

# The air pollution caused by the burning of fireworks during the lantern festival in Beijing

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## Abstract

The effects of the burning of fireworks on air quality in Beijing was firstly assessed from the ambient concentrations of various air pollutants (SO<sub>2</sub>, NO<sub>2</sub>, PM<sub>2.5</sub>, PM<sub>10</sub> and chemical components in the particles) during the lantern festival in 2006. Eighteen ions, 20 elements, and black carbon were measured in PM<sub>2.5</sub> and PM<sub>10</sub>, and the levels of organic carbon could be well estimated from the concentrations of dicarboxylic acids. Primary components of Ba, K, Sr, Cl<sup>-</sup>, Pb, Mg and secondary components of C<sub>5</sub>H<sub>6</sub>O<sub>4</sub><sup>2-</sup>, C<sub>3</sub>H<sub>2</sub>O<sub>4</sub><sup>2-</sup>, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, C<sub>4</sub>H<sub>4</sub>O<sub>4</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> were over five times higher in the lantern days than in the normal days. The firework particles were acidic and of inorganic matter mostly with less amounts of secondary components. Primary aerosols from the burning of fireworks were mainly in the fine mode, while secondary formation of acidic anions mainly took place on the coarse particles. Nitrate was mainly formed through homogeneous gas-phase reactions of NO<sub>2</sub>, while sulfate was largely from heterogeneous catalytic transformations of SO<sub>2</sub>. Fe could catalyze the formation of nitrate through the reaction of α-Fe<sub>2</sub>O<sub>3</sub> with HNO<sub>3</sub>, while in the formation of sulfate, Fe is not only the catalyst, but also the oxidant. A simple method using the concentration of potassium and a modified method using the ratio of Mg/Al have been developed to quantify the source contribution of fireworks. It was found that over 90% of the total mineral aerosol and 98% of Pb, 43% of total carbon, 28% of Zn, 8% of NO<sub>3</sub><sup>-</sup>, and 3% of SO<sub>4</sub><sup>2-</sup> in PM<sub>2.5</sub> were from the emissions of fireworks on the lantern night.

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## 1. Introduction

Fireworks contain chemicals such as potassium nitrates, potassium chlorate, potassium perchlorate,

charcoal, sulfur, manganese, sodium oxalate, aluminum and iron dust powder, strontium nitrate, and barium nitrate, etc. (McLain, 1980). Burning of fireworks releases pollutants, like sulfur dioxide, carbon dioxide, carbon monoxide, suspended particles, and several metals like aluminum, manganese and cadmium, etc., which are associated with serious health hazards. Fireworks often result in serious accidents and lethal injuries (Bull et al., 2001), and the complex nature of firework particles

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with trace metals and organic compounds possess more threat to human health (Ravindra et al., 2001). Besides, the use of colored fireworks could generate ozone at the ground level, which is a strong and harmful oxidizing agent, and will put people at a high risk (Attri et al., 2001).

In despite of the harmful effects of fireworks on the environment and human health, there is a limited amount of literatures describing the physio-chemical characteristics of firework particles. During the Fourth of July holiday, Mg and Al in PM<sub>10</sub> aerosol particles revealed significant increase in Florida (Carranza et al., 2001). Following the Fourth of July holiday, significant increases in the levels of ambient air magnesium, aluminum, potassium, lead, barium, strontium, and copper have been found at the University of California in Riverside (Liu et al., 1997). During Diwali festival in India, Ba, K, Al and Sr went up to 1091, 25, 18 and 15 times higher (Kulshrestha et al., 2004), black carbon increased by a factor of over 3 (Babu and Moorthy, 2001), and SO<sub>2</sub>, NO<sub>2</sub>, PM<sub>10</sub>, TSP increased 2–10 times higher (Ravindra et al., 2003). During the Millennium fireworks in Leipzig, Germany, an increase of particle number and volume in the accumulation mode range (>100 nm) has been witnessed (Wehner et al., 2000). Besides the studies on the aerosols from firework burning, Fleischer and coworkers reported the concentrations of organic toxic species, including octachlorinated dioxins, furans, and hexachlorobenzene, in the remains of fireworks (Fleischer et al., 1999); Liu and coworkers reported the original chemical composition and particle size of typical firework mixtures (Liu et al., 1997).

The studies above only give limited informations on the chemical characteristics of the aerosols generated by fireworks. To date, there is still no such data available in China, which is mostly related to the banning of manufacture, sale, and use of fireworks since 1993. From then on, the conflict between competing interests in society-safety, health, and calm on the one hand, and tradition on the other hand, has evolved over time. As a result, the capital government allows the burning of fireworks in the 2006 spring festival in urban Beijing. This provides the first opportunity to detect the associated changes in ambient air pollutant levels caused by fireworks in Beijing. In this study, aerosol samples have been collected during the lantern festival, dating on 15 January in Chinese lunar calendar and known as one of the most

important feasts during the spring festival season. Ions, metals, and black carbon have been measured in aerosol samples. This effort was made to present an insight into the air pollution problem related to fireworks, taking the chemistry of fireworks as a focal point. The eruptive increase in the chemical components, the formation mechanism of secondary aerosols, as well as the quantitative estimate of the contribution of fireworks to the local environment have been elaborated. This study will give the government some clues on how to manage the firework issue and fill in the blanks in this research area.

## 2. Experimental

### 2.1. Sampling

PM<sub>2.5</sub> and PM<sub>10</sub> aerosols originating from the burning of fireworks were monitored over a 4-day period at urban Beijing during the lantern festival in 2006. A total of eight samples (four PM<sub>2.5</sub> and four PM<sub>10</sub>) were collected, i.e. on the night of the festival day (12 February, noted as sample #1), the daytime after the festival day (13 February, noted as sample #2), the nighttime after the festival day (13 February, noted as sample #3), and the normal day (14–15 February, noted as sample #4). The samples were collected on the roof (~40 m high) of a building in Beijing Normal University, a mixed residential and traffic site in Beijing. PM<sub>2.5</sub> and PM<sub>10</sub> were collected on Whatman<sup>®</sup> 41 filters (Whatman Inc., Maidstone, UK) by a medium-volume sampler (model: (TSP/PM<sub>10</sub>/PM<sub>2.5</sub>)-2, flow rate: 77.59 L min<sup>-1</sup>). Because there was a well-defined start time and end time for the burning of fireworks (19:00–24:00), the sampling time was regulated accordingly for a better understanding of the characteristics of firework particles. The detail sampling information was presented in Table 1. The samples were put in polyethylene plastic bags right after sampling and reserved in a refrigerator. All those filters were weighed before and after sampling with an analytical balance (Sartorius 2004MP, reading precision 10 µg) after stabilizing under constant temperature (20 ± 1 °C) and humidity (40 ± 2%) for over 24 h. The differences in the two totals were divided by the collected sampling volumes to obtain the corresponding concentrations. All the procedures were strictly quality-controlled to avoid any possible contamination of the samples.

Table 1  
Mass concentrations of PM<sub>2.5</sub> and PM<sub>10</sub> together with the meteorological conditions during the sampling period

		PM <sub>2.5</sub> ( $\mu\text{g m}^{-3}$ )	PM <sub>10</sub> ( $\mu\text{g m}^{-3}$ )	Temp. <sup>a</sup> (°C)	Dewp. <sup>b</sup> (°C)	RH <sup>c</sup> (%)	WS <sup>d</sup> ( $\text{m s}^{-1}$ )	Visibility (km)	Mixdepth (m)	Condition
Sample #1	Feb 12, 19:54–Feb 13, 07:45	184.3	466.2	−2.23	−4.00	88	1.69	1.81	250	Fog
Sample #2	Feb 13, 07:54–Feb 13, 19:50	142.5	406.9	2.00	−0.58	83	1.67	1.33	253	Fog
Sample #3	Feb 13, 19:50–Feb 14, 07:50	137.8	394.9	0.33	−2.25	85	3.08	1.69	257	Haze
Sample #4	Feb 14, 07:52–Feb 15, 07:52	26.1	85.6	4.38	−5.71	55	3.08	7.58	509	Sunny

<sup>a</sup>Temperature.

