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The impact of fireworks on airborne particles

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Abstract

Fireworks are one of the most unusual sources of pollution in atmosphere; although transient, these pollution episodes are responsible for high concentrations of particles (especially metals and organic compounds) and gases. In this paper, results of a study on chemical–physical properties of airborne particles (elements, ions, organic and elemental carbon and particles size distributions) collected during a fireworks episode in Milan (Italy) are reported. Elements typically emitted during pyrotechnic displays increased in 1 h as follows: Sr (120 times), Mg (22 times), Ba (12 times), K (11 times), and Cu (6 times). In our case study, Sr was recognised as the best fireworks tracer because its concentration was very high during the event and lower than, or comparable with, minimum detection limits during other time intervals, suggesting that it was mainly due to pyrotechnic displays. In addition, particles number concentrations increased significantly during the episode (up to 6.7 times in 1 h for the $0.5 < d < 1\,\mu m$ size bin). Contributions (e.g. Cu, elemental carbon and nitrogen oxides) to air pollution due to the large traffic volume registered during the same night were also singled out.

The original application of Positive Matrix Factorisation and Multiple Linear Regression allowed, as far as we know, here for the first time, the quantification of the fireworks contribution to atmospheric particulate matter (PM) and the resolution of their chemical profile. The contribution of fireworks to the local environment in terms of PM_{10} mass, elements and chemical components was assessed with 4-h time resolution. PM_{10} mass apportioned by fireworks was up to $33.6\,\mu g\,m^{-3}$ (about 50% of the total PM_{10} mass). Major contributors were elemental and organic carbon (2.8 and $8.1\,\mu g\,m^{-3}$, respectively) as well as metals like Mg, K, Sr, Ba, and Cu (0.4, 0.7, 0.07, 0.1, and $0.1\,\mu g\,m^{-3}$, respectively).

Keywords: Fireworks; Chemical composition; Number size distribution; PMF

1. Introduction

In recent years concern for air pollution effects both on short term and on long term has increased (Pope and Dockery, 2006; and therein literature). Therefore, many studies are currently carried out to characterise anthropogenic emissions especially in urban areas where large populations live.

One of the most unusual sources of pollution in atmosphere is the displacement of fireworks to celebrate festivities worldwide as well as specific

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events. The burning of fireworks is a huge source of gaseous pollutants such as ozone, sulphur dioxide, and nitrogen oxides (Attri et al., 2001; Ravindra et al., 2003) as well as of suspended particles. The aerosol particles emitted by fireworks are generally composed of metals (e.g. potassium, magnesium, strontium, barium, and copper), elemental carbon and secondary compounds like nitrate and organic substances (Kulshrestha et al., 2004; Drewnick et al., 2006; Moreno et al., 2007; Wang et al., 2007). The issue of exposure to elevated particle concentrations during celebrations with fireworks has implications in many countries of the world where pyrotechnic exhibitions often last for several hours/days (e.g. during Diwali Festival in India, Las Fallas in Spain, Lantern Festival in Beijing and New Year's celebration worldwide). The complex nature of particles emitted during fireworks may cause adverse health effects as reported in Ravindra et al. (2001). Nevertheless, some authors (Perry, 1999; Dutcher et al., 1999) concluded that fireworks unlikely pose a significant public health hazard, as they are relatively rare, detonate at altitudes well above the ground and generally burn outdoors, where the emitted pollutants can be dispersed in a large volume of air.

An additional effect of fireworks is the visibility reduction due to the generation of a dense cloud of smoke that drifts downwind and slowly disperses. The impact of fireworks on visibility and human health is particularly evident when the pyrotechnic exhibition is performed during stable meteorological conditions (Clark, 1997).

In this paper, we report on the chemical–physical characteristics of ambient aerosol measured during fireworks burnt in Milan (Italy) to celebrate the win of the football World Cup; due to the short duration of the fireworks exhibition, we considered it as a case study. The main goal of this paper is the assessment of the fireworks emissions environmental impact through the aerosol characterisation in terms of number (10-min resolution), mass and chemical composition (4-h time resolution) as well as 1-h resolution elemental data. In addition to particulate matter (PM), trace gases concentrations, meteorological parameters, and atmospheric stability conditions were taken into account. Owing to the occurrence of this episode during a longer monitoring campaign, the apportionment of the fireworks source was possible applying Positive Matrix Factorisation (PMF) and Multiple Linear Regression (MLR) to the whole data set; as far as we know, this is the first attempt to identify and quantify the fireworks source contribution using a receptor model.

2. Experimental

The effect of pyrotechnic displays on air quality was studied in Milan (Italy) in July 2006, during the night between 9th and 10th, when the Italian team was celebrated for the win of the 2006 FIFA World Cup.

2.1. Site and sampling

Major pyrotechnic displays were located in the Cathedral's square downtown Milan; additional celebrations with many minor fireworks displays and a huge amount of crackers and sparkles were burnt everywhere in the town, starting soon after the end of the football match (at about 10:45 p.m.). Due to the peculiarity of the episode, the duration of the celebrations was not easy to assess (a reasonable estimate might be approximately 1–2 h). The samplings were carried out at the University campus on the roof of the Institute of Physics, at about 10 m a.g.l. The monitoring station was about 3 km far from the city centre so that the measurement was related to the advected and diffused smoke cloud (as generally done in literature studies on this topic).

PM_{10} was sampled starting at 12 a.m., local time, from 9 to 11 July, every 4 h. Samplings were carried out in parallel on PTFE filters (diameter: 47 mm, pore size: 2 μm) and quartz fibre filters (diameter: 47 mm, pre-fired at 700 °C for 1 h) using CEN-equivalent samplers operating at a flow rate of $2.3\,m^3\,h^{-1}$.

