The impacts of fireworks burning at Chinese Spring Festival on air quality: insights of tracers, source evolution and aging processes

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Abstract:

To understand the impact of fireworks burning (FW) particles on air quality and human health during winter haze period, thirty-nine elements, ten water-soluble ions and eight fractions of carbonaceous species in atmospheric $PM_{2.5}$ at Nanjing were investigated during 2014 Chinese Spring Festival (SF). Serious regional haze pollution persisted throughout the entire sampling period, with $PM_{2.5}$ averaging at 113±69 μg m^{-3} and visibility at 4.8±3.2 km. The holiday effect led to almost all the chemical species decreasing during the SF, except for Al, K, Ba and Sr which were related to FW. The source contributions of coal combustion, vehicle emission and road dust decreased dramatically, whereas FW contributed to about half of the $PM_{2.5}$ during SF period. The intensive emission of FW particles at New Year's Eve accounted for 60.1% of the $PM_{2.5}$. Fireworks also obviously modified the chemical compositions of $PM_{2.5}$, with 39.3% contributed by increased organic matter, followed by steadly increased loadings of secondary inorganic ions. The aging processes of the FW particles lasted for about four days reflected by the variations of Ba, Sr, NH_4^+, NO_3^-, SO_4^{2-} and K^+, characterized by heterogeneous reactions of SO_2 and NO_x on crustal materials directly from FW, the replacement of Cl^- by NO_3^- and SO_4^{2-}, coating of NO_3^- and SO_4^{2-} on soot, formation of secondary organic aerosols and metal-catalyzed formation of NO_3^- and SO_4^{2-} at higher relative humidity. During aging, the main contributors to the extinction coefficient shifted from elemental carbon and organic matter to ammonium sulfate. The particles raised higher cancer risk of 1.62×10^{-6} by heavy metals (especially for Cd and As). This study provided detailed composition data and first comprehensive analysis of the aging processes of FW particles

during serious haze pollution period and their potential impact on human health.

Keywords: $PM_{2.5}$; chemical compositions; haze; fireworks burning particles; aging; health risk

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Abbreviations glossary:

FW-Fireworks burning
CNY-Chinese New Year day
SF-Spring Festival
LF-Lantern Festival
OC-Organic carbon
EC-Elemental carbon
BC-Black carbon
OM-Organic matter
RH-Relative humidity
ICP-MS-Inductively coupled plasma-mass spectroscopy
ICP-OES-Inductively coupled plasma-optical emission spectrometer
OPC-Optically detected pyrolized carbon
PCA-Principal component analysis
LADD-Lifetime average daily dose
InhR-Inhalation rate
EF-Exposure frequency
ED-Exposure duration
BW-Average body weight
AT-Averaging time
HQ-Hazard Quotient
RfD-Reference dose
HI-Hazard Index
MIN-Mineral matter
TE-Trace elements
SS-Sea salt
SIA-Secondary inorganic aerosol
UM-Unidentified matter
R^2-Correlation coefficient
WRF-Weather Research and Forecast model
Pre-CNY-The day before CNY
Pre-LF-The day before LF

Pre-SF-The period before Spring Festival
After-SF-The period after Spring Festival
PM_{cal}-Mass calculated by adding individual components
PM_{meas}-Gravimetrically measured particulate mass
V_{cal}-Visibility calculated by adding individual components
V_{meas}-Measured visibility
b_{ext}-Extinction coefficient

1 Introduction

Atmospheric pollutants emitted from fireworks burning (FW) at festivals or special celebration events around the world have recently received wide attention, such as Guy Fawkes' night at UK (Allan et al., 2010; Godri et al., 2010), Pyronale® 2009 and Pyromusikale® (Dutschke et al., 2011), Montréal International Fireworks competition (Joly et al., 2010), New Year's celebrations (Williams et al., 2005; Drewnick et al., 2006; Zhang et al., 2010; Do et al., 2012; Feng et al., 2012; Jiang et al., 2014; Jing et al., 2014; Tian et al., 2014; Ye et al., 2014), Diwali (Godri et al., 2010), Las Fallas in Valencia (Moreno et al., 2007), new Millennium in Germany (Wehner et al., 2000), 2006 FIFA World Cup (Vecchi et al., 2008) and Lantern Festival (Do et al., 2012; Tsai et al., 2012). Besides the direct possible dangers like the exposure to sound pressures (Dutschke et al., 2011) or firework-related injuries (Do et al., 2012), their burning results in massive quantities of pollutants, leading to degradation of air quality (Wang et al., 2007; Sarkar et al., 2010; Dutschke et al., 2011; Do et al., 2012; Feng et al., 2012; Tsai et al., 2012; Jiang et al., 2014; Jing et al., 2014; Tian et al., 2014; Yang et al., 2014) and raising serious human health concerns (Godri et al., 2010; Do et al., 2012). Evidence suggests that inhalation of fumes containing high levels of specific elements such as chlorine can cause mucosal irritation and acute respiratory distress syndrome (Joly et al., 2010). A toxicity study reported that the samples collected in the post-FW period were more toxic than those in the pre-FW period according to the viabilities of BEAS-2B cells after 24-h incubation with the particle extracts (Do et al., 2012). A positive significant relationship was also found between particulate matter oxidative burden and individual trace metals associated with FW (Godri et al., 2010).

China is the largest firework producing country in the world (Tian et al., 2014). For the Chinese New Year day (CNY, in the Spring Festival (SF) on Jan. or Feb. of lunar Chinese calendar, high-profile FW events occurred at the midnight of the CNY's Eve in national scale,

from small villages to megacities. It should be noted that FW events always occured in an already highly polluted urban air in China (Supplementary file S1). In winter, increased coal consumption for heating (Li and Zhang, 2014) and stable atmospheric conditions always raise serious haze pollution in central and eastern China. On January 2013, the whole central and eastern China was shrouded in a long-lasting severe haze episode (Wang et al., 2014). According to the Chinese Ministry of Environmental Protection, on Jan. 31, 2014, about 80% of 161 cities held average $PM_{2.5}$ concentrations higher than 150 μg m^{-3} (Ye et al., 2014). The addition of pollutants from FW deteriorates ambient air quality during the SF and its impact can vary significantly with FW duration and meteorological conditions (Vecchi et al., 2008; Yu et al., 2013).

Previous studies have extensively characterized the physicochemical signatures of FW emissions, such as gaseous pollutants (Wehner et al., 2000; Attri et al., 2001; Williams et al., 2005; Drewnick et al., 2006; Wang et al., 2007; Vecchi et al., 2008; Tan et al., 2009; Godri et al., 2010), particle size distribution and number concentration (Wehner et al., 2000; Drewnick et al., 2006; Vecchi et al., 2008; Zhang et al., 2010; Dutschke et al., 2011; Yang et al., 2014), chemical components including trace elements (Wang et al., 2007; Moreno et al., 2007; Vecchi et al., 2008; Estrellan and Iino, 2010; Godri et al., 2010; Joly et al., 2010; Do et al., 2012; Tsai et al., 2012; Tian et al., 2014; Yang et al., 2014), organic carbon (OC) and elemental carbon (EC) (Estrellan and Iino, 2010; Feng et al., 2012; Tsai et al., 2012; Tian et al., 2014; Yang et al., 2014) and water-soluble ions (Wang et al., 2007; Vecchi et al., 2008; Shen et al., 2009; Estrellan and Iino, 2010; Tsai et al., 2012; Wang et al., 2013; Jiang et al., 2014; Tian et al., 2014; Yang et al., 2014). Recently, single particle's chemical compositions (Drewnick et al., 2006; Allan et al., 2010; Jiang et al., 2014), morphology and mixing properties (Li et al., 2013) and optical properties (Yu et al., 2013) of FW particles had been reported. However, there are now still two issues needed to be explicitly addressed.

Firstly, no studies reported the chemical compositions (crustal elements, trace elements, water-soluble ions, OC and EC) of FW particles completely, considering the complex manufacture materials of FW (Supplementary file S2). Although Estrellan and Iino (2010), Feng et al. (2012), Yang et al. (2014) and Tian et al. (2014) reported the ions, elements and carbonaceous species synchronously, some important species were missed, such as Na, Mg, K, Ti, NH_4^+ and Cl^- in Tian et al. (2014), OC in Estrellan and Iino (2010) , Si and some heavy elements in Feng et al. (2012)

and crustal elements in Yang et al. (2014). These species are all highly elevated during FW events. Crustal elements including Na, Mg, Al, Si, K, Ca, Ti, Fe and Mn were always missing or not sufficiently studied in FW particles. However, except for inorganic and organic chemicals such as charcoal, potassium nitrate, potassium chlorate, potassium perchlorate, sulfur, manganese, sodium oxalate, aluminum, iron powder, strontium nitrate, and barium nitrate (Shen et al., 2009; Jing et al., 2014), clay is also used to seal the top and bottom of fireworks as shown in Supplementary file S3. 90% of the total mineral aerosol was from the emission of FW on the lantern night in Beijing (Wang et al., 2007). The incomplete compositions of FW particles may bias the identification of particle sources during FW period and limit our understanding of its aging processes. For example, crustal elements-Al, Si and Ca were thought to result from the resuspension of materials already deposited on the ground (caused by pyrotechnic device explosions) and hereby the resuspended dust was regarded as a contributor to atmospheric particles during SF (Tian et al., 2014). Without detecting the crustal and trace elements, secondary particulate matter accounted for 63-82% of $PM_{1.0}$ during FW periods in Beijing (Jiang et al., 2014).

Secondly, all the former studies unanimously agreed that FW contributed to elevated concentrations of particles and associated chemical species, but no studies concerned the aging processes of particles after emitted from intensive FW. The cocktail of primary pollutants released may exhibit varied interactions among themselves, and if aided by favourable atmospheric conditions, may lead to the formation of secondary pollutants (Sarkar et al., 2010). Do et al. (2012) pointed that the sub-micron aerosol or accumulation-mode particles from FW can suspend in the air for very long periods, from days to weeks, potentially causing pollution to large areas. Data in literature verified the exsitence of aging processes of FW particles, though it has not been discussed. For example, Li et al. (2013) indicated that emissions from FW changed the transformation pathway from SO_2 to SO_4^{2-} and the FW particles can influence the air at downwind site (50 km far away). And after about two days, the elevated $PM_{2.5}$ mass concentrations at CNY's Eve decreased to the level of the day before CNY (pre-CNY). In Beijng, $PM_{2.5}$ mass concentrations at CNY's Eve decreased to the level of pre-CNY in one day, while secondary ions (SO_4^{2-}, NH_4^+ and NO_3^-) and organic matter (OM) increased first and then decreased to the level of pre-CNY after three days (Wang et al., 2007). In Jinan, a "tailing" phenomena was found, indicating that NH_4^+ and NO_3^- did not increase (peaking at 8:00 and 12:00, respectively)

immediately with the concentrations of particles (peaking at 00:00) after emitted at CNY's Eve (Yang et al., 2014). In Shanghai, NH_4^+ and NO_3^- also increased in the first day after emitted at CNY's Eve and then decreased to the level of pre-CNY in the third day and the decreasing rate of $PM_{2.5}$ was faster than that for OC (Feng et al., 2012). Therefore, we still need to answer the following questions: (1) are the decreasing trends of particles and associated chemical components the same? (2) how long and how far can FW influence the air quality at certain meteorological conditions? (3) during aging and transport, which type of chemical reactions will the FW particles undergo and how will specific chemical ratios vary?

Due to rapid economic expansion and urbanization, the occurrence frequency of haze has increased rapidly in recent 30 years at the Yangtze River Delta region (Wang et al., 2014). As one of the central megacities of this region, Nanjing is suffering from serious air pollution and the occurrence of hazy days increased from 1961 to 2005 (Kang et al., 2013). Thus, it provides a unique site and opportunity to study the chemical composition evolution and source variation during haze-clear days with the injection of intensive FW at SF. The main purposes of this study are to: (1) characterize in detail the chemical compositions of atmospheric $PM_{2.5}$ before, during and after intensive FW events; (2) identify how long and how much can the FW particles influence $PM_{2.5}$ by tracer analysis and receptor models; (3) emphasize how can the FW particles affect visibility and human cancer and non-cancer risks; (4) analyze the FW particle aging processes by specific species and ratios. The data and analysis will improve the knowledge of chemical compositions of FW particles, their evolution during serious haze pollution periods and their influence on visibility and human health.

