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Impacts of firecracker burning on aerosol chemical characteristics and human health risk levels during the Chinese New Year Celebration in Jinan, China

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HIGHLIGHTS

- The effect of firecracker burning on aerosol characteristics and human health was assessed.
- The burning of firecrackers elevated the concentrations of particles and water-soluble ions.
- The burning of firecrackers varied the chemical composition of $PM_{2.5}$ and the number size distribution of particles.
- The burning of firecrackers did not alter the mass size distributions of the water-soluble ions.
- Pollutants emitted from the firecracker burning caused high non-carcinogenic risks to human health.

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ABSTRACT

Measurements for size distribution and chemical components (including water-soluble ions, OC/EC and trace elements) of particles were taken in Jinan, China, during the 2008 Chinese New Year (CNY) to assess the impacts of firecracker burning on aerosol chemical characteristics and human health risk levels. On the eve of the CNY, the widespread burning of firecrackers had a clear contribution to the number concentration of small accumulation mode particles (100–500 nm) and $PM_{2.5}$ mass concentration, with a maximum $PM_{2.5}$ concentration of 464.02 μg/m^3. The firecracker activities altered the number size distribution of particles, but had no influence on the mass size distribution of major water-soluble ions. The concentrations of aerosol and most ions peaked in the rush hour of firecracker burning, whereas the peaks of NO_3^- and NH_4^+ presented on the day following the burning of firecrackers. K^+, SO_4^{2-} and Cl^- composed approximately 62% of the $PM_{2.5}$ mass, and they existed as KCl and K_2SO_4 during the firecracker period. However, during the non-firecracker period, organic matter (OM), SO_4^{2-}, NO_3^- and NH_4^+ were the major chemical components of the $PM_{2.5}$, and major ions were primarily observed as $(NH_4)_2SO_4$ and NH_4NO_3. Estimates of non-carcinogenic risk levels to human health showed that the elemental risk levels during the firecracker period were substantially higher than those observed during the non-firecracker period. The total elemental risk levels in Jinan for the three groups (aged 2–6 years, 6–12 years and ≥70 years) were higher than 2 during the firecracker period, indicating that increased pollutant levels emitted from the burning of firecrackers over short periods of time may cause non-carcinogenic human health risks.

1. Introduction

Festivals worldwide, such as Independence Day in the US, France's Commemoration of the French Revolution, the Las Fallas in Spain, the Lantern Festival and Spring Festival in China, Diwali Festival during October/November in India, and New Year's Eve celebrations throughout the world, are often celebrated with the extensive burning of firecrackers. The burning of firecrackers is responsible for elevated levels of pollutants, including gaseous pollutants (e.g., SO_2, NO_x and O_3) (Attri et al., 2001; Ravindra et al., 2003; Moreno et al., 2007; Barman et al., 2008; Godri et al., 2010; Singh et al., 2010; Nishanth et al., 2012) and particles (e.g., TSP, PM_{10} and $PM_{2.5}$) with water-soluble ions and

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trace metals (Kulshrestha et al., 2004; Drewnick et al., 2006; Moreno et al., 2007; Vecchi et al., 2008; Camilleri and Vella, 2010; Moreno et al., 2010; Perrino et al., 2011). In addition, the burning of firecrackers often causes degradation in air quality (Clark, 1997; Vecchi et al., 2008) and health hazards (e.g., chronic lung diseases, cancer, neurological and haematological diseases) (Becker et al., 2000; Kamp et al., 2005; Godri et al., 2010; Moreno et al., 2010). As a result, the pollution caused by the burning of firecrackers has recently received serious attention in the scientific community. However, most of the above studies were located abroad in areas with relatively low air pollutant levels, but data is still limited for China.

The Spring Festival and the Lantern Festival are two important celebrations with intensive burning of various firecrackers in China, a country that already has suffered serious air pollution. In China, several studies have been conducted to characterise the impacts of firecracker burning on air quality. These studies have indicated significant increases in the levels of $PM_{2.5}$ and PM_{10} with elements and water-soluble ions (Wang et al., 2007; Chang et al., 2011; Huang et al., 2012), and in the number concentration of particles in the size range of 100–500 nm (Zhang et al., 2010) due to the extensive burning of firecrackers. Li et al. (2013) also found that the emissions from the firecracker burning significantly changed the morphology and chemical composition of individual airborne particles and the transformation pathway from SO_2 to SO_4^{2-}. The above studies provided limited information regarding the aerosols, water-soluble ions and metal components emitted from the burning of firecrackers. However, the impacts of firecracker burning on aerosol chemical characteristics, especially for $PM_{2.5}$ and its chemical components, and human health risk levels have not been systematically studied in China.

To investigate the impacts of firecracker burning on aerosol chemical characteristics and human health risk levels, a campaign was conducted from February 3rd to 26th 2008 in Jinan, China, which spans the Chinese New Year. Jinan is the capital of Shandong Province, the hometown of Confucius, and is often the site of Chinese New Year celebrations that include the extensive burning of firecrackers. In addition, Jinan suffers from serious air pollution, especially particulate matter pollution (Baldasano et al., 2003; Yang et al., 2007, 2012; Gao et al., 2011). Therefore, it is important to understand whether the extensive burning of firecrackers has significant impacts on aerosol chemical characteristics and human health risk levels in this highly polluted region. In this manuscript, we discuss the impacts of firecracker burning on the mass size distribution of water-soluble ions, number concentration and size distribution of particles, and the chemical compositions of $PM_{2.5}$ during the firecracker period. And then we choose three highly sensitive groups, including children aged 2 to 6 years, children aged 6 to 12 years and older adults (≥70 years) to assess the potential health impact of $PM_{2.5}$ from the firecracker burning.

