Fluorescence (ED-XRF) technique (details on the technique set up are reported in Marcazzan et al. 2004), allowed the determination of concentration values for Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Sr, Ba and Pb on PTFE filters. The minimum detection limit (MDL) was in the range 2–20 ng m^{-3} for most elements. Experimental overall uncertainties were in the range 10–15%. Because of the well known self-absorption effect on low-energy fluorescence X-rays in large particles, particle size correction factors were applied to Na, Mg, Al and Si concentrations. Literature studies (Maenhaut and Cafmeyer 1998; D'Alessandro et al. 2003) determined these correction factors which resulted 2.0 for Na, 1.7 for Mg, 1.5 for Si and 1.3 for Al. Particle size correction factors for Na and Mg are lower and less accurate, so that data for these elements should be considered semi-quantitative.

One half of the quartz fibre filters was analysed for water-soluble inorganic major components (i.e. SO_4^{2-}, NO_3^-, and NH_4^+) and oxalate (as an organic ion) by ion chromatography (IC). A particular care must be used in IC analyses of particulate matter collected on quartz fibre substrates due to high blank levels (minimum detection limits: 167, 359 and 46 ng m^{-3} for SO_4^{2-}, NO_3^-, and NH_4^+, respectively). More information about extraction procedures and blanks correction can be found in Fermo et al. (2006). The overall uncertainty for ionic concentrations in 4-hours time-resolved samples was estimated to be 10%.

One punch (area: 1.5 cm^2) cut from each quartz fibre filter was analysed by TOT (Thermal-Optical Transmittance) method (Birch and Cary 1996) to quantify elemental and organic carbon. Five sub-fractions of OC were identified during the analysis: OC1, OC2, OC3, OC4 and PC (pyrolytic carbon). OC1–4 fractions were evaluated as the organic carbon evolved at 4 different, increasing, temperatures in He atmosphere. PC is formed during TOT analysis and it is mainly due to water-soluble organic carbon, which pyrolyses during the first part of the analysis, in He atmosphere. PC evolves during the second part of the analysis, in He-O_2 atmosphere, and it can be separated by EC using an optical correction. The technique detection limit was 0.2 μg C m^{-3} and the precision was 10%.

Nuclepore and Kapton substrates from the streaker sampler were analysed by Particle Induced X-ray Emission (PIXE) analysis at the LABEC-INFN accelerator facility in Florence, Italy, whose set up is described in Calzolai et al. (2006). PIXE detected the same elements as ED-XRF. The minimum detection limit was in the range 1–10 ng m^{-3} for most elements. The accuracy of hourly elemental concentrations was in the range 2–20%.

Additional measurements

An Optical Particle Counter (Grimm, mod.1.107) gave high time-resolved (10 minutes) information about number concentration in 31 size bins in the 0.25–32 μm range (details on this optical counter are given in Mazzei et al. 2007). From 21 November to 4 December a Condensation Particle Counter (TSI, mod.3775) was also operated, in order to obtain information about the number concentration of particles with $d > 4$ nm.

To evaluate atmospheric dispersion conditions, ^{222}Rn short-lived decay products measurements were performed using the experimental methodology reported in Marcazzan et al. (2003a). The evaluation of mixing layer heights (MLH) with hourly resolution was carried out using a box model suitably set up, using ^{222}Rn concentration measurements as input data (Pacifico 2005).

Meteorological parameters (wind speed and direction, temperature, relative humidity, pressure, solar radiation and precipitation) were also measured at the monitoring station.

Gaseous pollutants (NO_2, NO, O_3) hourly data recorded at monitoring stations located near the University campus as well as information on CO and hourly traffic volumes in the city centre were available by the Regional Environmental Protection Agency of Lombardy.

Results and discussion

Meteorological conditions and mass concentration

In Table 1, statistics of hourly-averaged meteorological parameters are reported.

During the summer campaign there were mainly good weather conditions with high temperature (about 30°C during day-time and above 20°C during night-time), and maximum solar radiation of about 800 W m^{-2}. Rainfalls were registered only on 29 June and on 6 July.

During the winter campaign, the weather was generally cloudy or rainy, except on five days (22, 23, 26, 30 November and 1 December). The temperature during cloudy/rainy days was about 10–12°C, with slight differences between daytime and nighttime. Rainfalls were frequently registered, but their intensity was at most 1 mm h^{-1}. During sunny days, temperatures up to 18°C during daytime and lower than 8°C during nighttime occurred and the solar radiation reached 400 W m^{-2}.

In Fig. 1, PM10 mass and ^{222}Rn concentration during both field campaigns are shown. PM10 concentrations were generally higher during wintertime, due both to additional sources (i.e. domestic heating) and to stability conditions, as evidenced by the analysis of ^{222}Rn temporal patterns.

Indeed, if average PM10 concentrations in the two seasons are compared, it can be noticed that winter values were on average 2 times summer ones (54.7 μg/m^3 and 110.5 μg/m^3 in summer and winter, respectively). Taking ^{222}Rn daily minimum concentrations as indication of the dispersion conditions of the atmosphere (as they are registered when mixing layer height is at its maximum) and averaging these values in the two seasons (Vecchi et al. 2004), it can be observed that winter values were 1.6 times the summer ones.

Table 1 Statistics of hourly-averaged meteorological parameters

		Temperature (°C)	Wind speed (m s^{-1})	Pressure (hPa)	R.H. (%)	Precipitation (mm h^{-1})	222Rn (Bq m^{-3})
Summertime	Average	26.5	1.36	1,001	49		10.5
	Std deviation	3.8	0.62	2	13		5.0
	Minimum	17.9	0.31	997	26		3.7
	Maximum	33.7	5.17	1,006	84	25.0	26.4
	Median	26.7	1.43	1,001	48		9.8
	10° percentile	21.7	0.51	999	34		4.7
	90° percentile	31.7	2.07	1,004	66		17.7
Wintertime	Average	10.5	0.89	1,004	78		13.6
	Std deviation	2.0	0.41	9	12		4.4
	Minimum	4.4	0.20	980	21		2.9
	Maximum	17.9	2.29	1,018	93	1.2	27.6
	Median	10.5	0.80	1,005	80		12.8
	10° percentile	8.4	0.45	991	64		9.0
	90° percentile	12.9	1.49	1,015	89		20.2

Therefore, it can be concluded that about 80% of the registered increase in concentrations during wintertime was due to atmospheric stability conditions and that additional sources contribute for about 20% to the average winter PM10 mass growth.

Mass closure

PM10 detailed chemical characterisation (elements, ions and carbon fractions) allowed the mass closure on quartz fibre filters.