2 Methodology

2.1 $PM_{2.5}$ collection

From 24 Jan. to 21 Feb. 2014, a sampling campaign of $PM_{2.5}$ was conducted on the rooftop (40 m high) of a building in Nanjing University of Information Science & Technology (Kang et al., 2013; Wang et al., 2014). It is a suburban site, surrounded by residential communities at the west, south, north and southeast directions. There is a steel factory 2 km to the east of the campus and a chemical industry park about 10 km to the northeast. It faced one road with heavy traffic, about 200 m in the east. Location of the sampling site was shown in Fig.1 and Supplementary file S4. During the sampling period, CNY on Jan. 30 and Lantern Festival (LF) on Feb.14 were included.

At CNY's and LF's Eve, numerous fireworks were consumed. The SF holiday was from Jan. 30 to Feb.7. Each day, $PM_{2.5}$ samples were collected at about 08:00 am for 24 h using two medium-volume air samplers (TH-150C, Wuhan Tianhong Ltd., China) on quartz fiber filters (baked at 800 ℃ for 2 h) and polypropylene fiber filters (baked at 80 ℃ for 0.5 h) at a flow rate of 100 L min^{-1}. The hourly online $PM_{2.5}$ mass concentrations for the nine monitoring sites set by Jiangsu Environmental Monitoring Center were collected from the pubic platform (http://218.94.78.75/jsair/) (their locations can be found in Supplementary file S4). Twenty-four pairs of filter samples were obtained (Supplementary file S5). By using a microbalance (Ohaus Discovery DV214CD) with balance sensitivity as ±0.010 mg, filters were weighed before and after sampling under controlled environment with temperature and relative humidity (RH) of 22 ℃ and 35%. Then they were stored at -20 ℃ until chemcial analysis. The quartz fiber filters were for analyzing water-soluble inorganic ions, OC and EC. Polypropylene fiber filters were for elemental analysis.

(Fig.1)

2.2 Chemical analysis

Inductively coupled plasma-mass spectroscopy (ICP-MS) (Agilent 7500a, Agilent Co. USA) was used for analyzing Li, Be, Na, Mg, Al, P, K, Ca, Sb, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, As, Rb, Y, Mo, Cd, Sn, Cs, La, Ce, Sm, W, Tl, Pb, Bi, Th and U. Nine elements including Si, Al, Ca, Mg, Fe, Ti, Ba, Sr and Zr were analyzed by inductively coupled plasma-optical emission spectrometer (ICP-OES). Al, Ca, Mg and Ti were analyzed by both ICP-MS and ICP-OES, and results from the latter were used as the analysis accuracy for the four elements by ICP-OES was better than that by ICP-MS (Kong et al., 2014a). Ten ions including NH_4^+, Na^+, Mg^{2+}, K^+, Ca^{2+}, F^-, Cl^-, NO_2^-, NO_3^- and SO_4^{2-} were analyzed by a professional Ion Chromatograph (Wan Tong 850, Switzerland). DRI Model 2001 (Thermal/Optical Carbon Analyzer) with the IMPROVE thermal/optical reflectance protocol was used for OC and EC analysis (Han et al., 2008; Han et al., 2010; Huang et al., 2012; Li et al., 2012; Wang et al., 2013; Kong et al., 2014a). A 0.188 cm^2 punch area from the quartz filter was heated to produce four OC fractions: OC1, OC2, OC3 and OC4 at temperatures of 120, 250, 450 and 550˚C in a non-oxidizing He atmosphere, three EC fractions: EC1, EC2 and EC3 at

550, 700 and 800˚C in an oxidizing atmosphere of 2% O_2/98% He and optically detected pyrolized carbon (OPC). OC is defined as OC1+OC2+OC3+OC4+OPC and EC is calculated by EC1+EC2+EC3-OPC. Char-EC is defined as EC1 minus OPC, and soot-EC is the sum of EC2 and EC3 (Han et al., 2008; Han et al., 2010). The pre-treatment and chemical analysis procedures and quality assurance and control are described detailedly in our previous works (Li et al., 2012; Kong et al., 2014a; 2014b; Li et al., 2014).

2.3 Meteorological parameters

The meteorological parameters including relative humidity (RH), visibility, wind speed, wind direction and temperature were recorded by the meteorological observatory of our university (http://qxt.nuist.edu.cn/). The rainfall information was obtained from http://www.wunderground.com/. According to China Meterological Administration, fog is defined as visibility <10 km and RH>90% and haze is defined as visibility <10 km and RH<80%. For visibility <10 km and 80%<RH<90%, it is fog-haze mixing day. Fig.2 shows that the visibilities are generally below 10 km (averaged as 4.8±3.2 km), indicating fog, haze or fog-haze mixing events frequently occurred. On Feb.4, a strong cold front passed through, leading to high visibility (14.7 km), low temperature (2.4˚C) and high wind speed (3.5 m s^{-1}). The wind speed remained mostly below 3 m s^{-1} (averaged as 2.2±0.7 m s^{-1}), suggesting stagnant weather conditions.

(Fig.2)

2.4 Data processing

2.4.1 Back trajectory calculation

Three-day air mass back trajectories are calculated using NOAA Air Resource Lab HYSPLIT 4.8 model, driven by the GDAS meteorological dataset (1 °×1 °) (Kong et al., 2014b). A 72 h back trajectory is adopted with the starting height of 500 m above ground level (Huang et al., 2012). Cluster analysis is adopted which results in sub-sets of trajectories with backward trajectories computed every six hours (00:00, 06:00, 12:00 and 18:00) each day. The clustering process is described in detail in Hysplit User˙ s Guide-Version 4. The mixing layer height is calculated every three hours each day by the NOAA's READY Archived Meteorology online calculating program (http://ready.arl.noaa.gov/READYamet.php). This program produces a time-series of calculated

boundary layer depth using the chosen meteorological data. As shown in Fig.3, 43% (cluster 3, 4 and 5) of the air masses origined from the Mongolia and crossed Chinese coastal seas; 31% (cluster 1) was from the north China and transported across Shandong peninsula; 26% (cluster 2) was from central China. Cluster 1 and cluster 2 transported for short distances, which may easily raise regional air pollution, as the Shandong peninsula and central and eastern China hold intensive anthropologic sources for air pollutants.

(Fig.3)

2.4.2 Principal component analysis

Principal component analysis (PCA) is used to identify the sources for particles at periods before (Jan. 24-29), during (Jan. 30-Feb. 6), after SF holiday (Feb. 12-Feb. 21) and the whole period. It can analyze multivariate data sets structure and identify a smaller number of independent factors to explain the data variance. Factor loadings are related to the source emission compositions. A varimax normalized rotation is adopted by SPSS 13.0 software in this study (Kong et al., 2010).

2.4.3 Health risk assessment of heavy metals

After emitted, the heavy metals in FW particles can raise risks to human health. To raise the attention of public on the health threat of FW particles, the average amount of heavy metal exposure by inhalation (D_{inh}) per an individual's body weight over a given time span for adult and childern was calcualted by following equation (Kong et al., 2012; Yang et al., 2014):

$$D_{inh}(mg \cdot kg^{-1} \cdot day^{-1}) = \frac{C \times InhR \times EF \times ED}{BW \times AT} \quad (1)$$

The lifetime average daily dose (LADD) of Co, Ni, As and Cd exposure through inhalation was used for assessing cancer risk as following:

$$LADD = \frac{C \times EF}{AT} \times \left(\frac{InhR_{child} \times ED_{child}}{BW_{child}} + \frac{InhR_{adult} \times ED_{adult}}{BW_{adult}}\right) \quad (2)$$

where C is exposure-point concentration. Its upper limit of the 95% confidence interval for the mean is calculated as:

$$C_{95\%UCL} = \exp\left(\overline{X} + 0.5s^2 + \frac{s \times H}{\sqrt{n-1}}\right) \quad (3)$$

where $\overline{X}$ is the arithmetic mean of the log-transformed data, s is the standard deviation of the log-transformed data, H is the H-statistic and n is the number of samples. InhR: inhalation rate, 7.6 and 20 m^3 day^{-1} for children and adult; EF: exposure frequency, 4 day $year^{-1}$ in this study (according to the discussion in Section 3.4.2); ED: exposure duration, 6 and 24 years for children and adult; BW: average body weight; 15 and 70 kg for children and adult; AT: the averaging time, for non-carcinogens, AT (days)=ED×365; for carcinogens, AT (days)=70×365=25, 550.

After the D_{inh} is calculated, a Hazard Quotient (HQ) for non-cancer toxic risk can be obtained by (Kong et al., 2012):

$$HQ = D/RfD \quad (4)$$

Considering the sensitive group, the reference dose (RfD) (mg/kg/day) is estimated as the maximum permissible risk on human by daily exposure. The threshold values of RfD indicate whether there is adverse health effect during a life time. Then Hazard Index (HI) can be obtained by suming up the individual HQ to estimate the total risks of all elements considered:

$$HI = \sum HQ_i \quad (5)$$

where i denotes different heavy metals. RfD values are 7×10^{-3}, 2.86×10^{-5}, 1.43×10^{-5}, 4.0×10^{-2}, 3.0×10^{-1} and 3.5×10^{-3} for the cancer risk estimation of V, Cr, Mn, Cu, Zn and Pb. For non-cancer risk estimation of Co, Ni, As and Cd, the RfD values are 5.71×10^{-6}, 2.00×10^{-2}, 3.00×10^{-4} and 1.00×10^{-3}, respectively (Kong et al., 2012). If HI≤1, there is no adverse health effects; if HI>1, likely adverse health effects exist. For carcinogens, the LADD is multiplied by the corresponding RfD value (they are 9.8×10^{0}, 8.4×10^{-1}, 1.51×10^{1} and 6.3×10^{0} for Co, Ni, As and Cd, respectively) (Kong et al., 2012). For cancer risk, the value of 10^{-6} is an internationally accepted precautionary or threshold value above which the risk is unacceptable (Granero and Domingo, 2002; Baptistaa and Miguel, 2005).

2.4.4 Mass closure of $PM_{2.5}$

To better understand the chemical compositions before, during and after SF, the chemical mass closure analysis was conducted. The chemical components are divided into six classes as follows: mineral matter (MIN), trace elements (TE), OM, EC, sea salt (SS), secondary inorganic

aerosol (SIA) and unidentified matter (UM). MIN is the sum of the common oxides of Al, Mg, Mn, Si, Na, K, Ca, Ti and Fe as:

$$MIN=2.14\times Si+1.67\times Ti+1.89\times Al+1.59\times Mn+1.67\times Mg+1.95\times Ca+1.35\times Na+1.21\times K+1.43\times Fe \quad (6)$$

As the existence of CaO and $CaCO_3$, a factor of 1.95 for Ca is used (Terzi et al., 2010). Except for the above elements in MIN, all other elements are sumed up to act as TE. OM is calculted by multiplying OC of a conversion factor, in accordance with the organic molecular carbon weight per carbon weight. The factor 2.0 is applied here, which is also used for spring festival period in Shanghai, another megacity at Yangtze Revier Delta region (Huang et al., 2012). In Allan et al. (2010), during bonfires and fireworks burning period at the Guy Fawkes' night, the OM/OC ratio ranged around 2.0 or higher than 2.0. The marine contribution is calculated based on a standard sea water composition, assuming that soluble Na^+ in aerosols only come from sea salt. Then,

$$\text{sea salt}= [Na^+]+[\text{ss-}Cl^-]+[\text{ss-}Mg^{2+}]+[\text{ss-}K^+]+[\text{ss-}Ca^{2+}]+[\text{ss-}SO_4^{2-}] \quad (7)$$

where $\text{ss-}Cl^-=1.8\times[Na^+]$, $\text{ss-}Mg^{2+}=0.12\times[Na^+]$, $\text{ss-}K^+=0.036\times[Na^+]$, $\text{ss-}Ca^{2+}=0.038\times[Na^+]$, and $\text{ss-}SO_4^{2-}=0.252\times[Na^+]$ (Terzi et al., 2010). SIA is the sum of $\text{nss-}SO_4^{2-}$, NO_3^- and NH_4^+. The concentrations of all these species in μg m^{-3} are adopted.

2.4.5 Visibility re-construction by chemical components

The mass scattering efficiency of spherical particles is a function of water and chemical components including $(NH_4)_2SO_4$, sea salt, mineral materials and carbonaceous species (Kimet al., 2001). To find which types of chemical components are the key for the visibility degration during sampling period and how can the injection of FW particles change the visibility, the IMPROVE equation was used to calculate the light extinction coefficient (b_{ext}) (Kim et al., 2001;Yang et al., 2007):

$$b_{ext} =3f(RH)\,[\text{ammonium sulfate}]+3f(RH)\,[\text{ammonium nitrate}]+4[OM]+1[\text{soil}]+10[BC] \quad (8)$$

The visibility can be calculated by $Vs= 3.91/b_{ext}$ (Yang et al., 2007). We used [ammonium sulfate]$=0.944\times[NH_4^+]+1.02\times[SO_4^{2-}]$, [ammonium nitrate]$=1.29\times[NO_3^-]$, [OM]$=2.0\times$[OC], [soil]=MIN and [BC]=[EC] (Yang et al., 2007; Tao et al., 2009). f(RH) is the RH growth function indicating how scattering efficiencies increase for SO_4^{2-} and NO_3^- as they absorb liquid water and detailed data can be found in Tao et al. (2009).