Fine ($d_{ae} < 2.5\,\mu m$) and coarse ($2.5 < d_{ae} < 10\,\mu m$) 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 $d_{ae} > 10\,\mu m$) and an impactor. The latter is made of a Kapton foil on which coarse particles are collected. The fine fraction is then sampled 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 ($1.8^\circ\,h^{-1}$); this produces a circular continuous deposition on both stages. It should be noted that mass concentration in streaker samples is not available. 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.

2.2. Laboratory analyses

Before and after the samplings the filters were exposed for 48 h on open but dust-protected sieve-trays in an air-conditioned weighing room ($T = 20 \pm 1\,^{\circ}C$ and $RH = 50 \pm 5\%$). The gravimetric determination of the mass was carried out using an analytical microbalance (precision 1 μg), which was installed and operated in the weighing room. Calibration procedures checked the microbalance performance.

PTFE filters were analysed for elemental composition by Energy Dispersive X-Ray Fluorescence technique (details can be found in Marcazzan et al., 2004), obtaining concentration values for Mg, Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, Sr, Ba, Pb. Other elements (i.e. V, As, Se, Zr, and Mo) were in principle detectable, but they often resulted below the minimum detection limit (MDL), which was in the range 2–20 $ng\,m^{-3}$ for most elements. Experimental overall uncertainties were in the range 10–15%.

One half of the quartz fibre filters was analysed for water-soluble major components (SO_4^{2-}, NO_3^-, and NH_4^+) by ion chromatography (IC). A special care was used in IC analyses of particulate matter collected on quartz fibre filters due to high blank levels (MDLs: 167, 359 and 46 $ng\,m^{-3}$ for SO_4^{2-}, NO_3^- and NH_4^+, respectively); information about extraction procedures and blanks correction can be found in Fermo et al. (2006). The overall uncertainty for ionic concentrations was estimated in 10%.

One punch (area: 1.5 cm^2) cut from the quartz fibre filter was analysed by thermal–optical transmittance (TOT) method (Birch and Cary, 1996) to quantify elemental and organic carbon. The technique detection limit was 0.2 $\mu g\,C\,m^{-3}$ and the precision was 5%.

Nuclepore and Kapton substrates from the streaker sampler were analysed by Particle Induced X-ray Emission analysis (PIXE) at the LABEC-INFN accelerator facility in Florence, Italy, whose set up is described in Calzolai et al. (2006). The concentration of 19 elements (Na, Mg, Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, Sr, Ba, Pb) was obtained. As for ED-XRF analysis, other elements were in principle detectable, but they often were below the MDL (lower than 10 $ng\,m^{-3}$ for V, As, Se, Zr, Rb, Mo). The accuracy of hourly elemental concentrations was in the range 2–20%.

2.3. Additional measurements

An optical particle counter (Grimm, mod.1.107) measured number size distributions in the 0.25–32 μm range (31 size bins).

To evaluate atmospheric dispersion conditions, ^{222}Rn short-lived decay products measurements were performed using the experimental methodology reported in Marcazzan et al. (2003). Mixing layer heights (MLHs) with hourly resolution were obtained by means of a box model suitably set up by the group of the Institute of Physics using ^{222}Rn concentration measurements as input data (Pacifico, 2005). MLH evaluations by our box model were in good agreement with thermal inversions heights from radio-soundings data by the nearby Milan-Linate airport as well as with other modelling studies based on thermodynamic variables (Casadei et al., 2006).

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

Trace gases data recorded at monitoring stations of the Regional Environmental Protection Agency were also available (Fig. 1): NO_2 and NO at the 1-J station (near the University campus and the motor-way) and NO_2, NO and CO at the 2-V station (city centre) and 3-L (on the ring-round). Moreover, hourly traffic volumes in the city centre were recorded at the station 4-S (city centre).

2.4. Receptor model

The fireworks episode occurred during a longer field campaign, which was performed during 2 weeks in summer and 2 weeks in winter 2006, with the same characteristics as those described in Sections 2.1–2.3. The complete PM_{10} data set (180 samples) was analysed by PMF to identify and apportion (by MLR) major aerosol sources. PMF resolved seven sources (re-suspended soil, construction works, industry, traffic, secondary sulphates, secondary nitrates and fireworks). In this paper, only results on the fireworks source will be

Fig. 1. Map of the monitoring stations.

described and discussed (another paper in preparation deals with the other six sources).

PMF is an advanced factor analysis technique computing a weighted, non-negative constrained least-squares fit. It imposes non-negativity constraints to the factors and uses realistic error estimates from data standard deviations, as described in Paatero (1997). Data values and errors, missing values and below detection limit data were calculated according to Polissar et al. (1998) and used in this work as inputs for the PMF.

In PMF studies, a weak variable (according to signal-to-noise ratio criterion, as in Paatero and Hopke, 2003) can sometimes be inserted in the fit with the normal variables if it represents a tracer of a specific source (Qin et al., 2006). This approach was here adopted for Sr, considered the best tracer of the fireworks source in our case study (see Section 3.3). It was not really a weak variable but it had a much lower signal-to-noise ratio with respect to other variables. In this work, instead of reducing the weights of Sr, we doubled them to highlight the role of this fireworks tracer in the fit. At the same time, it was necessary to down-weight some variables by increasing their uncertainties by a factor from 2 to 4 to obtain a better distribution of their scaled residuals (Kim et al., 2003). The coefficients of adjustment for the weights were determined with trial and error method until the model resolved the fireworks source, together with the same six sources found in a previous analysis where Sr was not used as input for PMF.

Rotational ambiguity is always a problem in factor analysis (Paatero et al., 2002); in this work, after a systematic study of the rotational range of the solution, FPEAK = 0 was chosen. MLR was performed to regress the total mass against the factor scores; the regression coefficients were then used to transform the factor profiles given in arbitrary units in parts per million ones and to quantitatively apportion the mass contributions among the resolved sources.