2. Methodology

2.1. Sampling site

The study was conducted at two urban sites in Jinan, the capital of Shandong Province (36°69′ N, 117°06′ E), from February 3rd to February 26th 2008. The filters for $PM_{2.5}$ and size-segregated aerosols were collected on the rooftop of a six-storied teaching building on the Centre Campus of Shandong University, approximately 20 m above ground level. Online instruments for particle number concentration and water-soluble ions in $PM_{2.5}$ were located at the rooftop (15 m above ground level) of public teaching building on the Hongjialou Campus of Shandong University, 1 km away from the Centre Campus. The inlets for aerosols were 1.5 m above the laboratory rooftop. These two sampling sites were surrounded by densely populated residential and commercial areas. The specific event of this study was the Chinese New Year and is characterised by the extensive burning of firecrackers from the night of February 6th to the morning of the following day when the city was shrouded in fume and smoke, particularly in the densely populated residential areas. In this study, we defined the day of February 6th as the firecracker period, while the other days as the non-firecracker period.

2.2. Instruments

2.2.1. Filter-based instruments

$PM_{2.5}$ samples were collected manually by using a Reference Ambient Air Sampler (Model RAAS 2.5–400, Thermo Andersen) with Teflon filters (Teflo™, 2 μm pore size and 47 mm diameter, Pall Inc.) at a flow rate of 16.7 L/min. Size-resolved aerosol samples were collected on aluminium substrates (MSP) by using the MOUDI (Micro-Orifice Uniform Deposit Impactor 110 with rotator, MSP) at a flow rate of 30 L/min. The MOUDI has eight stages with the size ranges of ≥18 μm, 10–18 μm, 5.6–10 μm, 3.2–5.6 μm, 1.8–3.2 μm, 1.0–1.8 μm, 0.56–1.0 μm, 0.32–0.56 μm and 0.18–0.32 μm. The sampling time for both $PM_{2.5}$ and size-resolved aerosol samples was approximately 24 h, normally from 9:00 a.m. to 8:45 a.m. the following day from February 3rd to February 26th 2008. A total of 20 samples for $PM_{2.5}$, and 13 sets of size-resolved aerosol samples with each set comprising of nine samples, were collected during the whole campaign. The flow rates of $PM_{2.5}$ sampler and MOUDI were calibrated before the field campaign, and field blanks were collected at the start and end of the field campaign. After sampling, all the filters were kept in plastic Petri dishes and then stored in a refrigerator at −4 °C for subsequent analysis in laboratory. In the laboratory, the concentrations of water-soluble ions were determined by ion chromatography (ICs, model Dionex 90) (Zhou et al., 2010), OC and EC in $PM_{2.5}$ were analysed by a semi-continuous OC/EC analyser (Sunset-DOSCOCEC, Sunset Lab, Portland, OR) (Wang et al., 2011), and trace metals in $PM_{2.5}$ were determined by using X-ray fluorescence (XRF) (Yang et al., 2013).

2.2.2. Real-time instruments

Particle number concentration at the range of 10 nm–10 μm was measured by a wide-range Particle Spectrometer™ (WPS model 1000XP, MSP Co., USA). This instrument combines the principles of differential mobility analysis (DMA), condensation particle counting (CPC), and laser light scattering (LPS). The detailed information for the principles of these parts can be found in Xu et al. (2011). The time of WPS measurements was from February 4th to February 9th 2008. Before and after the measurement, PSL spheres with sizes of (0.269 μm and 0.1007 μm mean diameter) and (0.701 μm, 1.36 μm, 1.6 μm, and 4.0 μm mean diameter) were used to calibrate DMA and LPS respectively. The DMA and CPC can measure particle number size distribution at the range of 10–500 nm in up to 96 channels. The LPS covers the 350–10,000 nm range in 24 additional channels. In this study we chose the sample mode with 60 channels in DMA and 24 channels in LPS. It took about 8 min for one complete scanning of the entire size range.

An ambient ion monitor (AIM; Model URG-9000B, URG Co.) was deployed to measure the hourly concentrations of water-soluble inorganic ions in $PM_{2.5}$. The AIM measurements started from February 3rd and ended on February 9th. Multi-point calibrations were performed every four days after changing the eluent solutions. The uncertainties were approximately 10%, and the estimated detection limits ranged from 0.010 to 0.084 $\mu g/m^3$ for all ions. The data from AIM had been compared to the filter samples, and they perfectly matched (Gao et al., 2011).

2.3. Elemental risk level calculations in $PM_{2.5}$

In this study, representative elemental components of $PM_{2.5}$ were applied to calculate elemental risk levels to assess the possible impacts on human health.