From elemental concentrations, crustal matter was estimated applying the sum of oxides algorithm, following Marcazzan et al. (2004) and using Si as reference element and the crustal composition given by Mason (1966). As Ca showed high enrichment factors (often higher than 4 in both seasons), only the natural fraction of Ca (its concentration divided by its enrichment factor) was inserted in the crustal matter calculation. Metal oxides were evaluated from Cu, Zn, Pb and the anthropogenic component of Fe; Br oxides were also added to this component, which was generically called "metal oxides" (Marcazzan et al. 2004).

Organic matter was obtained from OC, using a mean molecular to carbon ratio of 1.8, considering that in Milan area air masses are usually aged due to the frequently occurrence of stability conditions (Turpin and Lim 2001). Organic matter was the major contributor to PM10 mass (Fig. 2a), without significant seasonal differences (34% and 33% in summer and winter, respectively).

An important contribution to total PM10 mass in both seasons came also from other secondary compounds such as sulphate, nitrate and ammonium, which, summed up, accounted for 16% and 24% during summer and winter, respectively.

During summertime, crustal matter contribution was 14%, while during wintertime it was 6%. The larger summer values can be ascribed to drier conditions of the ground (that foster dust resuspension) and higher atmospheric turbulence, which slows the deposition of suspended particles. Moreover, local construction works occasionally affected PM10 mass. Particularly strong construction works contribution was

