



Seasonal variation and secondary formation of size-segregated aerosol water-soluble inorganic ions during pollution episodes in Beijing



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ABSTRACT

Particulate matter (PM) pollution is a serious issue that has aroused great public attention in Beijing. To examine the seasonal characteristics of aerosols in typical pollution episodes, water-soluble inorganic ions (SO_4^{2-} , NO_3^- , NH_4^+ , Cl^- , K^+ , Na^+ , Ca^{2+} and Mg^{2+}) in size-segregated PM collected by an Anderson sampler (equipped with 50% effective cut-off diameters of 9.0, 5.8, 4.7, 3.3, 2.1, 1.1, 0.65, 0.43 μm and an after filter) were investigated in four intensive campaigns from June 2013 to May 2014 in the Beijing urban area. Pronounced seasonal variation of TWSIs in fine particles (aerodynamic diameter less than 2.1 μm) was observed, with the highest concentration in summer ($71.5 \pm 36.3 \mu\text{g}/\text{m}^3$) and the lowest in spring ($28.1 \pm 15.2 \mu\text{g}/\text{m}^3$). Different ion species presented different seasonal characteristics of mass concentration and size distribution, reflecting their different dominant sources. As the dominant component, SO_4^{2-} , NO_3^- and NH_4^+ (SNA) in fine particles appeared to play an important role in the formation of high PM pollution since its contribution to the TWSIs and $\text{PM}_{2.1}$ mass increased significantly during pollution episodes. Due to the hygroscopic growth and enhanced secondary formation in the droplet mode (0.65–2.1 μm) from clean days to polluted days, the size distribution peak of SNA in the fine mode tended to shift from 0.43–0.65 μm to 0.65–2.1 μm . Relative humidity (RH) and temperature contributed to influence the secondary formation and regulate the size distributions of sulfates and nitrates. Partial correlation analysis found that high RH would promote the sulfur and nitrogen oxidation rates in the fine mode, while high temperature favored the sulfur oxidation rate in the condensation mode (0.43–0.65 μm) and reduced the nitrogen oxidation rate in the droplet mode (0.65–2.1 μm). The $\text{NO}_3^-/\text{SO}_4^{2-}$ mass ratio in $\text{PM}_{2.1}$ (73% of the samples) exceeded 1.0, suggesting that vehicle exhaust currently makes a greater contribution to aerosol pollution than stationary sources in Beijing.

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1. Introduction

Beijing is one of the most economically developed regions in China, with a population of more than 21 million and a vehicle fleet of approximately 5.4 million (Beijing Statistical Yearbook, 2014). In response to the rapid economic growth, population expansion, and sharp increase in motor vehicle numbers in Beijing and its surrounding industrialized areas (e.g., Tianjin, Hebei, Shandong, and Shanxi), emissions from anthropogenic sources have substantially increased and particulate pollution events have been frequently observed in recent years (Zhang et al., 2014; Zhao et al., 2013a). For example, in January 2013, extremely severe, persistent haze occurred in eastern and central China, raising considerable public concern (Wang et al., 2013b, 2014; Zhang et al., 2014). According to the statistics, a total of five haze pollution episodes occurred in this month, with the maximum hourly $\text{PM}_{2.5}$ mass concentration in Beijing even reaching $680 \mu\text{g}/\text{m}^3$ (Wang et al., 2013b). Lu et al.

(2013) reported January 2013 to be the haziest air pollution month in the past 60 years in Beijing.

Haze pollution is characterized by an elevated amount of fine particles, which have important effects on visibility, radiative forcing, and the deposition of acids and nutrients to ecosystems (Sun et al., 2013b; Ulbrich et al., 2009). The scattering effect of fine particles is the most important factor influencing visibility; the scattering coefficients of aerosols have been shown to account for more than 85% of light extinction coefficients in Beijing and surrounding areas (Tian et al., 2015; Yan et al., 2008; Zhao et al., 2013a). Meanwhile, human health concerns arise from particulate matter, since fine particles can penetrate deeply into the lungs, leading to adverse effects on the cardiopulmonary system (Pope and Dockery, 2006). Particulate matter (PM) is a mixture of a variety of chemical species (e.g., water-soluble inorganic ions, organic matter, black carbon, and crustal matter) originated from natural and anthropogenic sources (Sun et al., 2004). Water-soluble inorganic species are major components of PM, accounting for one third or more of fine particles (Kong et al., 2014; Zhao et al., 2013a). Systematic analysis of water-soluble ions has been carried out in many studies in Beijing. It has been commonly observed that secondary inorganic ions (SO_4^{2-} ,

