Supplementary Materials

Estimation of direct and indirect impacts of fireworks on the physicochemical characteristics of atmospheric fine and coarse particles

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2 Methodology

2.1 Sampling

The size-resolved PM samples were collected in Tianjin (a megacity in China). Tianjin, the largest harbor of Northern China, is a fast-growing and economically developed city who has a population of over 12 million and more than 1.5 million automobiles. The air quality of Tianjin declined with rapid urbanization and industrialization. The sampling site is sited at the rooftop of a six-story building which is located in a mixed residential and commercial area in Tianjin. Usually, substantial degradation would occur during the firework displays in such a mixed area. The map of the sampling site was indicated in Fig. S1.

The sampling campaign of PM_{10} and $PM_{2.5}$ was carried out from 30 January 2013 to 24 February 2013, including periods before, during, and after CNY (till to Lantern Festival). The sampling periods and the corresponding Chinese Lunar calendar were listed in Table S1. During the sampling periods, firework displays took place for celebration of the CNY holiday. For the period from CNY's Eve to Lantern Festival, fireworks are allowed in China and numerous fireworks were consumed, thus, this period is defined as heavy-firework period. For the period before the CNY's Eve, sporadic fireworks might be set off, so light-firework period is defined.

Based on our previous works and other related studies (Shi et al., 2009; Xue et al., 2010; Harrison et al., 2012; Tian et al., 2013; Zhao et al., 2013 a, b), the $PM_{2.5}$ and PM_{10} were simultaneously collected on quartz fiber filters (90 mm in diameter, 2500QAT-UP, Pall Life Sciences) and polypropylene fiber filters (90 mm in diameter,

Beijing Synthetic Fiber Research Institute, China) using medium-volume air samplers (TH-150) at a flow rate of 100 L/min. Before sampling, to remove any organic compounds that may be present on the filters, the quartz and polypropylene fiber filters were baked in the oven at 400-500 °C and 60°C, respectively. Before and after sampling, all the filters were equilibrated for 48 h in desiccators at room temperature. Then each filter was weighted more than 3 times by a sensitive microbalance with balance sensitivity ±0.010 mg. After weighing, the filters were stored at −4 °C until chemical analysis and the chemical analysis would be conducted in less than a month.

2.2 Chemical Analysis

The elemental compositions (Al, Si, Ca, V, Cr, Mn, Fe, Co, Cu, Zn, As and Pb) of the collected samples on polypropylene fiber filters were determined by inductively coupled plasma-mass spectrometry (ICP-AES) (IRIS Intrepid II, Thermo Electron). Before measured by ICP-AES, half of polypropylene filters were cut into fragments and placed into a conical flask. Acid solutions (15 mL of HNO3 and 5 mL of $HClO_4$) were added into the flask and the flask was heated by electric stove. The solution was evaporated until about 3 mL residual left. After being cooled and filtered, the solution was decanted into a test tube and diluted to 15 mL with deionized water. Alkali solution was used for measuring the concentrations of silicon. For QA/QC, standard reference materials were pre-treated and analyzed with the same procedure, with the recovered values for all the target elements falling into the range or within 5% of certified values.

The ion chromatography (DX-120, DIONEX) was used to analyze the water soluble ions (NO_3^-, SO_4^{2-}, Na^+, K^+ and Mg^{2+}) collected on quartz-fiber. A 1/8 piece of each quartz fiber filter was put into a glass tube and deionized water was used to extract. The extraction procedure was conducted for at least three times so that the water soluble ions of samples were extracted adequately into the solution. Before detection of ions, standard solutions were prepared and were detected for over three times; and low relative standard deviations were observed.

Organic carbon (OC) and elemental carbon (EC) concentrations of the samples was determined by means of DRI/OGC carbon analyzers, a technique based on the IMPROVE thermal/optical reflectance (TOR) protocol. The first sample was analyzed again every ten samples and the precision should be less than 2%. The calibration of the analyzer should be done before and after sample analysis every day.