Based on the US EPA (2001) and the experimental data in this study, the following equation was used to obtain one-sided (1-a) UCL on the mean:

$$UCL_{1-a} = \overline{X} + t_{a,n-1}S/\sqrt{n}, \quad (1)$$

where $\overline{X}$ is the mean concentration, S is the standard deviation, t is the Student's t value, which can be found in Gilbert (1987), and n is the sample size. To evaluate the long-term or chronic impact of pollutant exposure, the average amount of pollutant exposure per an individual's body weight over a given time span for the three sensitive groups (aged 2–6 years, 6–12 years and ≥70 years) was calculated as (USEPA, 1989):

$$DE = \frac{C \times I \times F \times D}{t \times W} \quad (2)$$

where the terms are DE: dose of exposure (mg/kg-day); C: mean concentrations (mg/m^3); I: inhalation rate (m^3/day); F: exposure frequency (days/year); D: exposure duration (years); t: average time; and W: body weight (kg). The elemental risk (R) was calculated by Eq. (3). Here RD is the reference dose (USEPA, 1989).

$$R = {}^{DE}/_{RD} \quad (3)$$

3. Results and discussion

3.1. Overview of measurement data

Fig. 1 depicts the daily concentrations of $PM_{2.5}$, water-soluble ions and OC/EC measured in Jinan from February 3rd to 26th 2008. From this figure, it can be observed that the $PM_{2.5}$ concentration in Jinan varied over a large range during the measurement period. Heavy aerosol pollution occurred on February 6th when the firecrackers were extensively displayed, with the daily $PM_{2.5}$ concentration of 464.02 μg/m^3. Light aerosol pollution was observed with the daily $PM_{2.5}$ concentration of 33.08 μg/m^3, slightly lower than the 24 h US National Ambient Air Quality Standard (35 μg/m^3).

Table 1 summarises the statistics of the $PM_{2.5}$, water-soluble ions and OC/EC for the study period, including subset intervals for periods with and without the firecracker burning. Overall, serious aerosol pollution was illustrated, especially during the firecracker period. During the study period, the average concentration (±standard deviation) of $PM_{2.5}$ was 134.51 (±97.40) μg/m^3, which is approximately nine times the annual US National Ambient Air Quality Standard of $PM_{2.5}$ (15 μg/m^3) and is substantially higher than the annual standard in China (35 μg/m^3). Water-soluble ions and carbonaceous species (OC + EC) contributed to 57% and 14%, respectively, of the $PM_{2.5}$ mass. Water-soluble ions were the most abundant species; among all ions observed, SO_4^{2-} was the most abundant composition, with a mean value of 26.41 (±20.25) μg/m^3, followed by NO_3^- and NH_4^+ with average concentrations of 18.07 (±11.99) and 12.21 (±6.93) μg/m^3, respectively. These three species together composed approximately 76% of all water-soluble ions. Cl^- and K^+ also had relatively large concentrations of 10.11 (±16.88) and 10.78 (±29.20) μg/m^3, respectively. Other ions (F^-, Na^+, Mg^{2+}, Ca^{2+}) normally were observed at very low concentrations, and accounted for a minor fraction of the total $PM_{2.5}$ water-soluble ions.

Table 1
Average concentration of chemical species in $PM_{2.5}$ in Jinan, China (unit: μg/m^3).

Species	$PM_{2.5}$	SO_4^{2-}	NO_3^-	Cl^-	F^-	Na^+
All data	134.51	26.41	18.07	10.11	0.43	0.69
Firecrackers	464.02	86.85	14.63	74.54	1.08	1.81
Non-firecrackers	113.92	22.64	18.29	6.08	0.39	0.62
Species	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	OC	EC
All data	12.21	10.78	0.69	0.76	14.77	1.70
Firecrackers	7.25	123.69	6.66	1.05	19.56	3.63
Non-firecrackers	12.52	3.72	0.32	0.74	14.47	1.58

3.2. Air pollution caused by the burning of firecrackers

3.2.1. Variation in $PM_{2.5}$ and water-soluble ion concentrations

The holiday for celebrating the 2008 Chinese New Year lasted seven days from February 6th to 12th, including the lunar New Year's Eve on February 6th, when firecrackers were displayed through the following morning. The mass concentration of $PM_{2.5}$ was high with daily value of 464.02 μg/m^3 during the firecracker period (Fig. 1 and Table 1), three times higher than the average values (113.92 μg/m^3) obtained during the non-firecracker period. Similarly, the total concentrations of water-soluble ions were also elevated, with hourly values (Fig. 2) at their highest concentrations of 1620.09 μg/m^3 at 1:00 a.m. on February 7th when firecrackers were extensively displayed. Because industrial activity and traffic are drastically reduced during the lunar New Year's Eve, anthropogenic emissions should only minimally contribute to air pollution during this period (Li et al., 2013). Thus, increased aerosol pollution can be attributed to firecracker emissions.

As shown in Fig. 2, water-soluble ions can be classified into two groups based on the variations in their concentrations: (1) K^+, Cl^-, SO_4^{2-}, Mg^{2+}, Ca^{2+}, F^- and Na^+, and (2) NO_3^- and NH_4^+. The ions K^+, Cl^-, SO_4^{2-}, Mg^{2+}, Ca^{2+}, F^- and Na^+ exhibited a sharp concentration

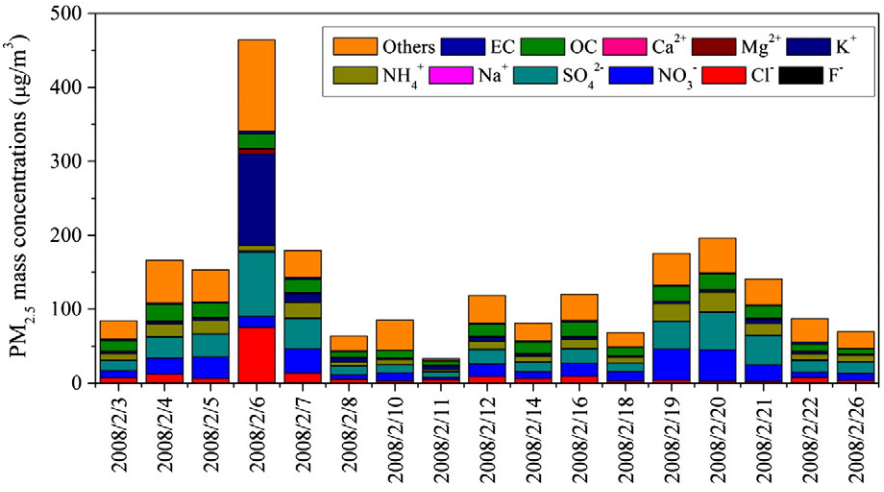

Fig. 1. Time series of daily concentrations of $PM_{2.5}$ and its chemical components in Jinan, China.

