Chemical characteristics and health risks of trace metals in PM$_{2.5}$ from firework/firecracker burning during the Spring Festival in North China

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Abstract. Firework/firecracker (FF) burning can significantly deteriorate air quality, whereas little is known about its influences on the elemental composition and associated health risks. Fine particles (PM$_{2.5}$) and trace elements were characterized based on a multi-site campaign at Chifeng, China around 2016 Chinese Spring Festival (SF). Severe pollution levels average of 57.70 µg m$^{-3}$ were observed during the SF with maximum to 471.00 µg m$^{-3}$ shortly after the intensive FF activities. Largely enhanced PM$_{2.5}$-bound metals were found in both urban and rural sites especially for K (8.27±5.36 µg m$^{-3}$) and Al (2.36±1.41 µg m$^{-3}$). Ba and Sr as the tracer of fireworks also increased more than 20-fold compared to non-SF period. Accordingly, FF burning factor identified via PMF model contributed significantly to the total elemental mass (71.34±24.94%) during the SF. Its major impacts on both crustal elements as Al, Ca, K and heavy metals as Cr, Cu and Pb were both identified. Elevated non-cancer risks (0.76 to children, 0.11 to adults) and cancer risks (3.96×10$^{-6}$) were assessed during the SF, with As, Cd, Pb exerted the most adverse threats. The FF burning contributed the second largest share of the health threats after coal combustion, accounted for 28.35% and 12.64% of non-cancer risks for children and adults, respectively, and 10.03% of cancer risks, respectively. This study provided scientific evidences for stricter firework/firecracker regulations to protect public health.

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1. Introduction
Festivals around the world, such as the Spring Festival in China, the Independent Day in the United States, are often celebrated with fireworks/firecrackers. On the one hand, cities are beautifully illuminated through the displays, while concerns for air pollution problem also arise [1], [2]. As one high-intensity emission activity, fireworks burning can generate massive containments, such as SO$_2$, NO$_2$, and fine particular matters (PM$_{2.5}$) [3], [4]. The serious air quality deteriorations have been reported during the firework displays worldwide, and the varying compositions especially highly toxic metal exposed to firework plumes also present potential health hazards [5]. Hence, advancing
understandings on the effects of fireworks on PM$_{2.5}$ and consequent health risks can provide scientific evidence for effective pollution regulation.

China, where firework originally invented, is the world’s largest producer and consumer of fireworks. The traditions of fireworks/firecrackers (FF hereafter) burning to celebrate the Spring Festival have been widely documented to directly cause severe pollution episodes [6]. Meanwhile, the indirect impacts, e.g., re-suspended dust due to explosion, secondary processes affected by emitted metals have also been reported [7]. Although the physicochemical nature of PM$_{2.5}$ has been extensively characterized in FF periods, several issues still needed to be further addressed.

Firstly, the FF burning was not the only major source to trace metals during the festival. The Chinese Spring Festival (SF hereafter) presents unique holiday effects with reduced industrial and motor vehicle activities, and increased emissions as cooking and FF [8]. Thus, the accurate quantification of FF impacts is a great challenge due to such complex sources. Secondly, most works focused on major PM$_{2.5}$ components as sulfate, nitrate, whereas studies on toxic species, e.g., trace metals are very scare [9]. Thirdly, linking the adverse health impacts to various sources is of significance for effective control, while such source-specific risk assessments are still very limited.

Therefore, to properly assess the contribution of FF burning on trace elements and consequent health risks, a systematic campaign was conducted at Chifeng, China during February 2016, which span the Chinese Spring Festival. PM$_{2.5}$ samples were collected at urban and rural sites and 21 trace elements were analysed. The relative contribution of FF burning was then explored via positive matrix factorization (PMF). The source-attributed health risks were also assessed, which provide implications for air pollution control and precautions.

2. Material and methods

2.1. Sampling and laboratory analyses

The whole campaign covered from January 2016 to January 2017 with 24-hr integrated PM$_{2.5}$ samples collected by air samplers (Junray Instrument Co., Ltd, ZR-3930B) at the flow rate of 16.7 L min$^{-1}$. Overall, 50 samples from four urban sites and one rural around the Spring Festival (SF) were selected. Specifically, three-day continuous campaign (7 Feb to 9 Feb, as New Year’s Eve, January 1st, January 2nd in Chinese Lunar Calendar) were conducted, in which the intensive FF activities occurred. Besides, the before Spring Festival (bef-SF) and after Spring Festival (aft-SF) periods are designate as 13, 14, 26 Jan and 16, 19, 25 Feb of 2016, respectively.

