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# Influence of fireworks displays on the chemical characteristics of $PM_{2.5}$ in rural and suburban areas in Central and East China

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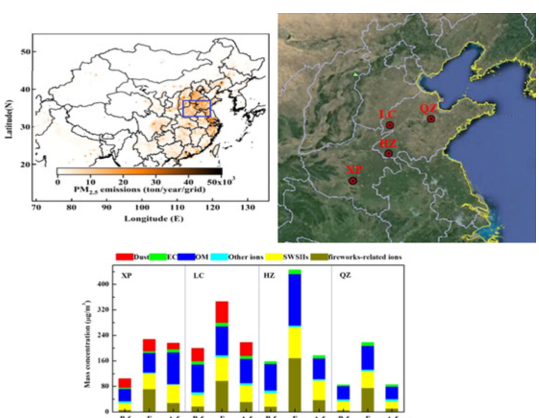
## HIGHLIGHTS

- Serious $PM_{2.5}$ pollution was found in rural and suburban areas of Henan and Shandong provinces.
- There was clear spatial variation in the main chemical components of $PM_{2.5}$ across the sampling areas.
- Firecrackers directly emitted $K^+$, $Cl^-$, $SO_4^{2-}$, K, Cl, S, Cu, Sr and other elements, and indirectly influenced $NO_3^-$ and $NH_4^+$.

## GRAPHICAL ABSTRACT

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## ABSTRACT

To explore the spatial and chemical characteristics of $PM_{2.5}$ pollution and the influence of fireworks displays on $PM_{2.5}$ and its chemical components in rural areas in Central and East China, $PM_{2.5}$ samples were collected at three rural sites and one suburban site in Henan and Shandong provinces during the 2016 Chinese New Year, and the chemical composition of $PM_{2.5}$, including water-soluble inorganic ions (WSIIs), organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC) and trace elements (TEs) was analysed. The concentrations of $PM_{2.5}$ at the four sites were significantly higher than the Grade I national standard of 35 μg/m$^3$, indicating serious $PM_{2.5}$ pollution in rural and suburban areas. The contributions of secondary WSIIs to total WSIIs at the four sites were lower than in urban areas. The TEs in XP and LC were significantly enriched in $PM_{2.5}$. A significant difference was found in the main chemical compositions of different sites. Fireworks displays directly increased the concentrations of $PM_{2.5}$ and many chemicals, especially $K^+$, $Cl^-$, K, Cl, S, Cu and Sr, and concentrations of $NO_3^-$ and $NH_4^+$ ions peaked after the fireworks period in the three rural sites, indicating the influence of firecrackers on the secondary formation of the precursors of $NO_2$. The ratio of WSOC/OC decreased during fireworks displays,

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indicating the direct influence of firecrackers on water insoluble organic matter. Fireworks-related ions were a key component of the aerosol at the four sites during fireworks displays, accounting for 28–38% of the total measured species.



## 1. Introduction

Atmospheric particulate matter (PM) pollution is recognised as a globally important environmental issue that has negative effects on human health, visibility, and the radiation balance of Earth's atmosphere. PM has been identified as carcinogenic by the International Agency for Research on Cancer (Loomis et al., 2013). In recent years, more and more studies have focused on short-term air quality degradation and the continuous adverse influence on human health.

Setting off fireworks and firecrackers is a celebratory tradition at popular fiestas all over the world, such as Bastille Day in France, Diwali in India, Independence Day in the USA, and the Lantern Festival in China. However, fireworks are an important source of PM and precursors such as $SO_2$, $NO_x$ and CO, which can contribute up to 29.66% of $PM_{2.5}$ (Tian et al., 2014a). The highest $PM_{2.5}$ concentration in 1 h has been shown to be nearly 1000 times the background level (10,000 μg/m$^3$) during exposure to firework plumes (Joly et al., 2010). High-intensity anthropogenic activities have also been shown to cause an increase in a number of harmful chemicals including colour-generating species such as Cu, Ba, Sr and Pb and Mg and oxidising agents such as chlorates, perchlorates and nitrates (Sarkar et al., 2010; Vecchi et al., 2008). Wang et al. (2007) reported that the concentrations of $Cl^-$, $SO_4^{2-}$ and $NO_3^-$ increased over five times in the lantern days than those in the normal days. Cheng et al. (2014) suggested that $K^+$ was 4.97 times higher during the fireworks period than that during non-fireworks periods. As fireworks activities tend to emit fine PM, which is easily inhaled during exposure to the smoke plume, a systematic and complete study of the chemical characteristics of the fine particles produced by fireworks activities was necessary.