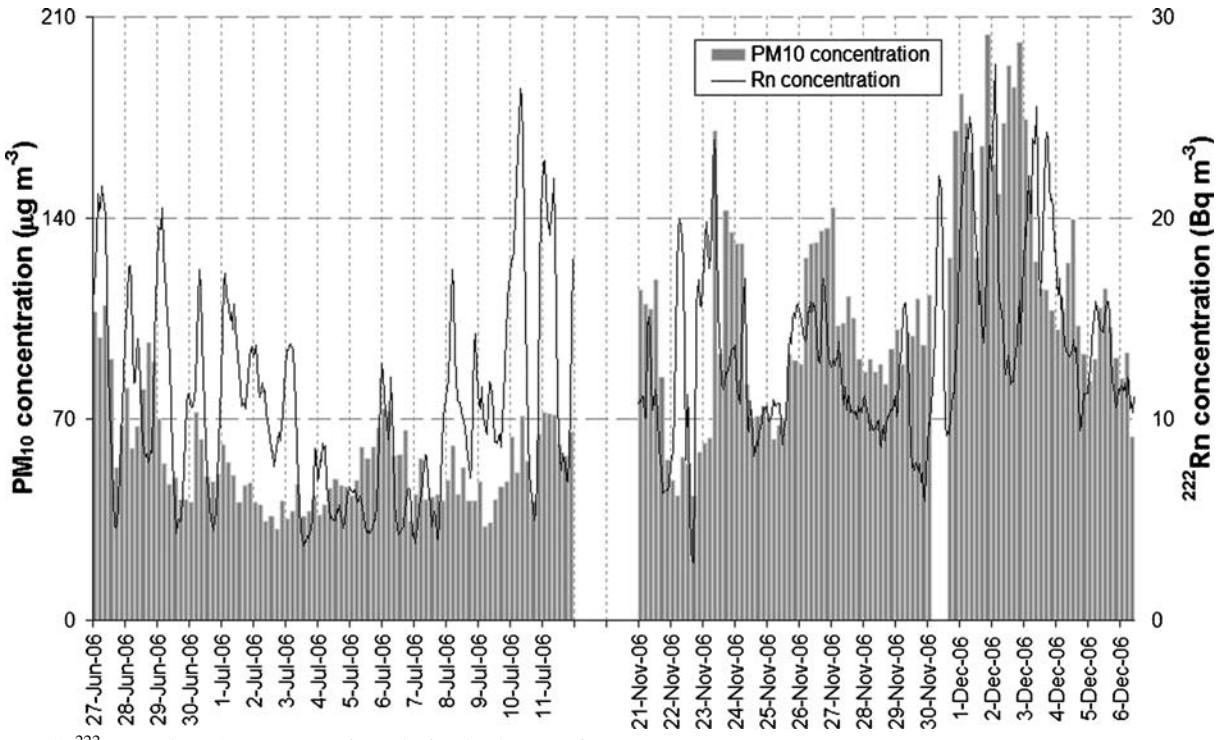

Fig. 1 ^{222}Rn and PM10 concentrations during both campaigns

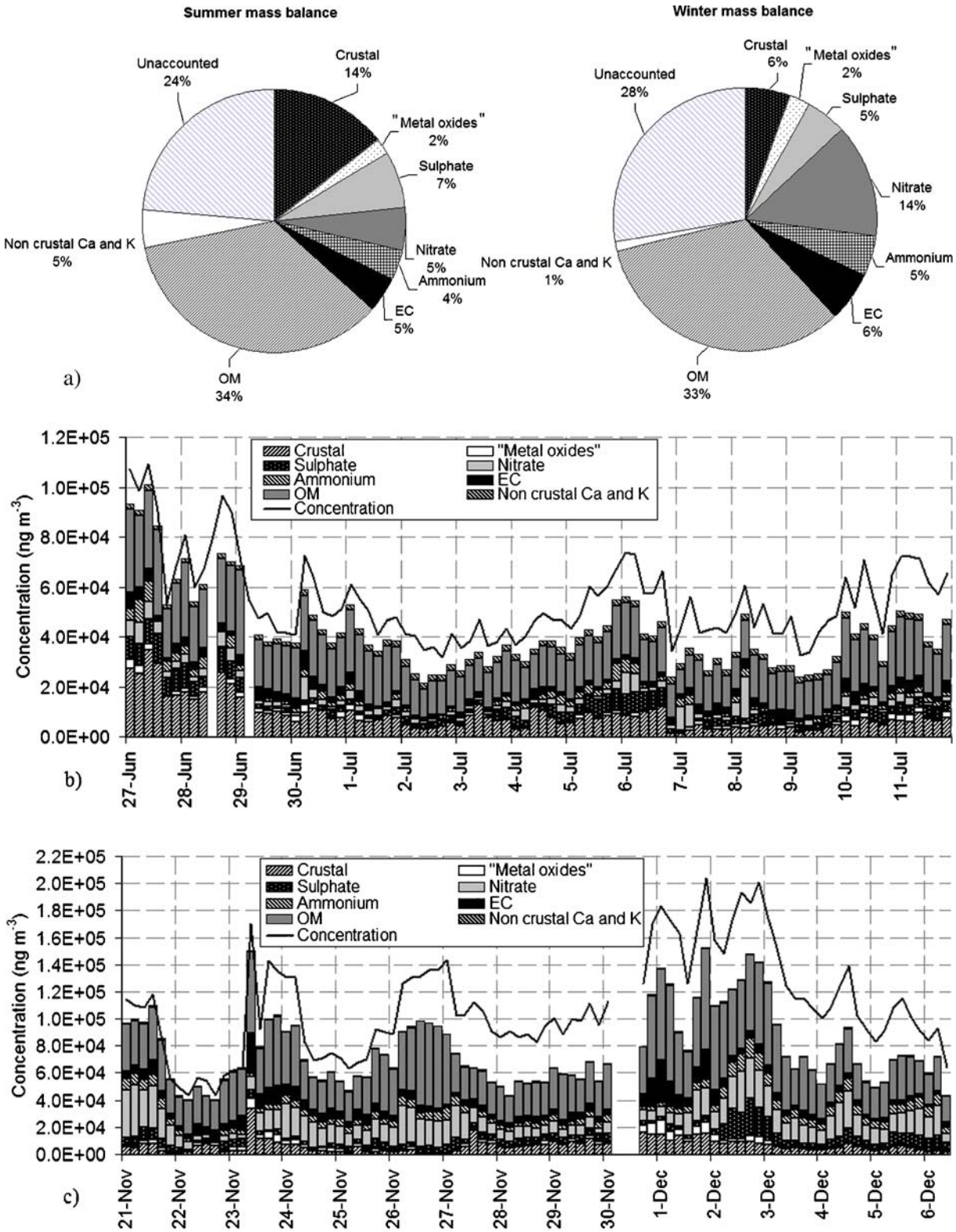

Fig. 2 (a) Summer and winter average mass closure. (b) Temporal trend of different PM10 components contribution (summer). (c) Temporal trend of different PM10 components contribution (winter)

Table 2 Average absolute and relative contribution of measured PM10 components in different time-intervals during both seasons

			PM10 mass	Crustal	Metal oxides	Sulphate	Nitrate	Ammonium	EC	OM	Non crustal Ca and K
Summer	12–04 a.m.	$\mu g\ m^{-3}$	58	8.1	1.6	3.8	4.0	2.4	3.0	20.7	2.3
		% PM10		12%	3%	7%	7%	4%	5%	36%	5%
	04–08 a.m.	$\mu g\ m^{-3}$	57	6.8	1.6	3.1	4.8	2.5	2.9	17.3	2.3
		% PM10		12%	3%	6%	8%	4%	5%	33%	5%
	08 a.m.–12 p.m.	$\mu g\ m^{-3}$	56	10.3	1.3	3.3	2.3	1.9	3.0	19.0	2.3
		% PM10		17%	2%	5%	4%	3%	5%	35%	5%
	12–04 p.m.	$\mu g\ m^{-3}$	53	7.9	0.4	3.7	1.7	1.4	1.6	16.7	2.1
		% PM10		15%	1%	7%	4%	4%	3%	35%	5%
	04–08 p.m.	$\mu g\ m^{-3}$	51	8.5	0.7	4.5	1.9	1.5	1.8	17.2	2.3
		% PM10		16%	1%	8%	4%	4%	4%	34%	5%
	08 p.m.–12 a.m.	$\mu g\ m^{-3}$	53	7.4	1.4	3.7	2.3	2.4	2.3	18.4	2.3
		% PM10		13%	3%	7%	4%	4%	5%	36%	5%
Winter	12–04 a.m.	$\mu g\ m^{-3}$	109	4.9	2.4	4.6	13.3	4.9	6.2	33.6	0.9
		% PM10		4%	2%	5%	14%	5%	6%	34%	1%
	04–08 a.m.	$\mu g\ m^{-3}$	105	4.0	1.9	5.3	14.9	5.4	5.3	33.9	0.9
		% PM10		4%	2%	5%	15%	6%	6%	35%	1%
	08 a.m.–12 p.m.	$\mu g\ m^{-3}$	111	7.4	2.2	5.5	14.1	4.7	6.8	32.1	0.9
		% PM10		7%	2%	5%	14%	5%	7%	32%	1%
	12–04 p.m.	$\mu g\ m^{-3}$	109	6.6	1.6	4.8	14.2	4.7	4.7	26.4	0.8
		% PM10		7%	2%	5%	15%	5%	6%	30%	1%
	04–08 p.m.	$\mu g\ m^{-3}$	111	6.9	2.8	5.5	13.6	5.0	5.9	32.9	0.9
		% PM10		7%	3%	5%	13%	5%	6%	33%	1%
	08 p.m.–12 a.m.	$\mu g\ m^{-3}$	113	5.7	3.0	5.5	12.0	4.9	6.8	35.1	0.9
		% PM10		5%	3%	6%	12%	5%	6%	35%	1%

identified on 3 July and on 23 and 27 November, using both information on Al, Si and Ca concentration and sudden and short-lasting increases in coarse-fraction particle number concentration (not shown).

The 4-hours temporal-resolution allowed the mass closure evaluation during different time-intervals. Figure 2b and c show the temporal pattern of the measured components. Differences in PM10 composition during the period and in particular during contiguous time-slots can be noticed (see as examples 30 June morning, 6 July evening, 23 November morning, 1–2 December, or summer differences in nitrates concentrations between daytime and nighttime) and they would not have been singled out using traditional 24 hours samplings. Moreover, intra-day variations were important for the identification of particular phenomena. In Table 2, the average absolute and relative contributions for different components are reported, while in Fig. 3 the pattern during the representative day (Nassetti 1996) for sulphates and nitrates is shown. For each PM component and each sampling day the squared differences between the concentration in each time interval and the correspondent concentration of another day were summed up. The day for which the sum of the above mentioned values on the whole period is minimum can be defined as the representative day. Thus, the representative day is a "real" day characterised by the minimum variation from all the others. From Table 2 and Fig. 3, it can be noticed that summer sulphates relative concentration began to rise from 12 P.M., reached a maximum between 04–08 P.M. and then lowered during nighttime. Indeed, the mixing layer reaches its maximum evolution during afternoon, and it can include sulphates produced by photochemical processes at higher altitudes (Raes et al. 2000). During the evening, mixing layer height decreases and the entrainment of sulphates from upper atmospheric layers is inhibited. Nevertheless, as secondary sulphates usually lay in smaller size ranges (Querol et al. 1998; Alastuey et al. 2004; and therein literature), their residence time is quite long and during the night, when larger particles deposit rapidly, their relative contribution to the mass does not change significantly. The minimum daily concentration was reached on average between 08 A.M. and 12 P.M. when other sources (resuspended dust, traffic, construction work) reactivated while mixing layer was not yet high enough to reach sulphates potentially present at higher altitudes.

It is noteworthy that nitrates relative contribution was higher during nighttime in summer, when lower temperatures both limited losses due to volatilisation and favoured condensation processes.

Seasonal average relative contributions showed that crustal matter had a slight diurnal trend in both seasons, with higher relative contributions during daytime when resuspension due to traffic and construction works was higher.