The trace elements (Na, Mg, Al, P, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, Ba, Ti, Pb, Th, U) in PM$_{2.5}$ was determined using an inductively coupled plasma mass spectrometry (ICP-MS, Thermo Electron Co., Ltd. USA) with detailed analytical procedures in our previous work [10]. Hourly PM$_{2.5}$, PM$_{10}$ and meteorological parameters were provided by local environmental agency.

2.2. Receptor model

EPA PMF 5.0, a well-established multivariate statistical model was applied to quantify the sources to PM$_{2.5}$-bound metals. The Positive Matrix Factorization (PMF) was described in elsewhere [11]. Since the number of samples around the SF was less than that typically required by PMF (>100), we utilized the full year datasets for PMF runs. Total 19 analyzed trace elements were chosen, while species frequently below the detection limit were excluded. The total elemental mass was also introduced as “total variable” for factor scaling, and set as “weak” species.

2.3. Health risk assessment

The non-cancer and cancer risks exposed to trace metals were assessed using US Environmental Protection Agency (US EPA) human health risk assessment model. The average daily dose (ADD) through three major pathways, i.e., ingestion, dermal absorption, and inhalation were firstly estimated. Then, a Hazard Quotient (HQ) for non-cancer risks was calculated by dividing the daily dose to a
specific reference dose (RfD) as HQ = ADD/RfD. The Hazard Index (HI) combining all pathway for multiple species was obtained as Eq (1):

$$HI = \sum HQ_i \quad i = \text{As, Cd, Co, Cr(VI), Cu, Mn, Ni, Pb, Zn}$$

(1)

where RfD refers to a maximum permissible risk shown in Table 1, and HQ>1 indicates likely adverse health risks on human pollution.

The cancer risks (CR) is an estimation of the incremental probability of an individual developing cancer exposure to the potential carcinogen via inhalation:

$$CR = LADD \times SF$$

(2)

where LADD refers to the lifetime average exposure, SF refers to the slope factor. The acceptable or tolerable CR is in the range of 10^{-6} to 10^{-4} [12].

The levels of Cr(VI) are estimated as 1/7 of the total Cr [13]. All the exposure parameters were obtained from US EPA Risk Assessment Guidance or previous researches in China [14], [15].

3. Results and discussion

3.1. Dataset overview

The time series of hourly PM$_{2.5}$, PM$_{10}$ and meteorological conditions in February 2016 are given in Fig. 1. The average PM$_{2.5}$ levels during the SF holiday was 57.70 µg m$^{-3}$, with three days (8 February, 11 February, 12 February) surpassed the China National Ambient Air Quality Standard (75 µg m$^{-3}$, 24 h average). Several dramatic fluctuations in short-term with extremely peaks (>200 µg m$^{-3}$) were clearly observed, which were distinct to the normal diurnal pattern. Such major peaks as on 8 February (Chinese New Year, CNY), 12 February (the God of Wealth’s birthday) and 22 February (the Lantern Festival) all coincided with the FF burning traditions. On the CNY, the most explosive PM$_{2.5}$ growth lasted for 4 hours (00:00-04:00 am) with the maximum up to 471.0 µg m$^{-3}$. Meanwhile, the average ratio of PM$_{2.5}$/PM$_{10}$ (0.67±0.09) was higher than the average over the month (0.53±0.23), indicating more impacts on fine particles. Also noted that PM$_{2.5}$ elevations still lasted for 5 days with increases till 13:00 on 13 February, coincidently corresponding to a gradual increase of wind speed (~2 m/s to ~6 m/s). Similar long-lasting pollution episodes during the SF has been observed over China, suggesting the persistent health risks affected by FF events [8]. The filter-based PM$_{2.5}$ also showed significantly higher levels (63.06±37.00 µg m$^{-3}$) during the SF and no significant differences were identified between urban and rural sites over Chifeng (one-way ANOVA, p>0.1).