Some chemical residues may be dissolved into the solution during laboratory analysis. Thus, background contamination was routinely monitored through blank tests. Enough blank tests were conducted and used to valid and correct corresponding data. Certified reference materials (CRM, produced by National Research Center for Certified Reference Materials, China) were used to ensure QA/QC. Blanks and duplicate sample analyses were carried out for nearly 10% of samples. The pre-treatment procedure, chemical analysis and QA/QC were referred to our previous works and other related studies (Bi et al., 2007; Shi et al., 2009; Kong et al., 2010; Xue et al., 2010; Zhao et al., 2013 a, b).

In addition, scanning electron microscopy (SEM) determinations were performed

by a JEOL JSM-7500F equipped with an X-ray energy dispersive spectrometer (EDS), to investigate morphology characterization and chemical analysis of individual particles.

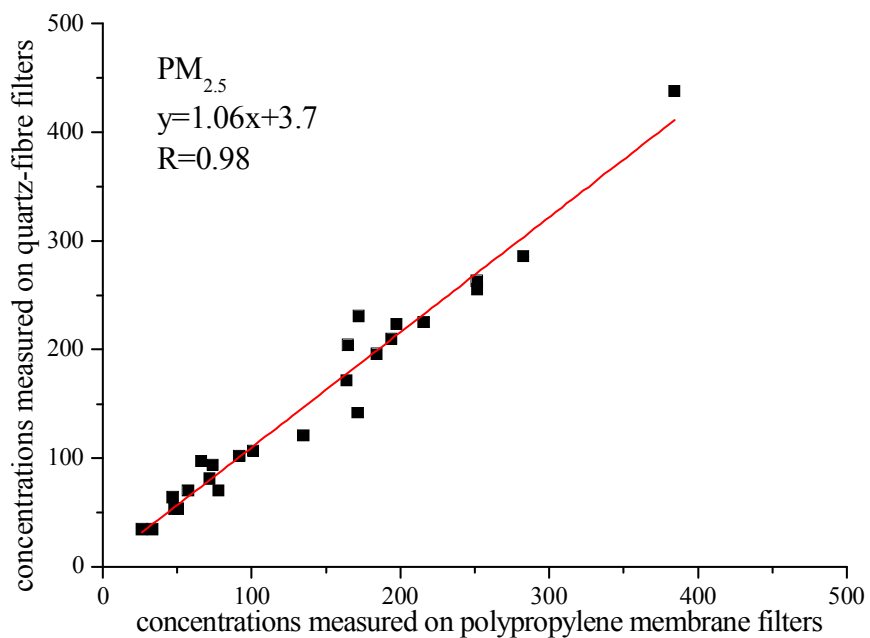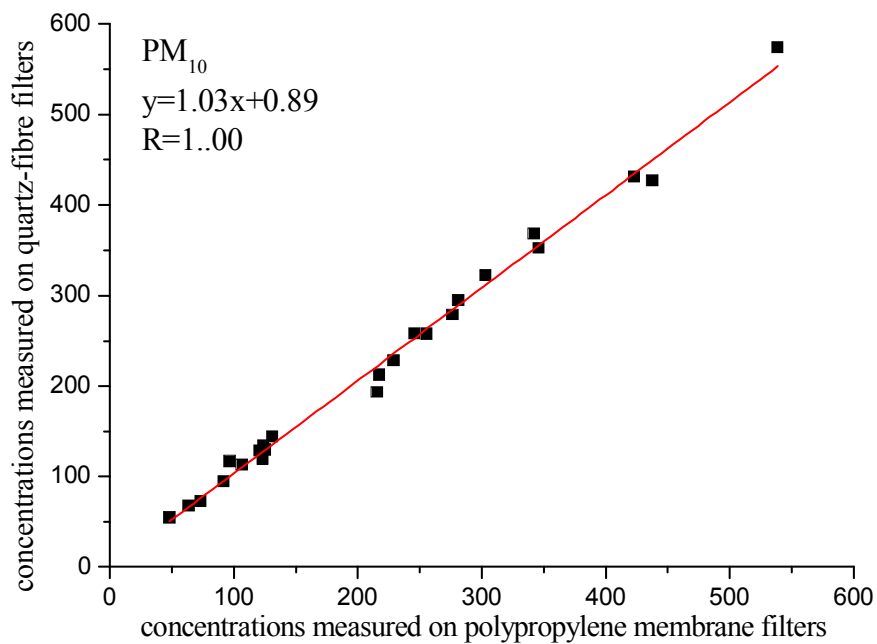**Fig. S1** The map of sampling site, in a megacity in China.

