Size-resolved aerosol water-soluble ions during the summer and winter seasons in Beijing: Formation mechanisms of secondary inorganic aerosols

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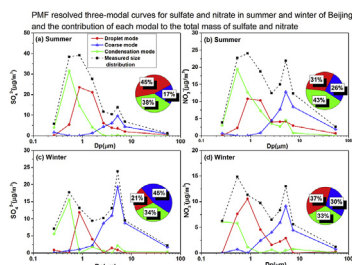
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HIGHLIGHTS

- SIA in the range of 0.65—2.1 μm exhibited the most dramatic increase in PM events.
- Dust particles enhance sulfate and nitrate concentration in fine and coarse particles.
- The formation of SIA in fine particles was mainly attributed to in-cloud process.
- The coarse mode nitrate formation was different from sulfate.

GRAPHICAL ABSTRACT

PMF resolved three-modal curves for sulfate and nitrate in summer and winter of Beijing, and the contribution of each modal to the total mass of sulfate and nitrate

ABSTRACT

Size-segregated water-soluble ionic species (WSIs) were measured using an Anderson cascade impactor from Jul. to Aug. 2008 and from Dec. 2009 to Feb. 2010 in urban Beijing. The results showed that fine particles (PM$_{2.1}$, Dp < 2.1 μm) accounted for ~49% (summer) and ~34% (winter) of the total particulate mass, and WSIs accounted for 23—82% of the mass concentration of PM$_{2.1}$. Secondary inorganic aerosols (SIAs, the sum of SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$) accounted for more than 30% of the fine particles, which were greatly elevated during particle pollution events (PM events), thereby leading to an alteration of the size distributions of SO$_4^{2-}$ and NO$_3^-$ to nearly single fine-mode distributions peaking at 0.65—2.1 μm. This finding suggests that heterogeneous aqueous reactions were enhanced at high RH values. SIAs also increased during dust events, particularly for coarse mode SO$_4^{2-}$, which indicated enhanced heterogeneous reactions on the dust surface. The positive matrix factorization (PMF) model was used to resolve the bulk mass size distributions into condensation, droplet, and coarse modes, representing the three major sources of the particles. The formation of SO$_4^{2-}$ was attributed primarily to in-cloud or aerosol droplet processes during summer (45%), and the heterogeneous reaction of SO$_2$ on mineral dust surfaces was an important formation pathway during winter (45%). The formation pathways of NO$_3^-$ in fine particles were similar to those of SO$_4^{2-}$, where over 30% were formed by in-cloud processes. This work provides important field measurement-based evidence for understanding the formation pathway of secondary inorganic aerosols in the megacity of Beijing.

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1. Introduction

Atmospheric aerosol is a mixture of primary particles generated from both anthropogenic and natural sources and secondary particles produced by gas-to-particle conversion processes. These particles are ubiquitously suspended in Earth's atmosphere, have a significant impact on air quality and visibility (Watson, 2002; Molina and Molina, 2004) and are detrimental to human health (Pope III et al., 2002; Liu et al., 2013). The size distribution and chemical composition of aerosols play essential roles in their transport, transformation, and removal mechanisms (Hinds, 1999). In the environment, the most important aerosol processes occur over the following size modes: Aitken (<0.1 μm), condensation (~ 0.1−0.5 μm), droplet (~ 0.5−2.0 μm), and coarse (>2.0 μm) (Seinfeld and Pandis, 2006). Droplet-mode particles are produced by in-cloud processing or aqueous reactions (Chen et al., 2016), whereas coarse-mode aerosols are typically derived from different sources than smaller aerosols.

Water-soluble ionic species (WSIs) are major components of atmospheric aerosols, and sulfate (SO_4^{2-}), nitrate (NO_3^-) and ammonium (NH_4^+) are the main secondary inorganic aerosol (SIA) components in WSIs. Previous research suggests that sulfate is mostly contained in the non-coarse modes, with the condensation-mode of sulfate produced by homogeneous gas-phase photochemical oxidation of SO_2 followed by gas-to-particle conversion (Seinfeld and Pandis, 2006) and the droplet-mode of sulfate produced by the condensation and coagulation of smaller particles, in-cloud processes and condensation-mode growth via the addition of sulfate and water (aerosol droplet process). The coarse-mode of sulfate can be attributed to heterogeneous reactions of SO_2 on mineral particles (Zhuang et al., 1999). In contrast, nitrate usually has a bimodal distribution, with peaks in both the fine and coarse modes. The formation of fine-mode nitrate is dominated by the reactions of gaseous HNO_3 or the heterogeneous hydrolysis of N_2O_5 on aerosol surfaces (Seinfeld and Pandis, 2006; Pathak et al., 2009), whereas coarse-mode nitrate is often observed because of the effect of chloride depletion of sea salt aerosols (Pierson and Brachaczek, 1998). Ammonium is mostly found in the fine mode, and it is chemically associated with sulfate and nitrate.