Uncertainties on mass closure were calculated following Andrews et al. (2000): an uncertainty of 50% was given to crustal matter and metal oxides, as their evaluation comes from assumptions on principal oxides, while an analytical uncertainty of 10% was given to sulphate, nitrate, ammonium, EC and OM. The total uncertainty on mass closure was thus estimated to be about 10%. This was not enough to justify the PM10 unexplained mass, which was about 25% in both seasons. However, it should be considered that there are components, i.e. carbonates and water, which were not measured with our analytical techniques. Inorganic carbonate carbon (CC) presents an analytical interference with OC during standard TOT analysis (Chow and Watson 2002), but it is in general a minor fraction of total carbon. However, the conversion between CC and carbonate mass is 5.0, very high if compared with the 1.8 factor used for OC–OM ratio. So, if only 5% of carbon considered as OC were CC, considering a factor of 5.0 instead of 1.8 for carbon to mass conversion for this small carbon fraction, carbonate matter would accounts for 5% to total PM10 mass. Moreover, water content at 50% R.H. can give a contribution of about 10% (McMurry 2000). In particular, K (Andrews et al. 2000), sulphates and nitrates (Hueglin et al. 2005) can be responsible for water contents in particulate matter. The larger discrepancies in mass closure observed during wintertime may be explained considering that higher nitrate concentration (on average 14%) and R.H. (on average 78%) registered in this season might have increased water content in PM10. Sea salt

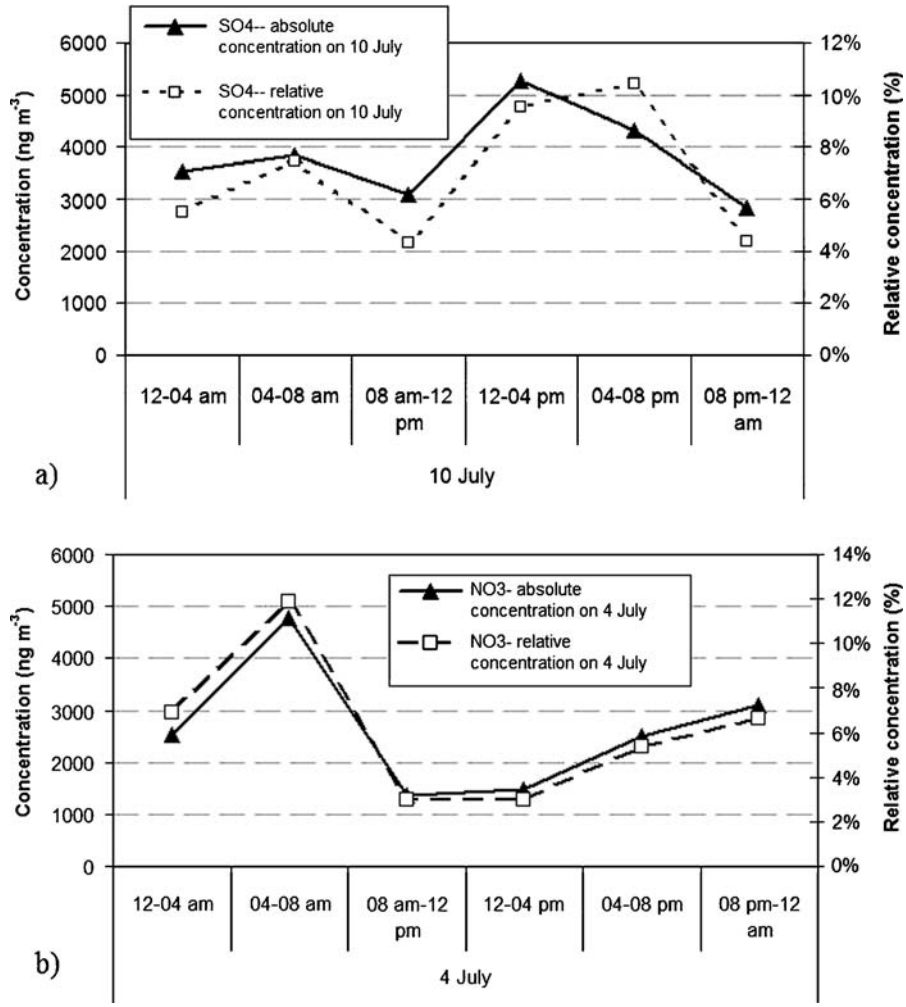

Fig. 3 (a) Representative day calculated for absolute and relative sulphate summer concentrations (10 July). (b) Representative day calculated for absolute and relative sulphate summer concentrations (5 July)

(Maenhaut et al. 2002) is another possible PM10 component that was here neglected because in Milan its average contribution was 1–2% at most. Therefore, if we consider about 15–20% of contribution coming from H_2O and carbonates, our mass closure approaches to 100% within the evaluated uncertainties.

Evaluation of secondary contribution

A subject of great concern in aerosol science is the identification of primary and secondary contributions. The biggest problem in identifying these components consists in the separation of contributions from organic carbon. Different approaches can be found in the literature, but the most used is still the EC-tracer method (Turpin and Huntzicker 1995). This method operates the separation of the two contributions, using the ratio between OC and EC in primary sources $(OC/EC)_{pri}$.

The model used here was $OC_{pri} = EC \cdot (OC/EC)_{pri}$, with two different values used for $(OC/EC)_{pri}$ during summer and winter. During summertime, as traffic is the main EC source in the city, $(OC/EC)_{pri} = 1.34$ was used, as reported by Giugliano et al. (2005) for tunnel measurements in Milan. On the contrary, during wintertime that value could not correctly represent primary emissions, as oil combustion for domestic heating or biomass burning might provide quite important contributions to EC concentration. Thus, pollution episodes dominated by primary contribution from a complex mixture of sources were identified and the average OC/EC ratio

during these episodes was chosen as representative for primary OC/EC during wintertime, so $(OC/EC)_{pri} = 1.58$ was used during this season.

In this way, in both seasons OC_{pri} took into account only OC coming from combustion processes, while non–combustion primary emissions were included, together with secondary OC, into $OC_{res} = OC–OC_{pri}$. Non combustion primary emissions were especially biogenic debris, which were estimated about 8% of OM in the urban area of Vienna by Puxbaum and Tenze-Kunit (2003).

Applying this model, organic matter from combustion processes ($OM_{pri} = 1.8\ OC_{pri}$) accounted for 11% to PM10 mass during summertime and 16% during wintertime.

In Fig. 4, primary (crustal matter, "metal" oxides, EC, OM_{pri}, non-crustal Ca and K) and OM_{res} together with nitrate, sulphate, ammonium absolute contributions (named "secondary" in Fig. 4), compared to PM10 concentrations, are shown. During summertime the two contributions were comparable (on average 36% primary and 40% secondary contribution, with 24% of unidentified mass), while during wintertime primary contribution was reduced (32% on average) and secondary contribution was estimated on average 40%. During summertime, relative primary and secondary contributions showed few differences during the whole period, while some episodes were detected during wintertime with a predominance of primary or secondary contributions. Some of these episodes will be analysed in next paragraphs. As already noticed for sulphate relative concentration also OM_{res} exhibited maxima during summer afternoons (likely due to higher photochemical activity) and morning minima (due to the high contribution of other primary sources, i.e. resuspended dust, traffic, construction works, and to the low photochemical activity). On the contrary, during wintertime the strongest secondary OM contributions were registered during night-time, probably due to condensation processes, which are favoured by lower temperatures.