Fig. S2 The comparisons between concentrations measured on polypropylene fibre filters and that on quartz fibre filters.
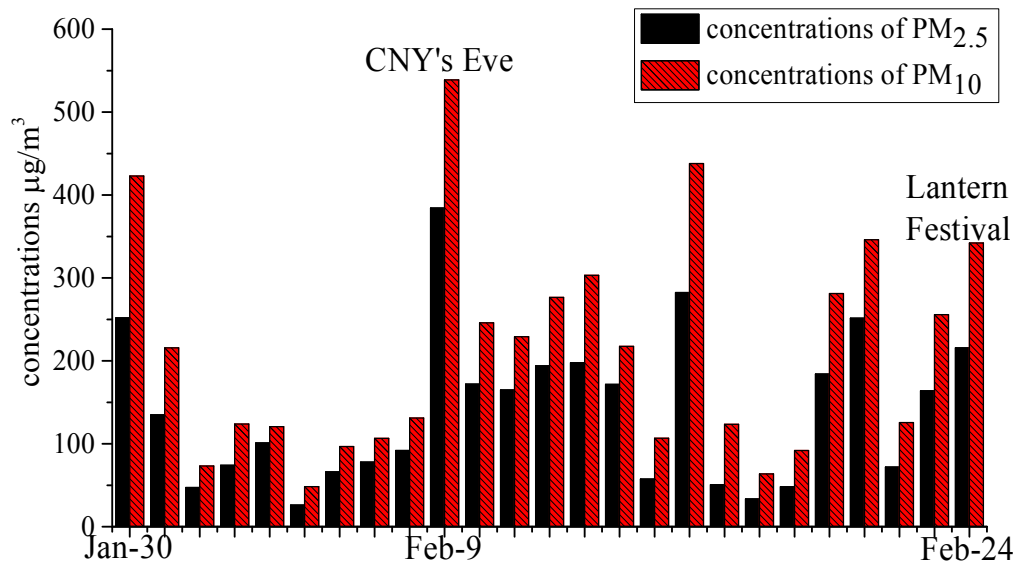
Fig. S3 The concentrations of the PM_{10} and $PM_{2.5}$ in Tianjin during sampling periods