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NO_3^- and NH_4^+) dominate the water-soluble ions and are considered as important contributors to the issue of visibility impairment (Jung et al., 2009; Wang et al., 2015b). In addition, previous results have also shown that secondary inorganic species play an enhanced role in haze formation, as suggested by their elevated contributions during haze episodes in Beijing (Sun et al., 2012, 2014b; Tian et al., 2014; Zhang et al., 2014). However, most previous studies mainly focused on the average conditions or examined pollution episodes that specifically took place only during one or two seasons. The typical pollution characteristics of water-soluble species throughout all four seasons have seldom been compared or analyzed comprehensively in Beijing. In addition, water-soluble ions in integrated particles, such as $\text{PM}_{1.0}$, $\text{PM}_{2.5}$, PM_{10} and total suspended particles, have been investigated generally, but few studies have examined the mass size distribution, which strongly affects the optical properties of PM (Contini et al., 2014; Tang, 1996) and could provide valuable information about particle formation, conversion, transportation and removal processes (Liu et al., 2008). Some studies reported that secondary sulfates and nitrates often exhibited a sharp increase in the droplet mode when fine particle pollution occurred and the concentration peak for fine mode particles shifted to a larger size (Sun et al., 2013b; Tian et al., 2014; Wang et al., 2012). The remarkable secondary formation of droplet-mode sulfate and nitrate was primarily attributed to the enhanced heterogeneous aqueous transformation from SO_2 and NO_x under high relative humidity (RH) during haze episodes.

To better understand the development process of particle pollution, size-segregated aerosol sampling was performed at an urban site in Beijing in this study. The samples were collected in four intensive campaigns and were expected to reflect the seasonal pollution characteristics of water-soluble ions, including changes in the components and particle size evolution in the pollution process. Furthermore, the correlation of sulfur and nitrogen oxidation rates with relative humidity and temperature were investigated to clarify the dominant meteorological factors affecting the secondary formation of sulfate and nitrate in different size fractions.

2. Methods

2.1. Collection of size-segregated particles

Four sampling campaigns, each of 11 consecutive days, were carried out across four seasons in Beijing: summer sampling from June 19–July 2, 2013; autumn sampling from October 24–November 4, 2013; winter sampling from January 8–January 19, 2014; and spring sampling from April 26–May 7, 2014. Sample collection was performed on the rooftop of a two-story building located in the courtyard of the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences (CAS). The observation site was located between the north 3rd Ring Road and north 4th Ring Road, an area under the influence of residential housing, traffic, and construction emissions and could be considered representative of urban Beijing. Ambient air was sampled at approximately 8 m above ground.

During observation, size-segregated PM samples were collected daily (beginning at 10:00 am each day and ending at 09:30 the following day) using a cascade impactor (Anderson Series 20-800, USA) at a flow rate of 28.3 L/min with cut-off points as 9.0, 5.8, 4.7, 3.3, 2.1, 1.1, 0.65 and 0.43 μm aerodynamic diameter. An after filter collected all particles < 0.43 μm . All the samples were collected onto cellulose membranes, 81 mm in diameter. After sampling, the filters were individually placed in petri dishes and stored at -20°C immediately before analysis. All the filters were weighed before and after sampling using a micro-electronic balance with a reading precision of 10 μg after a 48-h equilibration inside a constant temperature (25 $^\circ\text{C}$) and humidity (50%) chamber. The airflow rate of the sampler was calibrated before and after the sampling to ensure that the instrument was working at the

specified flow rate. All the procedures were strictly quality-controlled to avoid any possible contamination of the samples.

