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Characterization of the size-segregated water-soluble inorganic ions in the Jing-Jin-Ji urban agglomeration: Spatial/temporal variability, size distribution and sources

Xingru Li [a], Lili Wang [b], Dongsheng Ji [b], Tianxue Wen [b], Yuepeng Pan [b], Ying Sun [a], Yuesi Wang [b,*]

[a] Department of Chemistry, Analytical and Testing Center, Capital Normal University, Beijing 100048, China
[b] State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

HIGHLIGHTS

- The concentrations of water-soluble ions in the Jing-Jin-Ji urban agglomeration.
- The spatial variability of those compounds was discussed.
- The seasonal variations and size distributions of those compounds were discussed.
- The sources and formation mechanisms of secondary water-soluble ions were discussed.

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ABSTRACT

To investigate the characteristics of aerosols in north China, the samples of water-soluble ions, including anions (F^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}) and cations (NH_4^+, K^+, Na^+, Ca^{2+}, Mg^{2+}) in 8 size-segregated particle fractions, are collected using a sampler from Sep. 2009 to Aug. 2010 at four sites in urban areas (Beijing, Tianjin and Tangshan) and a background region (Xinglong) in the Jing-Jin-Ji urban agglomeration. High spatial variability is observed between the urban areas and the background region. The results of chemical composition analysis showed that secondary water soluble ions ($SO_4^{2-} + NO_3^- + NH_4^+$) (SWSI) composed more than half the total ions, and are mainly found in fine particles (aerodynamic diameters less than 2.1 μm), while Mg^{2+} and Ca^{2+} contributed to a large fraction of the total water-soluble ions in coarse particles (aerodynamic diameters greater than 2.1 μm and less than 9.0 μm). The concentrations of SO_4^{2-}, NO_3^- and NH_4^+ are higher in summer and winter and lower in spring and autumn. Mg^{2+} and Ca^{2+} are obviously abundant in winter in Beijing, Tianjin and Tangshan. In contrast, Mg^{2+} and Ca^{2+} are abundant in autumn in Xinglong. The SWSI showed a bimodal size distribution with the fine mode at 0.43–1.1 μm and the coarse mode at 4.7–5.8 μm, and had different seasonal variations and bimodal shapes. NH_4^+ played an important role in the size distributions and the formations of SO_4^{2-} and NO_3^-. Heterogeneous reaction is the main formation mechanism of SO_4^{2-} and NO_3^-, which tended to be enriched in the coarse mode of aerosol. The sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR) indicated high photochemical oxidation property over the whole Jing-Jin-Ji urban agglomeration.

1. Introduction

Atmospheric aerosols are among the most important classes of atmospheric pollutants. These aerosols can scatter or absorb both incoming solar radiation and thermal radiation emitted from the Earth's surface, directly changing the radiation balance (Bellouin et al., 2005; Buseck et al., 2000; Haywood and Boucher, 2000; Wang et al., 2009), and, thus, contributing to climate effects (Giorgi et al., 2002; Gustafson et al., 2011; Ramachandran and Kedia, 2010). Atmospheric aerosols, especially particles with small sizes, also have a serious impact on human health, increasing respiratory and cardiovascular diseases and reducing life expectancy (Andreae et al., 1998; Rupp, 2009; Shen et al., 2009; Vedal et al., 2009). Atmospheric particulate matter in urban areas is composed of a

* Corresponding author. Tel.: +86 01082080530.
E-mail addresses: lixr@dq.cern.ac.cn (X. Li), wys@dq.cern.ac.cn (Y. Wang).

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complex mixture of inorganic substances (e.g., metal ions, sulfate, ammonium, and nitrate) and hundreds of different organic compounds (Shrestha et al., 2010; Holzinger et al., 2010; Spencer et al., 2008). Water-soluble ions are major components of atmospheric aerosols, especially $PM_{2.5}$ (Lin et al., 2012; Zhao et al., 2011), and can compose up to 50–60% of the mass of $PM_{2.5}$ during haze period (Shen et al., 2009). Therefore, observations on the chemical composition of size-segregated water-soluble ions would be valuable for understanding their physical/chemical characteristics, their sources, and their behaviour and formation mechanisms.

In recent years, the Jing-Jin-Ji economic circle located in the center of the vibrant economic area of Northern China has become one of the world's fastest-developing economic zones (http://www.stats.gov.cn/tjsj/ndsj/2010/indexch.htm) (Lu et al., 2010). The Jing-Jin-Ji region consists of Beijing, Tianjin and the province of Hebei. Beijing, the political, economic and cultural center of China, has a population of nearly 20 million and 5 million mobile vehicles within an area of 16 800 km^2. Tianjin and Hebei, surrounding Beijing, have become China's workshop and a major manufacturing base for items such as oil, steel, cement, electronics, and a range of other heavy industrial products (Pathak et al., 2009). Various anthropogenic emissions, especially motor vehicle exhaust and volatile solvent usage in this region and industrial emissions in Tianjin and Hebei, have increased significantly and have been transported to impact the air quality within the region.

To further control air pollution in the Jing-Jin-Ji region over Northern China after the Olympics, the "Project of Atmospheric Combined Pollution Monitoring over Beijing and its Surrounding Areas" is organized by the Chinese Ecosystem Research Network (CERN), the Institute of Atmospheric Physics (IAP), and the Chinese Academy of Sciences (CAS) to provide in-depth understanding and a comprehensive record of aerosol particles and other air pollutants in this quickly developing region of China. Chemical compositions, size distributions and sources of aerosol particles are determined by the participation of 4 air-quality network stations to provide a comprehensive picture of the aerosol particles on a regional scale.