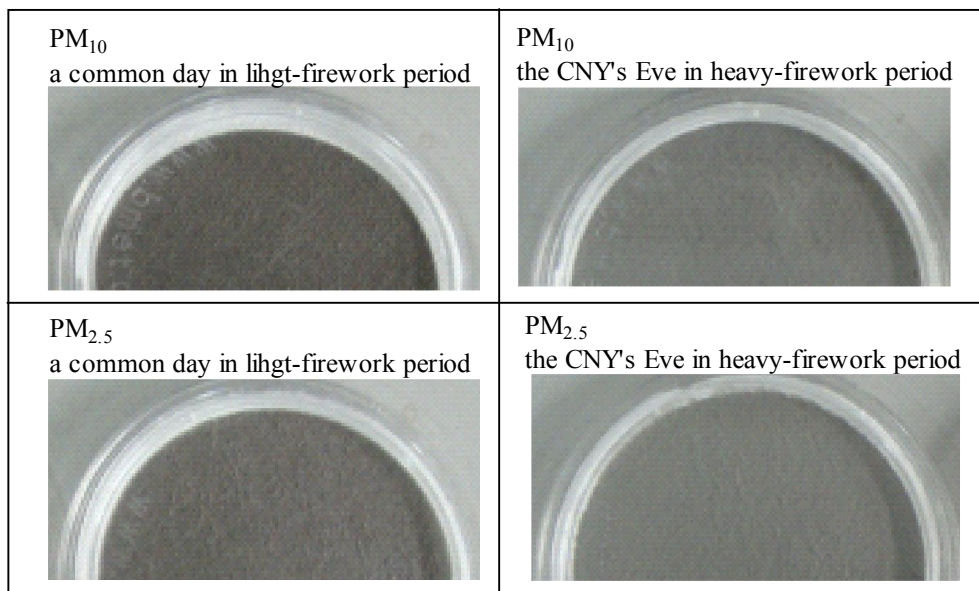
Fig. S4 Photos of quartz filters for PM_{10} and $PM_{2.5}$ samples in two cases: a common day in the light-firework period and the CNY's Eve in the heavy-firework period.
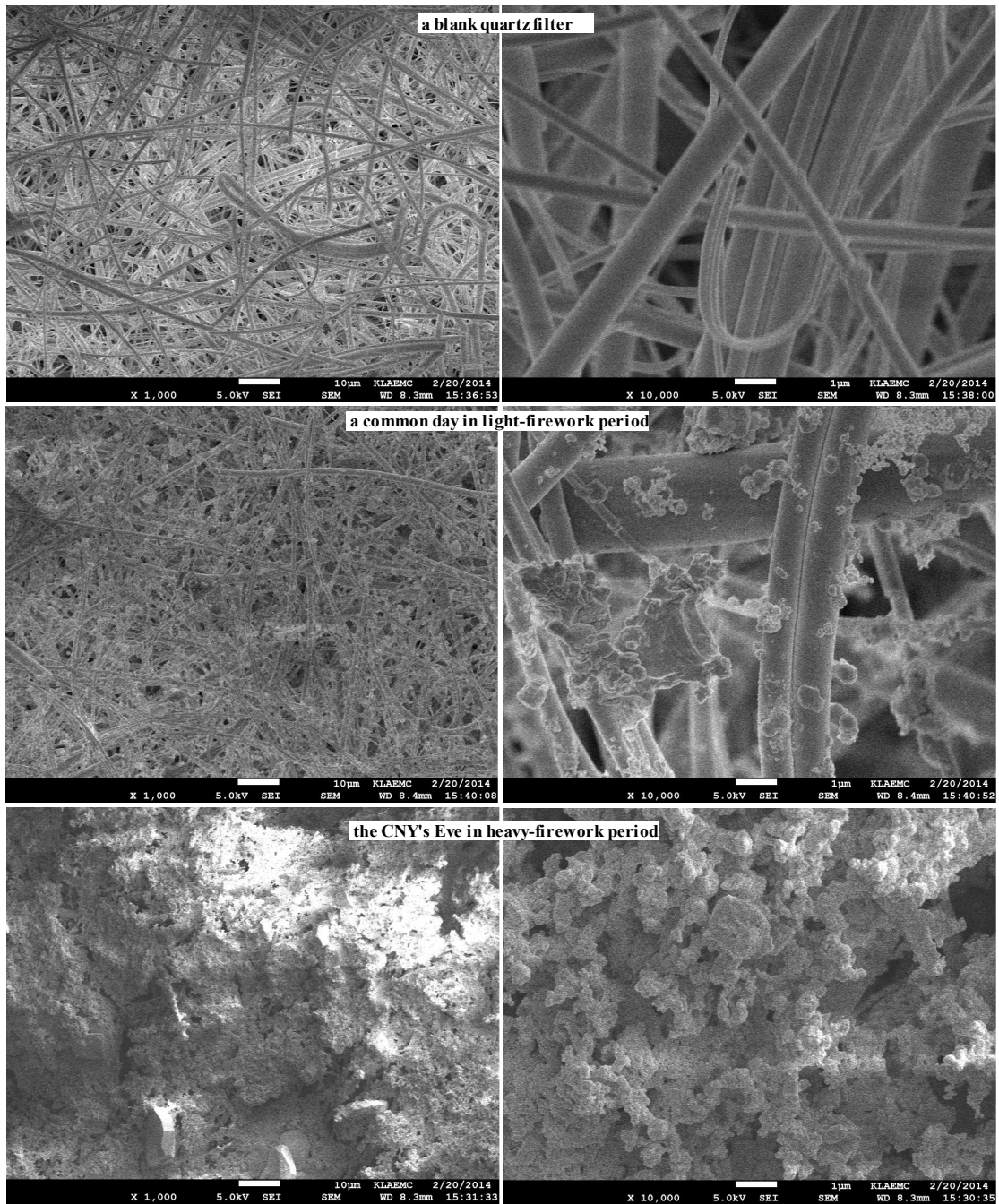