China is the world's largest fireworks producing country, and firecracker displays are a traditional way for the Chinese to celebrate Chinese New Year all over the country. This folk-custom is very important for Chinese culture but simultaneously brings dangerous side effects such as fires, injury and air pollution. Han et al. (2014) suggested that the influence of fireworks on air quality lasts for more than 15 h and estimated that the amount of $PM_{2.5}$ produced from fireworks in Wuhan in February 2013 was more than 39.57 tons. Verma and Deshmukh (2014) suggested that a huge amount of mineral aerosol (90%), Pb (98%), TC (43%), Zn (28%), $NO_3^-$ (8%) and $SO_4^{2-}$ (3%) in $PM_{2.5}$ is produced by fireworks displays on Lantern Day. Thus far, almost all surveys of fireworks displays have focused on the determination of the concentration of chemical components in urban regions such as Beijing (Wang et al., 2007), Shanghai (Feng et al., 2012), Taiwan (Tsai et al., 2012), Wuhan (Han et al., 2014) and Nanjing (Kong et al., 2015). In recent years, the Chinese government has begun to realise the seriousness of the problem and has introduced a series of policies to regulate the times and places of burning in megacities such as Beijing and Shanghai. Unfortunately, the intensity of fireworks burning in suburban and rural areas, which are not covered by the policies, has increased year by year as farmers' standard of living has increased. Air pollution in rural areas, where the burning of solid fuel and biomass with old technology is common, is serious but overlooked due to a lack of monitoring instruments. Atmospheric research in rural areas before, during and after fireworks displays is important for the understanding of rural air quality at Chinese New Year and to provide valuable information on regional air pollution.

Henan and Shandong, the two most populous provinces in China, have huge amounts of $SO_2$, $NO_2$ and $PM_{2.5}$ emissions. And the contribution from rural areas cannot be ignored. In this study, four typical areas – one rural site in Henan province, and two rural and one suburban sites in Shandong province – were selected for the collection of $PM_{2.5}$ samples before, during and after New Year's Eve. The main chemical components, including water-soluble inorganic ions (WSIIs), organic (OC) and elemental carbon (EC), water-soluble organic carbon (WSOC) and trace elements (TEs) were analysed to explore the influence of fireworks displays on air quality and as possible sources of $PM_{2.5}$ in rural and suburban areas.

## 2. Materials and methods

### 2.1. Research and sampling areas

The geographical locations of the four sampling sites are shown in Fig. 1. Three sites (Xiping, Liaocheng and Heze) are located in rural villages, and the fourth (Qingzhou) is in a suburban area of Qingzhou city. The sampling site (33.32°N, 113.72°E) in Xiping (XP) lies in the middle of a village area that is home to about 400 people. The village is surrounded by farmland, about 100 m away from the nearest provincial road, and 40 km to the closest county town. The sampling site (34.77°N, 115.88°E) in Heze (HZ) is encircled by farmland and residential zones (about 3000 people), approximately 1.8 km away from the closest traffic road and 12 km to the nearest county town. The sampling site (36.37°N, 115.87°E) in Liaocheng (LC) lies to the east of a village of about 400 residents, which is surrounded by farmland, 17 km from LC city, and 300 m and 1.7 km away from the nearest rural highway and urban traffic main road, respectively. The sample site in Qingzhou (QZ) (36.72°N, 118.51°E), which is home to about 400 people, is surrounded by road and urban areas, close to a national highway (619 m away) with busy traffic, 436 m from the provincial road, and 3 km from QZ city. In the study regions, the residents generally use coal gas, corn stalks, wood and solid coal for cooking three times a day and for heating in winter.

Field research at the four sites was carried out from 5 to 14 February 2016. It rained often after 10 February; samples from rainy days were excluded. The sampling sites in the three rural villages were on the roof, ~4 m above the ground and ~1 m above the roof. The sampling sites in QZ were ~1.5 m above the ground. Four $PM_{2.5}$ samplers (Model TH-150A; Wuhan Tianhong Corporation, China) with a flow rate of 100 L/min were used to collect samples on quartz filters (1 μm pore size and 88 mm diameter, Pall Gelman Inc., USA, baked at 600 °C for 6 h before use). The flow of the four samplers was corrected before and after sampling. MiniVol™ Tactical Air Samplers (TAS-50, USA) at a flow rate of 5 L/min were used to collect $PM_{2.5}$ samples with polypropylene fibre filters (Ø47 mm, Whatman) in XP and LC for element analysis. The six samplers ran and stopped simultaneously.

The sampling periods were 08:00–19:30 and 20:00–07:30 except on 7 February (New Year's Eve), when the sampling period was adjusted to 08:00–16:30 and 17:00–07:30 Lunar New Year's Day to collect the smoke plume from fireworks. Ten samples from each site were used to study the chemical components of $PM_{2.5}$ in detail. Two field blanks from each site were obtained and analysed by using the same methods with samples. The influence of fireworks displays on the samples collected before New Year's Eve was negligible, so a hypothesis was built that the air pollution characteristics before the fireworks display period (before-f) can represent the general air pollution status in winter at the sample sites. In this paper, intensive fireworks displays happened on