3. Results and discussion

3.1. Mass concentration and meteorological conditions

During the case study period, meteorological conditions were quite stable. The wind speed was about 1 m s^{-1} as average value between 10:30 p.m. and 12 a.m. on the fireworks night and the prevalent wind direction was changing from south-westerly to westerly direction.

During the fireworks night a ^{222}Rn strong accumulation was registered (Fig. 2); the variation

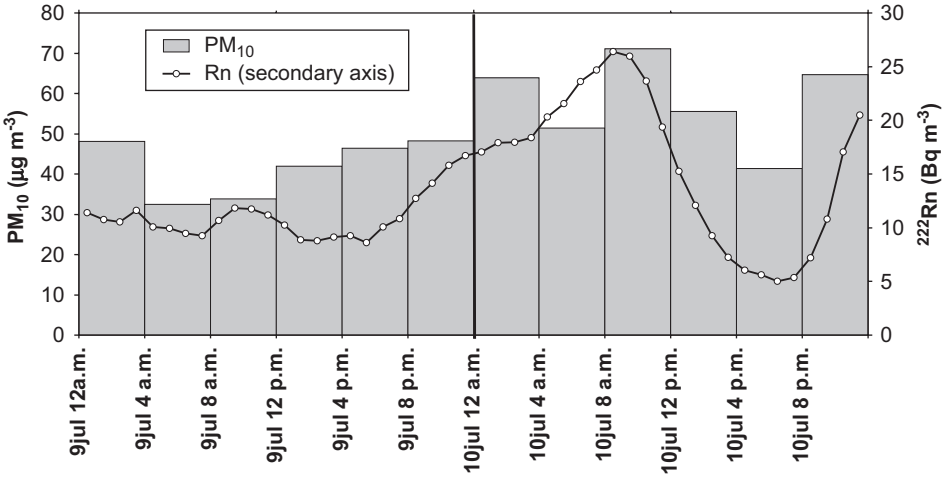

Fig. 2. PM_{10} mass (in $\mu g\,m^{-3}$) and ^{222}Rn concentration (in $Bq\,m^{-3}$) on 9–10 July 2006 in Milan.

of Radon concentration between the minimum ($8.6\,Bq\,m^{-3}$) on 9 July afternoon and the maximum ($26.4\,Bq\,m^{-3}$) in the following day was a good indicator of the nocturnal mixing layer depth, which was lower than 100 m.

In Fig. 2, PM_{10} mass and ^{222}Rn concentration on 9–10 July 2006 are shown. On 10 July, PM_{10} concentration increased up to $63.9\,\mu g\,m^{-3}$ in the time interval between 12 and 4 a.m., when the pyrotechnical displays contribution was maximum at our monitoring station, as singled out by the chemical markers analysis (see Section 3.3). However, fireworks were not likely the only cause of PM_{10} growth during that night; indeed, the concomitant strong accumulation of ^{222}Rn concentration suggests that this increase was likely due both to sources emissions and to the strong atmospheric stability.

As far as we know, currently in the literature there is no quantification of the fireworks contribution to the PM mass, as this estimation is difficult and not straightforward. With the aim of apportioning the fireworks source, in this paper the receptor model approach has been possible owing to the availability of a large number of chemically characterised PM samples with 4-h temporal resolution. According to the PMF source apportionment the fireworks contribution began to be remarkable in the 8 p.m.–12 a.m. time interval, accounting for $13.1\,\mu g\,m^{-3}$of the PM_{10} mass (27%), reached its maximum at $33.6\,\mu g\,m^{-3}$ (53%) in the 4 h after midnight and decreased to $4.2\,\mu g\,m^{-3}$ (8%) from 4 to 8 a.m.

3.2. Gaseous pollutants

CO concentration and traffic volumes increased soon after the end of the match (10:45 p.m.) at the monitoring stations 2-V and 4-S near the Cathedral's Square, as shown in Fig. 3a. A similar pattern in CO concentration, i.e. maximum value between 11 p.m. and 12 a.m. with a 3-fold increase in 1 h, was also recorded at the station 3-L, located next to the city ring-road (see Fig. 1) and about 1.5 km far from major pyrotechnic displays. In Fig. 3b NO_2 temporal patterns recorded at the stations 2-V, 3-L and 1-J are reported. At the 2-V and 3-L stations the concentration increase was recorded simultaneously with the CO increase while at the station 1-J (near University campus) a delay in the maximum concentration occurred.

Ravindra et al. (2003) observed NO_2 increases during the pyrotechnic displays. On the contrary, in our case the experimental results indicate that the increase in trace gases concentration was mainly due to the high number of vehicles circulating soon after the end of the match to celebrate the national team more than to fireworks emissions. Indeed, it is important to observe that the location of the 3-L monitoring station compared to the city centre and the prevalent wind direction (see Section 3.1) suggest that fireworks unlikely affect air quality in that area. Moreover, the NO_2 temporal trend observed at the station near major pyrotechnic displays (2-V) and at the 3-L station are comparable, indicating that no significant NO_2 emissions can be ascribed to fireworks in our case study.