Fig. S5 Micrographs of PM$_{2.5}$ for a blank quartz filter, a common day in light-firework period and the CNY's Eve in heavy-firework period.
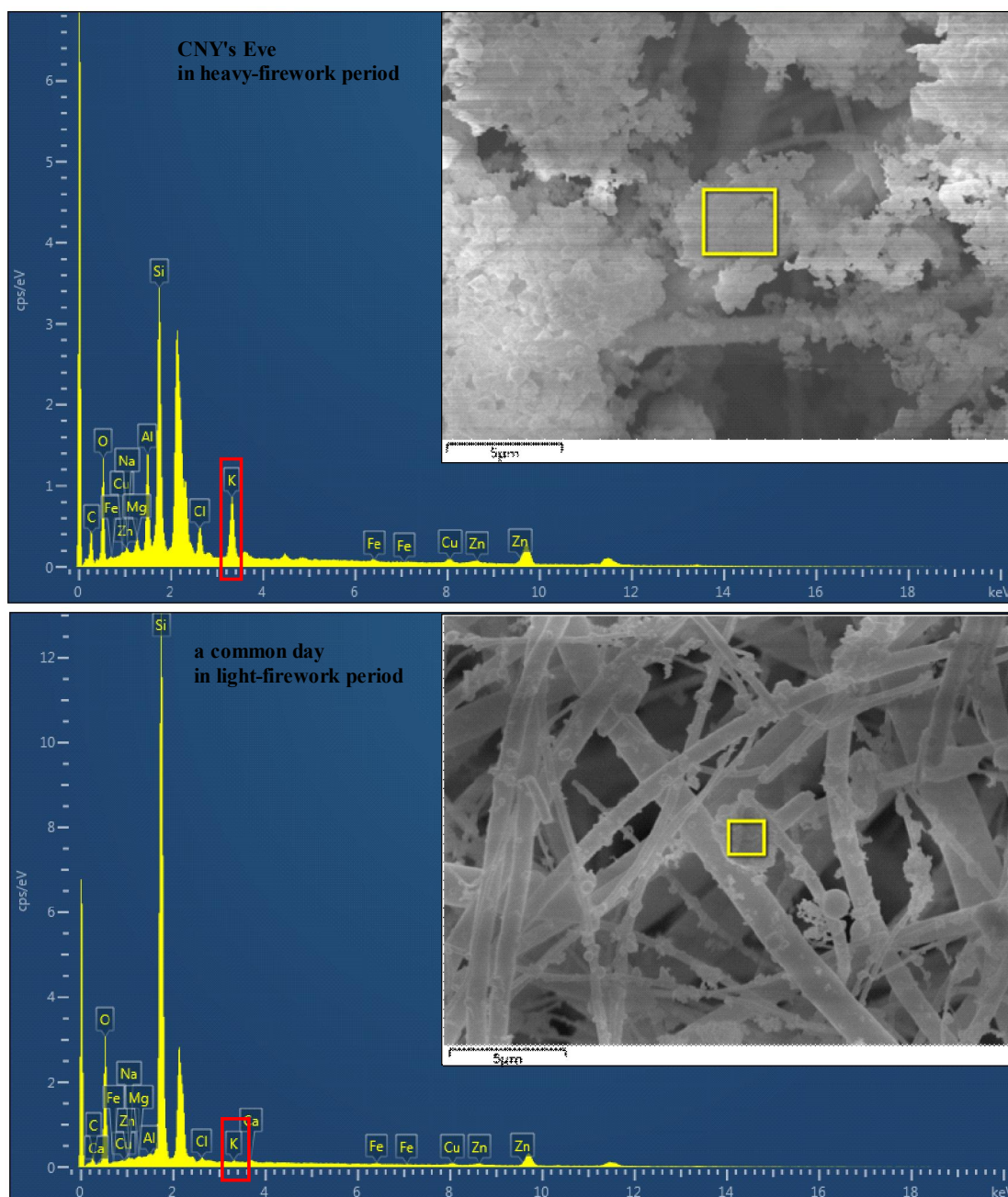
Fig. S6 SEM micrographs and EDS spectra of particles in two cases: a common day