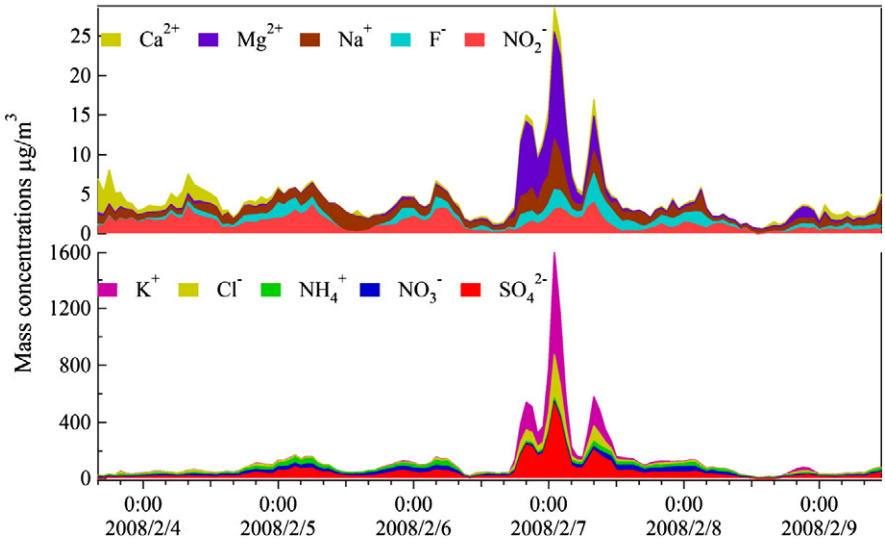

Fig. 2. Hourly concentrations of water-soluble ions during sampling period in Jinan, China.

peak on the night when firecrackers were extensively displayed, followed by a rapid decrease in their concentrations the following day. Thus, these ions were most likely released from the burning of firecrackers, with weak contribution from other local sources. Figs. 1 and 2 showed that NO_3^- and NH_4^+ had lower concentrations during the extensive firecracker burning period, and their concentrations gradually increased the following day. The concentrations of K^+, Mg^{2+}, Cl^-, SO_4^{2-}, F^- and Na^+ in $PM_{2.5}$ were approximately 33, 21, 12, 4, 3 and 3 times greater, respectively, during the firecracker period compared to the period when the firecrackers were not displayed (Table 1). K^+ was found in large quantities and showed the largest increase during the firecracker burning. The daily and hourly K^+ concentrations reached values of 123.69 and 717.49 μg/m^3, respectively, due to the extensive firecracker burning, which indicated that potassium salts might be one of the major compounds used in the firecrackers. KNO_3, $KClO_3$ and $KClO_4$ are often widely used as oxidiser that sustain the burning of firecrackers and are restored into KNO_2 and KCl (Wang et al., 2007). In this study, NO_2^- varied little during the firecracker burning (Fig. 2), whereas Cl^- was highly elevated, suggesting that $KClO_3$ and $KClO_4$ were used as the major oxygen sources in the firecrackers. However, the concentrations of NO_3^- and NH_4^+ peaked the day following the firecracker burning. The concentration peaks for NO_3^- and NH_4^+ occurred at 8:00 and 12:00, respectively, on the day following the extensive firecracker burning. In contrast, their concentration peaks occurred before dawn on days without firecracker use. The moderate elevation in NO_3^- just after dawn suggested that the peak was primarily attributed to firecracker emissions, and less to anthropogenic activities (e.g., coal burning and traffic exhausts). This "tailing" phenomena suggested that NO_3^- may be from the secondary formation of NO_x emitted from the burning of firecrackers.

3.2.2. Number concentration and size distribution

Hourly number concentration of particles in different size bins during the sampling period (02/04/2008–02/09/2008) is exhibited in Fig. 3. During the sampling period, the total particle number concentration ranged from 5377 cm^{-3} to 47,888 cm^{-3}, with the average value (±standard deviation) of 19,928 (±8590) cm^{-3}. Aitken mode and accumulation mode particles were the dominant size fractions, accounting for 57% and 42%, respectively, of the total particle number concentration. The nucleation mode particles showed much lower number concentration (average value: 204 cm^{-3}) and had little variation. Examination of the data revealed that there was no spontaneous burst in the number concentration of nucleation mode particles, therefore, no new particle formation events were observed during the sampling period. However, one particle growth process was clearly observed in the afternoon on February 6th. The growth rate (GR) was calculated to be 6.7 nm h^{-1} following the methods by Kulmala et al. (2004), which was within the typical urban particle GR range (1–20 nm/h) in previous study (Kulmala et al., 2004; Gao et al., 2012).