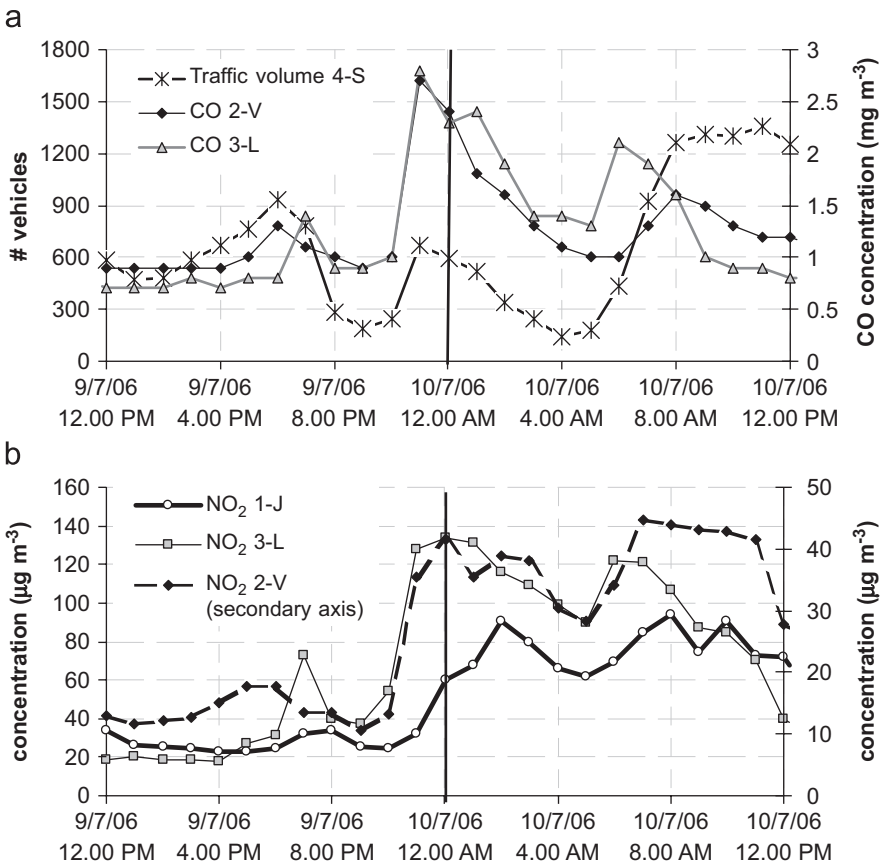

Fig. 3. (a) CO (in mg m^{-3}) and traffic volume (number of vehicles) and (b) NO_2 (in µg m^{-3}) concentrations at three different monitoring stations on 9–10 July 2006 in Milan.

The NO_2 peak occurring at 2 a.m. in the 1-J station was explained by traffic flows, likely due to people going back home, as also confirmed by Cu temporal pattern (another traffic tracer) represented in Fig. 4.

3.3. Chemical composition

On 9 July, starting from 11 p.m., the hourly concentrations of some elements in the fine fraction strongly increased. Similar results were also found PM_{10} elemental data with 4-h resolution (in Table 1 mass and chemical components concentrations are given for the episode); nevertheless, for sake of brevity, the data with the highest time resolution are represented in Fig. 4. At our monitoring station, the highest values were registered on 10 July between 1 and 2 a.m.; this is consistent with the location of major fireworks considering wind speed and direction. To quantify the elements concentration increase during the episode, the maximum concentration was compared to the value of the day before (9 July, not affected by fireworks), averaged between 12 a.m. and 10 p.m. In case of below MDL hourly data, one-half of the MDL value was used. Remarkable increases in Sr (120 times), Mg (22 times), K (12 times), Ba (11 times) and Cu (6 times) concentration were observed. No increases were detected in the coarse fraction elemental concentrations and Sr, Mg, K, Ba and Cu concentrations were below or comparable to MDL (not shown), indicating that ambient aerosol after the fireworks event was preferably confined in the fine fraction.

Sr, Ba and Cu compounds are used to give red, green, and blue fireworks, respectively (Kulshrestha et al., 2004; Wang et al., 2007; Moreno et al., 2007). Different Ba compounds can give the green colour, but the increase in chlorine concentration measured during the fireworks night and the nitrate concentration comparable or lower than other nights one, suggested that $Ba(ClO_3)_2$ was more likely used (Perry, 1999). K is one of the major components of

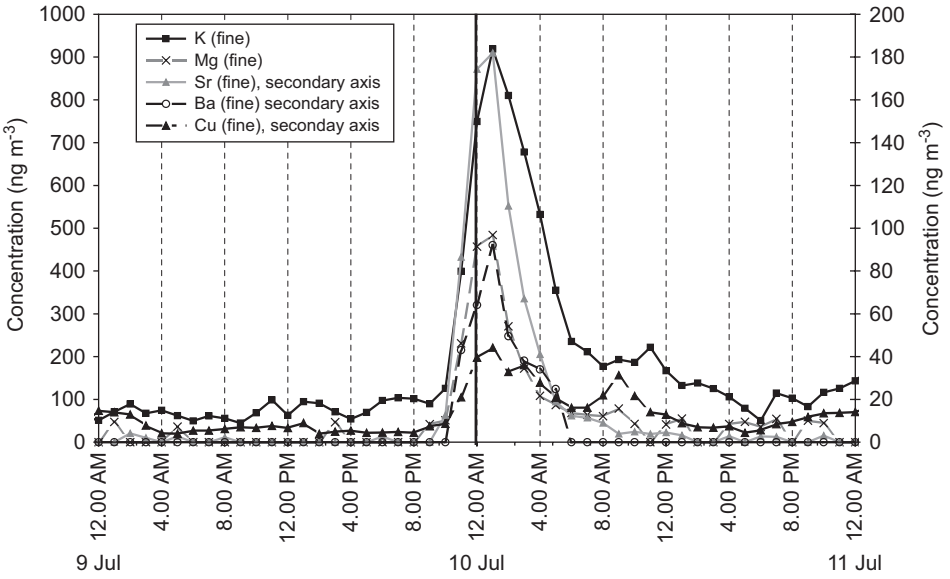

Fig. 4. Fireworks elemental markers, fine fraction data with hourly resolution (in ng m^{-3})

Table 1
4-h resolution chemical components and elemental concentrations (in ng m^{-3}) during the fireworks episode