in the light-firework period and the CNY's Eve in the heavy-firework period.
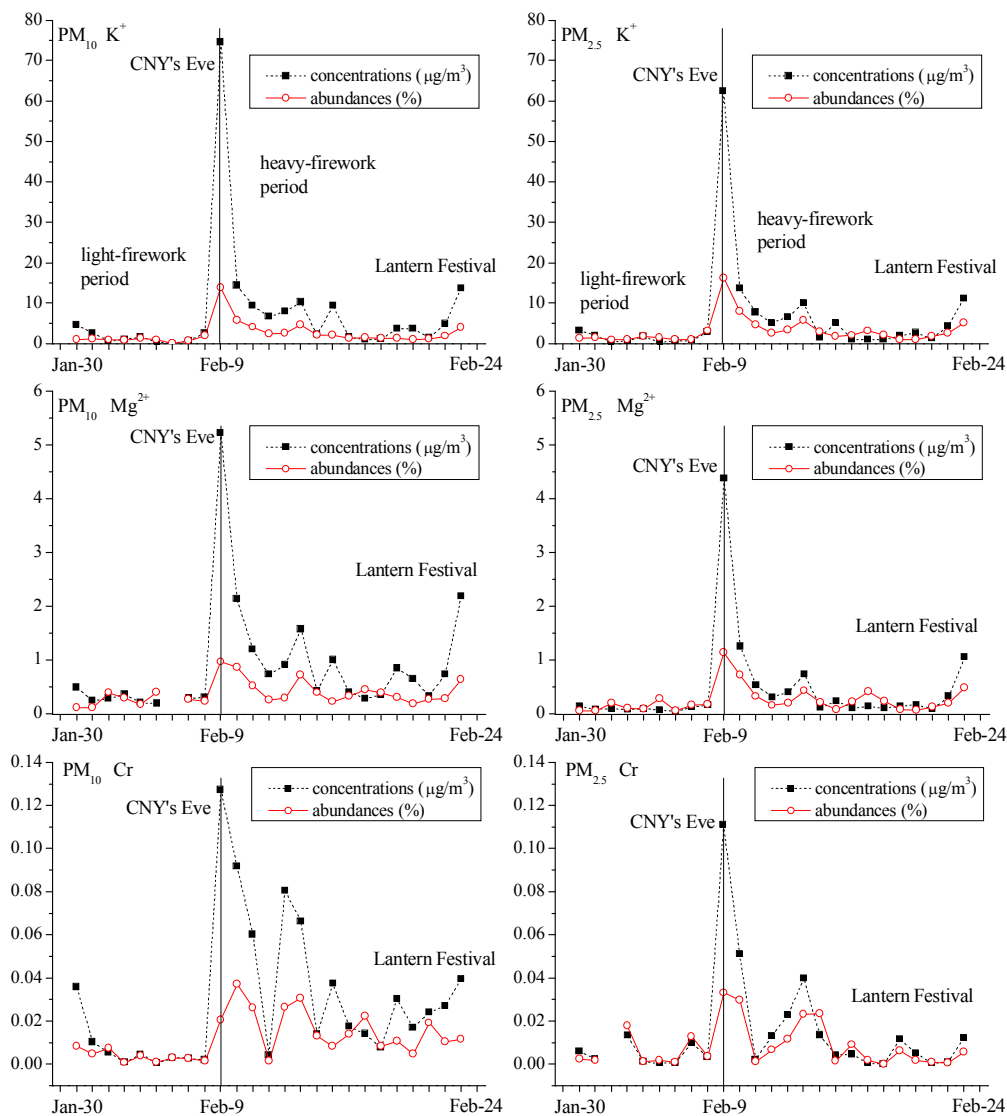
Fig. S7 The daily variations of concentrations and abundances of the most firework-influenced species (K$^+$, Mg^{2+} and Cr).