2.2. Ion analysis

A quarter of each sample was ultrasonically extracted with 25 mL deionized water (specific resistivity of 18.2 $\text{M}\Omega/\text{cm}$) for 30 min. After passing through microporous membranes of 0.22 μm pore size, the extracted solutions were analyzed using an ion chromatograph (IC) system (Dionex ICS-90, USA). The anions (Cl^- , SO_4^{2-} and NO_3^-) were determined by the IC system with an AS14A 4×250 mm analytical column, while the cations (NH_4^+ , K^+ , Na^+ , Ca^{2+} and Mg^{2+}) by the same IC system with a CS12A 4×250 mm column. Sample volume of 100 μL was used for both anion and cation analyses, respectively. Before analysis of the samples to be tested, external standard solutions (Merck, Germany) were used for making the standard curve, and correlation coefficients greater than 0.999 were required. The detection limits of the methods for the eight ions measured were all lower than 0.03 $\mu\text{g}/\text{m}^3$. The relative standard deviation was less than 5% for the reproducibility test.

2.3. Gaseous pollutants and meteorology data

Commercial instruments from Thermo-Fisher Scientific, USA were used to measure gaseous pollutants, such as O_3 (Model 491), $\text{NO}/\text{NO}_2/\text{NO}_x$ (Model 421), CO (Model 481) and SO_2 (Model 431). $\text{PM}_{2.5}$ was measured using a tapered-element oscillating microbalance method (R&P TEOM 1405DF, USA). Meteorological parameters, including ambient temperature, RH, wind direction and wind speed were observed using an automatic meteorological observation instrument (Milos520, Vaisala, Finland), located at the 8 m measurement height.

3. Results and discussion

3.1. Seasonal variation of water-soluble ions

3.1.1. Mass concentrations of water-soluble ionic species

Fig. 1(a, b) shows the hourly meteorological data, including temperature, RH, precipitation, wind direction and wind speed during the four seasons in Beijing. During the campaign, the temperature and RH were highest in summer, and lowest in winter. No precipitation occurred during the autumn and winter periods. The hourly concentration of $\text{PM}_{2.5}$ is given in Fig. 1(c), showing that high $\text{PM}_{2.5}$ loading usually occurred under stable synoptic conditions (e.g., high RH, low wind speed).

Since a cut-off size of 2.5 μm is not available in an Anderson sampler, 2.1 μm was chosen to separate the particles into fine and coarse particles. Therefore, $\text{PM}_{2.1}$ and $\text{PM}_{2.1-9.0}$ were presented as the fine and coarse particle fractions, respectively. The average concentration of $\text{PM}_{2.1}$ was $146.7 \pm 73.2 \mu\text{g}/\text{m}^3$, $143.2 \pm 86.0 \mu\text{g}/\text{m}^3$, $138.2 \pm 114.6 \mu\text{g}/\text{m}^3$ and $86.9 \pm 38.7 \mu\text{g}/\text{m}^3$, comprising around 61.0%, 54.2%, 55.0% and 43.0% of the $\text{PM}_{9.0}$ mass concentration during the summer, autumn, winter and spring intensive campaigns, respectively. The total water-soluble ions (TWSIs) were concentrated mainly in fine particles, averaging $53.8 \pm 39.2 \mu\text{g}/\text{m}^3$ in $\text{PM}_{2.1}$ and $22.2 \pm 9.5 \mu\text{g}/\text{m}^3$ in $\text{PM}_{2.1-9.0}$ during the campaign and contributing 41.8% and 21.4% of the $\text{PM}_{2.1}$ and $\text{PM}_{2.1-9.0}$ aerosol mass, respectively. This observation is consistent with the predominance of insoluble mineral dust in coarse particles observed by Kumar and Sarin (2010). Due to the continuous changes in source emissions, meteorology, photochemical reactions, planetary boundary layer heights, regional transport, etc. (Sun et al., 2012), the inorganic species showed temporally dynamic variations (Fig. 2). Seasonal variation of water-soluble ionic concentrations was also significant, with the average concentration of TWSIs in fine particles being higher in summer ($71.5 \pm 36.3 \mu\text{g}/\text{m}^3$) and autumn ($67.7 \pm 45.5 \mu\text{g}/\text{m}^3$) than in winter ($47.9 \pm 40.7 \mu\text{g}/\text{m}^3$) and spring ($28.1 \pm 15.2 \mu\text{g}/\text{m}^3$), constituting 48.7%, 47.3%, 34.6% and 32.3% of the $\text{PM}_{2.1}$ mass concentration, respectively. The smallest contribution of TWSIs to $\text{PM}_{2.1}$ mass in spring was probably

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