The results presented in Fig. 4 suggested also an outcome on future abatement strategies: considering the possibility to completely eliminate primary PM contribution and using the EU daily

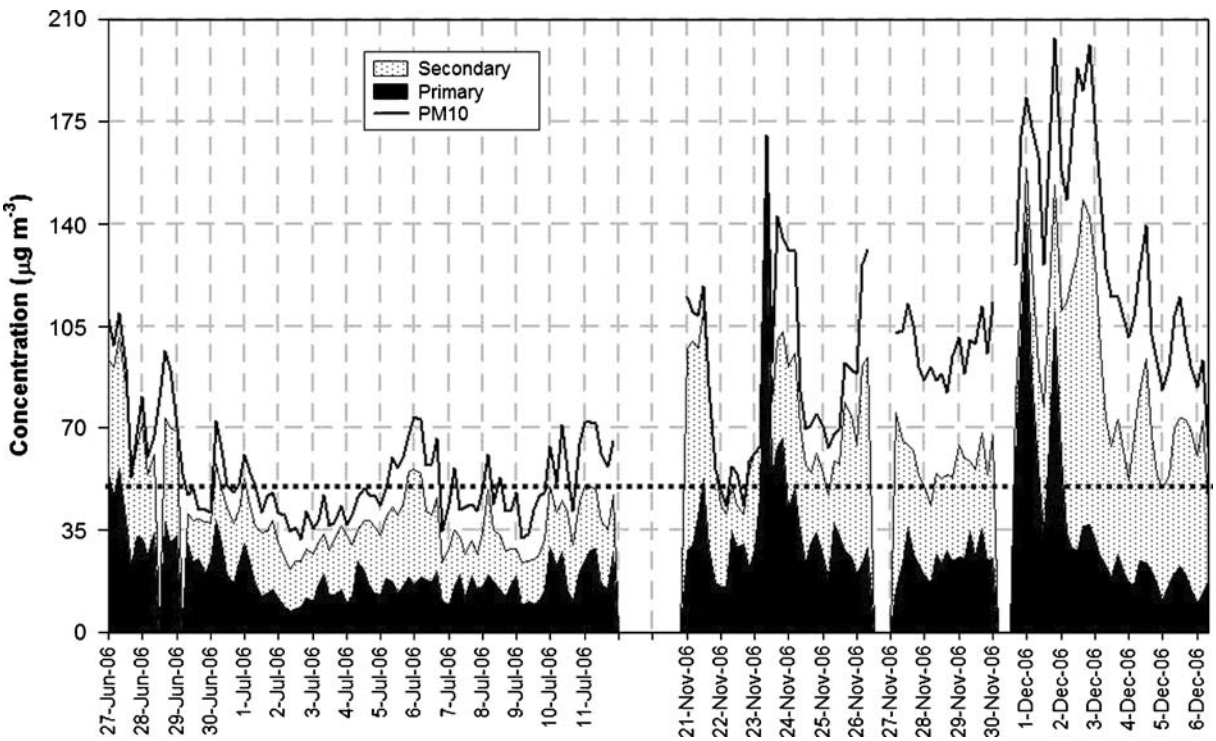

Fig. 4 "Primary" and "secondary" PM10 components

limit of 50 μg m^{-3}, it was noticed that summer exceedances on 24 hour basis (60% of the sampling days) would be completely eliminated. On the contrary during wintertime, this reduction would be really poor (from 100% to 81%), due both to higher PM10 concentration and secondary contribution. This means that it will not be enough to decrease primary emissions in future abatement strategies, but these will have to include also plans for gaseous precursors emissions reduction.

Separating working days from Sundays data, it was observed that the not explained PM10 mass was always higher during Sundays (summer: 23% during working days and 29% during Sundays; winter: 28% during working days and 32% during Sundays). The evaluation of primary and secondary OC also evidenced that during Sundays the secondary OC percentage was higher than during working days (summer: 80% secondary OC versus total OC during Sundays and 67% during working days; winter: 70% during Sundays and 49% during working days). These data might indicate that during Sundays the air mass contained a higher proportion of aged OC (which can have a higher OC–OM conversion factor) as the primary contribution was lower. This result suggests that a single OC–OM conversion factor cannot likely be used for all samples. However, due to the limited number of Sundays analysed in this work, further studies are needed to better understand this phenomenon and work on this topic is still in progress.

Episodes

The high-time resolution of the samplings allowed a detailed study of production/formation, transport, removal and settling of the particles in atmosphere and helped in the detection of different sources acting contemporaneously. As examples, in the following paragraphs some episodes are described and analysed in detail.

Effect of the rainfalls

Rainfall episodes were registered during both seasons; one episode during summertime (6 July evening) and another during wintertime (3–4 December) were studied. These episodes differed for rainfalls duration and intensity: in particular, an event during a short-lasting thunderstorm of high intensity, with 34 mm of rainfall in 4 hours (25 mm between 7 P.M. and 8 P.M.) and wind speed