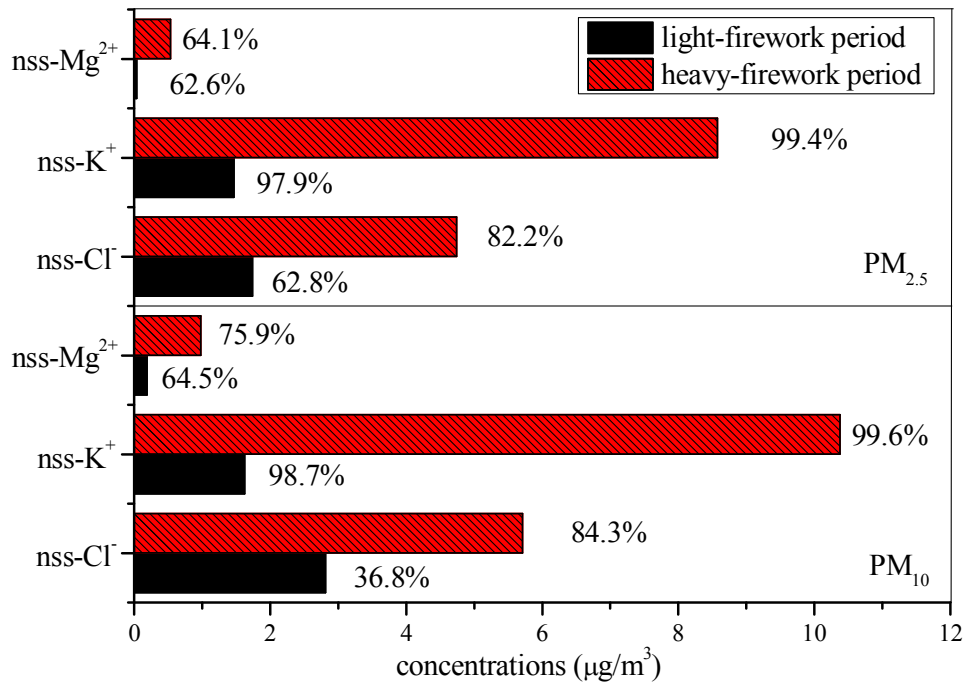
Fig. S8 The concentrations of nss-Cl⁻, nss-K⁺ and nss-Mg²⁺ as well as their percentages in total ions.
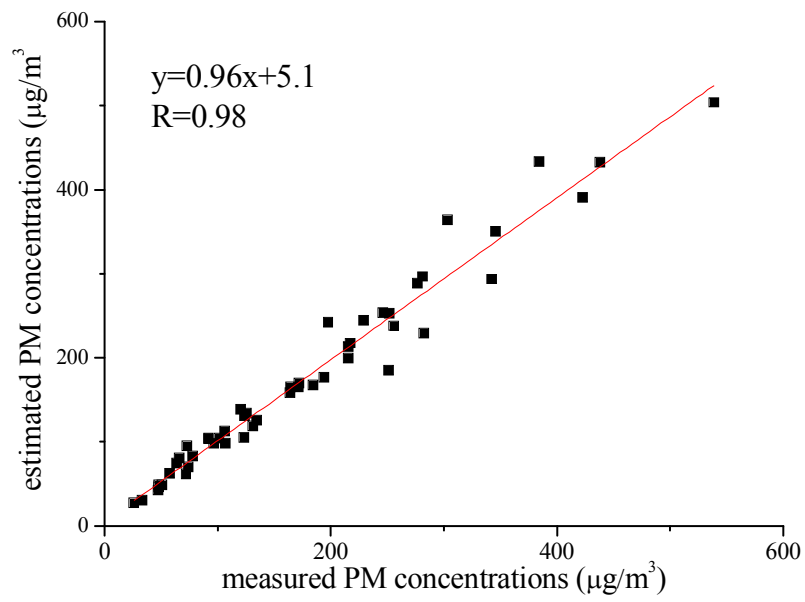
Fig. S9 The fitting plot between the measured and estimated PM concentrations by PMF.