The episode of extensive firecracker burning started at ~18:00 LT on February 6th and ended with the high point after midnight (1:00 LT) on February 7th. Fig. 3 showed that a significant increase in the number concentration of large particles, which also lead to an elevation of geometrical mean diameter (GMD). During the firecracker period the average total number concentration was 24,783 cm^{-3}, which increased 30.3% compared to the non-firecracker period. Moreover, the number concentration of accumulation mode particles increased to 15,023 cm^{-3} (60.8% of the total) during the firecracker period, much higher than 7007 cm^{-3} (36.9% of the total) during the non-firecracker period, which was in accordance with some previous studies (Agus et al., 2008; Mönkkönen et al., 2004; Zhang et al., 2010). In contrast, the number concentration of nucleation and Aitken mode particles reduced by 15% and 19%, respectively, during the firecracker period compared to the non-firecracker period, which was due to the large coagulation sink (Zhang et al., 2010). Therefore, we concluded that the intensive firecracker burning released a large amount of accumulation mode particles, and changed the particle number size distribution.

3.2.3. Size distribution of major water-soluble ions for different periods

The size distribution for major water-soluble ions (i.e., NH_4^+, K^+, Cl^-, SO_4^{2-} and NO_3^-) is depicted in Fig. 4 during four different periods, including the whole sampling period (February 3rd to 26th), the "firecracker period" (February 6th), the "non-firecracker period" (February 3rd to 26th except for February 6th), and the day following the firecracker burning (February 7th). During the whole sampling period (Fig. 4), these five ions generally existed in the fine particles with fractions of 87% for NO_3^-, 78% for SO_4^{2-}, 85% for Cl^-, 85% for K^+ and 98% for NH_4^+ being present in $PM_{1.8}$ (there is no 2.5 μm cut point for MOUDI). K^+, Cl^-, SO_4^{2-} and NO_3^- exhibited a bimodal distribution, with a predominant peak in the fine mode in the size range of 0.32–0.56 μm and a small peak in the coarse mode in the size range of 3.2–5.6 μm. NH_4^+ had a single peak in the size range of 0.32–0.56 μm.

As mentioned above, the burning of firecrackers can emit a large amount of the K^+ in $PM_{2.5}$. During the firecracker period, the size distribution of K^+ was in accordance with that during the other periods, indicating no change in the mass size distribution for K^+. However, the concentration varied depending on the time period. For each size-bin, the K^+ concentration during the firecracker period was 20–80 times

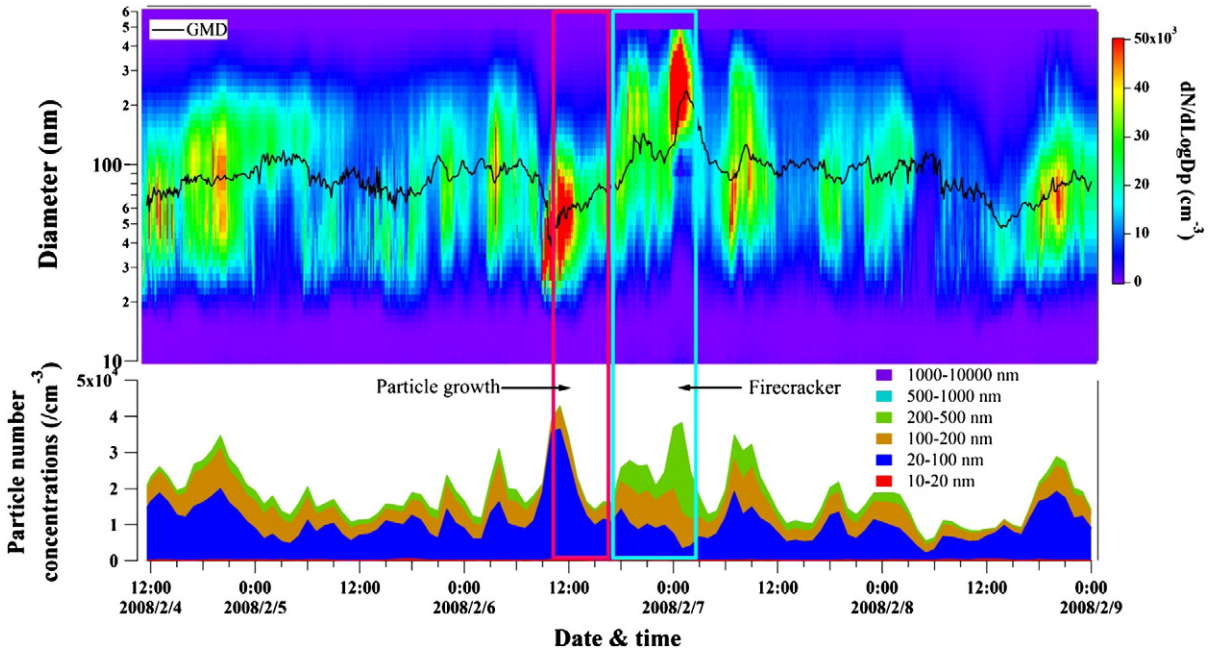

Fig. 3. Number size distribution and concentration of different size bins from February 4th to 9th, 2008.

that of the non-firecracker period. The K^+ concentration then decreased rapidly to the average value for each size-bin on the day following firecracker burning, which suggested that the firecracker burning made a strong contribution while other local sources made a weak contribution to the K^+ concentration. Variations in Cl^- size distribution and concentration were in accordance with those in K^+, and Cl^- showed strong correlation with K^+ for all size-bins ($R = 0.97$, $p \ll 0.01$). Thus Cl^- likely originated from the same source (i.e., firecracker burning) as K^+. The variation in SO_4^{2-} was similar to that of K^+; the only difference was the concentration variation on the day following the firecracker burning (February 7th). Similarly, the SO_4^{2-} concentration declined after the burning of firecrackers. However, the SO_4^{2-} concentration in the fine particles was still higher than the average value in all samples. This result indicated that primary particles emitted directly from the firecracker burning could be quickly removed by dry deposition, whereas pollution gases from the burning activities were likely to be oxidised to secondary inorganic components and retained in the particles. NO_3^- and NH_4^+ showed similar characteristics in size distribution variation, with no change over all the periods. However, their concentration peaks appeared on the day following firecracker burning (February 7th), which was in contrast with the peak in K^+ concentration during the firecracker period (February 6th). These results indicated that NO_3^- and NH_4^+ were not directly produced by the burning of firecrackers, unlike K^+, and that they may have been formed from the gases emitted by the burning of firecrackers.