<sup>b</sup>Dew point.

<sup>c</sup>Relative humidity.

<sup>d</sup>Wind speed.

## 2.2. Chemical analysis

### 2.2.1. Pretreatment of the sample filters

One-fourth of each sample and blank filter was extracted ultrasonically by 10 mL deionized water (resistivity:  $18 \text{ M}\Omega \text{ cm}^{-1}$ ). After passing through microporous membranes (pore size,  $0.45 \mu\text{m}$ ; diameter, 25 mm; made by the affiliated plant of Beijing chemical school), the filtrates were determined for pH with a pH meter (model, Orion 818). Ions and elements in those filtrates were measured by ion chromatography (IC) and inductively coupled plasma atomic emission spectroscopy (ICP-AES), respectively. This part was denoted as water-soluble ions and elements.

The residues after filtration was digested at  $170^\circ\text{C}$  for 4 h in high-pressure Teflon digestion vessel with 3 mL concentrated  $\text{HNO}_3$ , 1 mL concentrated  $\text{HClO}_4$ , and 1 mL concentrated HF. After cooling, the solutions were dried, and then added 1 mL concentrated  $\text{HNO}_3$ , and diluted to 10 mL with deionized water (resistivity of  $18 \text{ M}\Omega \text{ cm}^{-1}$ ). Elements in them were measured by ICP-AES and denoted as water-insoluble elements.

### 2.2.2. Ion and element analysis

Thirteen anions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{NO}_2^-$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{C}_3\text{H}_2\text{O}_4^{2-}$ ,  $\text{C}_4\text{H}_4\text{O}_4^{2-}$ ,  $\text{C}_5\text{H}_6\text{O}_4^{2-}$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{HCOO}^-$ , MSA) and five cations ( $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ) were analyzed by IC (model, Dionex 600), which consists of a separation column (Dionex

Ionpac AS11 for anion and CS12A for cation), a guard column (Dionex Ionpac AG 11 for anion and AG12A for cation), a self-regenerating suppressed conductivity detector (Dionex Ionpac ED50), and a gradient pump (Dionex Ionpac GP50). The gradient weak base eluent ( $76.2 \text{ mM NaOH} + \text{H}_2\text{O}$ ) and the weak acid eluent ( $20 \text{ mM MSA}$ ) were used for anion and cation detection, respectively. The recovery of those ions was in the range of 80–120%. The relative standard deviations were less than 5%. The limits of detection ( $S/N = 3$ ) were less than  $0.04 \text{ mg L}^{-1}$  for anions and  $0.006 \text{ mg L}^{-1}$  for cations. The quality assurance was routinely carried out by using Standard Reference Materials (GBW 08606) produced by National Research Center for Certified Reference Materials, China.

Twenty elements (Ag, Al, As, Ba, Bi, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Sr, V, Zn, S) were measured by ICP-AES (model, ULTIMA, made by JOBIN-YVON Company, France). The recovery of those elements was in the range of 95–105%. The relative standard deviations were generally below 10%. The detection limits ( $S/N = 3$ ) were less than  $0.02 \text{ mg L}^{-1}$ . Blank values were subtracted from sample determinations. The detailed analytical procedures were given elsewhere (Yuan et al., 2003; Zhuang et al., 2001).

### 2.2.3. Black carbon analysis

Black carbon (BC) in the sample filters was determined by an EEL smokestain reflectometer

(Model 43D, Diffusion systems Ltd, London). A light source shines its light on the filter, and the reflected light is measured by photocells located in a black housing. The reflector reading is obtained directly from the DS 29 universal digital readout, and converted to output voltage ( $U = 0.0777 \times \text{reading}$ ). The output voltage is then converted to a measure of blackness, which is uniquely determined from the three output obtained from (1) the aerosol filter to be evaluated, (2) the one which is totally black, and (3) the one which is totally white. The blackness is essentially determined by the use of Lambert–Beer’s law (Gagel, 1996). Provided that thin layers of aerosol particles are collected on the filter (“a single dust layer”), the equation relating the output voltages to the “black smoke number” is:

$$RZ = RZ_{\max}(U_{RZ0} - U_{RZ}) / (U_{RZ0} - U_{RZ\max}),$$

where,  $U_{RZ0}$ ,  $U_{RZ}$ , and  $U_{RZ\max}$  are the output voltages of the total white filter spot, the actual filter spot, and the total black filter spot, respectively.  $RZ_0$ ,  $RZ$ , and  $RZ_{\max}$  are “black smoke numbers” for these three types of filters, respectively. The equation used for converting “black smoke number” to concentration of black particles ( $C_R$ ) is:

$$C_R = -(RM/V) \ln(1 - (RZ - RZ_0)/kRZ_{\max}),$$

where  $V$  is the sampled air volume,  $k$  and  $RM$  are calibration constants. Here,  $k = 0.95$ ,  $RM = 11.2 \mu\text{g}$ ,  $U_{RZ\max} = 0.5$ ,  $U_{RZ0} = 8$ ,  $RZ_{\max} = 9$  were used. Finally,  $C_R$  is adjusted by a multiplication constant (the ratio of the filter area to the black spot area) to get the total BC concentration. The relative standard deviation and the detection limit of BC are 0.12% and  $0.01 \mu\text{g m}^{-3}$ , respectively. Regular linearity check was performed by a white/grey standard supplied with the instrument.

### 2.3. The meteorological data and the pollution gases

The meteorological data, including temperature, dew point, relative humidity (RH), wind speed,

visibility, mixdepth, etc., during the sampling period were downloaded from <http://www.wunderground.com> and <http://www.arl.noaa.gov/>, and presented in Table 1. Air Pollution Index (API, API = 100 corresponds to Chinese air quality standard II) of  $\text{SO}_2$ ,  $\text{NO}_2$ , and  $\text{PM}_{10}$  in Beijing were collected from <http://www.bjee.org.cn/> and converted to concentrations. The formulas used for converting API to concentration is

$$C = C_{\text{low}} + [(I - I_{\text{low}}) / (I_{\text{high}} - I_{\text{low}})] \times (C_{\text{high}} - C_{\text{low}}),$$

where  $C$  is the concentration and  $I$  is the API value.  $I_{\text{high}}$  and  $I_{\text{low}}$ , the two values most approaching to value  $I$  in the API grading limited value table, stand for the value higher and lower one than  $I$ , respectively;  $C_{\text{high}}$  and  $C_{\text{low}}$  represent the concentrations corresponding to  $I_{\text{high}}$  and  $I_{\text{low}}$ , respectively.

## 3. Results and discussion

### 3.1. The heavy pollution caused by fireworks

Daily variations of  $\text{SO}_2$ ,  $\text{NO}_2$ , and  $\text{PM}_{10}$  during the spring festival period in 2005 and 2006 were presented in Fig. 1.

The red and green arrows in the figure denote the New Year’s Eve and the lantern day, respectively. Clear elevation of  $\text{SO}_2$ ,  $\text{NO}_2$ , and  $\text{PM}_{10}$  in these two days in 2006 and minor changes of them in 2005 were observed.  $\text{SO}_2$ ,  $\text{NO}_2$ , and  $\text{PM}_{10}$  levels showed an increase of up to 57%, 25%, and 183%, respectively, in the lantern day compared to the previous day in 2006. The concentrations of  $\text{SO}_2$  and  $\text{NO}_2$  were moderately higher than the maximum allowed limits ( $150 \mu\text{g m}^{-3}$  for  $\text{SO}_2$  and  $80 \mu\text{g m}^{-3}$  for  $\text{NO}_2$ ), and the concentration of  $\text{PM}_{10}$  was largely double of the maximum prescribed limit ( $150 \mu\text{g m}^{-3}$ ) in the lantern day in 2006.