Date	9/7	9/7	10/7	10/7	10/7	10/7
Time interval	4–8 p.m.	8 p.m.–12 a.m.	12–4 a.m.	4–8 a.m.	8 a.m.–12 p.m.	12–4 p.m.
PM_{10} mass	46,400	48,200	63,900	51,400	71,100	55,500
SO_4^{2-}	4232	3130	3622	2687	2830	5147
NO_3^-	<360	1115	4499	2326	2326	3683
NH_4^+	1169	1102	1575	868	1644	2548
OC	7870	9806	13,491	11,672	12,071	10,490
EC	1293	1959	5372	4070	4694	1748
Mg	<100	183	598	246	127	182
Al	355	519	680	451	720	609
Si	802	1023	1368	967	1790	1344
S	1303	803	1176	1276	1024	1759
Cl	<70	<70	233	98	115	121
K	158	369	991	369	364	267
Ca	308	369	645	723	1475	744
Ti	28	32	46	37	53	34
V	<6	<6	<6	<6	<6	<6
Cr	<4	<4	11	10	<4	<4
Mn	7	16	30	35	30	20
Fe	468	847	1731	1581	1374	586
Ni	4	2	5	7	6	5
Cu	20	43	105	56	65	25
Zn	82	85	190	270	276	90
Br	5	6	9	12	6	4
Pb	9	16	57	25	41	14
Sr	<3	55	139	18	11	<3
Ba	<20	41	156	22	31	24

fireworks (Liu et al., 1997; Dutcher et al., 1999; Perry, 1999; Kulshrestha et al., 2004; Drewnick et al., 2006): 74% of black powder consists of KNO_3, which provides the main oxidiser to the burning. Also potassium perchlorate or, less commonly, chlorate can be used in the black powder. Mg gives

origin to bright electric white fireworks and it is used as metallic fuel (Moreno et al., 2007; Wang et al., 2007).

In this work, Sr was recognised as the best fireworks tracer because its concentration was very high during the event and lower than, or comparable with, MDL during other time intervals, suggesting that it was mainly due to pyrotechnic displays (see also PMF results in Table 2). On the contrary, Cu and Ba can also have a contribution coming from traffic (Vecchi et al., 2007 and therein literature) and K and Mg are widespread elements emitted by many sources (e.g. biomass burning for K and soil dust for Mg).

From 4-h resolution PM_{10} data, the concentration ratios between levels registered in the 12–4 a.m.

Table 2
Contribution to PM_{10} mass and major chemical components concentration (in ng m^{-3} and as percentage of their measured concentration) due to the fireworks source obtained by PMF

	9/7 4–8 p.m.	9/7 8 p.m.–12 a.m.	10/7 12–4 a.m.	10/7 4–8 a.m.	10/7 8 a.m.–12 p.m.	10/7 12–4 p.m.
EC						
ng m^{-3}	<MDL	1101	2827	357	211	<MDL
(%)		(56)	(54)	(9)	(6)	
OC						
ng m^{-3}	<MDL	3144	8075	1019	601	<MDL
(%)		(39)	(52)	(9)	(5)	
Mg						
ng m^{-3}	<MDL	168	433	<MDL	<MDL	<MDL
(%)		(62)	(81)			
Al						
ng m^{-3}	<MDL	102	262	<MDL	<MDL	<MDL
(%)		(20)	(38)			
Si						
ng m^{-3}	<MDL	151	387	49	29	<MDL
(%)		(15)	(29)	(5)	(2)	
K						
ng m^{-3}	<MDL	269	692	87	52	<MDL
(%)		(64)	(77)	(27)	(13)	
Ca						
ng m^{-3}	<MDL	111	284	36	21	<MDL
(%)		(30)	(44)	(5)	(1)	
Mn						
ng m^{-3}	<MDL	5.2	13	<MDL	<MDL	<MDL
(%)		(33)	(44)			
Fe						
ng m^{-3}	10.3	400	1028	130	77	10
(%)	(2)	(48)	(57)	(10)	(5)	(1)
Cu						
ng m^{-3}	<MDL	27	70	9	5	<MDL
(%)		(66)	(68)	(14)	(9)	
Zn						
ng m^{-3}	<MDL	38	98	12	7	<MDL
(%)		(45)	(52)	(5)	(3)	
Sr						
(ng m^{-3}	<MDL	54	140	18	10	<MDL
(%)		(100)	(100)	(99)	(98)	
Ba						
ng m^{-3}	<MDL	51	130	16	<MDL	<MDL
(%)		(90)	(91)	(47)		
PM_{10} mass						
ng m^{-3}	<MDL	13,087	33,610	4240	<MDL	<MDL
(%)		(27)	(53)	(8)		

By convention, concentration values lower than experimental minimum detection limits have been labelled as <MDL.

time interval and the average values of the day before (during the period free from the event, i.e. between 12 a.m. and 8 p.m.) were calculated; results for elements, organic and elemental carbon, and ions are reported in Fig. 5. As expected, the most significant increases were observed for Sr, Mg, Ba, K and Cu (elements ratios were smaller than those reported for 1-h resolution elemental data because the longer sampling time included periods with lower concentrations). Indeed, these elements can be all considered fireworks tracers.

The nitrate concentration ratio was comparable to the one measured during other summer nights at the same sampling site (as an example, see the comparison with 6 July night, in Fig. 5) because of the lower nighttime temperature, which limited losses due to volatilisation. In agreement with results by Drewnick et al. (2006), in our case study no nitrate increase due to fireworks was observed.

The EC ratios (3.1) found in this work are in good agreement with black carbon increases reported by Babu and Moorthy (2001) and by Wang et al. (2007).

Opposite to what found by Wang et al. (2007), no anomalous growth in secondary components was observed the day after the pyrotechnical displacement: the increases in sulphate and ammonium were similar to the ones measured during other summer afternoons at the same sampling site. However, it should be taken into account that secondary compounds formation may change in relation to local meteorological condition, pollutants mixture and duration and strength of the episode.