3.2.4. Chemical composition of $PM_{2.5}$

Particles emitted from firecracker burning are likely to have different chemical compositions compared with the normal aerosols. To identify the variation in chemical composition, the chemical composition of $PM_{2.5}$ was determined under four assumptions. First, the concentration of organic matter (OM) was calculated as 1.8 times the concentration of OC, according to the revised IMPROVE formula. Second, the soil dust concentration was assumed to be the sum of the oxides of the main crustal elements (Kim et al., 2001): $[Soil] = 2.20 * [Al] + 2.49 * [Si] + 1.63 * [Ca] + 2.42 * [Fe] + 1.94 * [Ti]$. Third, the concentration of trace metal was assumed to be the sum of the oxides of the corresponding elements, except for Al, Si, Ca, Fe and Ti. Fourth, the firework matter was calculated as the sum of K^+ and Cl^-, as their concentrations were highly elevated during the night of firecracker burning and could serve as firecracker indicators (Wang et al., 2007). The contributions of different components of $PM_{2.5}$ during the firecracker and non-firecracker periods are depicted in Fig. 5.

The results showed that, for the samples collected during the non-firecracker period, the pattern was dominated by secondary inorganic matter (the sum of SO_4^{2-}, NH_4^+ and NO_3^-; 47%) and organic matter (23%) in $PM_{2.5}$. The contribution of firework matter (the sum of K^+ and Cl^-) was relatively lower (9%). However, the samples collected during the firecracker period showed a different pattern, with greater amounts of firework matter (43%) and less secondary inorganic (24%) and organic matter (7%). This finding suggested that the chemical components of $PM_{2.5}$ were significantly influenced by the burning of firecrackers. The reduced fraction of secondary inorganic matter associated with the burning of firecrackers was due to the lower amounts of NH_4^+ and NO_3^-. The fraction of SO_4^{2-} in $PM_{2.5}$ was 19% during the firecracker period and 20% during the non-firecracker period, whereas NH_4^+ and NO_3^- declined from 11% and 16%, respectively, during the non-firecracker period to 1% and 3%, respectively, during the firecracker period.

To further identify the chemical forms of the major ions (i.e., SO_4^{2-}, NH_4^+, NO_3^-, K^+ and Cl^-), the correlation among ion concentrations was analysed using the hourly data for the firecracker and non-firecracker periods, respectively, and the results are shown in Table 2. During the non-firecracker period, SO_4^{2-} showed stronger correlations with NH_4^+ ($R = 0.96$, $p \ll 0.01$). The RMA slope of the regression between equivalent concentrations of NH_4^+ and SO_4^{2-} was 1.34, which indicated the complete neutralisation of SO_4^{2-} by NH_4^+. The RMA slope of the regression between equivalent concentrations of NH_4^+ and $(SO_4^{2-} + NO_3^-)$ was 1.00 ($R = 0.96$, $p \ll 0.01$), which implied complete neutralisation of SO_4^{2-} and NO_3^- by NH_4^+. K^+ showed little correlation with SO_4^{2-}, NO_3^- or Cl^-. These results indicated that $(NH_4)_2SO_4$ and NH_4NO_3 were the major chemical species in $PM_{2.5}$ during the non-firecracker period. However, during the firecracker period, different results were obtained. SO_4^{2-} showed stronger correlations with K^+, Na^+, Mg^{2+}, and Ca^{2+} ($R = 0.98$, 0.91, 0.91 and 0.89, respectively, $p \ll 0.01$) rather than NH_4^+ ($R = 0.07$, $p = 0.78$). K^+ can serve as a tracer for firecracker emissions. This finding indicated that SO_4^{2-} was largely produced from the firecracker burning and existed as K_2SO_4, and Na_2SO_4, $MgSO_4$ and $CaSO_4$ were also other major existing forms of SO_4^{2-}. Cl^- was highly correlated with K^+, Na^+, Mg^{2+}, and Ca^{2+}, with