338 **2.4.6 WRF-FLEXPART modeling**

339 To see the transport distance and decreasing trend of the highest mass concentrations of
340 $PM_{2.5}$ at CNY ś Eve, Weather Research and Forecast model (WRF) version 3.4 was used to
341 provide meteorological inputs of FLEXPART, with the NCEP global reanalysis meteorological
342 dataset (1 °×1 °) as initial and boundary conditions. The time step is set as 180 s. The grid system is
343 divided into 28 layers in the vertical direction. Two domains are adopted, with the grid resolutions
344 of 30 and 10 km. The simulating time period is 02:00-11:00 of Jan.31, 2014. The output of 10 km
345 evolution wind farms is used as the input of FLEXPART. For forward simulating of FLEXPART
346 model, Nanjing (N31°14′-32°37′， E118°22′-119°14′, height as 50 m) is considered as a whole
347 source region. In this study, we only considered the dry and wet deposition of particles at CNY ś
348 Eve. The average mass concentration of 572 μg m^{-3} is used as the initial particle concentration.

349 **3 Results and discussion**

350 **3.1 Comparison of particles before, during and after Chinese Spring Festival**

351 **3.1.1 $PM_{2.5}$ mass concentrations**

352 The concentrations of $PM_{2.5}$ (averaged as 113±69 μg m^{-3}, min-max: 21-318 μg m^{-3}) in this
353 study by filter sampling varied consistently with those for the nine online monitoring sites set by
354 local government at urban Nanjing (averaged as 112±70 μg m^{-3}, min-max: 13-385 μg m^{-3})
355 (Fig.2b). They correlated well with correlation coefficient (R^2) higher than 0.95 (P>0.01)
356 (Supplementary file S6), indicating that a regional air pollution occurred in Nanjing (visibility<10
357 km as Fig.2a shown) during study period. The $PM_{2.5}$ concentrations all peaked on CNY (Jan. 30)
358 and LF (Feb.14) and the peaking values on CNY were 4-5 times of the secondary standard of
359 China National Ambient Air Quality (75 μg m^{-3}, 24 h average). Results suggested that FW have
360 obvious impacts on fine particle pollution. At CNY's Eve, two massive FW events usually occur
361 at the evening (around 19:00-20:00 h for the family reunion dinner) and midnight (00:00-02:00 h
362 for celeberating the new year). $PM_{2.5}$ showed the maximum concentrations for the two episodes as
363 426±236 (20:00 h) and 572±136 μg m^{-3} (02:00 h), respectively (Fig.4). After 02:00, obviously
364 decreasing trend was pronounced as exponential form (R^2=0.99). The concentrations decreased to
365 195±16 μg m^{-3} at 13:00, which was similar to that of 178±16 μg m^{-3} at 17:00, Jan. 30 before
366 extensively FW activities (Fig.4). Note that on Jan. 30 and Jan. 31, the mixing layer heights were
367 only 257 and 227 m, the wind speeds were 1.7 and 2.1 m s^{-1} and the RH were 88 and 80%, all

favoring the accumulation of pollutants and regional air pollution formation. It was verified by the WRF-FLEXPART results which indicated that the particles with highest mass concentrations at 02:00 moved outside of Nanjing in the following nine hours. The center with peaked particle mass concentrations transported about 285 km to the north of Naning (Supplementary file S7) and the decreasing trend was in accordance with the real particle concentrations decreasing (Fig.5). The injection of FW particles deteriorated the air quality, with visibilities decreasing to 1.4-6.2 km in the following four days. Therefore, the $PM_{2.5}$ pollution raised by FW can last for about four days under unfavorable weather conditions (visibility was strongly related to $PM_{2.5}$ mass in Jan 30-Feb.3, R^2=0.82). On Feb.3 and Feb.5, $PM_{2.5}$ was cleaned effectively by the rainfall (precipitation as 0.3 and 9 mm), descreasing by 5.6-10.6 times for the ten sites.

(Fig.4)

(Fig.5)

3.1.2 Characterization of chemical species

Table 1 and Table 2 summarized the statistics of $PM_{2.5}$, water-soluble ions, OC and EC before, during and after SF. The data of CNY and LF were listed separately for intensive FW activities. The ratios of $PM_{2.5}$ and chemical species on CNY and LF with those for the day before them were also listed. For elements, K, Si, Al, Na, Ca and Fe were the most abundant species, totally accounting for 85%-90% of all the elements at these five periods. Without considering the data for CNY, elements Al, K, Ba and Sr at SF still elevated when compared with those for Pre-SF, whereas all other elements descrased during SF. This was related to the weakened sources, like construction activities, vehicle emission and industrial activities in the national holiday. For ions, NO_3^- was most abundant, averaging as 5.9 (±3.7) μg/m^3 for the days without intensive FW activities, then followed by SO_4^{2-} and NH_4^+, with average concentrations of 5.0 (±3.7) and 4.8 (±2.4) μg m^{-3}, respectively. K^+ and Cl^- also had relatively high concentrations of 0.9 (±1.0) and 0.8 (±0.5) μg m^{-3}. It was similar to the results of Wang et al. (2014) that the secondary aerosols in Nanjing were dominated by nitrate in winter haze periods. Na^+, Ca^{2+}, Mg^{2+}, F^- and NO_2^- accounted for a minor fraction (totally of 4.2%). For carbonaceous species, OC3, OC4 and EC1

were most abundant, in combination accouting for 80% of the total carbon, indicating coal combusition and gasoline exhaust were important sources for $PM_{2.5}$ at Nanjing (Cao et al., 2005). OPC and OC1 also showed a higher values which may be related to biomass burning (Cao et al., 2005). NO_3^-, OC and EC were highest for Pre-SF period, as the "spring travel rush" effect, characterized by extremely high traffic flows (Huang et al., 2012). The $PM_{2.5}$ concentrations decreased for about 10 μg m^{-3} during SF, implying that the reduction of anthropogenic sources in this national holiday (Feng et al., 2012). The particle concentration lower than that for pre-holiday period was also found in Shanghai (Huang et al., 2012).

During CNY with intensive FW, concentrations of Ba and Sr exhibited the most significant increase, by factors of 99.1 and 79.4 compared to the day before CNY (Pre-CNY). Ba and Sr also showed the highest ratios for LF/Pre-LF (the day before LF), as 9.7 and 5.7, respectively. Then followed by EC2, OC1, K, K^+, Al, Bi, SO_4^{2-}, OC2, EC1 and OC, going up to 4.1-37.7 times for CNY/Pre-CNY, respectively. Other species increased by 1.2-3.8 times except for W (0.6), Na^+ (0.7), NO_2^- (0.8) and OC4 (0.9). It implied that Na^+ was not affected by the FW and can be used as the tracer of sea salt. Most species also increased on LF when compared with Pre-LF, but the increasing ratios were much lower than those on CNY. It can be explained as the FW activities on LF (there are only organized FW activities by some organizations at cities) were less intensive than those on CNY (FW activities are national spread, from city to small villages). Crustal elements like Li, Be, Si, Na, Ca, Ti and Mn increased by about 1-2 times during FW, indicating the use of clay in firework production. Ca^{2+} and EC1 decreased by factors of 0.8 and 0.9, suggesting the increase of construction activities and vehicle emissions after SF. Meanwhile, Ba and Sr tend to be tracers of firework (R^2=0.99), consistent with former studies (Estrellan and Iino, 2010; Sarkar et al., 2010; Feng et al., 2012). As shown in the supplementary file S2 and literature (Moreno et al., 2007; Vecchi et al., 2008; Joly et al., 2010; Sarkar et al., 2010; Richard et al., 2011; Do et al., 2012; Tsai et al., 2012; Jing et al., 2014), the compounds of these elments are important FW manufacturing materials. Barium compounds can be used as oxidiser ($BaClO_3$ and $Ba(NO_3)_2$). $Sr(NO_3)_2$ can be used to give red color fireworks and potassium compounds are the most important compositions of black powder (as KNO_3 or $KClO_3$). Al is used alone as a common constituent for fuel, or to form sparks and glitter effects or as alloy magnalium (50:50 Mg:Al) for sparks and crackling stars. Fireworks also contain charcoal (Joly et al., 2010; Sarkar et al., 2010;

Tsai et al., 2012) and organic materials are used as adhesive, such as polyvinyl alcohol, polyoxyethylene, phenol formaldehyde resin and shell-lac. They are responsible for the elevated concentrations of EC2 (Joly et al., 2010; Sarkar et al., 2010; Tsai et al., 2012) and OC1 during FW periods.

(Table 1)

(Table 2)

3.2 Mass closure and re-construction of visibility

Fig. 6 illustrates the $PM_{2.5}$ mass balance of MIN, TE, OM, EC, SS, SIA and UM. About 60% of the chemical species in $PM_{2.5}$ were detected. The unaccounted PM mass were explained by the following four reasons: (1) non-C atoms in organic aerosols; (2) sampling and measurement artifacts; (3) conversion factors used for OM and MIN calculating; (4) aerosol water content (Tsyro, 2005; Terzi et al., 2010). Water constituted 20-35% of the annual mean PM_{10} and $PM_{2.5}$ concentrations (Tsyro, 2005). On Feb. 6, the water content in $PM_{2.5}$ was high to 72%, indicating the influence of rainfall and high RH (90%). These also lead to the gravimetrically measured particulate mass (PM_{meas}) higher than the mass calculated by adding individual components (PM_{meas}), while tight correlations still existed between them ($PM_{meas}=1.52PM_{cal}+14.5$, $R^2=0.91$). The slope was similar to those as 1.02-1.42 in Terzi et al. (2010).

(Fig.6)

The averaged chemical components of $PM_{2.5}$ profiles exhibited OM (26%)>SIA (18%)>MIN (9%)>EC (3.9%)>SS (1.7%)>TE (0.67%). The mass percentages of OM, TE and EC decreased in SF (as 23%, 0.6% and 2.7%) when compared with those at Pre-SF (as 34%, 0.7% and 6.2%). These changes reflected the holiday effect i.e. at the SF holiday, the new injection of FW particles cannot offset the reduced particles from vechicle emission and/or to industrial sources, especially for organic matter, trace elements and elemental carbon, which are important compositions of vehicle exhausts and industrial activities. On CNY, obviously elevated OM was observed,

458 accounting for 39.3% of $PM_{2.5}$. While SIA was only 14.4%, with the peak values occurred on
459 Feb.3 (as 36%), suggesting that after intensive emission of FW pollutants on CNY's Eve,
460 secondary ions were gradually formed during aging processes through gas-particles transformation
461 of SO_2 and NO_x, etc. It should be emphasized that MIN and TE were both important components
462 of $PM_{2.5}$, totally accounting for 5.8%-18.5%. In a recent study by AMS for aerosols during
463 Chinese Spring Festival at Beijing, organics, nitrate, sulfate, ammonium, BC and chloride,
464 accounted for 43%, 22%, 14%, 13%, 5% and 3% of $PM_{1.0}$ with no elements considered (Jiang et
465 al., 2014). The combination of filter sampling-offline chemical analysis and online real-time
466 monitoring of chemcial species are desired for atmospheric aerosol studies.
467 Fig. 7a shows the calculated average values of extinction coefficient (b_{ext}). They varied
468 between 44 and 525 Mm^{-1}. The calculated visibility (V_{cal}) exhibited good correlations with the
469 measured one (V_{meas}) (V_{cal}=0.96V_{meas}+1.4, R^2=0.45, P<0.001). The discrepancy between the
470 measured and calculated values can be attributed to the influence of ambient water vapor (Huang
471 et al., 2012) which was a key component of aerosol particles in this study as discussed before. At
472 higher RH, the role of ambient water vapor on light extinction was more important (Huang et al.,
473 2012). The b_{ext} exhibited higher values on CNY and the following three days, in the range of
474 301-525 Mm^{-1}. $(NH_4)_2SO_4$ had the largest contribution to b_{ext}, accounting for 36.5±11.7%,
475 followed by NH_4NO_3 (25.8±8.2%), EC (21.8±9.0%), OM (10.8±4.2%) and soil (5.1±1.8%)
476 (Fig.7b). These results implied that sulfate was the largest contributor to visibility degradation
477 especially at SF period. Before SF, the contribution of EC can be as high as 34%-44% during
478 serious haze periods (Jan. 24-26, RH<51%). It highlights the importance of controlling vehicle
479 emissions in haze days. Sulfate and soot were also found as the main contributors to visibility
480 degradation in other studies (Tao et al., 2009). The results obtained here were different from those
481 in Shanghai that organic aerosol had the largest contribution to the aerosol extinction as 47 %,
482 then followed by ammonium sulfate (22%), ammonium nitrate (14 %) and EC (12 %) (Huang et
483 al., 2012). The FW on CNY obviously changed the contributions of chemical species to scattering
484 coefficient. On CNY, the influence of FW particles on visibility was mainly controlled by
485 $(NH_4)_2SO_4$ (36%), NH_4NO_3 (26%), EC (15%) and OM (15%). During FW particle aging
486 processes, the contribution of $(NH_4)_2SO_4$ increased from 36% (Jan.30) to 67% (Feb.3), while for
487 NH_4NO_3, its contribution increased first to 28% on Jan.31 and then decreased to 10% (Feb.3).

