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# Individual metal-bearing particles in a regional haze caused by firecracker and firework emissions

Weijun Li [a,c,*], Zongbo Shi [b], Chao Yan [a], Lingxiao Yang [a], Can Dong [a], Wenxing Wang [a]

[a] Environment Research Institute, Shandong University, Jinan, Shandong 250100, China
[b] School of Geography, Earth and Environmental Sciences, University of Birmingham, UK
[c] State Key of Laboratory of Atmospheric Boundary Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

## HIGHLIGHTS

- TEM was used to observe the aged individual particles from firecrackers/fireworks during the Chinese New Year.
- Many fine metal-rich particles were emitted during fireworks and transported long distance.
- Emissions from fireworks/firecrackers can deteriorate air quality and cause a regional haze during the Chinese New year.

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## ABSTRACT

Intensive firecracker/firework displays during Chinese New Year (CNY) release fine particles and gaseous pollutants into the atmosphere, which may lead to serious air pollution. We monitored ambient $PM_{2.5}$ and black carbon (BC) concentrations at a regional background site in the Yellow River Delta region during the CNY in 2011. Our monitoring data and MOUDI images showed that there was a haze event during the CNY. Daily average $PM_{2.5}$ concentration reached 183 μg $m^{-3}$ during the CNY, which was six times higher than that before and after the CNY. Similarly, the black carbon (BC) concentrations were elevated during the CNY. In order to confirm whether the firecracker/firework related emission is the main source of the haze particles, we further analyzed the morphology and chemical composition of individual airborne particles collected before, during and after the CNY by using transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy (TEM/EDS). We found that sulfate and organic-rich particles were dominant in the atmosphere before and after the CNY. In contrast, K-rich sulfates and other metal (e.g., Ba-rich, Al-rich, Mg-rich, and Fe-rich) particles were much more abundant than ammoniated sulfate particles during the CNY. These data suggest that it was the aerosol particles from the firecracker/firework emissions that induced the regional haze episode during the CNY. In individual organic and K-rich particles, we often found more than two types of nano-metal particles. These metal-bearing particles also contained abundant S but not Cl. In contrast, fresh metal-bearing particles from firecrackers generated in the laboratory contained abundant Cl with minor amounts of S. This indicates that the firecracker/firework emissions during the CNY significantly changed the atmospheric transformation pathway of $SO_2$ to sulfate.



## 1. Introduction

Fireworks/firecrackers are frequently displayed throughout the world during ceremonies and traditional festivals. In China, the most intensive firecracker/firework event, which takes place throughout the country, occurs during the Chinese New Year (CNY) (the Spring Festival). In recent years, the size and variety of fireworks have increased markedly during national celebrations in rapidly developing China. The firework/firecracker displays cause severe regional air pollution, particularly high particulate pollution (Shen et al., 2009; Shi et al., 2011). As a result, many urban environmental bureaus issued health warnings during previous CNY celebrations. However, physical and chemical characteristics of air pollutants related to firework/firecracker displays are not well studied.

Fireworks/firecrackers contain various inorganic and organic chemicals, such as charcoal, sulfur, potassium, lead, aluminum, iron, and barium nitrate (Conkling, 1985; Steinhauser et al., 2008). Firework/firecracker displays can release gaseous pollutants (e.g., $SO_2$, $NO_2$, and $O_3$) and various fine particles (e.g., metals and organics) (Attri et al., 2001; Moreno et al., 2007; Wang et al., 2007; Godri et al., 2010). Pyrotechnic displays often cause severe air pollution events, such as those in Beijing, China (Wang et al., 2007); California, US (Liu et al., 1997); Valencia, Spain (Moreno et al., 2007); Diwali (Ravindra et al., 2003) and New Delhi (Agrawal et al., 2011), India; London, UK (Godri et al.,

* Corresponding author at: Environment Research Institute, Shandong University, Jinan, Shandong 250100, China.
*E-mail address:* liweijun@sdu.edu.cn (W. Li).

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2010); Malta (Camilleri and Vella, 2010) and Montréal, Canada (Joly et al., 2010). These short-term air pollution events often pose serious health hazards, especially for asthmatic children (Becker et al., 2000) and other respiratory-sensitive groups of the population. More recently, a positive and significant relationship was found between particulate oxidative burden and individual trace metals associated with fireworks/firecrackers, suggesting a potential negative impact of firework-emitted particles on human health (Godri et al., 2010).

Many studies have monitored air quality during firework displays and have investigated the chemical composition of aerosol particles using "bulk" techniques (Attri et al., 2001; Ravindra et al., 2003; Drewnick et al., 2006; Moreno et al., 2007; Wang et al., 2007; Shen et al., 2009; Godri et al., 2010). These studies generally showed that concentrations of water-soluble ions ($K^+$, $Cl^-$, and $SO_4^{2-}$), organic materials, and metals (e.g., Mg, K, Sr, Ba, Al, Cu, and Pb) in ambient aerosol particles were elevated during and shortly after the fireworks. By definition "bulk" techniques can determine the chemical composition of the total aerosol particle mass; they however cannot provide information on the properties of individual particles (Li and Shao, 2009). To date, characteristics of individual particles from firecracker/firework displays were rarely reported. However, morphology, size, and mixing properties of individual aerosol particles are critical in understanding their effects on human health and climate (Li et al., 2011). Moreover, knowledge of individual particles enables a direct tracing of those aerosol particles associated with fireworks/firecrackers.