In Fig. 6, the fireworks chemical profile obtained by PMF is also reported as an original contribution to the characterisation of fireworks emissions. Major components are carbon compounds (both EC and OC) and metals. The fireworks source profile confirms Sr as the best tracer in our case study as, contrarily to other fireworks indicators, it was found only in this chemical profile while, for example, Ba was also detected in the traffic profile, and K was found in a number of sources (not shown here). In Table 2, the PMF apportionment for major PM_{10} components detected during pyrotechnic displays is given. As already reported for PM_{10} mass concentrations, also elements, ions and carbon components peaked in the 12–4 a.m. time interval. Total carbon (TC = EC + OC) due to fireworks accounted for 11 $\mu g\,m^{-3}$ of the PM_{10} mass (i.e. about 50–55% of the measured total carbon). Major elemental contributions apportioned by PMF and due to the pyrotechnic displays were Mg (0.4 $\mu g\,m^{-3}$), K (0.7 $\mu g\,m^{-3}$), Cu (0.07 $\mu g\,m^{-3}$), Sr (0.1 $\mu g\,m^{-3}$) and Ba (0.1 $\mu g\,m^{-3}$) corresponding to 81%, 77%, 68%, 100% and 91% of their measured concentration, respectively. These results are in very good agreement with experimental observations discussed so far.

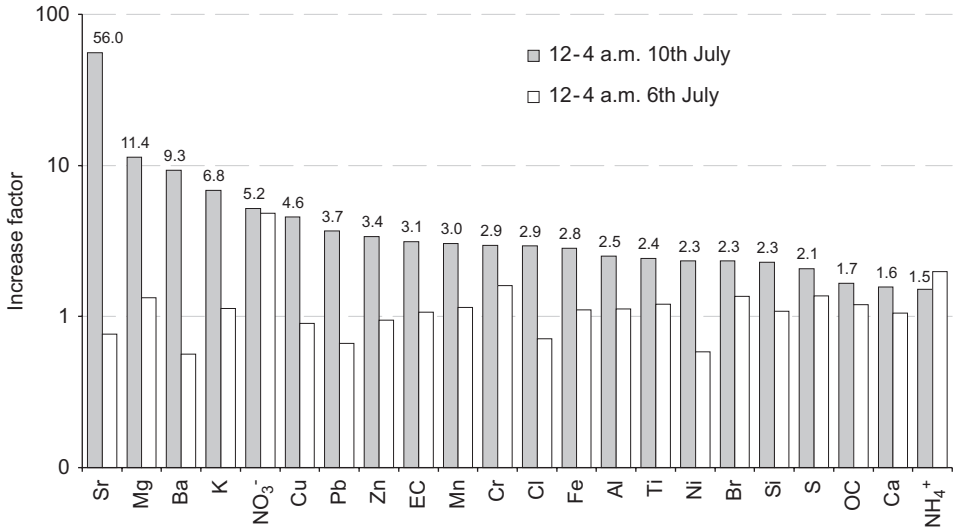

Fig. 5. Ratios between the concentration of different chemical components registered in the time interval 12–4 a.m. (fireworks displays) on 9–10 July night and the average value measured for the same species during the day before (grey). Similar ratios (white) calculated for the night between 6 and 7 July (free from fireworks) are given for comparison.

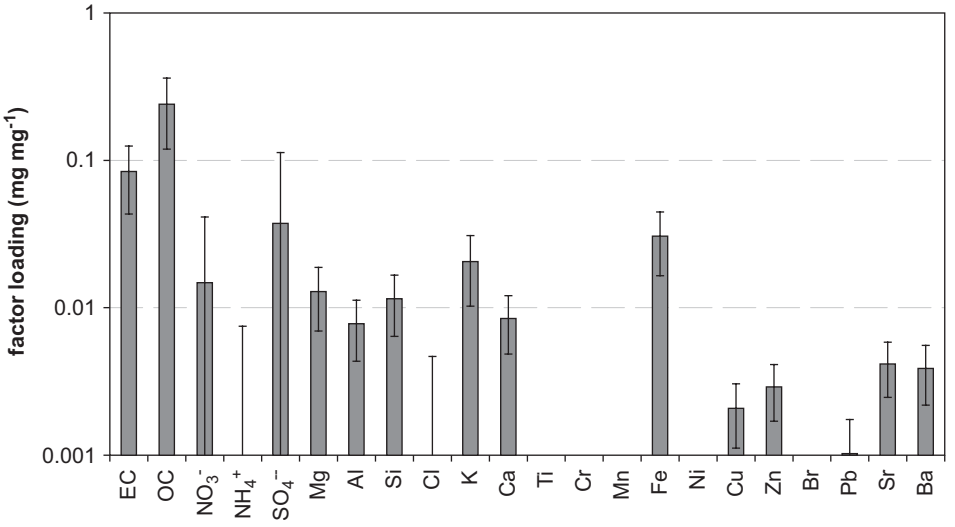

Fig. 6. Fireworks source profile (in mg mg^{-1}) as resolved by PMF.

3.4. Number size distribution

During the fireworks night, starting from 11 p.m., the number concentration in all size ranges increased. The growths were different for each size bin, but the maximum concentration was always found on 12:10 a.m. The ratios between the number of particles measured on 12:10 a.m. and 11 p.m. were as follows: 6.7 for particles in the range $0.5<d<1\,\mu m$, 2.8 for particles in the range $2.5<d<10\,\mu m$, 2.6 for particles in the range $1<d<2.5\,\mu m$ and 1.7 for particles with $d<0.5\,\mu m$.