Similar trend was found for EC, it increased to 22% (Feb.1) and then decreased to 7.6% (Feb.3). For OM, it exhibited decreasing trend, to the lowest value on Feb.2 (5.5%).

(Fig.7)

3.3 Source evolution

3.3.1 Contributions of fireworks burning to $PM_{2.5}$ on CNY and LF

The $PM_{2.5}$ concentrations peaked on CNY and LF in this study with intensive FW activities. Assuming that the $PM_{2.5}$ collected on CNY and LF was a simple combination of particles from FW and other emission sources, the contribution and compositions of the particles from FW can be estimated by substracting the contribution of the non-firework sources (Feng et al., 2012). An accumulation factor of 0.88 (mixing layer heights on Jan. 30 and Jan. 29 were 227 and 257 m, respectively) and 0.51 (mixing layer heights on Feb. 14 and Feb. 13 were 353 and 696 m, respectively) were used to eliminate the disperse impact caused by mixing height layer increasing (Feng et al., 2012; Deka and Hoque, 2014). About 60.1% and 10.9% of the $PM_{2.5}$ masses on CNY and LF were estimated to be from FW. The contributions to almost all species of FW on CNY were more obvious than those during LF (Fig.8). On CNY, OPC, EC3, Ba, Sr, Soot-EC, EC2 and OC1 maintained the higher contributions from FW, larger than 80%, followed by K, K^+, Al, Bi and Char-EC, with the contributions higher than 70%. On LF, 45% of Ba and 41% of Sr were from FW and the contributions to V, Bi, Fe, Be, K, K^+, Al, NO_2^- and Sb were higher than 20%.

(Fig.8)

3.3.2 Source variations by tracers and PCA analysis

In order to further identify the sources of particles, PCA results are shown in Fig.9 and supplementary file S8.

(Fig.9)

Five, five and eight factors were extracted for the dataset of Pre-SF, SF and After-SF period,

518 which explained 100%, 99.4% and 97.5% of the variance, suggesting almost all the sources have
519 been explained. Fireworks burning was the most important source for $PM_{2.5}$, contributing 24.0%
520 for the whole period. Coal combustion (including both local and regional transport) was also
521 important to $PM_{2.5}$ at this site in winter (contributing 19.3%). It was verified by the time series of
522 tracers (As and Sb, highly correlated with R^2=0.88) for coal combustion in Fig.10a. Extremly high
523 values can be found on Jan. 24, even higher than those for the intensive FW day. This can be
524 explained by two reasons: (1) on Jan. 24, it was a haze day with visibility and mixing layer height
525 as 8.2 km and 321 m, facilitating the acculumation of pollutants; (2) the air masses on Jan.24 were
526 classified as cluster 2 from central China where the Chang-Zhu-Tan region with intensive
527 non-ferrous metal metallurgy industries with huge coal consumption is located. On this day,
528 higher concentrations were also found for metals like Mg (228 ng m^{-3}), Cr (17 ng m^{-3}), Ca (782 ng
529 m^{-3}), Mn (85 ng m^{-3}), Fe (1014 ng m^{-3}), Co (0.61 ng m^{-3}), Ni (7.6 ng m^{-3}), Cu (124 ng m^{-3}), Mo
530 (4.4 ng m^{-3}), Cd (8.8 ng m^{-3}), Sn (16 ng m^{-3}) and Pb (359 ng m^{-3}). FW contributed about half of
531 the $PM_{2.5}$ during SF period. For Pre-SF and after-SF periods, its contributions were 9% and 14%.
532 As shown in Fig.10b, the tracers of Ba and Sr exhibited much higher values at SF, and there were
533 also some small peaks before SF (Jan. 27) and after SF (Feb. 14). During the one-week holiday,
534 most industrial activities shut down in China with low energy consumption during this period
535 (Feng et al., 2012; Huang et al., 2012; Li et al., 2013). As holiday effect, when compared the
536 source contributions at SF to those at Pre-SF, the contributions of coal combustion decreased from
537 46% to only 16%, the contributions of vehicle emissions decreased from 17% to 14% and the
538 contributions of dust also decreased. For After-SF period, along with the gradually re-starting of
539 industrial/contrustion activities and the increasing of traffic flows, the source contributions of coal
540 combustion, heavy oil burning, industrial processes and road dust increased, to 37%, 4%, 3.4%
541 and 5%, respectively. OC and EC were selected as the tracers of vehicle emission and their
542 correlation was higher to 0.80 without the data on CNY and LF. Ca was selected as the tracer for
543 construction activities or road dust (the main road was covered by abundant dust from subway
544 construction). Na^+ was used as the tracer of sea salt. Li, Be and Si were selected as the indicators
545 of soil (R^2 higher than 0.65 between them). The variations of mass concentrations of these tracers
546 before, during and after SF coincided with the contributions of corresponding sources.
547

(Fig.10)

3.4 Aging processes

3.4.1 The aging processes and mechanisms of fireworks burning particles

Previous studies indicated that the aerosol emission from FW activities is a short-term air quality degradation event (Jing et al., 2014), but no studies concerned how long the duration time is, and during the aging processes, what are the substantial hazard risk levels raised by elevated heavy metals from intensive FW. To better understand the influence of FW particles, its aging processes after emission were analyzed. It should be emphasized that during SF, contributions from other human sources were low (Fig.9), so the air quality in these days was mainly influenced by the highest contributor-FW particles' aging processes, including deposition, dispersion and transformations.

From Fig.2b and Fig.10b, it can be seen that it takes abut four days for the highest $PM_{2.5}$ and FW tracers-Ba and Sr on CNY to step down to the normal values of pre-CNY. The same situations were found for K^+, Cl^-, NH_4^+ and NO_3^- (Fig.11a). For SO_4^{2-}, on Feb.3, its mass concentrations decreased to a lower level of 6.1 μg m^{-3}. Then on Feb.4, it did not decrease immediately to the level of Jan. 29 until a rainfall (9 mm) on Feb.5. New emissions related with scattered fireworks burning at surroundings were thought to be introduced on Feb.4 as Ba, Sr, K^+, Ca^{2+}, Ca and Na^+ (they are all from primary emissions) slightly increased on Feb.4. Therefore, the variations of SO_4^{2-} on Feb.5 may not just related with the aging of the intensive FW particles at CNY's Eve. On Feb.1, though $PM_{2.5}$ has decreased from 317 to 185 μg m^{-3}, the visibility was still low as 2.2 km, with peak concentrations of NH_4^+, NO_3^- and SO_4^{2-} (they contributed 65% to the b_{ext}). On Feb.3, $PM_{2.5}$ decreased to 30 μg m^{-3}, haze pollution still existed with the visibility as 6.7 km, mainly contributed by ammonium sulfate (67%). It can be preliminarily concluded that the intensive FW particles at CNY's Eve can influence the air quality for about four days by changing the main contributors of extinction coefficient from EC+OM to ammonium sulfate. Drewnick et al. (2006) also found that after about three or four days, the aerosol mass concentrations droped to about one-third of the concentrations for Near Year's firework burning period, while the relative compositions of aerosols for the two periods were similar. And the mass concentrations of nitrate, sulfate and ammonium increased again after about three days.

(Fig.11)

Pollution gases (SO_2, NO_x, etc.) emitted during FW events may be oxidized to secondary organic and inorganic components that may be adsorbed onto particles (Sarkar et al., 2010). From Fig.11a, we can find that Ca^{2+}, NH_4^+, NO_3^- and SO_4^{2-} showed peak values on CNY and two days after, suggesting the directly emission from FW and secondary formations through heterogeneous reactions of SO_2 and NO_x on crustal materials. Higher correlations were found for NO_3^--Ca^{2+} (R^2=0.64) and SO_4^{2-}-Ca^{2+} (R^2=0.70). The lower wind speed (1.7-2.6 m s^{-1}) and mixing layer heights (257-284 m) helped to capture pollution gases near the ground and higher RH (74%-88%) favored their secondary transformation and following condensation onto pre-existing aerosols at the initial four days after intesive FW emissions on CNY.

From Jan. 30 to Feb. 4, the ratios of soot-EC/NO_3^-, Cl^-/K^+, NO_3^-/SO_4^{2-} and Ca^{2+} decreased first and then increased again, while to the opposite for SO_4^{2-}/K^+, suggesting the secondary formation (Fig.11b). Secondary formations of NH_4^+, NO_3^- and SO_4^{2-} from the gases emitted from FW were also found in other cities (Wang et al., 2007; Yang et al., 2014). During aging, the direct emission of KCl from fireworks (Drewnick et al., 2006) (R^2=0.85 for K^+-Cl^-) can react with H_2SO_4 and HNO_3 to form SO_4^{2-} (R^2=0.76 for K^+-SO_4^{2-}) and NO_3^- (R^2=0.96 for K^+-NO_3^-), leading to the desreasing of Cl^-/K^+ ratio and increasing of SO_4^{2-}/K^+ ratio. Li et al. (2013) drew the same conclusion through single particle analysis as that K-rich particles containing significant amounts of S in the form of K_2SO_4 at a background site under the influence of FW. It implied the existence of the aging of fresh FW particles via heterogeneous reactions during long-range transport. Soot (soot-EC) can be directly introduced by firework displays (Do et al., 2012) which showed moderate correlations with NO_3^- and SO_4^{2-} (R^2=0.47 and 0.56, respectively) in this study, indicating the coating of NO_3^- and SO_4^{2-} on soot. The OC/EC ratio peaked on CNY (as 6.8) which was mainly contributed by the increasing of OC1,OC2 and OPC. They are related with volatilization of the organic materials used for fireworks producing. The smelting point temperatures for polyvinyl alcohol, polyoxyethylene and shell-lac are 230-240˚C, 212˚C, 115-120˚C and the softening point for phenol formaldehyde resin is 80-85˚C, all lower than the detecting temperature for OC2 (230˚C). Therefore, OC1, OC2 and OPC are more easily and