The severe air pollution caused by fireworks can also be revealed from the  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  aerosol samples collected in this work.  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$

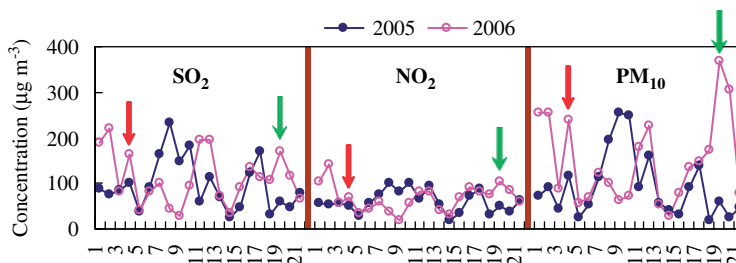


Fig. 1. Variations of  $\text{SO}_2$ ,  $\text{NO}_2$ , and  $\text{PM}_{10}$  during the spring festival period in 2005 and 2006.

exhibited the highest concentrations of 184 and  $466 \mu\text{g m}^{-3}$  on the night of the lantern day (sample #1), which were over six and four times higher than those in the normal day (sample #4) (Table 1). These high levels of pollutants on the lantern night may be related to both the heavy source emissions and the calm meteorological conditions (low wind speed and low mixdepth, Table 1). However, the increase of suspended particles ( $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ ), especially the fine part ( $\text{PM}_{2.5}$ ), were much more than the pollution gases ( $\text{SO}_2$  and  $\text{NO}_2$ ), indicating that changes in the meteorology alone can not explain the observed changes. Burning of fireworks might be a strong source of suspended particles. Large amount of soot and various metal oxides particles could be emitted into the air during the burning. These high-temperature derived particles are mostly in the fine mode and the large amount of soot and metals in them could catalyze atmospheric reactions. Therefore, the chemistry of firework particles might be very different from those of typical urban aerosols. The characteristics of the firework particles will be investigated in the following sections.

### 3.2. The increase of chemical components in the firework period

The concentrations of various species during the lantern festival days were shown in Figs. 2a–h.

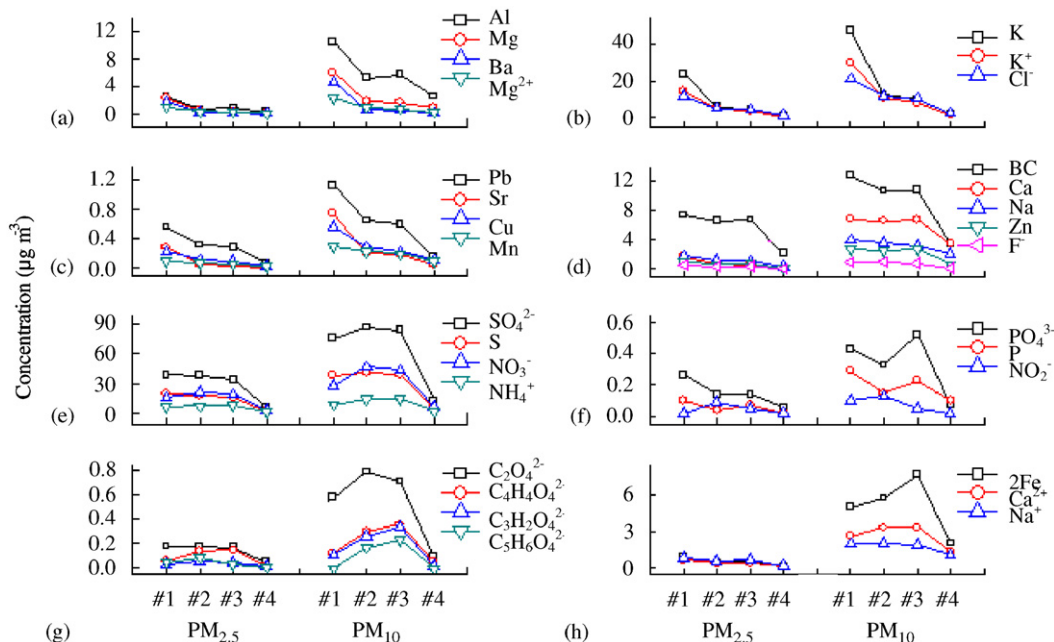


Fig. 2. Variations of the measured species in  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  during the lantern festival. Please consult Table 1 for the sampling information of sample #1, #2, #3, and #4.

The concentrations of elements on the night of lantern festival was observed to be in the order of  $\text{K} > \text{S} > \text{Al} > \text{Mg}$ ,  $\text{Na}$ ,  $\text{Ca}$ ,  $\text{Ba} > \text{Zn} > \text{Pb} > \text{Fe} > \text{Sr} > \text{Cu} > \text{Mn} > \text{P} > \text{As} > \text{V} > \text{Bi} > \text{Ni} > \text{Cd} > \text{Ag}$ , and the concentrations of BC and ions followed the order of  $\text{SO}_4^{2-} > \text{NO}_3^-$ ,  $\text{K}^+ > \text{Cl}^- > \text{BC} > \text{NH}_4^+ > \text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+ > \text{F}^- > \text{PO}_4^{3-}$ ,  $\text{C}_2\text{O}_4^{2-} > \text{C}_4\text{H}_4\text{O}_4^{2-} > \text{C}_3\text{H}_2\text{O}_4^{2-} > \text{C}_5\text{H}_6\text{O}_4^{2-} > \text{NO}_2^- > \text{CH}_3\text{COO}^-$ ,  $\text{HCOO}^-$ ,  $\text{MSA}$ .  $\text{As}$ ,  $\text{V}$ ,  $\text{Bi}$ ,  $\text{Ni}$ ,  $\text{Cd}$ ,  $\text{Ag}$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{HCOO}^-$ , and  $\text{MSA}$  were excluded in this study for their low concentrations and large uncertainties.

Figs. 2a–c showed the variations of  $\text{Al}$ ,  $\text{Mg}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}$ ,  $\text{K}$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{Pb}$ ,  $\text{Sr}$ ,  $\text{Cu}$ , and  $\text{Mn}$ . These components, noted as group 1, had very sharp peaks on the night of firework burning, and showed quick decrease after the burning. Their sharp peaks on the night of lantern festival clearly indicates the strong contribution of fireworks, and the rapid decrease in the next day suggests the weak contribution of other local sources. Fig. 2d showed the variations of  $\text{F}^-$ ,  $\text{Zn}$ ,  $\text{BC}$ ,  $\text{Ca}$ , and  $\text{Na}$ . The concentrations of these components, noted as group 2, on the firework night were moderately higher than those in the normal days. However, different from the species in group 1, they only exhibited a slight decrease in the next day, suggesting that local emissions besides firework burning could also contribute to the accumulation of these

species in the atmosphere. Figs. 2e–f showed the variations of  $\text{SO}_4^{2-}$ , S,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ , P,  $\text{NO}_2^-$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{C}_4\text{H}_4\text{O}_4^{2-}$ ,  $\text{C}_3\text{H}_2\text{O}_4^{2-}$ ,  $\text{C}_5\text{H}_6\text{O}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ , and Fe. These species, noted as group 3, had the highest concentrations one day after the burning night, indicating that they were not from the fireworks directly. They may be formed from the gases emitted by the burning of fireworks. It should be noticed that the variations of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  were different from those of Na and Ca.  $\text{Na}^+$  and  $\text{Ca}^{2+}$  are supposed to be of secondary origin, formed from the reactions of primary basic particles containing Na and Ca with secondary acidic species.