Mass size distributions can provide evidence for examining the formation pathways of water-soluble ions (Guo et al., 2010; Zhang et al., 2008). Non-sea salt sulphate and ammonium are found to be predominantly in the fine mode, while sea spray SO_4^{2-}, Cl^-, Na^+, Mg^{2+}, and Ca^{2+} are more abundant in the coarse fraction (Li et al., 2012; Miyazaki et al., 2012). The size distribution of NO_3^- is determined by the process through which they are formed and by the amount of ammonia (Lee et al., 2008; Wang et al., 2011; Zhuang et al., 1999). Apparently, the particle size distributions vary greatly with season, location, and air-mass origin (Ahrens et al., 2012; Fisseha et al., 2006; Zhang et al., 2008).

Many studies on the chemical compositions of PM_{10} and $PM_{2.5}$ in Beijing (Guo et al., 2010; He et al., 2001; Li et al., 2012; Song et al., 2012; Sun et al., 2012) and Tianjin (Li and Bai, 2009) have been reported in the last few years. Seasonal size distributions of water-soluble ionic aerosol compositions can help us understand the transformation, transport, and fate aerosols, but only a few studies have focused on the seasonal variations and size distributions of atmospheric particles in the Jing-Jin-Ji region (Li et al., 2012; YongQiao et al., 2005). Moreover, most of the previous studies in the Jing-Jin-Ji region are single-site measurements and concentrated on urban areas such as Beijing and Tianjin. There have been very few experimental studies characterizing the regional particle pollution of the Jing-Jin-Ji region (Jones, 1998). It is even rare to find a quantification of the pollution characteristics of the background area. Thus, it is necessary to study the size distributions of water-soluble ions in the Jing-Jin-Ji region.

In this study, we present analyses of the size characteristics of water-soluble inorganic ions and their sources from Sep. 2009 to Aug. 2010. The goal of this study is to understand the variations in the constituent concentrations, chemical composition, particle size distribution and formation of aerosols as well as the effects of pollution control measures on these variables. The results of this work will help researchers better understand the mechanisms of particulate matter pollution and abatement in megacities.

2. Experimental details

2.1. Sampling site

The network comprises four air-quality monitoring stations in the Jing-Jin-Ji urban agglomeration (Fig. 1), including three urban sites (Beijing, Tianjin, Tangshan) and a background site (Xinglong). The four sampling sites are selected to characterize the representative regional air pollution across North China according to the meteorological conditions, wind directions, urban size, industrial structure and ecotypes. The specific characteristics of the individual stations are described in detail in Table 1. To avoid interference from local air pollutants, all the sites are located far from specific point emission sources and are selected to be broadly representative of air pollution levels for a selected site.

2.2. Sampling collection

Two eight stage samplers (Andersen Series 20-800, USA) is used to simultaneously sample particles at a flow rate of 28.3 L min^{-1} with cutoff points of 0.43, 0.65, 1.1, 2.1, 3.3, 4.7, 5.8, and 9.0 μm from Sep. 2009 to Aug. 2010. Each set of the size-segregated samples is continuously collected for 24 h (in Xinglong for 48 h) on a bi-weekly basis. The substrates used in the Andersen sampler are quartz fiber filters and the mixed cellulose ester filters that are each 47 mm in diameter. The quartz fiber filters are wrapped with aluminum foil and pre-heated at 450 °C for 4 h to remove all organic material, then conditioned in a constant humidity desiccator (temperature: 25 °C; humidity: 50%) for 24 h before weighing. After sampling, the mixed cellulose ester filters are individually placed in plastic bags and then placed in a freezer (−20 °C) prior to transport and subsequent analysis (water-soluble ions and elements). The quartz fiber filters are wrapped with aluminum foil and returned to the desiccator (temperature: 25 °C; humidity: 50%) for 24 h. After weighing, the filters are stored in a freezer (−20 °C) prior to subsequent analysis (EC, OC and main organic compounds).

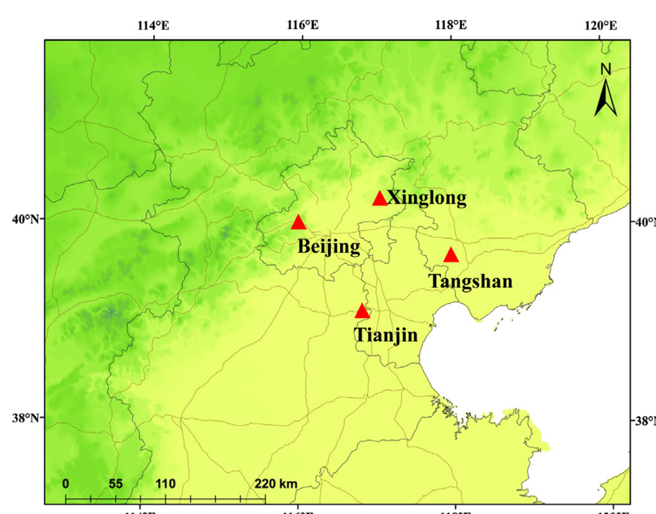

Fig. 1. The air-quality network in Jing-Jin-Ji city agglomeration.