608 directly emitted from FW. The iniatially decreasing OC/EC ratio indicated the gradual formation
609 of secondary (aged) organic aerosols (Feng et al., 2012). To summarize, the heterogeneous
610 reactions of SO_2 and NO_x on crustal materials directly from FW, the replacement of Cl^- by NO_3^-
611 and SO_4^{2-}, coating of NO_3^- and SO_4^{2-} on soot and formation of secondary organic aerosols are the
612 main aging mechanisms of FW particles.
613 Previous studies also indicated that metals like Fe, Cu and Mn can catalyze the formation of
614 NO_3^- and SO_4^{2-} (Wang et al., 2007; Do et al., 2012; Feng et al., 2012). Wang et al. (2007)
615 indicated that the heterogeneous formation of sulfate through reacting with a-Fe_2O_3 exsited under
616 moist atmosphere and was a function of RH and HNO_3. As shown in Fig.12 and Supplementary
617 file S9, significant correlations are found between NO_3^- and Fe, Cu and Mn and between SO_4^{2-} and
618 Fe, Cu and Mn at higher RH. It indicated the mechanism of metal-catalyzed formation of NO_3^-
619 and SO_4^{2-} was more likely to occur at higher RH. On the day of CNY and Feb.2, the RH was 88%
620 and 87%, implying the occurrence of metal-catalyzed reactions, which may also explain the higher
621 NO_3^- and SO_4^{2-} concentrations at these days. The R^2 increased with the elevated RH. There are
622 obvious increases of R^2 for Fe-NO_3^-, Mn-NO_3^- and Cu-NO_3^- when RH were >85%, >85%
623 and >65%, respectively. For the correlations of Fe-SO_4^{2-}, Mn-SO_4^{2-} and Cu-SO_4^{2-}, clear
624 increasings in R^2 were found when RH were >85%, >85% and >55%. Then we can conclude that
625 for Fe-catalyzed and Mn-catalyzed reactions, the threhold of RH was around 85%; for
626 Cu-catalyzed formation of NO_3^- and SO_4^{2-}, the threholds of RH were around 65% and 55%,
627 respectively. For RH higher than 90%, R^2 decreased for Fe-NO_3^-, Cu-NO_3^-, Fe-SO_4^{2-} and
628 Mn-SO_4^{2-} which needs more data in the future to be verified and explained.
629
630 (Fig.12)
631
632 **3.4.2 Potential health risks during the aging of fireworks burning particles**
633 After they are emitted from the intensive FW at CNY's Eve, heavy metals including Vi, Cr,
634 Mn, Co, Ni, Cu, Zn, As, Cd and Pb decreased directly in the following four days (Supplementary
635 file S10). It indicated that they were emitted from FW primarily and were removed mainly by
636 dispersion and deposition during aging. Then we can assume that: (1) other emisson sources (coal
637 combustion, vehicle exhaust and industrial processes were their main sources) for these metals

were stable during SF period; (2) the highest concentrations of them were just the combinations of particles from the FW on Jan. 30 and other sources on Jan. 29. We subtract the concentrations of elements on Jan. 29 from the corresponding values on Jan.30, Jan.31, Feb.1 and Feb.2 for each element, respectively, to obtain the element concentrations just related with the FW particles. Considering the variations of mixing layer height (as 306, 257, 227, 284 and 248 m for the five days of Jan.29-Feb.2) and accumulation effect, the concentrations of these elements on Jan. 30, Jan.31, Feb.1 and Feb.2 were transferred by factors of 0.84, 0.74, 0.93 and 0.81, respectively. Then the $C_{95\%UCL}$ values raised by FW particles were 7.4, 21.2, 12.0, 23.7, 0.42, 5.2, 54.5, 11.7, 126 and 837 ng m^{-3} of the ten elements, respectively, for the four days. The non-cancer risks raised just by FW particles at CNY's Eve were below 1 (0.03 and 0.02 for childern and adult) (Fig.13), indicating no adverse health effects. However the cancer risk was 1.62×10^{-6}, higher than 10^{-6}, suggesting the FW particles were important carcinogens and should be controlled effectively especially for the contained Cd and As. Meanwhile, the risk level for childern was higher than that for adult, which meant that children were more sensitive to non-carcinogenic effects and should be kept from possible exposure to them (Yang et al., 2014). The FW should be restricted at SF from the view of their cancer risks to human health.

(Fig.13)

4 Conclusions

Thirty-nine elements, ten water-soluble ions and eight fractions of carbonaceous species were measured to fully characterize the chemcial compositions in atmospheric $PM_{2.5}$ in Nanjing during the 2014 Chinese Spring Festival (SF). Serious regional haze pollution occurred and lasted during the whole sampling period. At the Chinese New Year (CNY)'s Eve, after it peaked at 02:00, $PM_{2.5}$ exponentially decreased in the following 11 hours to the level before extensive fireworks burning (FW) activities. Due to holiday effect, almost all elments decreased during SF except for Al, K, Ba and Sr which were related with FW. As the "spring travel rush" effect, NO_3^-, OC and EC showed highest values for periods before SF, indicating the extremely high traffic flows. At the New Year's Eve, about 60.1% of the $PM_{2.5}$ mass was estimated to be from FW. Highly elevated Ba and Sr were also found (highly correlated with each other), indicating they can be used as the tracers

of FW. The intensive FW at CNY's Eve obviously changed the chemical compositions of $PM_{2.5}$, with elevated organic matter (OM) immediately, contributing 39.3% of $PM_{2.5}$. The contributions of secondary ions formed by gas-particle transformations gradually increased during FW particles ´ aging processes. After FW particles emitted on CNY, the contribution of $(NH_4)_2SO_4$ to extinction coefficient increased from 36% to 67%; while for NH_4NO_3 and EC, their contributions increased first and then decreased. According to tracers and principle component analysis, fireworks burning was the most important source of $PM_{2.5}$ at this site. They contributed about half of $PM_{2.5}$ during SF. Tracers for various sources (As and Sb for coal combustion, Ba and Sr for FW, OC and EC for vehicle emission, Ca for construction or road dust, Na^+ for sea salt and Li, Be and Si for soil) performed well and they varied accordantly with the contributions of corresponding sources. The FW particles emitted from CNY's Eve may undergo about four days' aging processes from the variations of Ba, Sr, NH_4^+, NO_3^-, SO_4^{2-} and K^+. The aging processes were characterized by heterogeneous reactions of SO_2 and NO_x on crustal materials directly from FW, the replacement of Cl^- by NO_3^- and SO_4^{2-}, coating of NO_3^- and SO_4^{2-} on soot, formation of secondary organic aerosols and metal-catalyzed formation of NO_3^- and SO_4^{2-} at higher relative humidity. For Fe-catalyzed and Mn-catalyzed reactions, the threholds of RH were around 85%; while for Cu-catalyzed formations of of NO_3^- and SO_4^{2-}, the threholds of RH were around 65% and 55%, respectively. During the aging processes, FW particles on CNY obviously changed the main contributors to the extinction coefficient from EC+OM to ammonium sulfate. Meanwhile, higher cancer risks raised by heavy metals (especially for Cd and As) only related with FW particles emitted at CNY's Eve was 1.62×10^{-6}, which also imposed higher non-cancer risks to childern than adult. The results in this study will be useful for understanding the detailed compositions and aging processes of FW particles and also highlight the importance of controlling intensive fireworks burning in order to protect air quality and reduce the cancer risks.

Acknowledgment. This work was funded by the National Natural Sciences Foundation of China (No. 41030962), Scientific and technological cooperation between the Government of China-Serbia (2013(158)2-10), the grant of China Scholarship Council and the Priority Academic Program Development (PAPD) of Jiangsu Higher Education Institution.

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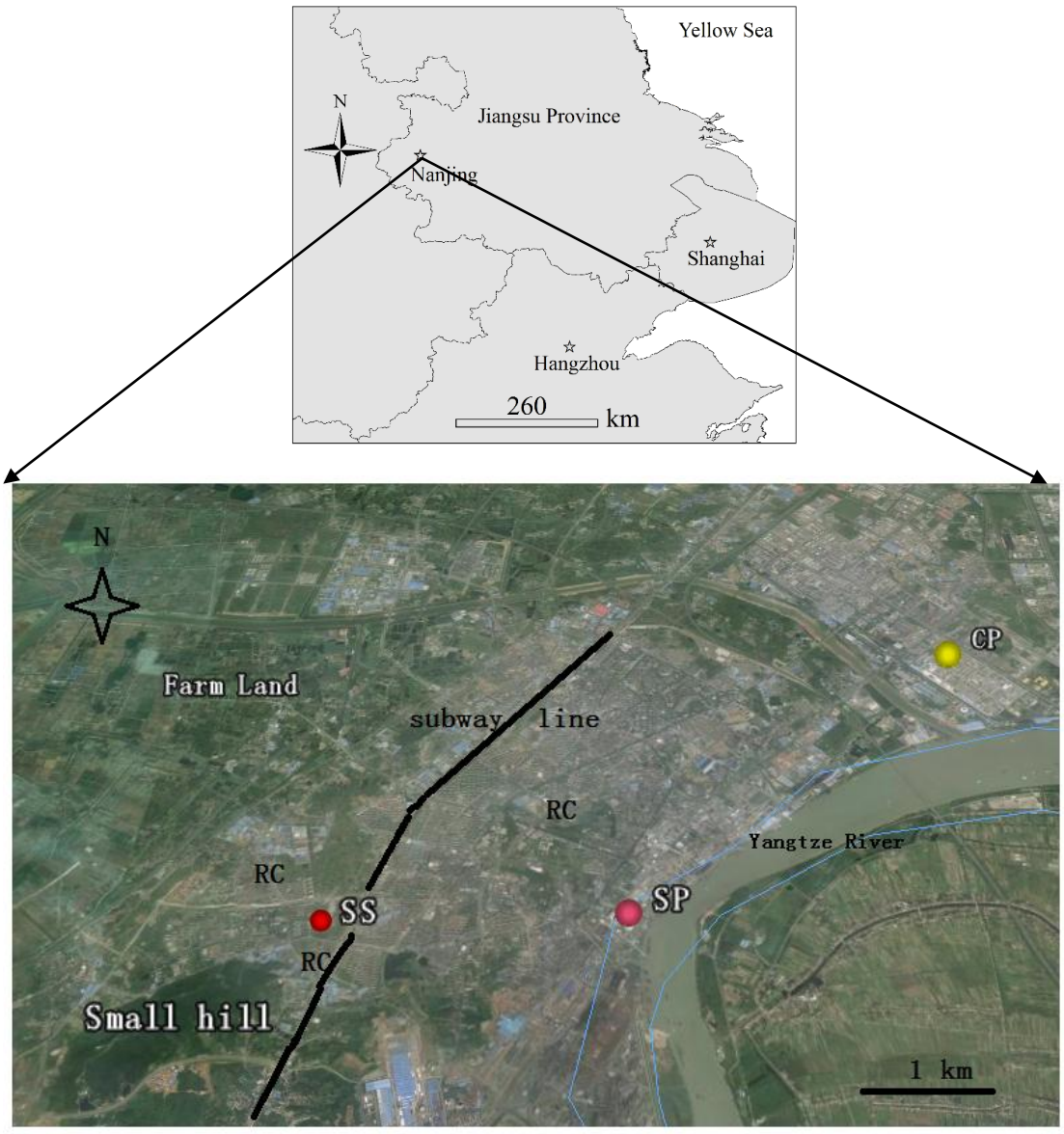
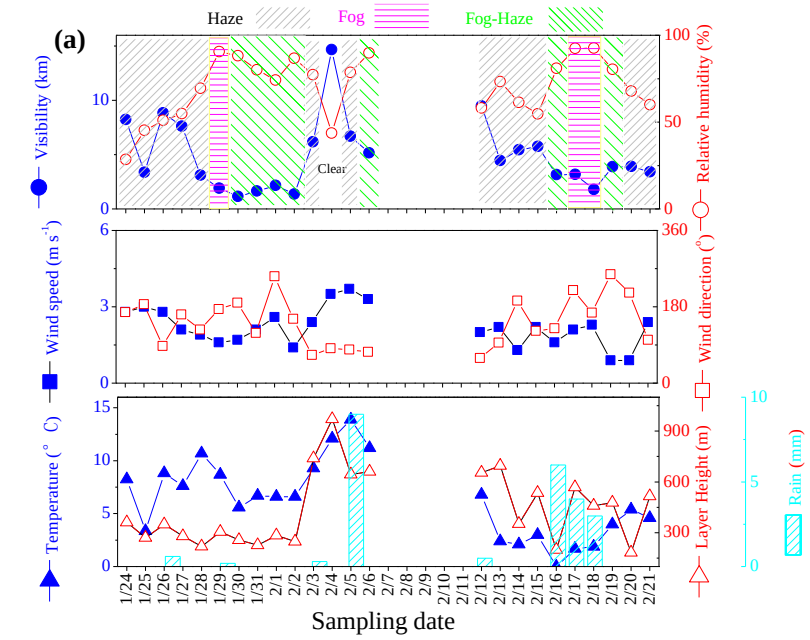


Fig. 1 Location of the sampling site (the red dot, SS). SP: iron smelt plant; CP: chemical industrial park; RC: residential community. The black line indicates the subway line near SS.



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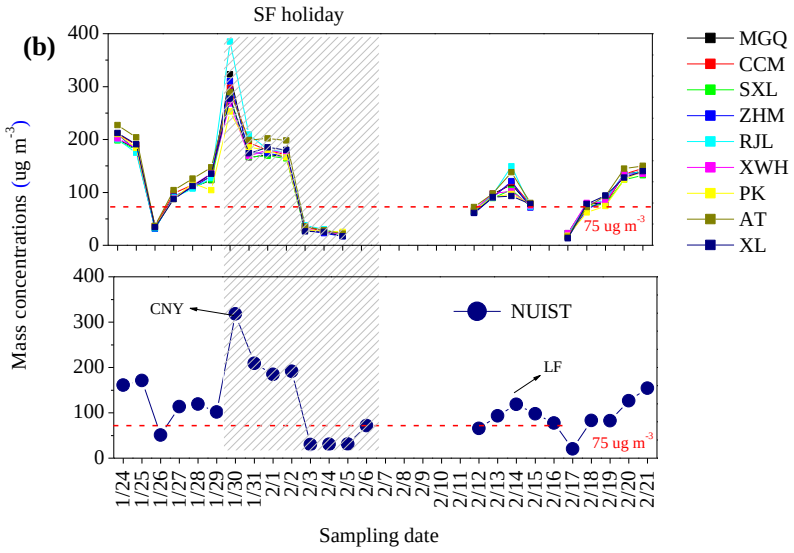

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892 Fig.2 Daily variation of meteorological factors (a) and mass concentrations of $PM_{2.5}$ (b) during
893 sampling periods. MGQ, CCM, SXL, ZHM, RJL, XWH, PK, AT and XL indicate the nine urban
894 air quality monitoring sites set by Jiangsu Environmental Monitoring Center as Supplementary file
895 S4 shown. NUIST indicates the sampling site of this study at Nanjing University of Information
896 Science and Technology. SF means Spring Festival (between Jan. 30-Feb.7); CNY means Chinese
897 New Year day (Jan.30); LF means Lantern Festival day (Feb. 14). 75 μg m^{-3} is the 24 h-averaged
898 secondary standard value for $PM_{2.5}$ of China National Ambient Air Quality.