Table S1 Sampling periods of this work.

light-firework period	Date in 2013	30 Jan	31 Jan	1 Feb	2 Feb	3 Feb	4 Feb	5 Feb	6 Feb	7 Feb	8 Feb
	Chinese Lunar calendar	19	20	21	22	23	24	25	26	27	28
heavy-firework period	Date in 2013	9 Feb	10 Feb	11 Feb	12 Feb	13 Feb	14 Feb	15 Feb	16 Feb	17 Feb	18 Feb
	Chinese Lunar calendar	CNY's Eve	CNY	2	3	4	5	6	7	8	9
	Date in 2013	19 Feb	20 Feb	21 Feb	22 Feb	23 Feb	24 Feb				
	Chinese Lunar calendar	10	11	12	13	14	Lantern Festival				

Table S2 The abundances of species (fractions of species in PM) in PM_{10} and $PM_{2.5}$ (%).

	PM10			PM2.5		
	light-firework period	heavy-firework period	H/L[a]	light-firework period	heavy-firework period	H/L
Al	5.45	6.53	1.20	4.38	4.99	1.14
Si	7.24	9.24	1.28	7.00	8.63	1.23
Ca	7.38	10.36	1.40	4.48	8.44	1.89
V	0.02	0.01	0.73	0.01	0.01	0.85
Cr	0.00	0.02	**4.44**	0.00	0.01	**2.06**
Mn	0.05	0.06	1.12	0.04	0.04	1.02
Fe	1.95	3.57	1.83	0.92	1.25	1.35
Co	0.00	0.00	0.72	0.00	0.00	0.89
Cu	0.04	0.04	0.99	0.04	0.05	1.16
Zn	0.28	0.23	0.82	0.27	0.23	0.85
As	0.00	0.00	0.99	0.00	0.00	0.97
Pb	0.21	0.22	1.01	0.24	0.26	1.05
OC	7.35	6.54	0.89	8.22	7.33	0.89
EC	4.19	2.97	0.71	4.43	3.12	0.70
Cl^-	3.95	3.77	0.95	3.59	4.22	1.18
NO_3^-	12.64	9.47	0.75	15.77	10.53	0.67
SO_4^{2-}	22.03	15.52	0.70	25.11	19.07	0.76
Na^+	0.89	0.89	1.00	0.68	0.64	0.93
K^+	1.05	3.24	**3.08**	1.52	4.06	**2.68**
Mg^{2+}	0.25	0.45	**1.78**	0.14	0.32	**2.37**

[a] H/L: the ratios of abundances in heavy-firework period to those in light-firework period.

Table S3 Performance indices (R^2, χ^2 and the percent mass) of CMB results.

	PM	χ^2	R^2
PM_{10}	95.35	2.65	0.96
$PM_{2.5}$	104.03	3.37	0.97