The delay (about 1.5 h) in the occurrence of the maximum concentration compared to end of the match may be explained considering the distance of our sampling site from the city centre (where the major fireworks exhibition was performed and the largest traffic volume observed) together with the low wind speed, the wind direction and the atmospheric stability conditions. From 12:10 to 1:40 a.m. the particles number concentration in all size ranges decreased as follows: −20% for particles with $d<0.5\,\mu m$, −70% for particles in the range $0.5<d<1\,\mu m$, −50% for particles in the $1<d<2.5\,\mu m$ range and −35% for particles in $2.5<d<10\,\mu m$ range. Between 1:40 and 3 a.m. another increase was observed in all size bins, and particularly in particles with diameters smaller than 0.4 μm. It is interesting to note that a growth in Cu hourly concentration (fine fraction) and in NO_2 concentration (at 1-J monitoring station near the University campus) was also measured between 2 and 3 a.m. (see Figs. 3b and 4). As these increases were contemporary, the growth in particle number concentration might be ascribed to traffic (contributing to Cu, NO_2, and fine particles), because of people going back home after celebrations. Moreover, these results suggested that traffic emissions were mainly in the finest fractions. After 3 a.m., particles number concentrations definitively decreased until the next morning, when the number of particles increased again because of typical working day's activities.

Particles number temporal pattern in each size range was compared to Sr concentration (taken here as fireworks tracer). The correlation coefficients between Sr (fine fraction) and number concentration were calculated using hourly resolved data between 10 p.m. on 9 July and 10 a.m. on 10 July. The highest correlation coefficients ($R>0.95$) were registered in the 0.45–1 μm, and particularly in the 0.70–0.80 μm, size bin ($R=0.98$). The high correlation between Sr and the 0.7–0.8 μm size range is consistent with what found by Perry (1999), who reported 0.7 μm as mass mean diameter of potassium (in that work considered the indicator for fireworks) observed after fireworks emissions transport.

In Fig. 7, Sr temporal pattern (1-h resolution) and particles number concentrations (10-min resolution) in the 0.25–0.3, 0.70–0.80, and 8.5–10 μm size intervals are shown, as examples. A very good agreement between Sr and particle number in the 0.70–0.80 μm size range in the increase phase and in

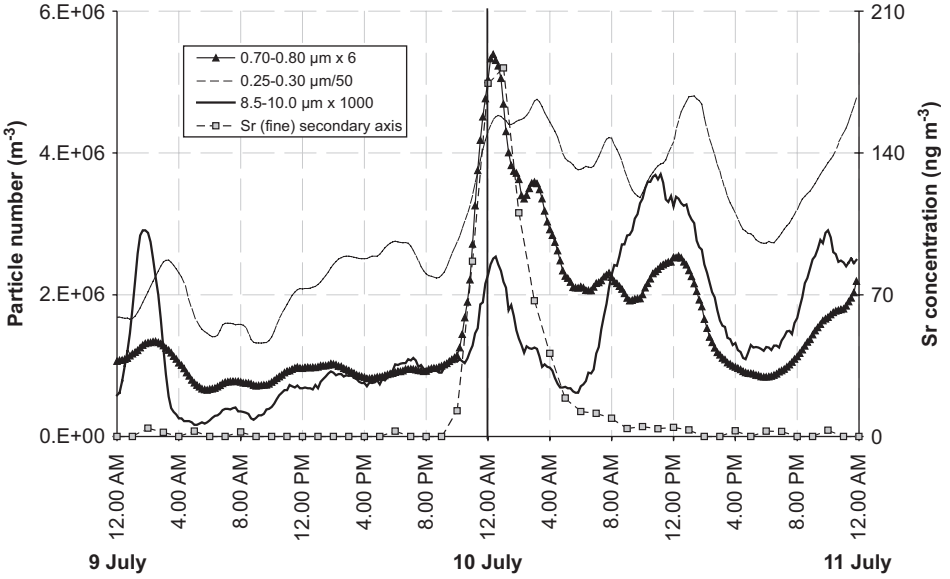

Fig. 7. Sr hourly temporal pattern (in ng m^{-3}) together with particles number concentration (particles m^{-3}) in the 0.25–0.30, 0.70–0.80 and 8.5–10 μm size intervals.

the first part of the decrease phase was evident, while differences can be noticed after 2 a.m. However, it must be considered that, in this case study, fireworks display was the only source of Sr while airborne particles in general can be originated by different sources. In Fig. 7 can also be noted that, even if particles in the 0.25–0.3 and 8.5–10 μm size ranges increased during the fireworks period, a poorer correlation ($R = 0.72$ and -0.13, respectively) was found with Sr concentration.

Taking into account the good correlation between Sr and particles in 0.4–1 μm size range during the increase phase, and evaluating the time necessary to Sr to reach values similar to those presented before fireworks, a rough estimate of the time necessary to particles in this size range to diffuse (with low wind speed conditions) can be evaluated in about 12 h.

4. Conclusions

The fireworks exhibition was used to study the chemical composition and the size distribution of airborne particles observed during such events. The influence of additional emissions due to the traffic registered just after the football match was also discussed.

Atmospheric aerosols originated by fireworks had a typical signature as singled out by the few works on this topic (see references given in the text). Results obtained by hourly elemental analysis showed that in the fine fraction many metals (i.e. Sr, Mg, K, Ba and Cu) increased significantly during the celebrations (e.g. Sr up to 120 times in 1 h) while no differences were observed in the coarse fraction concentrations. It is worth noting that, although fireworks cause short-lived air pollution events, fine particles are responsible for adverse health effects, and the bioreactivity of fine metal aerosols is of particular concern (Moreno et al., 2007; and therein cited literature).

The availability of a large number of chemically characterised samples allowed the PM_{10} and major chemical components apportionment during the pyrotechnic displays. Although our fireworks event had short duration, the PM_{10} concentration ascribed by PMF to the fireworks source was not negligible (up to 33.6 μg m^{-3}). In addition, fireworks accounted for a large part of the metal concentrations (e.g. up to 70–100% of the measured values for Mg, K, Cu, Sr and Ba). Obviously, the impact of this source type can vary considerably in relation to fireworks duration and type, being more serious when stable atmospheric conditions occur (Clark, 1997). The assessment of the fireworks source chemical profile and of the contribution of fireworks to local environment gives an original contribution towards understanding the aerosol characteristics and burden during fireworks displays.

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References

Attri, A.K., Kumar, U., Jain, V.K., 2001. Formation of ozone by fireworks. Nature 411, 1015.