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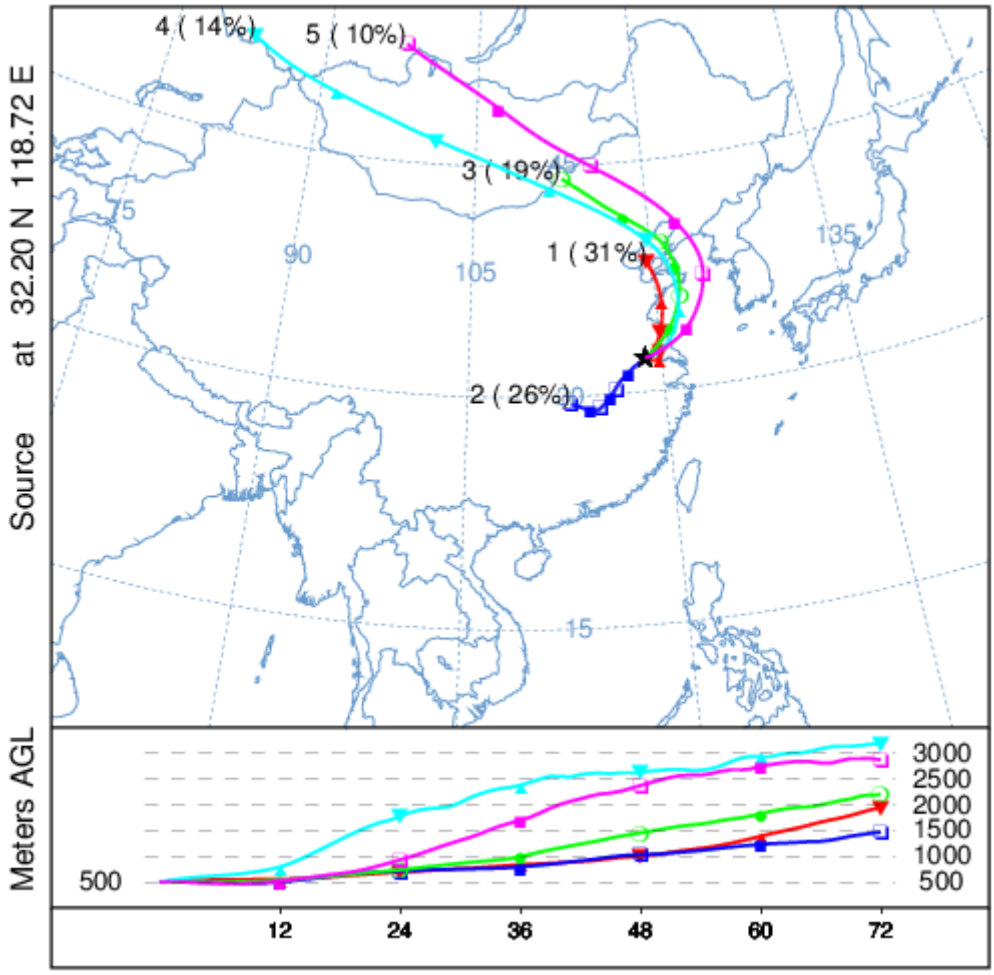


Fig.3 Cluster analysis for backward trajectories of air masses during the whole sampling periods. The different colors indicated different clusters of the backward trajectories.

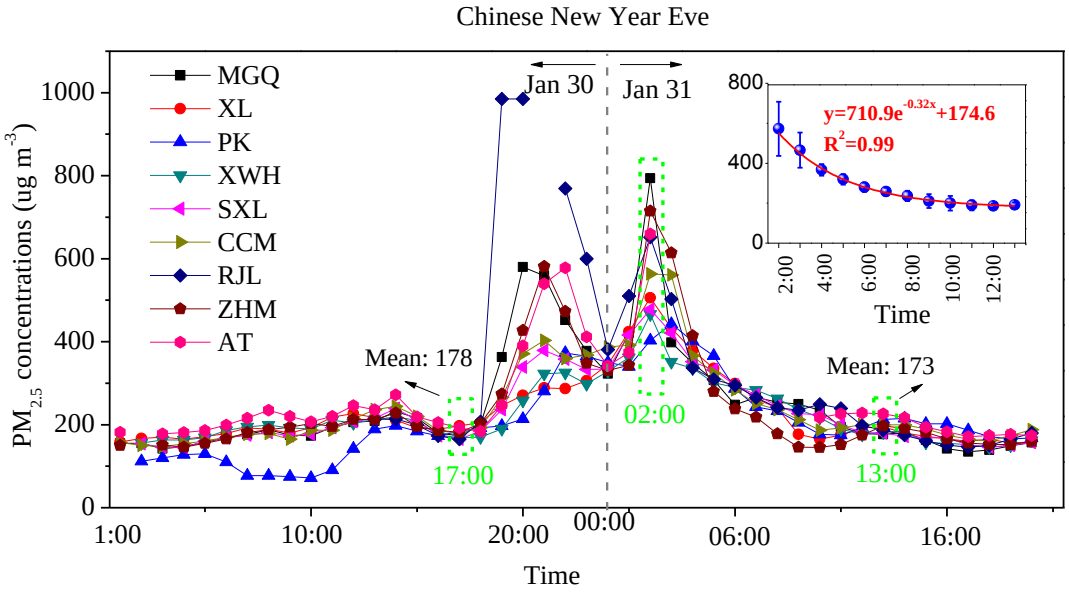


Fig.4 Hourly $PM_{2.5}$ concentrations before, during and after Chinese New Year (CNY) ́s Eve of 2014 at Nanjing. The figure at the top-right corner indicates the decreasing trend of averaged $PM_{2.5}$ mass concentrations after 02:00 of CNY ́s Eve (on Jan. 30, 2014). Hourly data for the nine sites in urban Nanjing (locations were shown in supplementary file S4) were collected from the public platform at http://218.94.78.75/jsair/.

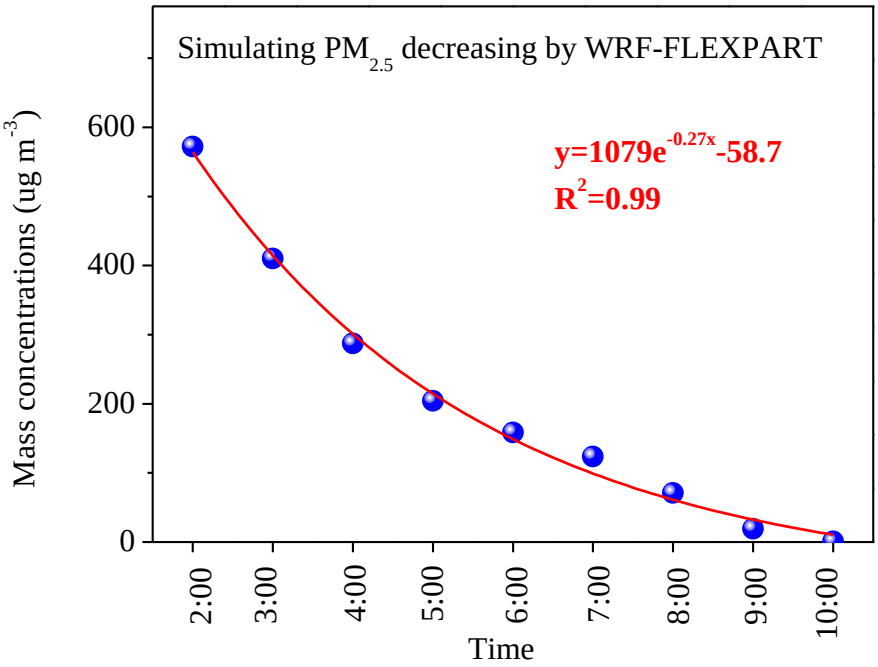
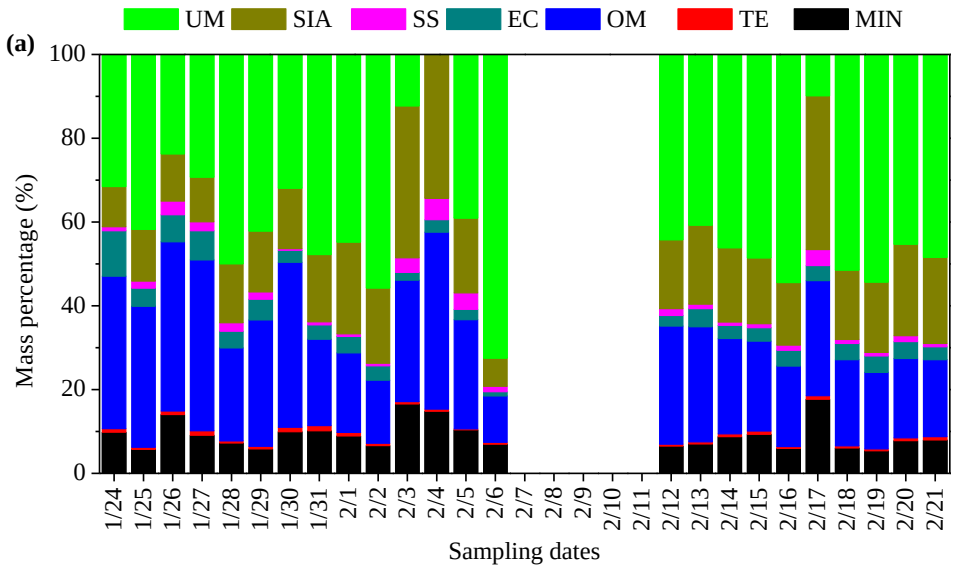


Fig.5 Particles decreasing trend at Chinese New Year ́s Eve by WRF-FLEXPART simulating. The particle concentrations decreased to 0.76 μg m^{-3} after nine hours, faster than the real decrease as Fig.4 shows. It can be explained as that we did not consider the injections of particles during simulating course, which biases the result.



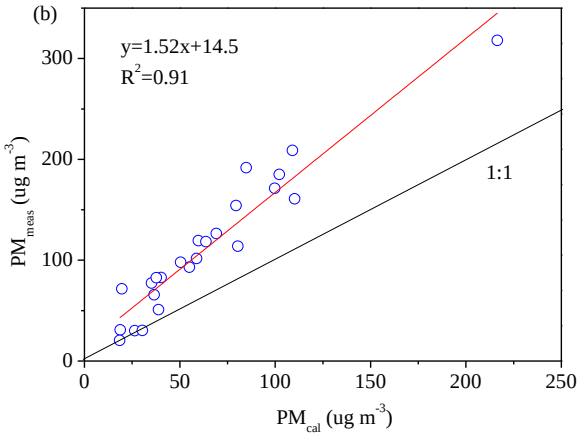


Fig.6 Mass balance of chemical species in $PM_{2.5}$ at sampling periods (a) and relationship between the mass calculated by adding individual components and the gravimetrically measured particulate mass (b).

MIN=2.14×Si+1.67×Ti+1.89×Al+1.59×Mn+1.67×Mg+1.95×Ca+1.35×Na+1.21×K+1.43×Fe.

Trace elements (TE) indicated the sum of all other elements except for those used in calculating MIN. Sea salt (SS)=[Na^+]+[ss-Cl^-]+[ss-Mg^{2+}]+[ss-K^-]+[ss-Ca^{2+}]+[ss-SO_4^{2-}]; ss-Cl^-=1.8×[Na^+]; ss-Mg^{2+}=0.12×[Na^+]; ss-K^-=0.036×[Na^+]; ss-Ca^{2+}=0.038×[Na^+]; ss-SO_4^{2-}=0.252×[Na^+]. Secondary inorganic aerosol (SIA) was calculated as the sum of nss-SO_4^{2-}, NO_3^- and NH_4^+. Organic matter (OM)=2.0×OC. UM indicated unidentified matter. Jan.30-Feb.7 belongs to the Chinese Spring Festival in 2014; Jan. 30 is the Chinese New Year day; Feb. 14 is the Lantern Festival day.