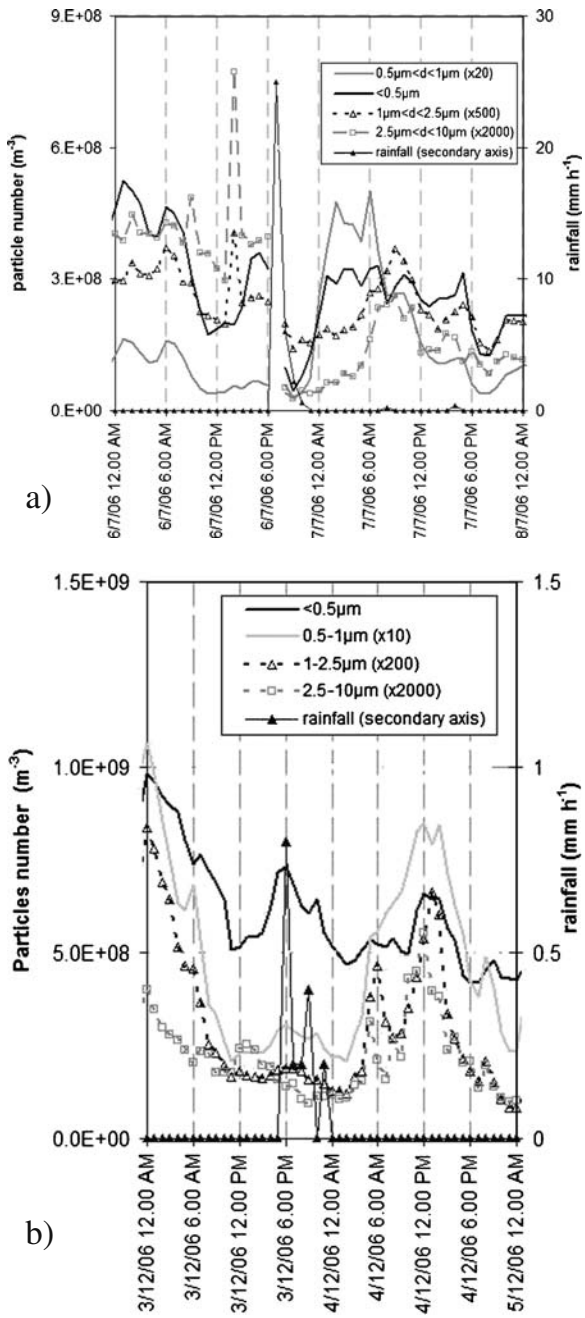

Fig. 5 Particle number concentration in different size-ranges and precipitation intensity during: (a) 6–7 July 2006; (b) 3–4 December 2006

up to 7.5 m s^{-1} (averaged on 10 minutes), occurred during summertime, while the wintertime episode lasted for several hours, but the rainfall rate was always below 1 mm h^{-1}.

Particles removal depended on the characteristics of the phenomenon. Figure 5a shows that precipitations of high intensity were efficient in removing very fine particles (<0.5 μm) and particles in the coarse fraction (2.5 μm < d < 10 μm), with decreases of 70% and 90%, respectively. Less significant decreases (about −25%) were registered for particles in the range 0.5–2.5 μm. This experimental result was in agreement with the so-called Greenfield gap (Greenfield 1957), generally reported in theoretical studies (Seinfeld and Pandis 1998; Chate 2005). It consists in low removal efficiency for particles with diameters between a few hundreds nm and about 2.0 μm, due to the low collision efficiency for particles in this size range. Our experimental data showed also that a lower rainfall rate caused a small or even no effect on the particles removal in all size ranges (Fig. 5b).

During the summer thunderstorm, the mass concentration was halved. Strong reductions were registered in sulphates and oxalate concentrations (−85% and −75% respectively), due to the high solubility of these compounds. Also Al, Si, K, Ca and Ti concentrations decreased more than 80%, as they are mainly found in larger particles (coarse mode) which are efficiently removed by strong rainfalls. As an additional result, Fe, Mn, Ni, Cu, Zn, Br and Pb and ammonium concentrations were reduced more than 40%, while nitrate and EC did not show significant variations during the period.

During the winter episode, which had lower intensity, no relevant differences were registered both in mass, elements, ions and carbon fractions concentrations, highlighting the importance of the rainfall rate in the particles removal process.

Local production

A remarkable increase in Cl, Cr, Mn, Fe, Ni, Cu, Zn, Pb and EC concentrations, in particle with $d >$

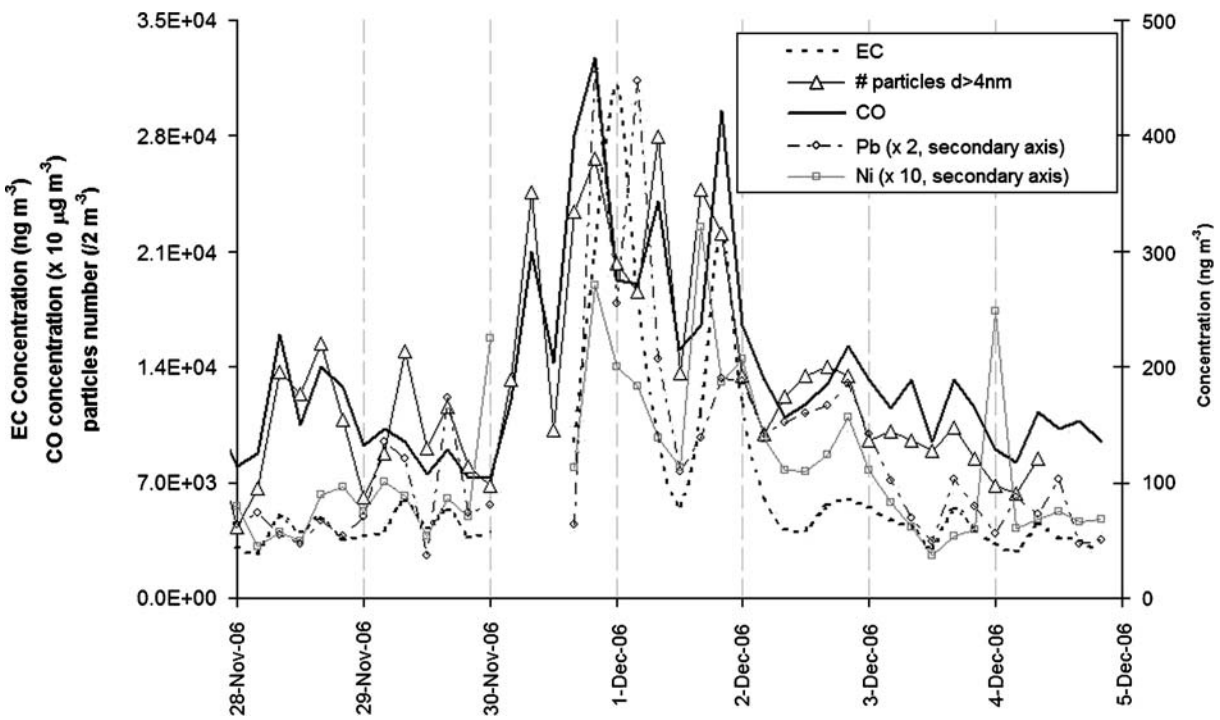

Fig. 6 EC, Pb, Ni and CO concentration together with concentration patterns particles with $d > 4$ nm during 28 November–4 December 2006

4 nm number and in primary gaseous pollutants (CO and NO) concentrations was registered during the nights between 30 November–1 December and 1–2 December (see Fig. 6 as an example). The average values for all these components during the two periods were 3 times higher (2 times for particle with $d > 4$ nm) than the values registered during 28–29 November (before the episode) and 3–4 December (after this episode; data registered on 2 December were excluded because of another episode analysed in the following paragraph). It is noteworthy that all the listed components were of primary origin while secondary components did not show any significant increase during the episode. EC is the tracer for traffic emission (Querol et al. 2004), as well as Fe, Cu and Cr (Marcazzan et al. 2003b; Vecchi et al. 2007). Mn and Zn are associated to industrial emissions in this area (Marcazzan et al. 2003b). CO and NO are typically emitted during combustion processes while Cl, Ni and Pb may be emitted by incinerators or by oils combustion (Artaxo et al. 1999; Song et al. 2001; Thomaidis et al. 2003; Qin and Oduyemi 2003; Graney et al. 2004).