### 3.2.1. The increase of primary components

Figs. 2a–d showed that the concentrations of Ba, K,  $\text{K}^+$ , Sr,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ , Pb, Mg, Cu, Al,  $\text{F}^-$ , Zn, BC, Mn, Ca, and Na in  $\text{PM}_{10}$  were about 82, 22, 21, 17, 11, 9, 8, 8, 6, 6, 5, 5, 5, 4, 3, and 3 times higher on the firework night than those in the normal days, indicating the presence of highly toxic metals like Ba, Pb, Cu, Al, Mn, and Sr as well as other metals like K, Mg, Zn, Ca, and Na in the fireworks. Carbonaceous components and water-soluble salts containing  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{F}^-$  might also present.

Fig. 3 compared the abundance of primary species in aerosols collected on the firework night and in the normal days. Potassium was found in huge quantities in the firework particles. The mean levels of potassium reached 131 and  $103 \text{ mg g}^{-1}$  in  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  on the firework night, which were

about three times higher than those in the normal days, indicating that potassium salts might be one of the major compounds used in the fireworks and potassium could serve as a tracer of the emissions from fireworks. Actually potassium salts, such as nitrates, chlorates, and perchlorates, are widely used as oxygen donors (oxidisers) in the fireworks. The corresponding chemical equations are  $2\text{KNO}_3 = 2\text{KNO}_2 + \text{O}_2$ ,  $2\text{KClO}_3 = 2\text{KCl} + 3\text{O}_2$ , and  $\text{KClO}_4 = \text{KCl} + 2\text{O}_2$ , respectively. Fig. 2f showed that nitrite remained low during the sampling period, even on the night of firework burning, while chloride was highly elevated, indicating that the oxidiser used in the fireworks might be mainly of chlorates and perchlorates.

Interestingly, K showed stronger correlations with Mg, Ba, Pb, and Sr ( $r = 0.99, 0.98, 0.92,$  and  $0.99$ ) than with Al, Na, Ca, Zn, Cu, and Mn ( $r = 0.83, 0.66, 0.53, 0.60, 0.84$  and  $0.76$ ), indicating that Mg, Ba, Pb, and Sr are largely from the fireworks, while Al, Na, Ca, Zn, Cu, and Mn might also be contributed by other sources, such as road dust (Al, Ca), fossil fuel combustion (Al, Na, Ca), vehicular traffic emissions (Zn, Cu), and metal alloy industry emissions (Al, Zn, Cu, Mn) etc. In fact, Al and Mg are widely used as metallic fuels in pyrotechnics. Al is also used to give a silver or ‘flitter’ type effect. Sr, Na, Cu, Ba, and Ca are used to give red, yellow, blue, green, and orange colors, respectively. Pb could help to achieve a steady and reproducible burning rates (Conkling, 1985). Furthermore,  $\text{Cl}^-$  was found to be well correlated

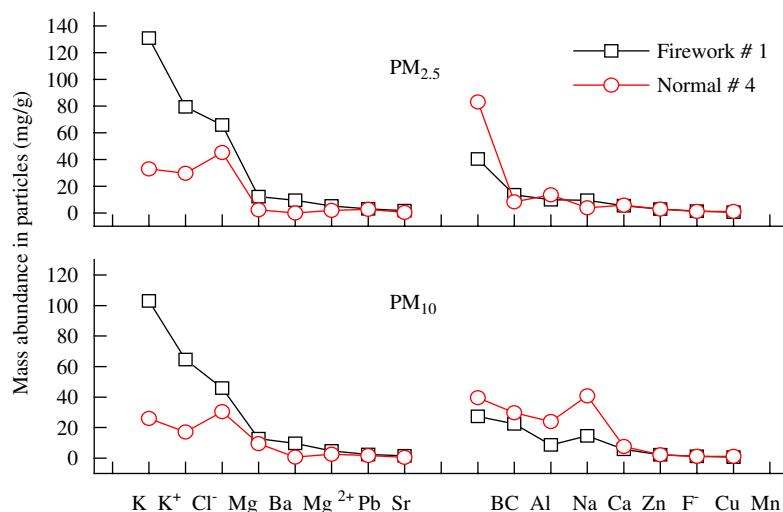


Fig. 3. Mass abundance of primary species in  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  collected on the firework night and in the normal days.

with K, Mg, Ba, Pb, and Sr, with correlation coefficients of 0.947, 0.996, 0.958, 0.990, and 0.988, respectively, suggesting that chloride salt might be the main chemical form of these metals in the fireworks. This coincided with the fact that chlorine was very important in the color effects, and “color species” were known to be  $\text{CaCl}^+$ ,  $\text{SrCl}^+$ ,  $\text{BaCl}^+$ , etc. (Helmenstin, 2005).

### 3.2.2. The increase of secondary components

Figs. 2e–h showed that the concentrations of  $\text{C}_5\text{H}_6\text{O}_4^{2-}$ ,  $\text{C}_3\text{H}_2\text{O}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{C}_4\text{H}_4\text{O}_4^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ , Fe,  $\text{Ca}^{2+}$ , and  $\text{Na}^+$  peaked after the burning night, and were about 23, 14, 11, 9, 8, 7, 7, 6, 5, 3, 3, and 2 times higher than those in the normal days in  $\text{PM}_{10}$  samples. This “tailing” phenomena suggest that a significant amount of these species may be from the secondary formations. Non-metallic fuels including charcoal, sulfur, and red phosphorus are generally used in the fireworks. The burning of these fuels can emit large amounts of pollution gases, such as CO,  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{P}_2\text{O}_5$  and carboneous particles. The low wind speed on the firework night and the following day (Table 1) could favor the accumulation of these pollution gases near the ground, and the high humidity might accelerate the secondary transformation progress. As a result, secondary acidic components—sulfate, nitrate, nitrite, and phosphate, as well as oxalate, malonate, succinate, and glutarate—were present in larger amount in the next day.

High concentrations and moderate elevations of sulfate and nitrate suggested that these two acidic species might come from both the special firework emissions and the typical anthropogenic activities, such as coal burning and traffic exhausts. This was the same with nitrite, phosphate, oxalate, malonate, and succinate, which have been frequently detected in typical urban aerosols. The clear enhancement of glutarate indicates its predominant source of firework burning.

### 3.3. Chemical composition of aerosols in the firework period

Particles generated from fireworks are likely to possess unique chemical compositions, which might be different from ambient normal aerosols. In order to present the composition scheme clearly, six chemically specific categories, i.e. secondary inorganic aerosol, geologic material, organic

matter, firework matter, black carbon, and trace species, were introduced. (1) The concentrations of secondary inorganic aerosol was obtained by summing up the concentrations of ammonium, nitrate, and sulfate. (2) Geologic material refers to the oxides of elements primarily associated with the earth’s crust. The mass of geologic material is calculated by dividing the concentration of Al with its proportion in the earth’s crust, i.e. 8%, in this work. (3) The firework matter is calculated as the sum of potassium and chloride, as they two were highly elevated on the lantern night and could be served as firework indicators. However, this is just an indicator or surrogate of the emissions from fireworks, because we don’t know the exact chemical forms of those species emitted. (4) The concentration of black carbon is got directly from the reflectometer. (5) Trace species is estimated by summing up all the ions and elements measured except those mainly presented in the other five list categories, i.e.  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , Al, Ca, Fe, K, Mg, Mn, Na, S,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{C}_3\text{H}_2\text{O}_4^{2-}$ ,  $\text{C}_4\text{H}_4\text{O}_4^{2-}$ ,  $\text{C}_5\text{H}_6\text{O}_4^{2-}$ , and BC. (6) The organic matter (OM) is often obtained by multiplying the organic carbon (OC) content by a factor of 1.4–2.1 (Turpin and Lim, 2001). However, OC has not been quantified because of the cellulose filter used. In this study “the mass difference between the aerosol particles and the above five categories” correlated well with “the total concentration of the four dicarboxylic acids” with a linear regression equation of “mass difference =  $92.198 \times (\text{oxalate} + \text{malonate} + \text{succinate} + \text{glutarate}) + 10.188$ ” and a correlation coefficient of 0.95, respectively. Since the mass difference is mainly related to organic matter, the mass of organic matter could be estimated by multiplying the total mass of oxalate, malonate, succinate, and glutarate with a factor of 92.198. In this way, organic matter was found to comprise 16.1–37.7% of the particle mass, which was similar to the value of 13.3–30.9% reported in Beijing in 2002–2003 (Sun et al., 2004), showing the reliability of this method in estimating organic matter.