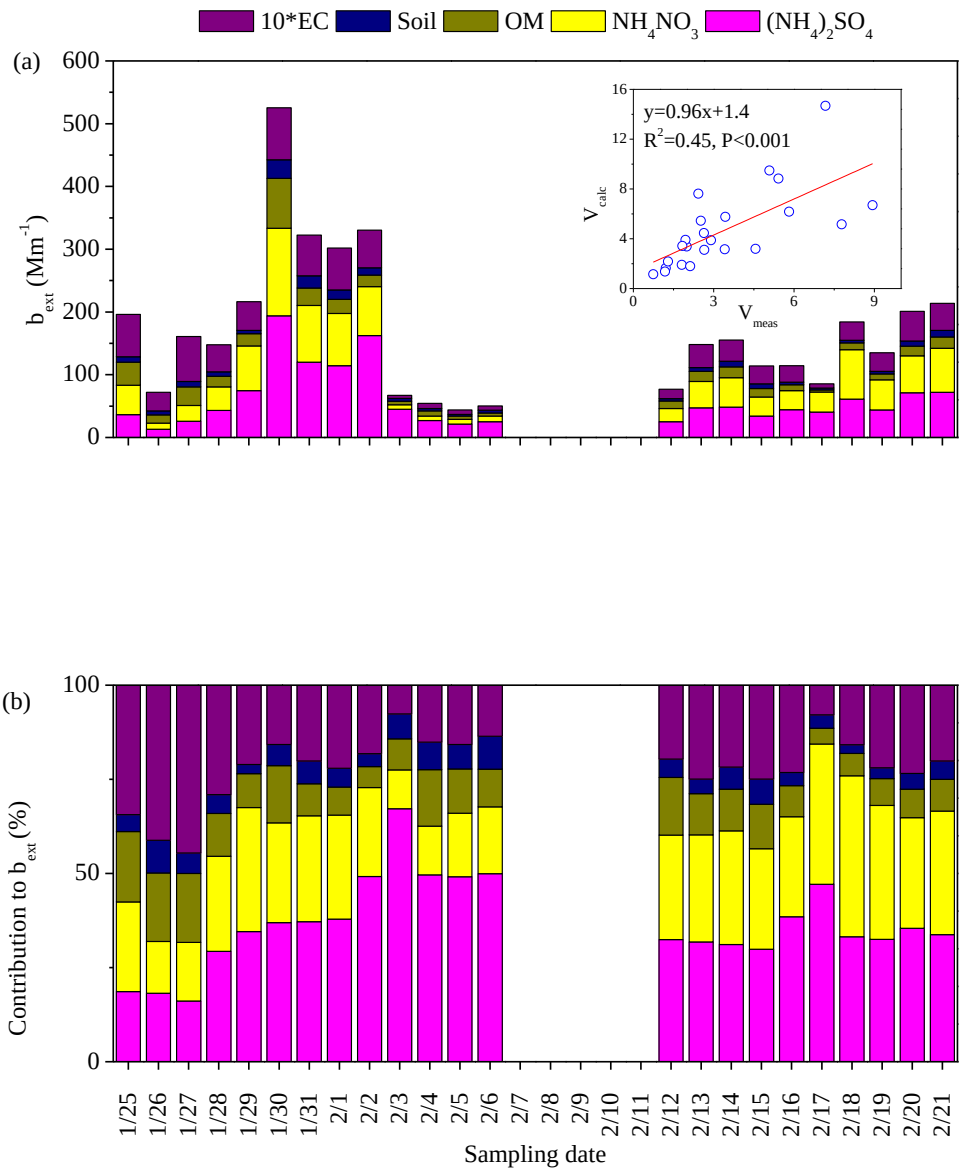


Fig.7 Extinction coefficients of chemical components in $PM_{2.5}$ at Nanjing (a) and relative contribution to light extinction of chemical components in $PM_{2.5}$ (b). Jan. 30-Feb.7 belongs to the Chinese Spring Festival in 2014; Jan. 30 is the Chinese New Year day; Feb. 14 is the Lantern Festival day. V_{cal} indicates the visibility calculated by adding individual components; V_{meas} is the measured visibility.

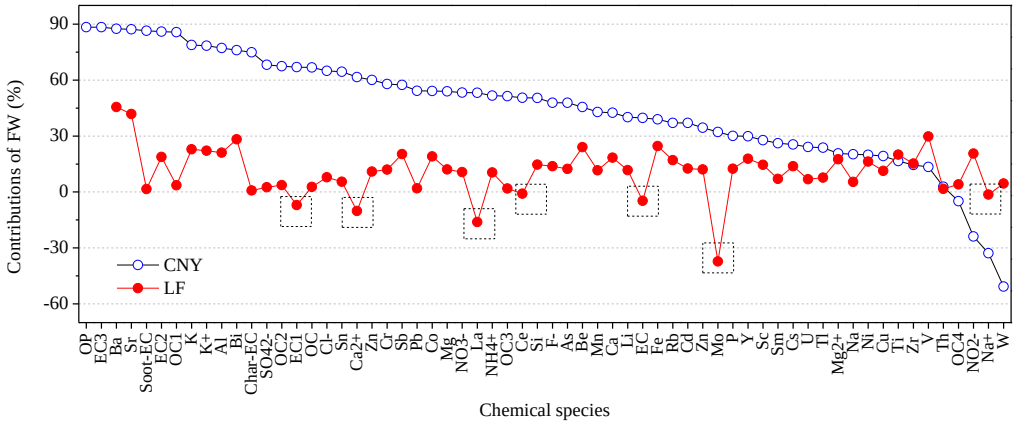


Fig.8 Contributions of fireworks burning (FW) on CNY and LF to chemical species in $PM_{2.5}$. CNY means Chinese New Year day (Jan. 30); LF means Lantern Festival day (Feb. 14).

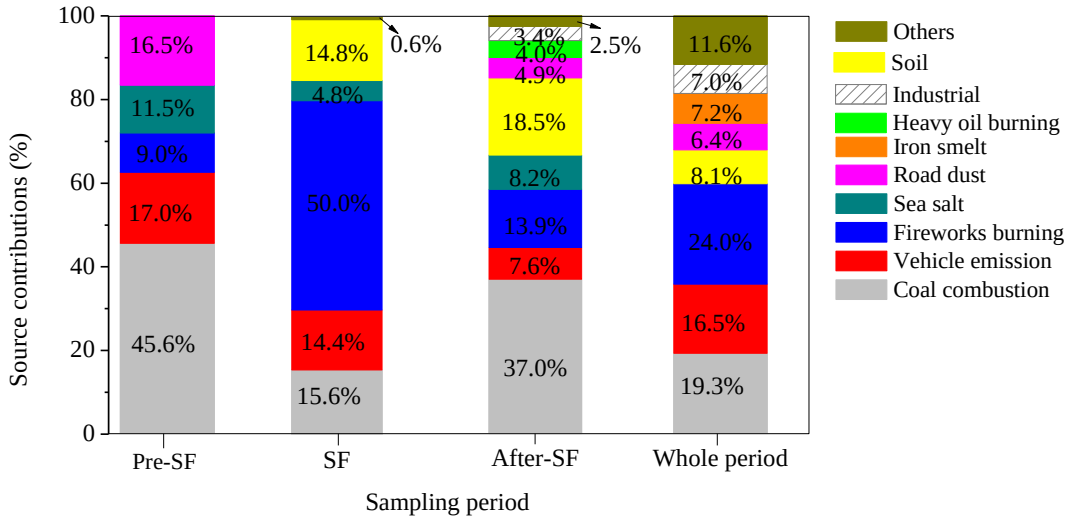


Fig.9 Source contributions to atmospheric $PM_{2.5}$ before, during, after 2014 Spring Festival (SF) and the whole period by principal component analysis. Pre-SF indicated the period before SF, covering the days from Jan. 24 to Jan. 29; SF indicated the period during SF, covering the days from Jan. 30 to Feb. 6; After-SF indicated the period after SF, covering the days from Feb.12 to Feb.21. The whole period included Pre-SF, SF and After-SF period.

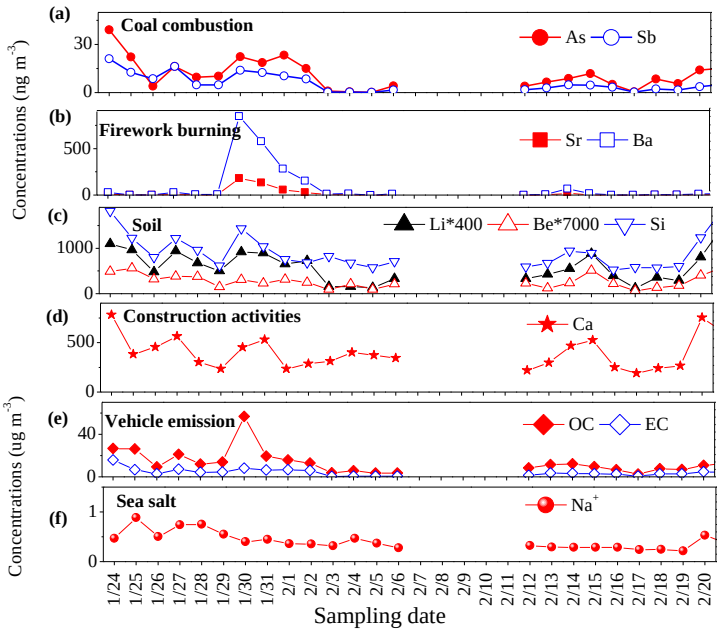
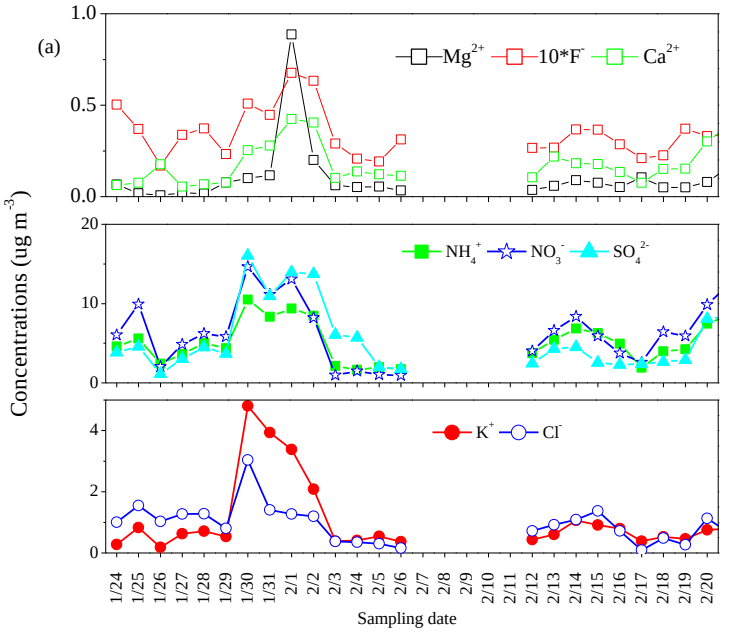


Fig.10 Time series of tracers for (a) coal combustion, (b) fireworks burning, (c) soil, (d) construction activities or road dust, (e) vehicle emission and (f) sea salt. The Y-axis units for (a), (b), (c) and (d) are ng m^{-3} and are ug m^{-3} for (e) and (f). Jan. 30-Feb.7 belongs to the Chinese Spring Festival in 2014; Jan. 30 is the Chinese New Year day; Feb. 14 is the Lantern Festival day.



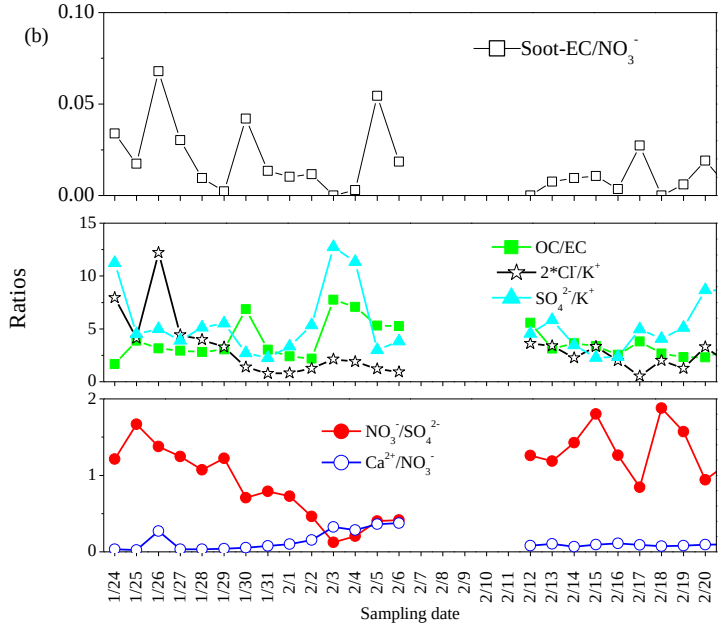


Fig.11 Time series of ions (a) and specific ratios (b) during sampling period. Jan. 30-Feb.7 belongs to the Chinese Spring Festival in 2014; Jan. 30 is the Chinese New Year day; Feb. 14 is the Lantern Festival day.