Transmission electron microscopy (TEM) is a powerful tool to analyze internally mixed fine particles (Li et al., 2011). In the current study, we investigate the chemical composition and morphology of individual aerosol particles associated with fireworks/firecrackers during the CNY using TEM coupled with energy-dispersive X-ray spectrometry (EDS). Given their potential toxicity, we paid particular attention to what metals were present and how they were mixed with other aerosol species.

## 2. Experimental section

### 2.1. Sampling site description

The samples were collected at a rural site (38°03′N, 118°44′E, 3 m a.s.l) in the Yellow River Delta (YRD) in the northern part of Shandong Province, China. The YRD covers an area of 4167 $km^2$ and is an ecological reserve, which is part of China's national wetlands. The sampling site is approximately 13 km south-west of the Bohai Sea and 50 km north of Dongying City (population > 18 million). The influence of local air pollutant emissions on the site is limited to a few oil drilling stations and sparse villages in the wetland. In winter, air masses usually originate from the Chinese continent (Figure S1); long-range transport of particles has been identified as the major source of aerosol particles in this area. The site is often under the influence of regional pollution in North China.

### 2.2. Instrumentation

Thirteen $PM_{2.5}$ samples were collected on quartz filters by a MiniVol sampler (Ametrica, USA) with a constant airflow of 5 l $min^{-1}$. The samples were taken from 8:00 am to 7:30 am of the following day. The collected samples were immediately put in a polyethylene plastic box and stored in a refrigerator. The filters were weighed before and after sampling with an electronic microbalance (Sartorius-ME5, ±1 μg) after equilibrating over 24 h under constant temperature (20 ± 1 °C) and humidity (50 ± 2%). Mass concentrations of black carbon (BC) were measured continuously by an Aethalometer (Magee AE21).

### 2.3. TEM analysis

Aerosol particles were collected on copper TEM grids coated with carbon film (carbon type-B, 300 mesh copper, Tianld Co., China) using a single-stage impactor with a 0.5 mm diameter jet nozzle and an airflow rate of 1.0 l $min^{-1}$ (Li and Shao, 2009). The samples were collected before (27 January to 1 February), during (2 to 5 February), and after (6 to 8 February) the CNY (Table S1). In addition, we collected three source samples immediately after firecracker explosion from an experimental tank (80 (length) × 60 (width) × 50 cm (height)) in our laboratory. Detailed sampling information is listed in Table S1 of the supporting information.

Individual aerosol particles were analyzed with a JEM-2100 TEM operated at 200 kV. Elemental composition was determined semi-quantitatively by using an EDS that can detect elements heavier than C. Cu was excluded from the analyses because the TEM grids are made of Cu. The distribution of aerosol particles on TEM grids was not uniform, with coarser particles occurring near the center, and finer particles occurring on the periphery. Therefore, to ensure that the analyzed particles were more representative, five areas were chosen from the center and periphery of the sampling spot on each grid. Every particle in the selected area was analyzed. Through a labor-intensive operation, thousands of individual aerosol particles in the samples were analyzed. To understand the details of internally mixed aerosol particles, we also analyzed the composition of different components of individual particles, such as coatings, inclusions, and aggregations.

## 3. Results and discussion

### 3.1. Air pollution events during the CNY

The CNY holidays usually last four days from the end of December to early January of the Lunar Calendar. The most important day of the CNY celebration is the lunar New Year's Eve. In 2011, intensive firework and firecracker displays lasted from the evening of 2 February through to the following morning. In addition, many pyrotechnical displays for the CNY celebration took place throughout China during the CNY holidays (3 to 5 February).

Fig. 1 shows daily $PM_{2.5}$ and BC mass concentrations from 27 January to 9 February, 2011 at the rural background site. The daily $PM_{2.5}$ exhibited a high mass concentration with an average value of 183 μg $m^{-3}$ (range: 117–217 μg $m^{-3}$) during the CNY. This is six times higher than the average values before and after the CNY (Fig. 1). Similarly, BC concentrations were also elevated from 2 μg $m^{-3}$ before the CNY to 6 μg $m^{-3}$ during the CNY (Fig. 1). Furthermore, average $PM_{10}$ mass concentrations in most cities close to the YRD were elevated during the CNY (Figure S2). In addition, the visibility during the CNY was less than 10 km. These data suggest that there was a haze event during the CNY at the background site in the YRD. MODIS images provided further evidence that a regional haze occurred in East China (Figure S3). It should be noted that most industrial activity stops during the CNY and anthropogenic emissions (other than firework emissions) are at their lowest level on CNY eve. This suggests that the haze may be caused by the firework and firecracker emissions. In the following section, we will investigate the morphology and chemical composition of individual particles collected before, during and after the CNY in order to confirm the main source of the haze particles.

### 3.2. Composition, morphology, and mixing state of individual aerosol particles

We examined the morphology of 3616 particles using high-resolution TEM and analyzed chemical composition of 2771 particles using TEM/EDS. Fig. 2 shows different types of particles and their chemical compositions observed. Individual particles were classified based on the criteria in Li and Shao (2009). Sulfates (ammoniated), organic, fly ash, mineral, and soot were identified. We also identified K-rich, organic-rich, and metal particles (excluding K) during the CNY. At the background site, most of