^{222}Rn analysis showed a strong stability in atmospheric conditions (see Fig. 1) with both daily minima and maxima concentration growing from 29 November to 2 December morning. The strong daytime (low concentration)–nighttime (high concentration) modulation of the analysed components was mainly ascribed to mixing layer evolution. On 30 November–1 December maxima mixing layer heights were 229 m and 153 m, low values if compared to 400–500 m generally reached during the other days of the winter campaign. During nighttime, ground-based inversions were registered, with very low mixing layer heights (<50 m). Maxima concentrations for the above-mentioned components were not registered during the same time-intervals (Fig. 6), indicating that the components came from different sources. The increase and modulation in these components concentration was well described by local emissions (in the urban or suburban area) from different sources and by atmospheric stability.

As in these episodes some prevailing primary sources were identified, the average OC/EC ratio registered during these two nights (1.58) was chosen as representative for $(OC/EC)_{pri}$ during wintertime and it was used for the identification of OC_{pri} during this season, as explained in paragraph 3.3.

Long range transports

Looking at S concentration temporal pattern with 4 hours resolution, two peculiar behaviours were noted on 5–6 July and 2–3 December. During both episodes, there was a good correlation (R^2 = 0.85 between 12.00 A.M. on 5 July and 12.00 A.M. on 7 July; R^2 = 0.78 between 12.00 P.M. on 2 December and 4 P.M. on 3 December) between S and pyrolitic carbon (PC) concentration temporal trends. Literature studies report on the possibility of secondary organic formation, as result of acid-catalysed reactions between acidic sulphate and volatile organic compounds (Jang et al. 2003), fostering PC generation during TOT analysis. Moreover, volatile organic compounds can condense on sulphate particle surface (Kim and Hopke 2006) and sources of PC-rich secondary sulphates were also detected by PMF analysis in different sites (Kim and Hopke 2006; Begum et al. 2005).

During the summer episode (5–6 July), both S and PC (see Fig. 7) concentrations almost doubled (1.9 times) in comparison with the average levels registered during the summer campaign. More-

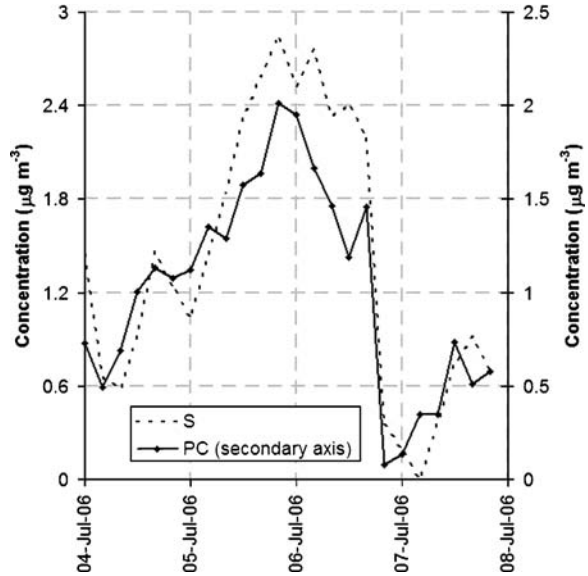

Fig. 7 S and PC concentration (4-hours resolution) during 4–6 July 2006

over, their relative contribution to the total mass increased, indicating that the growth was not due to stability condition, but to additional sources. On 5–6 July, sulphates and organic carbon fraction detected as PC during TOT analysis summed up to 13% of PM10 mass, which was higher than the average value of 8% registered during the rest of the summer campaign. It is also noteworthy the absence of daytime–nighttime modulation during the episode; on the contrary, no anomalous trends were registered for other PM10 components or gaseous pollutants. As O_x (NO_2+O_3, taken as photochemical indicator) did not show any anomalous behaviour compared with previous days, the hypothesis of photochemical production was rejected and the possibility of a long-range transport was considered. The wind speed was about 1.8 m s^{-1} and wind direction was E both during daytime and night-time during the episode; moreover, looking at back trajectories (Fig. 8) calculated using NOAA-Hysplit model (Draxler and Rolph 2003; Rolph 2003) it was observed that the air mass on Milan on 5 July had travelled through eastern Europe countries during previous days. Fuels containing high quantities of S are still largely used in those countries, so that