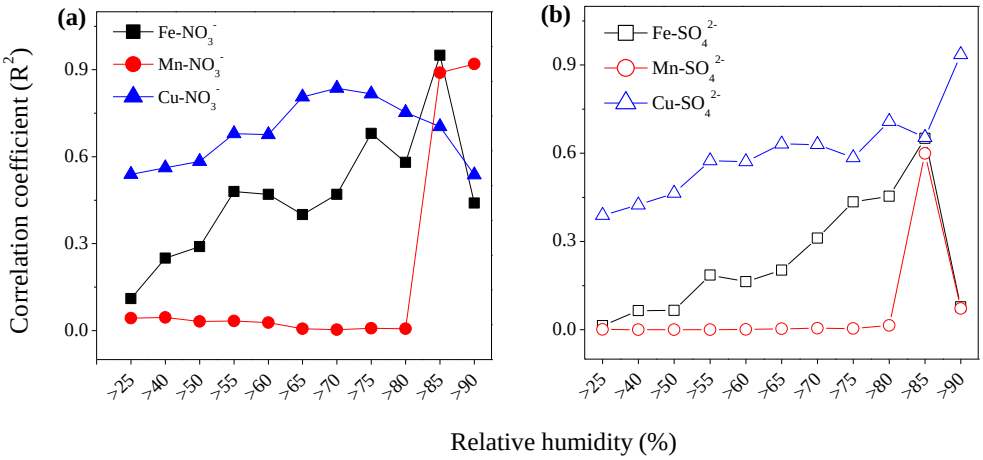


Fig.12 Correlation coefficients (R^2) of NO_3^- and metals-Fe, Mn and Cu under certain relative humidity bins (a); correlation coefficients of SO_4^{2-} and metals-Fe, Mn and Cu under certain relative humidity bins (b). For each time of calculating the R^2, the data of NO_3^- or SO_4^{2-} and each metal were used for corresponding relative humidity bins.

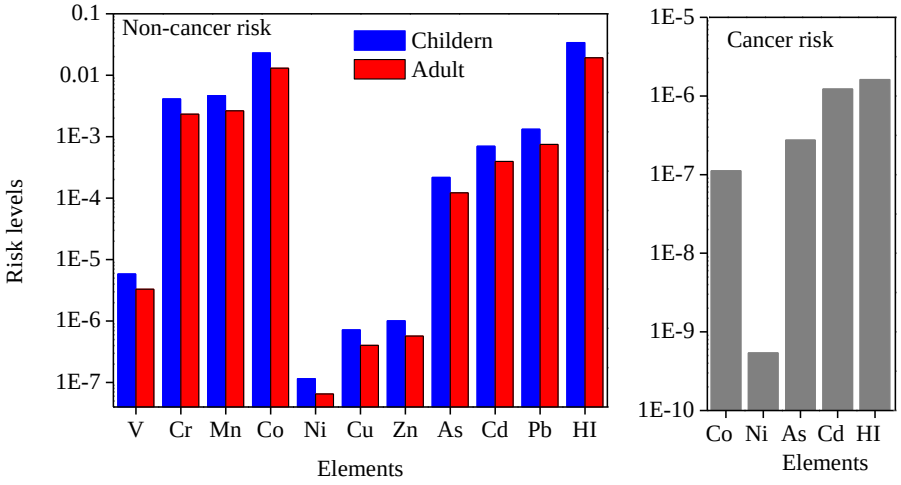


Fig.13 Non-cancer and cancer risks for heavy metals raised by intensive fireworks burning at Nanjing.

1136 Table 1 Mass concentrations of elements in $PM_{2.5}$ before, during and after 2014 Chinese Spring Festival at Nanjing (ng m^{-3})

Elements	Pre-SF	SF (without CNY)	After-SF (without LF)	CNY	LF	CNY/pre-CNY	LF/pre-LF
Li	1.9±0.7	1.1±0.8	1.4±1.0	2.3	1.4	1.8	1.3
Be	0.1±0.0	0.0±0.0	0.0±0.0	0.0	0.0	2.1	1.9
Na	826±209	417±196	435±172	563	506	1.3	1.1
Mg	124±79	97±89	106±30	196	124	2.6	1.3
Al	612±234	802±550	530±230	3127	811	7.9	1.7
Si	1105±420	752±147	847±422	1431	943	2.3	1.4
P	66±35	35±20	29±13	42	35	1.5	1.3
K	1940±725	3330±3848	1276±817	14336	2940	9.3	1.8
Ca	454±198	355±95	383±193	454	469	1.9	1.6
Sc	0.1±0.0	0.1±0.0	0.1±0.1	0.1	0.1	1.5	1.4
Ti	31±27	14±8	24±28	20	15	1.2	1.7
V	7.7±2.3	7.0±7.8	6.6±4.6	9.4	10.5	1.2	2.4
Cr	10.4±4.0	7.9±5.7	8.7±3.4	17.4	10.2	2.9	1.3
Mn	48±22	22±19	67±67	47	50	1.9	1.3
Fe	385±342	160±140	261±172	304	300	1.8	1.9
Co	0.4±0.1	0.4±0.4	0.4±0.2	0.6	0.5	2.6	1.6
Ni	8.5±6.0	4.5±3.1	8.9±5.6	5.9	7.6	1.3	1.5
Cu	102±30	81±63	77±25	170	116	1.3	1.3
Zn	257±145	93±81	194±154	242	174	1.6	1.3
As	17±13	9.0±9.8	8.0±4.6	22	8.8	2.2	1.3
Rb	8.5±2.2	4.7±4.2	5.7±4.5	12	6.5	1.7	1.5
Sr	5.1±3.9	34±49	4.9±5.9	181	20.5	79.4	5.7
Y	0.2±0.1	0.1±0.1	0.2±0.1	0.1	0.2	1.5	1.5
Zr	1.9±0.7	1.6±0.6	1.9±1.3	1.6	2.3	1.2	1.4

Mo	2.7±1.0	1.3±1.2	2.9±1.8	2.8	2.7	1.6	0.6
Cd	3.4±2.8	1.3±1.4	1.1±0.7	4.1	1.3	1.7	1.3
Sn	9.0±5.6	5.0±6.1	4.6±3.5	18.0	4.5	3.7	1.1
Sb	11±6.5	4.8±5.4	3.0±1.6	13.9	4.8	2.9	1.7
Cs	1.8±1.0	0.7±0.8	1.4±1.5	1.9	1.2	1.4	1.4
Ba	14±12	152±216	14.4±20.4	850	70.1	99.1	9.7
La	0.7±0.6	0.6±0.5	0.6±0.5	0.6	0.5	2.5	0.8
Ce	0.8±0.5	0.4±0.3	0.6±0.6	0.6	0.5	2.3	1.0
Sm	0.1±0.0	0.0±0.0	0.0±0.0	0.0	0.0	1.4	1.2
W	4.3±2.4	3.1±2.9	3.2±1.3	4.7	5.4	0.6	1.1
Tl	1.4±0.7	0.5±0.5	0.8±0.5	1.4	0.8	1.4	1.2
Pb	187±96	116±132	91±54	425	127	2.6	1.0
Bi	7.3±5.4	9.1±13.0	3.0±2.2	36.9	6.5	7.2	2.3
Th	0.6±0.0	0.5±0.0	0.6±0.0	0.6	0.6	1.0	1.0
U	0.1±0.0	0.0±0.0	0.1±0.1	0.1	0.1	1.4	1.2

Pre-SF indicated the period before 2014 Chinese Spring Festival (SF), covering the days from Jan. 24 to Jan. 29; SF indicated the Spring Festival period, covering the days from Jan. 30 to Feb.6; After-SF indicated the period after Spring Festival, covering the days from Feb.12 to Feb.21. CNY indicates the Chinese New Year (CNY) day and in 2014, it is Jan. 30; pre-CNY is the day before CNY and is Jan. 29. LF indicates the Lantern Festival (LF) day and in 2014, it is 14. Feb; pre-LF is the day before LF and is Feb.14. On CNY and LF, intensive fireworks were burned. Therefore, the mass concentrations of $PM_{2.5}$ and associated chemical species of the two days were listed seperately. CNY/pre-CNY indicates the ratios between mass concentrations of $PM_{2.5}$ and associated chemical species on CNY and the day before CNY (pre-CNY). LF/pre-LF indicates the ratios between mass concentrations of $PM_{2.5}$ and associated chemical species at LF and the day before LF (pre-LF).

1148 Table 2 Mass concentrations of ions and carbonaceous species in $PM_{2.5}$ before, during and after 2014 Chinese Spring Festival at Nanjing ($\mu g\ m^{-3}$)

Elements	Pre-SF	SF (without CNY)	After-SF (without LF)	CNY	LF	CNY/pre-CNY	LF/pre-LF
Na^+	0.65±0.17	0.37±0.07	0.31±0.09	0.40	0.29	0.7	1.0
NH_4^+	4.26±1.12	4.81±3.68	5.33±1.98	10.5	6.85	2.4	1.3
K^+	0.49±0.31	1.59±1.55	0.67±0.22	4.81	1.06	8.9	1.8
Ca^{2+}	0.09±0.05	0.23±0.14	0.19±0.09	0.25	0.18	3.3	0.8
Mg^{2+}	0.03±0.03	0.20±0.31	0.08±0.04	0.10	0.09	1.3	1.5
F^-	0.03±0.01	0.04±0.02	0.03±0.01	0.05	0.04	2.2	1.4
Cl^-	1.16±0.26	0.72±0.54	0.75±0.40	3.04	1.09	3.8	1.2
NO_2^-	0.02±0.01	0.04±0.01	0.04±0.01	0.02	0.05	0.8	1.7
NO_3^-	5.81±2.54	5.27±5.38	6.59±2.98	14.6	8.36	2.5	1.3
SO_4^{2-}	3.46±1.28	7.74±5.17	4.05±2.34	16.1	4.54	4.4	1.1
OC	18.2±7.45	9.38±6.70	8.95±3.15	56.9	12.2	4.1	1.1
EC	6.93±4.64	3.12±3.06	2.96±1.20	8.29	3.38	1.8	0.9
OC1	1.87±1.40	0.40±0.23	0.50±0.16	16.1	0.64	33.2	1.1
OC2	4.32±1.65	2.56±1.75	2.36±0.74	14.8	2.86	4.2	1.1
OC3	5.46±2.69	2.77±2.09	2.90±1.15	9.10	4.28	2.4	1.0
OC4	5.44±1.52	3.27±3.03	2.94±1.36	5.81	4.46	0.9	1.1
EC1	7.92±5.07	3.44±2.64	3.15±1.00	18.8	3.30	4.1	0.9
EC2	0.12±0.07	0.07±0.06	0.06±0.05	0.50	0.08	37.7	1.6
EC3	0.00±0.00	0.00±0.00	0.00±0.00	0.11	0.00	-	-
OPC	1.12±2.43	0.39±0.39	0.24±0.43	11.09	0.00	-	-
$PM_{2.5}$	119.6±43.4	106.9±84.1	88.9±37.4	318.0	118.4	3.1	1.3

1149 - Not detected in the day before CNY and LF.

1150 Pre-SF indicated the period before 2014 Chinese Spring Festival (SF), covering the days from Jan. 24 to Jan. 29; SF indicated the Spring Festival period, covering

1151 the days from Jan. 30 to Feb.6; After-SF indicated the period after Spring Festival, covering the days from Feb.12 to Feb.21. CNY indicates the Chinese New Year

(CNY) day and in 2014, it is Jan. 30; pre-CNY is the day before CNY and is Jan. 29. LF indicates the Lantern Festival (LF) day and in 2014, it is 14. Feb; pre-LF is the day before LF and is Feb.14. On CNY and LF, intensive fireworks were burned. Therefore, the mass concentrations of $PM_{2.5}$ and associated chemical species of the two days were listed seperately. CNY/pre-CNY indicates the ratios between mass concentrations of $PM_{2.5}$ and associated chemical species on CNY and the day before CNY (pre-CNY). LF/pre-LF indicates the ratios between mass concentrations of $PM_{2.5}$ and associated chemical species on LF and the day before LF (pre-LF).