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Heavy haze episodes in Beijing during January 2013: Inorganic ion chemistry and source analysis using highly time-resolved measurements from an urban site

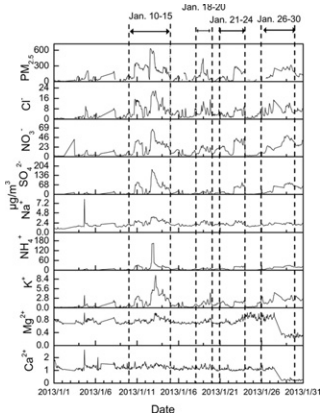
Bin Han [a], Rui Zhang [a,b], Wen Yang [a], Zhipeng Bai [a,*], Zhiqiang Ma [c], Wenjie Zhang [a]

[a] State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing, China
[b] Beijing Municipal Research Institute of Environmental Protection, Beijing, China
[c] Institute of Urban Meteorology, China Meteorological Administration, Beijing, China

HIGHLIGHTS

- Sulfate was one of key reasons of heavy haze episodes Beijing.
- RH and temperature played important roles in formation of SNA.
- Coal/biomass combustion, secondary nitrate and sulfate were sources of heavy haze.

GRAPHICAL ABSTRACT



Variation of $PM_{2.5}$ and ions concentrations in the sampling site in January 2013. The peak period of $PM_{2.5}$ are marked between the dote lines (μg/m³).

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ABSTRACT

The heavy air pollution that occurred in Beijing in January of 2013 attracted intense attention around the world. During this period, we conducted highly time-resolved measurements of inorganic ions associated with $PM_{2.5}$ at an urban site of Beijing, and investigated ion chemistry and potential sources. Hourly concentrations of Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+} were measured. Peak concentrations of SO_4^{2-} and NO_3^- were observed on the 10th–15th, 21st–24th, and the 26th–30th during this monitoring campaign. The percentages of SO_4^{2-} and NH_4^+ in total ion concentration increased with the enhancement of $PM_{2.5}$ concentrations, indicating that high concentrations of SO_4^{2-} and NH_4^+ may play important roles in the formation of haze episodes. The ratio of $[NO_3^-]/[SO_4^{2-}]$ was calculated, revealing that the sources of SO_4^{2-} would contribute more to the formation of $PM_{2.5}$ than mobile sources. Diurnal variations of SO_4^{2-}, NO_3^-, NH_4^+ (SNA) exhibited a similar pattern, with high concentrations at night and low levels during the day, revealing that meteorological conditions, such as mixing layer height, relative humidity, were likely to be responsible for high levels of SNA at night. The roles of meteorological conditions were further discussed in the formation of secondary inorganic ions. Relative humidity and temperature played key roles and exhibited positive correlations with secondary inorganic ions. An aerosol inorganics simulation model showed that SNA existed mainly in the aqueous phase during the sampling period. Furthermore, potential sources were identified by applying positive matrix factorization model. Secondary nitrate, secondary sulfate, coal combustion and biomass burning, as well as fugitive dust, were considered to be major contributors to total ions.

* Corresponding authors.

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1. Introduction

As the capital of China, Beijing (39.9°N, 116.4°E) has more than 20 million inhabitants distributed over 16,800 km^2. The city has been facing serious air pollution problems. During the past two decades, Beijing experienced a rapid increase in energy consumption, vehicle quantities, construction activities and urban sizes, which greatly enhanced the air pollution level of Beijing. Since 2000, air pollution control measures have been designed and implemented to reduce local emission and improve air quality. However, after the 2008 Olympic Games, the regional pollution and visibility in the whole area became worse (Zhang et al., 2010), and serious haze episodes occurred frequently (Cao et al., 2012; Huang et al., 2010; Sun et al., 2013; Wang et al., 2009). High concentrations of $PM_{2.5}$ were believed to be largely responsible for the deterioration of air quality and visibility. China's new National Ambient Air Quality Standard for $PM_{2.5}$ (75 μg/m^3 for a 24-h average and 35 μg/m^3 for the annual average) was issued in 2012 and will be implemented in 2016, which means more challenges arose to improve air quality in megacities (Hu et al., 2014).

Some previous studies found that secondary inorganic aerosols (SIA), such as sulfate, nitrate and ammonium (SNA), were the dominant ions in atmospheric $PM_{2.5}$ of Beijing (Cao et al., 2012; Duan et al., 2003; He et al., 2001; Pathak et al., 2009; Yao et al., 2002; Zhang et al., 2013). These components have effects on the hygroscopicity and acidity of aerosols, which are important factors in influencing aerosol-phase chemistry and the uptake of gaseous species by particles (He et al., 2001; Ocskay et al., 2006; Shon et al., 2012; Xue et al., 2011). While most of the previous studies used filter-based methods to collect PM samples, with each sample covering hours to days. Such low temporal resolution data have limitations when used for investigating secondary aerosol formation and time evolution. Highly time-resolved measurements have been reported for a wide range of $PM_{2.5}$ components, including inorganic compounds. Data from the high resolution instruments offer significant advantages over traditional 24-h integrated filter-based measurements (Vedantham et al., 2014). To investigate the impacts of control measures and regional transport, Gao et al. (2013) conducted highly time-resolved measurements of SO_4^{2-}, NO_3^-, and NH_4^+ in $PM_{2.5}$ simultaneously at an urban site and a downwind rural site in Beijing during the 2008 Olympics. Hu et al. (2014) monitored hourly water-soluble inorganic ions in $PM_{2.5}$ and gaseous precursors during June–November 2009 at an urban site in Beijing. The average mass concentration of the total water-soluble ion accounted for 38% of $PM_{2.5}$. SNA were the dominant ions. Kong et al. (2014) conducted hourly measurement of water-soluble inorganic ions in Shanghai, Hangzhou and Guangzhou from 2009 to 2011, and examined the relationship between SO_4^{2-} and NO_3^- based on the highly time-resolved measurement.