As the capital of China and a major megacity, Beijing has been experiencing serious air pollution due to the large quantity of air pollutants emitted by anthropogenic activities, e.g., traffic, industry, and power plants (Chan and Yao, 2008). In Beijing, a master plan (Blue Sky Project) was established in 1998 to improve the capital's poor air quality, and more than 200 environmental measures have been implemented in 14 stages until 2008, including moving high-polluting industries out of Beijing, replacing coal fuel with natural gas, and phasing out leaded gasoline (www.bjepb.gov.cn). Thus, the concentration of the primary air pollutant, PM_{10}, has been reported to have a decreasing trend (He et al., 2011), with an annual reduction rate at 1.7 μg m^{-3} yr^{-1} reported by Liu et al. (2015) from 2004 to 2012. Opposite to this improvement in air quality is the frequent severe haze episodes that have occurred mainly in winter. Sulfate, nitrate and ammonium typically compose approximately 30−40% of the total $PM_{2.5}$ mass annually (Cao et al., 2012) and over 50% of the $PM_{2.5}$ mass during certain heavy haze pollution episodes (Liu et al., 2016). The large fraction of the SIA concentration in $PM_{2.5}$ indicates that its formation is essential to the formation of haze. However, large amounts of SIAs were not reproduced in a modelling study of the haze events on the North China Plain (Gao et al., 2016a), which was likely caused by missing formation mechanisms in the current models, including heterogeneous chemistry (Gao et al., 2016b). Determination of the size distributions of aerosol WSIs can help understand aerosol transformation, transport, and fate, but only a few studies have focused on particle size distributions in Beijing (Yao et al., 2003; Hu et al., 2005; van Pinxteren et al., 2009; Guo et al., 2010a; Huang et al., 2016). Moreover, most of the previous studies in Beijing have focused only on single season measurements, and distinctive seasonal variations due to different meteorological and anthropogenic activities have rarely been discussed (Zhang et al., 2013; Huang et al., 2016; Shen et al., 2016).

In this study, size-resolved samples were collected by an Anderson cascade impactor at an urban site during summer and winter campaigns. The size-resolved characteristics of particle masses and WSIs were investigated to explore possible formation pathways of secondary compounds.

2. Experimental methods

2.1. Aerosol sampling

An Anderson cascade impactor (Anderson Series 20-800, USA) was used to collect size-segregated samples with nominal cut sizes of 9 (inlet), 0.43, 0.65, 1.1, 2.1, 3.3, 4.7, 5.8, 9.0 and 50 μm. The sampler was located on the rooftop of a two-story building in the courtyard of the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences (CAS). The observation site is located between the north 3rd Ring Road and north 4th Ring Road, which is an area under the influence of residential, traffic, and construction emissions and could be representative of urban Beijing. Ambient air was sampled at approximately 8 m above ground, and the sampler was operated at a flow rate of 28.3 L min^{-1}. The flow rate was checked before and after every sampling event. Two sampling campaigns were conducted in Beijing in the summer season (July-August 2008) and winter season (December 2009−February 2010). Sampling was conducted for 23.5 h, starting at 10:00 a.m. each day and ending at 09:30 the next day. All samples were collected onto mixed cellulose ester filters with diameters of 81 mm. Forty-two sets of samples and 20 sets of samples were obtained in the summer and winter campaigns, respectively. A set of field blank samples was also collected in each season by loading the sampler for the same sampling duration but without pulling air through the sampler.

2.2. Chemical analysis

After sampling, the filters were individually placed in petri dishes and stored at −20 °C immediately before analysis. All filters were then weighed before and after sampling using a micro-electronic balance with a reading precision of 10 μg after 48 h of equilibration inside a constant temperature and humidity chamber (RH = 50%, T = 25 °C). All procedures were strictly quality controlled to avoid any possible contamination of the samples. The size-segregated samples were analysed for water-soluble ionic species. One-quarter of each filter substrate was extracted with 25 mL deionized water in a PET vial for 30 min. After passing through microporous membranes with a 0.22 μm pore size, the extracted solutions were analysed via an ion chromatograph (Dionex ICS-90, USA). The anions (Cl$^-$, SO_4^{2-} and NO_3^-) were determined by ion chromatography with an AS19 analytical column (2 × 250 mm^2, Dionex), whereas the cations (NH$_4^+$, K$^+$, Na$^+$, Ca^{2+} and Mg^{2+}) were analysed via an IC system with a CS12A analytical column (2 × 250 mm^2, Dionex). A weak base gradient eluent (3.5 mmol L^{-1} Na$_2$CO$_3$; 1 mmol L^{-1} NaHCO$_3$) was used for anion detection, whereas a weak acid eluent (22 mmol L^{-1} methane sulfuric acid (MSA)) was used for cation detection. Before performing a targeted sample analysis, a standard solution and blank test were performed, and the correlation coefficient of the standard samples was more than 0.999. The detection limits for all anions