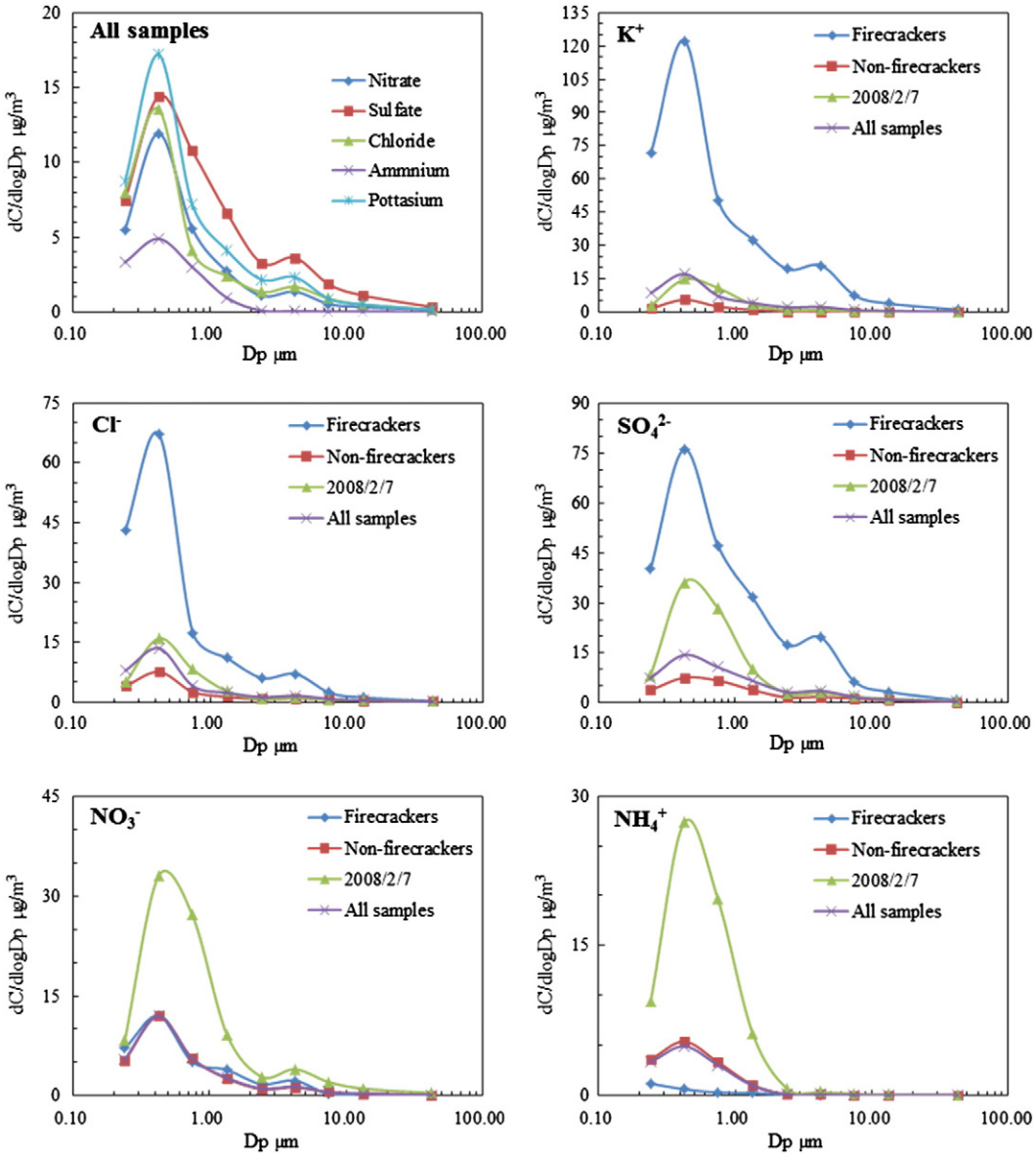

Fig. 4. Mass size distribution of major water-soluble ions during the four sampling periods.

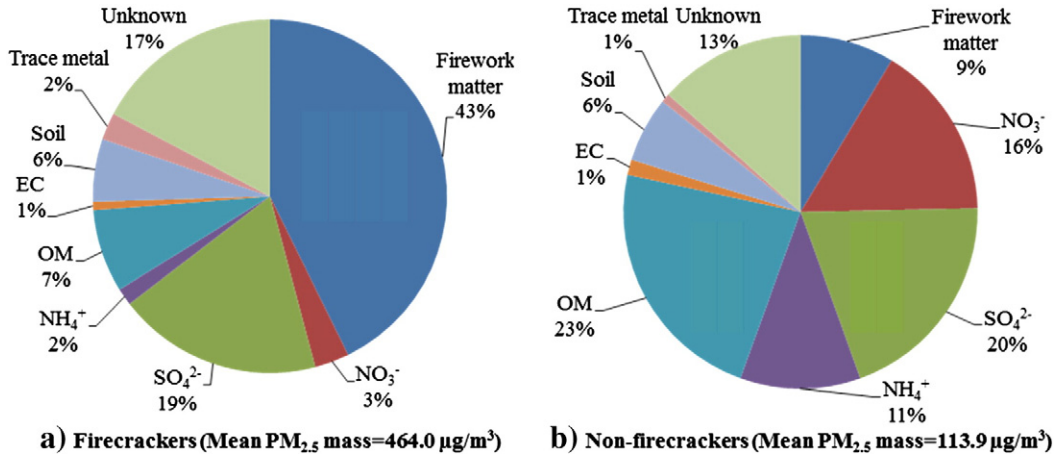

Fig. 5. Chemical composition of $PM_{2.5}$ in Jinan during (a) the firecracker period and (b) the non-firecracker period.

Table 2
Correlation between water-soluble ions using the hourly data for (a) the non-firecracker period and (b) the firecracker period.