In January of 2013, Beijing, along with the rest of the mideastern region of China, experienced massive, severe air pollution episodes (Ouyang, 2013). Five haze pollution episodes were identified in the Beijing–Tianjin–Hebei (Jing–Jin–Ji) area, and the maximum hourly $PM_{2.5}$ mass concentrations in Beijing were 680 and 530 μg/m^3, respectively(Wang et al., 2014c). As an urgent countermeasure, some industries and construction activities were interrupted. The heavy haze episodes also led to some adverse health effects. The term "Beijing cough" has been in use since as early as the 1990s among foreigners, many of whom experienced chronic respiratory problems when they arrived in Beijing due to dry and polluted air. However, it did not become well-known until recently, when more health problems were directly attributed to the current heavy air pollution (Chen et al., 2013). Gao et al. (2015) assessed the health impacts during this period, showing that the $PM_{2.5}$ concentrations in January might cause 690 premature deaths, 45,350 cases of acute bronchitis and 23,720 asthma cases in the Beijing area. The results of the economic loss assessments suggest that the haze in January 2013 might lead to 253.8 million USD losses, accounting for 0.08% of the total 2013 annual gross domestic product (GDP) of Beijing.

Several recent studies have attempted to determine the reasons for these heavy haze episodes in Beijing by using satellite- and surface-based aerosol optical depth (AOD) observations (Che et al., 2014; Tao et al., 2014), numeric model simulation (Wang et al., 2014a; Wang et al., 2014b; Wang et al., 2014d; Zhang et al., 2015a; Zheng et al., 2015) and monitoring data (Ji et al., 2014; Tian et al., 2014; Wang et al., 2014c; Wang et al., 2015; Zhang et al., 2015b; Zhang et al., 2014; Zheng et al., 2015).

Wang et al. (2014c) and Ji et al. (2014) found that the unusual atmospheric circulation, the depression of strong cold air activities, the very unfavorable dispersion, and secondary aerosol accumulation were the main causes for haze episodes. Wang et al. (2015) also concluded that increasing relative humidity and stable synoptic conditions may lead to enhanced water uptake by the hygroscopic submicron particles and formation of secondary aerosols, which might be the main reason for the severity of the haze episode. Zheng et al. (2015) also concluded that secondary species, including organics, SNA, were the major constituents of $PM_{2.5}$ during this period. Model simulations indicated that regional transport played an important role in the formation of regional haze over the Beijing-Tianjin-Hebei area (Wang et al., 2014b; Wang et al., 2014d). Zhang et al. (2015a) used WRF-Chem to simulate the four winter haze episodes in 2010–2014, and suggested the emissions in Beijing were still the major contributor (61–77%) to surface-layer $PM_{2.5}$ over the urban area in recent winter episodes. Zhang et al. (2015b) indicated that the formation of secondary particulate matter, made important contributions to the haze occurrences in Beijing, and haze could accelerate the formation of secondary particle matter especially under high humidity conditions. By daily size-resolved filter sampling in the haze episodes, Tian et al. (2014) found that secondary inorganic aerosols (36%) and organic matter (26%) dominated the fine particle mass on heavily polluted days more so than on clear days (29% for secondary inorganic aerosols and 18% for organic matter). Most presently available reports focused on the reasons for the formation of haze episodes. Secondary aerosol formation, regional transport, and high relative humidity were considered to be potential main causes of haze episodes, with the explosive growth of secondary aerosol playing an important role. Better understanding the characterizations of secondary aerosol will be helpful in the analysis of the mechanisms of episode formation.

This study focuses on the inorganic part of secondary aerosols and other inorganic ions, considered by the earlier studies to be the major contributors to $PM_{2.5}$. We analyzed the highly time-resolved measurements of inorganic ions associated with $PM_{2.5}$ throughout the entire period of heavy haze episodes in January of 2013, and investigated the characterization of inorganic ions, the impact of meteorological factors, as well as potential sources and their contributions. The paper will improve our understanding of the haze episodes in Beijing.

2. Experiment and methods

2.1. Sampling site

The field campaign was conducted in January of 2013. The sampling site was on the rooftop of a building in the Chinese Research Academy of Environmental Sciences (CRAES, 40°2′29.46″N, 116°24′51.00″E), which is located 4 km north of the 5th Ring Road and 15 km from the city center as shown in Fig. 1.

2.2. Instruments

The hourly concentrations of Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} associated with $PM_{2.5}$ were simultaneously measured by an ambient ion monitor (Model URG 9000B, URG Corporation, USA). This instrument draws air in through a $PM_{2.5}$ sharp-cut cyclone at a volumetric flow-controlled rate of 3 L/min to remove the larger particles from the air stream. Then, the air stream is drawn through a liquid diffusion