The mass percentages of those six categories in  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  aerosols were calculated and presented in Fig. 4. It showed that secondary inorganic aerosol, organic matter, geologic material, and firework particles were the four dominant fractions, which totally comprised 83.6–95.9% of the particle mass concentration. Specifically, the four categories

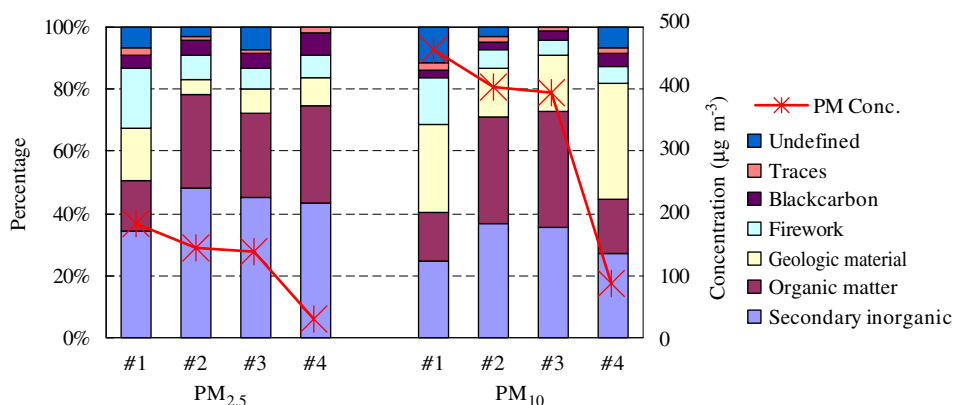


Fig. 4. Chemical composition of PM<sub>2.5</sub> and PM<sub>10</sub> during the lantern festival.

accounted for 24.5–48.0%, 16.1–37.7%, 5.0–37.2%, and 5.17–19.6%, respectively. The remaining undefined part of <11% could be partly attributed to water.

The results showed that for the samples collected in typical winter days (#4), the pattern was dominated by secondary inorganic (43%) and organic components (31%) in PM<sub>2.5</sub> and geologic material (37%) in PM<sub>10</sub>, respectively. The contribution of firework particles was low (6–7%). However, the samples from the lantern night (#1) showed a pattern with greater amounts of firework and crustal particles and less amount of secondary components, suggesting that the ambient concentrations are influenced by the proliferation of fireworks. Interestingly, for the samples taken just after the firework night (#2 and #3), the contribution of firework particles was similar with that in typical winter aerosol samples (#4), but the fraction of secondary inorganic and organic components was obviously higher than those in the firework samples (#1). This indicated that primary particles emitted directly from the fireworks could be quickly wiped off by dry deposition, while pollution gases from the burning activities were likely to be oxidized to secondary inorganic or organic components and retained in the particles.

### 3.4. The partitioning of chemical species in PM<sub>2.5</sub> and PM<sub>10</sub>

Fig. 5 showed the distributions of the major components between PM<sub>2.5</sub> and PM<sub>10</sub>. Typically primary elements were mostly distributed in the coarse fraction, with PM<sub>2.5</sub> to PM<sub>10</sub> ratios below 0.5, while soluble ions were almost evenly distributed in the fine and coarse fraction, with PM<sub>2.5</sub> to

PM<sub>10</sub> ratios fluctuating around 0.5. Fig. 5 also indicated how the distributions of major primary and secondary species altered over the firework period. The PM<sub>2.5</sub> to PM<sub>10</sub> ratio of primary components, shown in the left part of the figure, generally had the highest value on the firework night, then decreased along with the phasing out of the firework particles, ending at the lowest value in the normal days. However, the PM<sub>2.5</sub> to PM<sub>10</sub> ratio of secondary inorganic and organic components, shown in the right part of the figure, were higher both on the firework night and in the normal days, but they were lower in the day after the burning of firework. This variations of the size distributions indicated that the increase of fine particles was apparent on the firework night, while the secondary formation processes were mostly taken on the coarse particles after the burning night.

### 3.5. The acidity of aerosols in the firework period

Fig. 6 showed that pH of the aerosol filtrates during and after the firework burning (#1, #2, and #3) were lower than those in the normal days (#4) and the blank value of 6.25, indicating that burning of fireworks would likely aggravate the tendency of acidification. pH in PM<sub>2.5</sub> were higher than those in PM<sub>10</sub> for samples collected during and after the firework burning (#1, #2, and #3), indicating that more acidic anions were newly formed on the coarse particles. This accorded with the big elevation of the total equivalent concentrations of anions in PM<sub>10</sub> samples of #1, #2, and #3, and the high Anion/Cation ratios (1.60–2.10) in these samples.

The total equivalent concentrations (µeq m<sup>-3</sup>) of anions correlated well with those of cations, with a



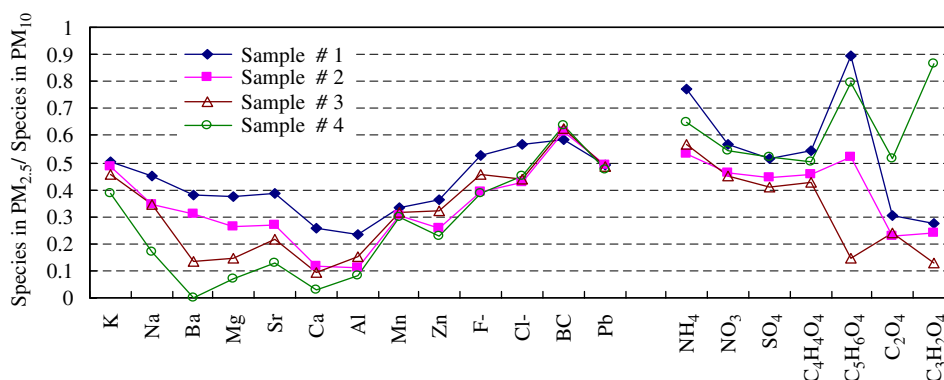


Fig. 5. Distribution diagrams of the measured species in  $PM_{2.5}$  and  $PM_{10}$ .

linear regression equation of “Cation =  $0.53 \times$  Anion ( $r = 0.97$ )”. The slope of the regression line was much lower than unity. This lack of cations might be partly due to the abundance of soluble transition metals, such as  $Al^{3+}$ ,  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Mn^{2+}$ ,  $Sr^{2+}$ , and  $Zn^{2+}$ , which are used as additives in the fireworks, but not included in the cation calculation. The solubility of the above transition metals was calculated from their concentrations in the water extracts (water-soluble) and in the residues (water-insoluble). The formula used is:

$$\text{Solubility} = \frac{\text{Concentration in the water extract}}{\text{Concentration in the water extract} + \text{Concentration in the residues}}$$

The results were presented in Fig. 7. It shows that the solubility of these elements increased after the burning of fireworks (#2 and #3). The solubility of Al, Pb, Cu, Mn, Sr, and Zn correlated well with the ratio of Anion/Cation, with correlation coefficients of 0.62, 0.91, 0.95, 0.92, 0.71, and 0.80, respectively. Thus, the formation of acidic inorganic and organic acids in the plume of the firework burning would make transition metals much more soluble. Soluble metals are known to be more harmful to the ecosystem and more poisonous to the human being (Dat, 1991), and people should be warned on the harmful effects of the fireworks.