Babu, S.S., Moorthy, K.K., 2001. Anthropogenic impact on aerosol black carbon mass concentration at a tropical coastal station: a case study. Current Science 81, 1208–1214.

Birch, M.E., Cary, R.A., 1996. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. Aerosol Science and Technology 25, 221–241.

Calzolai, G., Chiari, M., García Orellana, I., Lucarelli, F., Migliori, A., Nava, S., Taccetti, F., 2006. The new external beam facility for environmental studies at the Tandetron accelerator of LABEC. Nuclear Instruments and Methods in Physics Research B 249 (1–2), 928–931.

Casadei, S., Giugliano, M., Lonati, G., Pacifico, F., Valli, G., Vecchi, R., 2006. Valutazione dell'altezza dello strato rimescolato nell'area urbana di Milano nel biennio 2003–2004. Ingegneria Ambientale XXXV (4), 155–168 (in Italian).

Clark, H., 1997. Light blue touch paper and retire…. Atmospheric Environment 31, 2893–2895.

Drewnick, F., Hings, S.S., Cutius, J., Eerdekens, G., Williams, J., 2006. Measurement of fine particulate matter and gas-phase species during the new year's fireworks 2005 in Mainz, Germany. Atmospheric Environment 40, 4316–4327.

Dutcher, D.D., Perry, K.D., Cahill, T.A., Copeland, S.A., 1999. Effects of indoor pyrotechnic displays on the air quality in the Houston Astrodome. Journal of Air & Waste Management Association 49, 156–160.

Fermo, P., Piazzalunga, A., Vecchi, R., Valli, G., 2006. Set-up of extraction procedures for ions quantification in aerosol samples. Chemical Engineering Transactions 10, 203–208.

Kim, E., Larson, T.V., Hopke, P.K., Slaughter, C., Sheppard, L.E., Claiborn, C., 2003. Source identification of $PM_{2.5}$ in an arid Northwest US city by positive matrix factorization. Atmospheric Research 66, 291–305.

Kulshrestha, U.C., Nageswara Rao, T., Azhaguvel, S., Kulshrestha, M.J., 2004. Emissions and accumulation of metals in the atmosphere due to crackers and sparkles during Diwali festival in India. Atmospheric Environment 38, 4421–4425.

Liu, D.Y., Rutherford, D., Kinsey, M., Prather, K.A., 1997. Real-time monitoring of pyrotechnically derived aerosol particles in the troposphere. Analytical Chemistry 69, 1808–1814.

Marcazzan, G.M., Caprioli, E., Valli, G., Vecchi, R., 2003. Temporal variation of ^{212}Pb concentration in outdoor air of Milan and a comparison with ^{214}Bi. Journal of Environmental Radioactivity 65, 77–90.

Marcazzan, G.M., Ceriani, M., Valli, G., Vecchi, R., 2004. Composition, components and sources of fine aerosol fractions using multielemental EDXRF analysis. X-ray Spectrometry 33, 267–272.

Moreno, T., Querol, X., Alastuey, A., Minguillón, M.C., Pey, J., Rodriguez, S., Miró, J.V., Felis, C., Gibbons, W., 2007. Recreational atmospheric pollution episodes: inhalable metalliferous particles from fireworks displays. Atmospheric Environment 41, 913–922.

Paatero, P., 1997. Least squares formulation of robust non-negative factor analysis. Chemometrics and Intelligent Laboratory Systems 37, 23–35.

Paatero, P., Hopke, P.K., 2003. Discarding or downweighting high-noise variables in factor analytic models. Analytica Chimica Acta 490, 277–289.

Paatero, P., Hopke, P.K., Song, X., Ramadan, Z., 2002. Understanding and controlling rotations in factor analytical models. Chemometrics and Intelligent Laboratory Systems 60, 253–264.

Pacifico, F., 2005. Il Radon come tracciante dell'altezza dello strato rimescolato: sviluppo di un modello a box. Degree Thesis in Physics, University of Milan, Italy (in Italian).

Perry, K.D., 1999. Effects of outdoor pyrotechnic displays on the regional air quality of Western Washington State. Journal of Air & Waste Management Association 49, 146–155.

Polissar, A.V., Hopke, P.K., Paatero, P., Malm, W.C., Sisler, J.F., 1998. Atmospheric aerosol over Alaska. 2. Elemental composition and sources. Journal of Geophysical Research 103, 19045–19057.

Pope III, C.A., Dockery, D.W., 2006. Health effects of fine particulate air pollution: lines that connect. Journal of Air and Waste Management Association 56, 709–742.

Prati, P., Zucchiatti, A., Tonus, S., Lucarelli, F., Mandò, P.A., Ariola, V., 1998. A testing technique of streaker aerosol samplers via PIXE analysis. Nuclear Instruments and Methods in Physics Research B 136–138, 986–989.

Qin, Y., Kim, E., Hopke, P.K., 2006. The concentrations and sources of $PM_{2.5}$ in metropolitan New York City. Atmospheric Environment 40, S312–S332.

Ravindra, K., Mittal, A.K., Van Grieken, R., 2001. Health risk assessment of urban suspended particulate matter with special reference to polycyclic aromatic hydrocarbons: a review. Reviews on Environmental Health 16 (3), 169–189.

Ravindra, K., Mor, S., Kaushik, C.P., 2003. Short-term variation in air quality associated with fireworks events: a case study. Journal of Environmental Monitoring 5, 260–264.

Vecchi, R., Marcazzan, G., Valli, G., 2007. A study on nighttime–daytime PM_{10} concentration and elemental composition in relation to atmospheric dispersion in the urban area of Milan (Italy). Atmospheric Environment 41, 2136–2144.

Wang, Y., Zhuang, G., Xu, C., An, Z., 2007. The air pollution caused by the burning of fireworks during the lantern festival in Beijing. Atmospheric Environment 41, 417–431.