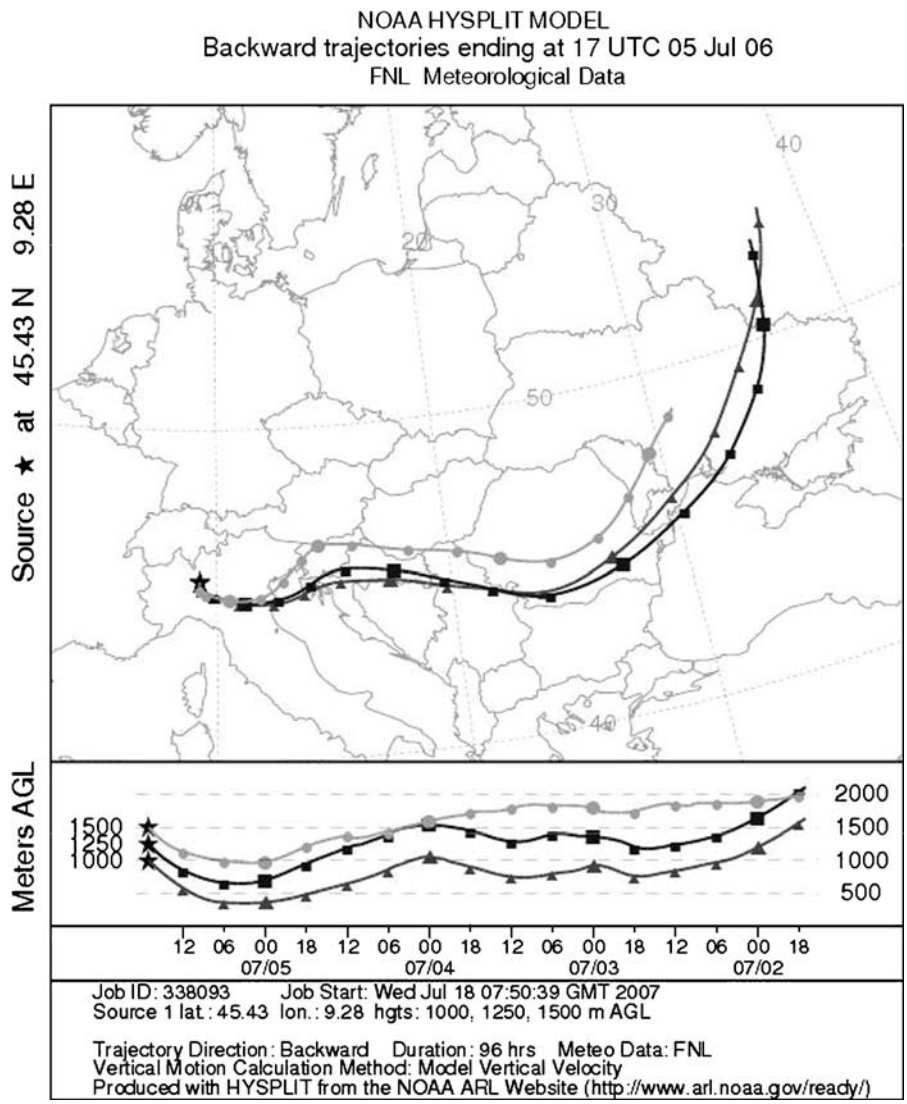

Fig. 8 backtrajectories on Milan during 5 July 2006

sulphates and/or their precursors, together with other components (e.g. organics) are occasionally transported to Northern Italy. Therefore, a long-range transport likely caused the observed episode.

The S temporal pattern obtained by streaker samples with hourly resolution (see Fig. 9) presented two narrow peaks on the gross modulation due to the transport event. These peaks were coincident to the ones recorded in Ca and number of particles with $d > 2.0$ μm concentrations and they were attributed to local construction works: resuspended construction matter (i.e. cement, dust, gypsum) and machineries exhausts were likely sources for Ca and S narrow peaks.

The importance of high-time resolved samplings is remarkable in the detection of these episodes, which would not have been singled out with standard 24-hours samplings, as the concentration values maxima were similar to the ones registered during other days in the same period. Instead, 4-hours resolution samplings allowed the detection of the long-range transport and 1-hour resolved samplings revealed the contribution of a local source (i.e. construction works).

During the winter episode (2–3 December) a significant sudden growth in S concentration was also observed (see Fig. 10) both in absolute values (that reached almost 10 μg m^{-3} as S average concentration on 4 hours) and in relative values: sulphate concentration increased from 4% (as average value during the rest of the period) to 12% during the episode. Increases were also detected in absolute concentrations for ammonium, nitrate, PC and Na (+2% for nitrate and ammonium, +3% for PC and +0.6% for Na). Back trajectories showed that the air mass on Milan on 2 December had travelled during the previous 5 days through the Po Valley (during 48 hours) and still before over the Adriatic sea, where the detected components could have been added to the air mass.

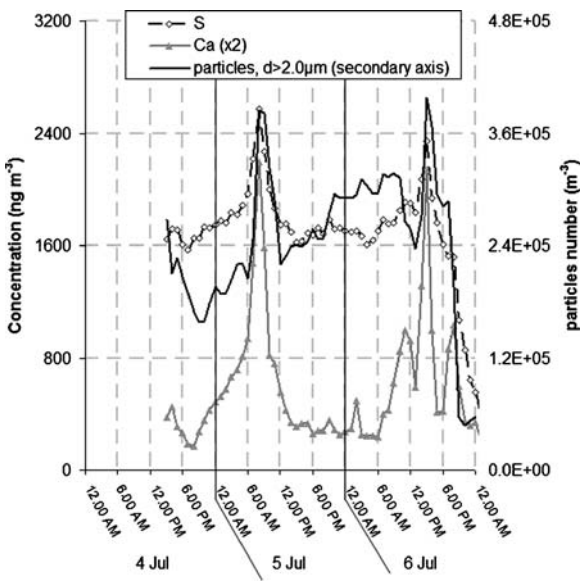

Fig. 9 S, Ca and particles ($d > 2$ μm) number concentration with 1-hour resolution during 4–6 July 2006

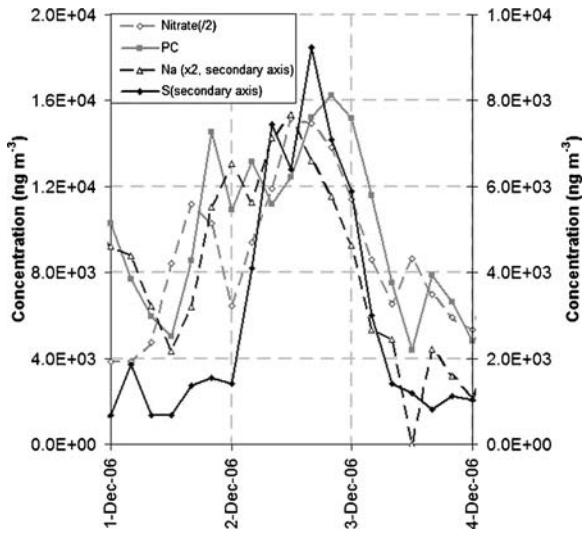

Fig. 10 NO_3^-, S, Na and PC concentration during 1–3 December 2006

It is worthy to note that during this episode the PM10 mass concentrations were comparable to previous days ones. However, during both episodes remarkable differences in PM10 composition (Fig. 2c) and in relative contributions by primary and secondary components (Fig. 4) were observed.

Conclusions

Elemental, ions and OC/EC fractions characterisation with high temporal resolution allowed to obtain the mass closure during the two analysed

periods and to single out daily variations. It showed that in summer sulphates presented daytime maxima (due to photochemical activity), while nitrates had higher relative contribution during night-time, due to the lower temperatures. During both seasons the crustal component showed higher relative concentrations during daytime, when emissions by resuspension sources were higher. Looking at the temporal pattern of the different components, significant variations in aerosol composition were often registered during contiguous time-intervals, highlighting that 24-hour samplings can limit the understanding of the actual impact of different sources on sampled aerosol.

Moreover, 4-hours resolution samplings allowed the identification of time-intervals when primary contribution dominated. This enabled the estimation of $(OC/EC)_{pri}$ during wintertime, when factors derived by tunnel measurements might be not representative of the primary sources mixture influencing the urban area. During summertime, primary OM was almost 11% and secondary OM was about 25% of total PM10 mass concentration, while during wintertime the two contributions were 14% and 19%, respectively. The higher summer contribution of secondary component was due to photochemical activity, while during wintertime, as the temperature was not too low (10.5°C on average), secondary contribution due to condensation was probably limited.

High time resolved samplings allowed also the identification of events, which would not have been identified with 24-hours resolved samplings. Removal of particles in different size-bins due to precipitations, local accumulation due to strong stability conditions and a long range transport episode were identified. During the last episode, the availability of 4-hours detailed characterisation and 1-hour resolved elemental characterisation led to the identification of a short-lasting local source (construction works) piled up to the contribution due to long range transport. This result emphasises that the higher is the sampling resolution, the better detailed is the information about processes influencing the measured aerosol concentration and composition.

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