### 3.6. Formation mechanism of secondary aerosols

#### 3.6.1. Sulfate and nitrate

Sulfur oxidation ratio defined as  $SOR = n\text{-SO}_4^{2-} / (n\text{-SO}_4^{2-} + n\text{-SO}_2)$  and nitrogen oxidation ratio defined as  $NOR = n\text{-NO}_3^- / (n\text{-NO}_3^- + n\text{-NO}_2)$  could be the indication of the secondary transformation processes. The relations of SOR and NOR to

meteorological factors and selected species were presented in Table 2.

There are many mechanisms reported for the formation of  $SO_4^{2-}$  from  $SO_2$ , such as gas-phase reaction of  $SO_2$  and OH radical, aqueous transformation processes (metal catalyzed oxidation or  $H_2O_2/O_3$  oxidation), and in-cloud processes (Ziegler, 1979; Meng and Seinfeld, 1994; Yao et al., 2002; Xiu et al., 2004). The gas-phase oxidation of  $SO_2$  to  $SO_4^{2-}$  by OH radical is a strong

function of temperature (Seinfeld, 1986). The heterogeneous formation of sulfate was reported to be a function of RH and particulate loading (Liang and Jacobson, 1999), and when  $RH > 75\%$  sulfate was largely from heterogeneous reactions (McMurry and Wilson, 1983). Table 2 showed that SOR was well correlated with particle mass (PM,  $r = 0.977$ ) and RH ( $r = 0.733$ ), but poorly with  $SO_2$  ( $r = -0.082$ ) and temperature ( $r = -0.668$ ). Moreover, RH was high during the sampling periods (Table 1). Thus the formation of sulfate in the firework plume might be mainly from heterogeneous process. Interestingly, SOR showed obvious correlations with transition metals (Cu, Fe, Mn), basic species (Al, Na, K, Mg, Ca), and BC (Table 2). Transition metals and BC can catalyze the formation of sulfate, while basic components may favor the absorbance of acidic  $SO_2$  and accelerate its reactions on the surface of particles. This indicated the dominance of metal-catalyzed heterogeneous formation of sulfate during the firework period.

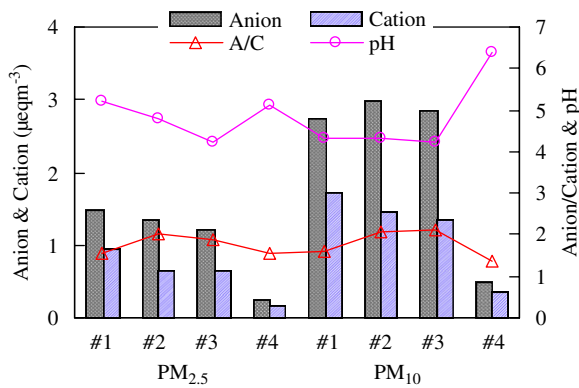


Fig. 6. pH of the aerosol filtrates, the equivalent concentrations of total anions and cations, and their ratios in PM<sub>2.5</sub> and PM<sub>10</sub> during the lantern festival.

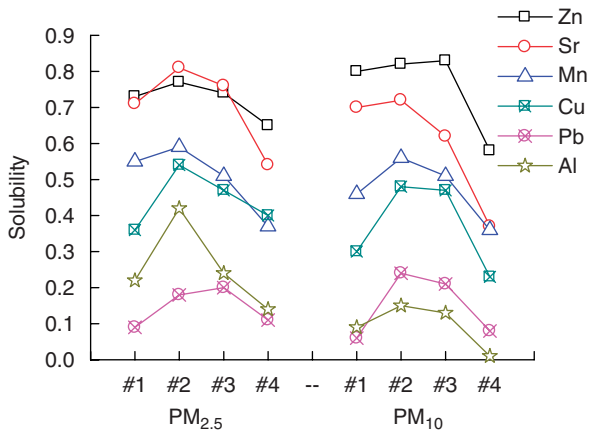


Fig. 7. solubility of several metals in PM<sub>2.5</sub> and PM<sub>10</sub> during the lantern festival.

NOR did not show strong correlations with RH, PM, BC, transition (except water-soluble Fe) and basic metals, but it was highly correlated with pollution gases (SO<sub>2</sub> and NO<sub>2</sub>) in the air and ammonium in the particles. Thus the formation of nitrate might be through homogeneous gas-phase reactions of NO<sub>2</sub> with OH or O<sub>3</sub> to form HNO<sub>3</sub>, which then reacts with NH<sub>3</sub> to form NH<sub>4</sub>NO<sub>3</sub>. The formation of NH<sub>4</sub>NO<sub>3</sub> can be verified by the strong correlations between ammonium and nitrate ( $r = 0.989$ ). The weaker correlation of NOR with basic metals indicated that NO<sub>2</sub> was quickly oxidized to HNO<sub>3</sub> before it was absorbed by particles. This agreed with the fact that the formation rate of nitrate was approximately ten times higher than that of sulfate (Hewitt, 2001).

Although NOR didn't show any correlations with most transition metals presented in Table 2, it was significantly correlated with water-soluble Fe (Table 2). Evidence showed that HNO<sub>3</sub> can dissociatively and irreversibly adsorb to form surface nitrate on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, and H<sub>2</sub>O adsorbed on the particle surface can solvate the nitrate ion and increases the initial uptake coefficient (Goodman et al., 2001). Thus, HNO<sub>3</sub> can react with  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in the aerosol particles under moist atmosphere in the firework period. This reaction would shift the equilibrium of "NH<sub>4</sub>NO<sub>3</sub>  $\rightleftharpoons$  NH<sub>3</sub> + HNO<sub>3</sub>" to the right side, and in return accelerate the secondary formation of nitrate and increase the concentration of water-soluble Fe. In this way, strong correlations between NOR and water-soluble Fe can be well founded. Different from NOR, SOR showed stronger correlations with total Fe than with water-soluble Fe (Table 2), suggesting that the mechanism between S

Table 2

Correlation coefficients of SOR and NOR with selected species and meteorological factors

	RH	Temp.	SO <sub>2</sub>	NO <sub>2</sub>	PM	NH <sub>4</sub> <sup>+</sup>	BC		
SOR	<b>0.733</b>	-0.688	-0.082	-0.176	<b>0.977</b>	0.788	<b>0.978</b>		
NOR	0.298	0.152	<b>0.792</b>	<b>0.765</b>	0.444	<b>0.803</b>	0.400		
Water-soluble	Cu	Fe	Mn	Al	Na	K	Mg	Ca	
SOR	<b>0.996</b>	0.651	<b>0.973</b>	<b>0.992</b>	<b>0.882</b>	<b>0.849</b>	<b>0.874</b>	<b>0.803</b>	
NOR	0.298	0.911	0.392	0.290	0.494	-0.225	-0.167	0.618	
Total	Cu	Fe	Mn	Al	Na	K	Mg	Ca	
SOR	<b>0.915</b>	<b>0.773</b>	<b>0.940</b>	<b>0.886</b>	<b>0.911</b>	<b>0.785</b>	<b>0.825</b>	<b>0.833</b>	
NOR	-0.045	0.624	0.273	0.078	0.375	-0.333	-0.237	0.454	

and Fe might be different from that between N and Fe. There might be active “Fe–O” or “Fe–OH” sites on the surface of atmospheric particles containing Fe. Since catalytic gas-to-particle conversion was suggested to be the major formation route of sulfate, the attachment of SO<sub>2</sub> to these sites and its further oxidation to sulfate could take place. The number of “Fe–O” or “Fe–OH” sites is proportional to the total Fe content in the particles. This might be the reason of the better correlation of SOR with total Fe than with water-soluble Fe. Besides Fe, other metals, like Cu and Mn, can also catalyze the formation of sulfate through the supply of active sites like “M–O” or “M–OH”. However, SOR exhibited stronger correlations with Cu and Mn than with Fe (Table 2), indicating that the supply of active “Fe–O” or “Fe–OH” sites cannot explain the entire effect of Fe. Actually, Fe can take part in the oxidation progress of SO<sub>2</sub>. The coupling between Fe and S has been widely studied (Zhuang et al., 1992), and the mechanism is known to be “Fe(III) + S(IV) → Fe(II) + S(VI)”.