The total concentrations of analysed metals during the SF was 13.91 µg m$^{-3}$, which enhanced to totally accounted for 19.37% of PM$_{2.5}$. As shown in Fig. 2, K and Al increased to the most abundant elements, which increased to 16.78, 6.90 times of those in bef-SF period, respectively, with maximum up to 22.33 µg m$^{-3}$, and 6.74 µg m$^{-3}$ on the CNY. Potassium compounds as KNO$_3$, KClO$_3$ are the important oxidizers for fireworks, while aluminium is the most common fuel and also serves as one additive for producing bright silver sparks [2]. Similarly, Ba, Sr typically served as the tracers of fireworks to impart green and red colours increased by a factor of, 27.99, 23.75, respectively. Differently, elements as Ca, Ti, Mn, Zn, Pb showed comparable or lower levels during the SF, suggesting the impact of fireworks were less crucial. The mass fraction of Ca, which was most abundant on normal days, even decreased ~50%, ascribing to fewer construction activities on the holiday. Additionally, enhanced heavy metals as Pb (97.71 ng m$^{-3}$), As (5.31 ng m$^{-3}$), V (2.60 ng m$^{-3}$), Cd (1.41 ng m$^{-3}$) revealed the raised potential health risks to human health. Although chemicals as PbO$_2$, As$_2$S$_3$ are also used for fireworks, other sources, e.g., fossil fuel combustion, might also contribute notably [16].
3.2. Source contributions on trace metals
The most physically plausible result was the eight-factor solution and the factor of FF burning was successfully identified, with high abundances of Al, Mg, K, Ba, Sr, Cu in the profiles. It mainly represented the directly emitted species, e.g., K₂S originated from the gunpowder burning (2KNO₃+S+3C→K₂S+N₂+3CO₂). The significant contributions were merely observed on the SF with the maximum contributions (35.81 µg m⁻³) estimated on the CNY. Specifically, FF burning was the dominated contributor to PM₂.₅-bound metals, which comprising 71.34±24.94% of the total elemental masses during the SF. Even in rural site XS with fewer FF activities, this factor still accounted for 48.25% of PM₂.₅ masses on the CNY, further highlighting its significant impacts on both urban and rural area. As shown in Fig. 3, most Al, Ca, Ti, Mg, Sr, Ba, K, Co, Cr, Cu, and Pb were associated with contributions ranging from 32.96% to 98.33%. As for Na, Fe, As, Zn, Cd, limited effects from FF burning were found. Additionally, coal combustion contributed the most to heavy metals as As and Cd.

![Figure 1](image1.png)

![Figure 2](image2.png)

![Figure 3](image3.png)
3.3. Health effects of trace metals
The non-cancer risks (represented as HI) during the SF period were ~5 times of those in non-SF periods, while were still under safe limit (1). As for children, HI values (0.76) was greater than those to adults by approximately 6 times, suggesting that children are more sensitive to non-cancer effects. Moreover, the toxicity of those elements followed as As > Pb > Cd > Mn > Cu > Cr(VI) > Co > Zn > Ni with the ingestion pathway presented the most adverse effects. Significant enhanced cancer risk were also estimated (3.96×10⁻⁶), which was ~10 times of non-SF periods. The decreasing order of CR for toxic metals followed as As > Cd > Cr(VI) > Co > Ni.

The source-attributed risk assessments revealed that FF burning contributed to 28.35%, 12.64% of non-cancer risks to children and adults, respectively. Meanwhile, the FF factor was merely responsible for 11.32% of the total cancer risks. Also noted that the actual health effects from FF burning should be more severe because the risks exposed to other toxic species, e.g., polycyclic aromatic hydrocarbons were not included.

![Figure 4](image-url) The non-cancer risks to children (A) and cancer risks (B) respective to different sources during the non-SF and SF periods.

4. Conclusions
The PM₂.₅ pollutions were observed at Chifeng during the Spring Festive (57.70 μg m⁻³) with significant impacts from FF burning were confirmed. On the Festival Eve with the most intensive FF activities, PM₂.₅ dramatically increased (>400 μg m⁻³) within a few hours. Moreover, largely enhanced levels of trace metals were identified, totally contributing to 19.37% of PM₂.₅ during the SF. K and Al increased to the largest abundant metals. Ba and Sr as typical fireworks tracers also significantly increased (>20 times). The PMF-identified FF burning was the largest contributor to PM₂.₅-bound metals during the festival especially to Al, Ca, Ti, Mg, Sr, Ba, K, Co, Cr, Cu, and Pb (32.96% to 98.33%). Elevated actual health risks were also identified for both children (0.76) and adults (0.11) compared to non-SF period. The cancer risks (3.96×10⁻⁶) were also largely enhanced (~10 times) with As and Cd exerted the highest threats. Importantly, the factor of FF burning was estimated as one major contributor to HI for children (28.35%) and adults (12.64%) and also partly responsible to the elevated cancer risks (11.31%) during the SF. Those findings provide potential insights for effective firework regulation over China.

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