(a)	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Cl^-	1								
NO_2^-	0.54**	1							
NO_3^-	0.45**	0.37**	1						
SO_4^{2-}	0.48**	0.49**	**0.86****	1					
Na^+	0.01	0.17	0.28**	0.42**	1				
NH_4^+	0.46**	0.60**	**0.84****	**0.96****	0.40**	1			
K^+	0.42**	−0.16	0.26**	0.26**	−0.06	0.1	1		
Mg^{2+}	0.25**	−0.16	−0.13	−0.06	−0.18**	−0.18*	0.78**	1	
Ca^{2+}	0.11	0.28**	−0.31**	−0.35**	−0.05	−0.28**	−0.21*	0.04	1

(b)	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Cl^-	1								
NO_2^-	0.54*	1							
NO_3^-	−0.29	−0.01	1						
SO_4^{2-}	**0.96****	0.50*	−0.35	1					
Na^+	**0.92****	0.45	−0.4	**0.91****	1				
NH_4^+	0.18	0.61**	**0.71****	0.07	0.03	1			
K^+	**0.99****	0.51*	−0.32	**0.98****	**0.92****	0.11	1		
Mg^{2+}	**0.84****	0.33	−0.58**	**0.91****	**0.84****	−0.26	**0.87****	1	
Ca^{2+}	**0.94****	**0.73****	−0.33	**0.89****	**0.84****	0.26	**0.92****	**0.77****	1

The bold and underlined values indicate strong correlation.
* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

correlation coefficients of 0.99, 0.92, 0.84 and 0.94, respectively. These correlation patterns suggested that chloride salt might be the main chemical form for these metals in the firecrackers. Furthermore, NH_4^+ and NO_3^- showed moderate correlation, but they showed a smaller or negative correlation with other ions (e.g., K^+, Na^+, Mg^{2+}, and Ca^{2+}). This result reinforced that NH_4^+ and NO_3^- were not directly emitted from the burning of firecrackers.

3.3. Assessment of health risk levels from metals in $PM_{2.5}$

The burning of firecrackers can release a large amount of heavy metals into the atmosphere (Gao et al., 2002; Wang et al., 2007). Particles of these heavy metals can penetrate into the human body through direct inhalation, ingestion and dermal contact and then cause short- and long-term health problems, especially for children and elderly (Kong et al., 2012). Therefore, it is essential to evaluate the human health risks related to heavy metal exposure. In this study, nine major metals (Cu, Pb, Cr, Co, S, Mn, Zn, As and Ni) were used to assess the possible non-carcinogenic human health risks via direct inhalation during the firecracker burning and non-firecracker burning scenarios. The non-carcinogenic risk assessment results for the firecracker period and the non-firecracker period are listed in Table 3.

De Miguel et al. (2007) suggested that an elemental risk level larger than 0.1 had adverse health effects on children. As shown in Table 3, the metals in $PM_{2.5}$ with risk values higher than 0.1 for the study populations in Jinan were Mn, Co and S for the non-firecracker period and Mn, Co, S, Cr and Pb for the firecracker period. The risk values for Cu, Pb, Cr, Co, S, Mn, Zn, As and Ni were approximately 16, 9, 6, 4, 3, 3, 3, 2 and 2 times greater, respectively, during the firecracker period compared to the non-firecracker period. Considering the cumulative effect of the non-carcinogenic risk levels of heavy metals, the total risk values were summed for the nine metals. The total risk values were 0.83 for children aged 2–6 years, 0.85 for children aged 6–12 years, and 0.63 for elderly adults during the non-firecracker period, and these values exceeded 2.0 during the firecracker period. These results indicated that exposure to metals found in $PM_{2.5}$ may pose a serious public health risk in this study area and that the non-carcinogenic elemental inhalation risk is greatly increased due to the burning of firecrackers. Cu, used to make blue colours in firecrackers, and Pb, used to achieve a steady and reproducible burning rate, increased the most (Conkling, 1985). During the burning of firecrackers, a large amount of Cu and Pb was emitted into the atmosphere, causing increases in their concentrations (Gao et al., 2002; Wang et al., 2007). In addition, a comparison was conducted between children and adults, and the results showed that children were the most sensitive group to non-carcinogenic effects and should avoid possible exposure to these contaminants.

4. Summary

To assess the impacts of firecracker burning on aerosol chemical characteristics and human health risk levels, chemical components of $PM_{2.5}$, number concentration and size distribution of particles, and

Table 3
Health risks based on the chemical elemental components of $PM_{2.5}$ for the three groups during periods with and without firecracker detonation.

Firecrackers period				Non-firecrackers period		
Elements	Children (2–6)	Children (6–12)	Adult	Children (2–6)	Children (6–12)	Adult
S	0.49	0.50	0.38	0.16	0.16	0.12
Cr	0.43	0.44	0.33	0.08	0.08	0.06
Mn	1.11	1.12	0.84	0.39	0.39	0.29
Ni	1.61E−04	1.63E−04	1.22E−04	9.113E−05	9.251E−05	6.916E−05
Cu	2.45E−03	2.49E−03	1.86E−03	1.55E−04	1.57E−04	1.18E−04
Zn	6.29E−04	6.39E−04	4.78E−04	2.23E−04	2.27E−04	1.69E−04
Pb	0.11	0.11	0.09	1.25E−02	1.26E−02	9.45E−03
As	0.02	0.02	0.02	9.27E−03	9.41E−03	7.04E−03
Co	0.69	0.70	0.52	0.19	0.20	0.15
Total	2.86	2.90	2.17	0.83	0.85	0.63

mass size distribution of water-soluble ions were measured in Jinan during the 2008 Chinese New Year. The firecrackers displayed to celebrate the Chinese New Year elevated number concentration of particles and mass concentration of $PM_{2.5}$ and water-soluble ions, and varied the number size distribution and chemical components of $PM_{2.5}$; however, the firecracker burning only minimally altered the mass size distribution of major water-soluble ions. The results of elemental risk assessment suggested that the pollutants emitted from the burning of firecrackers even over a short duration may cause high non-carcinogenic risk levels to human health.

Conflict of interest

We declare that we have no conflict of interest.

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