In summary, nitrate is mainly formed through homogeneous gas-phase reactions of NO<sub>2</sub>. The dissociation of NH<sub>4</sub>NO<sub>3</sub> and subsequent reaction of HNO<sub>3</sub> with α-Fe<sub>2</sub>O<sub>3</sub> in the aerosols can accelerate the formation of nitrate. Sulfate is largely from heterogeneous catalytic transformation of SO<sub>2</sub> on the surface of atmospheric particles. Fe, unlike other transition metals, is not only the catalyst, but also the oxidant in the formation of sulfate.

### 3.6.2. Oxalate, malonate, succinate, and glutarate

SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and Ca<sup>2+</sup> were used as references to study the formation mechanism of dicarboxylic acids. The correlation coefficients between the diacid anions and the above inorganic ions were given in Table 3. Malonate (C<sub>3</sub>), succinate (C<sub>4</sub>), and glutarate (C<sub>5</sub>) showed higher correlations with nitrate and ammonium than with sulfate and calcium, while oxalate (C<sub>2</sub>) was highly correlated with sulfate and calcium, indicating that C<sub>3</sub>, C<sub>4</sub>, and C<sub>5</sub> were mostly attributed to gas-phase photochemical oxidation in the air, while C<sub>2</sub> was probably related to in-situ heterogeneous reactions on the particles.

Two types of chemical reaction mechanisms have been proposed for the formation of dicarboxylic acids in the atmosphere (Kawamura et al., 1996). One is the oxidation of unsaturated fatty acids. In this route, longer chain diacids are likely precursors

Table 3  
Correlation coefficients between dicarboxylic acids (right part) and those with NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, and Ca<sup>2+</sup> (left part)

	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>3</sub> :C <sub>4</sub>	C <sub>4</sub> :C <sub>5</sub>	C <sub>2</sub> :C <sub>3</sub>
NO <sub>3</sub> <sup>-</sup>	0.954	0.919	0.940	0.832	0.957	0.924	0.911
NH <sub>4</sub> <sup>+</sup>	0.914	0.900	0.944	0.843			
SO <sub>4</sub> <sup>2-</sup>	0.970	0.858	0.839	0.699	C <sub>3</sub> :C <sub>5</sub>	C <sub>2</sub> :C <sub>4</sub>	C <sub>2</sub> :C <sub>5</sub>
Ca <sup>2+</sup>	0.951	0.880	0.787	0.650	0.911	0.857	0.721

of lower chain ones, resulting in the good correlations among diacids. The other is the oxidation of aromatic hydrocarbons such as benzene and toluene. In this route, only C<sub>2</sub> can be produced through gas-to-particle conversion. The correlation coefficients between C<sub>2</sub>–C<sub>5</sub> were presented in Table 3. It is interesting to find that the strength of the correlation increases when the carbon number of the two diacids becomes nearer. This might suggest the successive oxidation of C<sub>5</sub>–C<sub>4</sub>, C<sub>4</sub>–C<sub>3</sub>, and C<sub>3</sub>–C<sub>2</sub>, and indicate the prevalence of the former route in the formation of C<sub>2</sub>–C<sub>5</sub>. In addition, the relative weak correlations between C<sub>2</sub> and C<sub>4</sub>–C<sub>5</sub> indicate that C<sub>2</sub> could also be from the second route, i.e. the oxidation of aromatic hydrocarbons.

### 3.7. The contribution of firework to ambient aerosols

As discussed above, firework might be one of the major sources for the severe air pollution during the lantern festival. We do need to know to what extent the burning of fireworks contributes to the degradation of air quality in Beijing? i.e. to estimate the contribution of firework to a certain component (X) in the aerosols.

K<sup>+</sup> is widely used as an indicator of biomass burning in atmospheric particles (Yamasoe et al., 2000; Ikegami et al., 2001). However, K was extremely elevated during the burning of fireworks, suggesting that it was mainly from the emissions of fireworks and could be served as an indicator of firework burning. Here, a simple method was developed to study the contribution of fireworks to X quantitatively. The principles and the assumptions for the estimation are: (1) K only originates from the firework burning, (2) X could be regarded as the sum of two fractions, one from the firework burning, and the other from other sources, (3) the ratio of X/K from the direct firework burning, (X/K)<sub>firework</sub>, is constant. According to the three

assumptions, the equation below, i.e.

$$X = (X/K)_{\text{firework}} \times K + (X)_{\text{non-firework}}$$

can be used to distinguish the contribution of the firework burning to  $X$ . Since no  $(X/K)_{\text{firework}}$  data has been reported in China,  $(X/K)_{\text{firework}}$  values calculated from the average composition of chemical species in the firework plumes during Diwali festival in India were used. These values are 0.0227 for Pb, 0.0112 for Zn, 0.5179 for TC, 0.0445 for  $\text{SO}_4^{2-}$ , and 0.0561 for  $\text{NO}_3^-$ , respectively ([www.indiatogether.org](http://www.indiatogether.org)). Pb, Zn, TC, and  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  were selected to be the representatives of highly elevated primary components (group 1 in Section 3.2), moderate elevated primary components (group 2 in Section 3.2), carbonaceous aerosol, and secondary aerosol (group 3 in Section 3.2), respectively. The contribution of firework to the  $X$  species was calculated from  $(X/K)_{\text{firework}} \times K/X$  and shown in Table 4.

Overall, the contributions of fireworks were about 2–8 times higher on the burning night than those in the normal days, and it was larger to the fine particles than to the coarse ones. Specifically, it contributed about 97.8%, 43.1%, 27.5%, 8.3%, 2.7% to Pb, TC, Zn,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  in  $\text{PM}_{2.5}$ , and 96.2%, 37.4%, 20.0%, 9.4%, 2.8% in  $\text{PM}_{10}$ , respectively, on the lantern night, verifying that the primary elements in group 1 were mainly from firework burning, while secondary components in group 3 were weakly influenced on the firework night.

In this study, the proportion of the local and long-range transport dust to the mineral aerosols has been estimated based on the ratio of Mg/Al (Sun et al., 2004; Han et al., 2005). The principles and the assumptions for the estimation are: (1) mineral aerosols could be regarded as the sum of two fractions, one from the local emissions, and the other from the long-range transport, (2) the composition of mineral aerosol from the source regions is constant during the transport, and (3) the ratio of Mg/Al from the local and the long-range transported dust are stable and statistically different. Based on the above assumptions, the equations below, i.e.

$$(\text{Mg}/\text{Al})_{\text{aerosol}} = m \times (\text{Mg}/\text{Al})_{\text{local}} + n \times (\text{Mg}/\text{Al})_{\text{transport}}$$

$$m + n = 1$$

could be used to estimate the relative contribution of local and long-range transported dust. Here,  $m$ ,  $n$  are contributions of local and long-range transported dust to the ambient mineral aerosols, respectively;  $(\text{Mg}/\text{Al})_{\text{aerosol}}$ ,  $(\text{Mg}/\text{Al})_{\text{local}}$ , and  $(\text{Mg}/\text{Al})_{\text{transport}}$  are the ratios of Mg/Al in the ambient aerosol, local dust, and transported dust, respectively. In our previous study (Sun et al., 2004), values of 0.45 and 0.18 have been used for  $(\text{Mg}/\text{Al})_{\text{local}}$  and  $(\text{Mg}/\text{Al})_{\text{transport}}$ , respectively. However, in this study the local condition is obviously different from the typical local conditions because of the burning of fireworks, so it is desirable to choose a new  $(\text{Mg}/\text{Al})_{\text{local}}$  value, which could better

Table 4

Values of several indicators used in the source apportionment and the contribution of firework to the local environment

	BC <sup>a</sup>	OM <sup>a</sup>	OC <sup>a</sup>	Mg/Al <sup>b</sup>	m <sup>c</sup> (%)	Pb <sup>d</sup> (%)	Zn <sup>d</sup> (%)	TC <sup>d</sup> (%)	NO <sub>3</sub> <sup>-d</sup> (%)	SO <sub>4</sub> <sup>2-d</sup> (%)
<b>PM<sub>2.5</sub></b>										
Sample #1	7.44	30.17	21.55	0.91	92.1	97.8	27.5	43.1	8.3	2.7
Sample #2	6.60	43.20	30.86	0.85	84.8	43.3	10.3	8.3	1.5	0.7
Sample #3	6.76	37.06	26.47	0.29	14.3	36.3	6.0	7.2	1.3	0.6
Sample #4	2.17	9.21	6.58	0.27	11.8	27.7	6.5	5.1	1.2	0.6
<b>PM<sub>10</sub></b>										
Sample #1	12.8	75.1	53.6	0.57	49.2	96.2	20.0	37.4	9.4	2.8
Sample #2	10.8	140.0	100.0	0.35	21.9	43.5	5.5	5.8	1.5	0.6
Sample #3	10.8	151.5	108.2	0.30	14.7	38.4	4.3	4.4	1.3	0.5
Sample #4	3.38	15.04	10.74	0.32	17.8	34.0	3.8	8.2	1.8	0.8

<sup>a</sup>Concentration in  $\mu\text{g m}^{-3}$ ,  $[\text{OM}] = 92.198 \times ([\text{C}_2\text{O}_4^{2-}] + [\text{C}_3\text{H}_2\text{O}_4^{2-}] + [\text{C}_4\text{H}_4\text{O}_4^{2-}] + [\text{C}_5\text{H}_6\text{O}_4^{2-}])$ ,  $[\text{OC}] = [\text{OM}]/1.4$ .

<sup>b</sup>Values in ratio.

<sup>c</sup>Contribution of local dust from firework burning to mineral aerosols, calculated from  $(\text{Mg}/\text{Al})_{\text{aerosol}} = m \times (\text{Mg}/\text{Al})_{\text{local}} + n \times (\text{Mg}/\text{Al})_{\text{transport}}$   $m + n = 1$ .  $(\text{Mg}/\text{Al})_{\text{local}} = 0.97$ ,  $(\text{Mg}/\text{Al})_{\text{transport}} = 0.18$ .

<sup>d</sup>Contribution of firework burning to the list species, calculated from  $(X/K)_{\text{firework}} \times [K]/[X]$  for species X;  $[\text{TC}] = [\text{BC}] + [\text{OC}]$ .

represent the local condition. Here, the value of Mg/Al from the pure firework particles is used for  $(\text{Mg}/\text{Al})_{\text{local}}$  on the assumption that the local contribution is predominantly from the fireworks during the festival period. Since the average concentrations of Mg and Al were reported to be 51.62 and 53.36  $\text{ng m}^{-3}$ , respectively, in the firework derived particles (Carranza et al., 2001), a value of 0.97 ( $= 51.62/53.36$ ) was used for  $(\text{Mg}/\text{Al})_{\text{local}}$  in this study.

The values of Mg/Al in  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  samples and the corresponding values of  $m$  calculated from the above method were listed in Table 4. It could be seen that on the night of firework burning (#1), the local firework emissions accounted for 92.1% and 49.2% of the total mineral aerosols in  $\text{PM}_{2.5}$  and in  $\text{PM}_{10}$ , respectively, which were about 8 and 2 times higher than those in the normal days (#4, 11.8% in  $\text{PM}_{2.5}$  and 17.8% in  $\text{PM}_{10}$ ). In addition, the local contribution presented a clear downtrend with the phase-out of the firework burning. This clearly demonstrated that the local firework burning contributed significantly to the mineral aerosols in the festival period. Table 4 also showed that the contributions from local firework emissions and from long-range transport were higher in  $\text{PM}_{2.5}$  in the firework and normal days, respectively, indicating that primary mineral particles from the firework burning and from the long-range transport are mainly in the fine fraction. The results using this technique quantitatively indicate that particulate pollution, especially the fine part, from the firework burning is extremely serious. Effective measures should be adopted to bring citizens a joyful and healthy holiday.

#### 4. Conclusions

$\text{PM}_{2.5}$  and  $\text{PM}_{10}$  aerosols were monitored in Beijing during the lantern festival to study the influences of fireworks on the ambient air. Eighteen ions, 20 elements, and black carbon in the aerosols have been measured by IC, ICP-AES, and smokes-tain reflectometer, respectively. Organic matter level could be well estimated from the concentrations of dicarboxylic acids through the equation of  $[\text{OM}] = 92.198 \times ([\text{oxalate}] + [\text{malonate}] + [\text{succinate}] + [\text{glutarate}])$ .

$\text{PM}_{2.5}$  and  $\text{PM}_{10}$  went up over 6 and 4 times in the lantern day compared to the normal days. Primary components of Ba, K,  $\text{K}^+$ , Sr,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ , Pb, Mg, Cu, Al,  $\text{F}^-$ , Zn, BC, Mn, Ca, and Na peaked on the

burning night and were about 82, 22, 21, 17, 11, 9, 8, 8, 6, 6, 5, 5, 4, 3, and 3 times higher than those in the normal days in  $\text{PM}_{10}$ . Secondary components of  $\text{C}_5\text{H}_6\text{O}_4^{2-}$ ,  $\text{C}_3\text{H}_2\text{O}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{C}_4\text{H}_4\text{O}_4^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ , Fe,  $\text{Ca}^{2+}$ , and  $\text{Na}^+$  peaked after the burning night, and were about 23, 14, 11, 9, 8, 7, 7, 6, 5, 3, 3, and 2 times higher. Primary aerosols from the burning of fireworks were mainly in the fine mode, while secondary formation of acidic anions mainly took place on the coarse particles. The firework particles were acidic and inorganic in nature with comparatively less amounts of secondary components.

Nitrate was mainly formed through homogeneous gas-phase reactions of  $\text{NO}_2$ , while sulfate was largely from heterogeneous catalytic transformation of  $\text{SO}_2$  on the surface of atmospheric particles. Fe could catalyze the formation of nitrate through the reaction of  $\alpha\text{-Fe}_2\text{O}_3$  with  $\text{HNO}_3$ , while in the formation of sulfate, Fe is not only the catalyst, but also the oxidant. Malonate, succinate, and glutarate were mainly from the gas-phase oxidation of unsaturated fatty acids, while oxalate could also derive from the heterogeneous reactions of aromatic hydrocarbons.

A revised method using the ratio of Mg/Al has been developed to quantitatively study the proportion of the local firework vs. long-range transport dust to the mineral aerosols in Beijing. On the night of firework burning, the local emissions have been found to account for 92.1% and 49.2% of the total mineral aerosol in  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ , respectively. A simple method using K as an indicator of firework burning was developed to study the contribution of firework burning to a certain species (X) in the aerosols. It showed that about 97.8% of Pb, 43.1% of TC, 27.5% of Zn, 8.3% of  $\text{NO}_3^-$ , and 2.7% of  $\text{SO}_4^{2-}$  in  $\text{PM}_{2.5}$ , and 96.2%, 37.4%, 20.0%, 9.4%, 2.8% in  $\text{PM}_{10}$ , were derived from firework burning on the lantern night.

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