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JES JOURNAL OF ENVIRONMENTAL SCIENCES www.jesc.ac.cn

Seasonal variations and size distributions of water-soluble ions in atmospheric aerosols in Beijing, 2012

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ARTICLE INFO

Article history:
Received 11 October 2014
Revised 11 December 2014
Accepted 14 January 2015
Available online 28 May 2015

Keywords:
Water-soluble ions
Size distribution
Hazy day
Foggy day
Beijing

ABSTRACT

The characteristics of water-soluble ions in airborne particulate matter in Beijing were investigated using ion chromatography. The results showed that the total concentrations of ions were 83.7 ± 48.9 μg/m^3 in spring, 54.0 ± 17.0 μg/m^3 in summer, 54.1 ± 42.9 μg/m^3 in autumn, and 88.8 ± 47.7 μg/m^3 in winter, respectively. Furthermore, out of all the ions, NO_3^-, SO_4^{2-} and NH_4^+ accounted for 81.2% in spring, 78.5% in summer, 74.6% in autumn, and 76.3% in winter. Mg^{2+} and Ca^{2+} were mainly associated with coarse particles, with a peak that ranged from 5.8 to 9.0 μm. Na^+, NH_4^+ and Cl^- had a multi-mode distribution with peaks that ranged from 0.43 to 1.1 μm and 4.7 to 9.0 μm. K^+, NO_3^-, and SO_4^{2-} were mainly associated with fine particles, with a peak that ranged from 0.65 to 2.1 μm. The concentrations of Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, Cl^-, NO_3^- and SO_4^{2-} were 2.69, 2.32, 1.01, 4.84, 16.9, 11.8, 42.0, and 44.1 μg/m^3 in particulate matter (PM) on foggy days, respectively, which were 1.4 to 7.3 times higher than those on clear days. The concentrations of these ions were 2.40, 1.66, 0.92, 4.95, 17.5, 7.00, 32.6, and 34.7 μg/m^3 in PM on hazy days, respectively, which were 1.2–5.7 times higher than those on clear days.

Introduction

For several years, atmospheric aerosols have received considerable attention because of their effects on human health, visibility, and global climate change (Cheng et al., 2011; Jung et al., 2009; Sheffield et al., 2011; IPCC, 2007). In fact, the chemical composition, particularly the size distributions of the chemical species, represents a key tool for understanding both anthropogenic and natural particle sources, and for characterizing the atmospheric chemical processes in which they are involved (Braziewicz et al., 2004; Karar and Gupta, 2007). Epidemiological studies have found that exposure to elevated concentrations of fine particulate matter (PM) is associated with adverse health effects (Dominici et al., 2005; Ostro et al., 2009). The smallest particles (ultrafine particles with diameters less than 100 nm) showed the ability to cross cell membranes (Li et al., 2003), which may influence their health effects. The size distribution of fine PM can provide information about the chemical and the physical processes affecting aerosol concentrations and compositions as they are transported in the atmosphere (Cabada et al., 2004). Recently, it has been shown that source apportionment of particle number populations can be successfully performed by statistically analyzing the size distributions (Dall'Osto et al., 2012).

According to relevant studies on aerosols, airborne ionic species are responsible for a large proportion of the visibility

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http://dx.doi.org/10.1016/j.jes.2015.01.025
1001-0742/

decrease and cloud formation in the air (Cheng et al., 2011; Jung et al., 2009; Lee and Sequerira, 2002). They can also play a major role in the acidification of precipitation and affect climate change (Khoder and Hassan, 2008). Water-soluble inorganic ions are the major components of atmospheric aerosols and can compose up to 60% to 70% of the total suspended PM mass (Ali-Mohamed, 1991; Wang and Shooter, 2001). The size distributions of water-soluble ions are basic and crucial characteristics of the particles, which provide detailed information on mode distributions and also provide evidence of particulate pollutant formation and transformation in the atmosphere.

Beijing has been experiencing heavy air pollution in the past two decades, with PM as one of the top pollutants (Chan and Yao, 2008). The hygroscopic growth of aerosol particles further increases the effect on atmospheric visibility (Quan et al., 2011). The situation is more serious on hazy and foggy days, which is a result of the excess PM in the atmosphere due to emission from anthropogenic sources and gas-to-particle conversion (Watson, 2002). The PM sources in Beijing include local primary emissions (Hao et al., 2005), secondary formation (Wang et al., 2005; Li et al., 2006), and regional transport (Chen et al., 2007; Streets et al., 2007). Many studies on the chemical compositions of PM10 and PM2.5 in Beijing (Guo et al., 2010; Song et al., 2012; Sun et al., 2012) have been reported in the last few years. Certain studies have focused on the seasonal variations and size distributions of atmospheric particles in the same area (Li et al., 2012; Sun et al., 2014).

In the present study, we conducted a four-season monitoring program to measure the water-soluble ions in PM and investigate the size distributions and characteristics during clear, hazy, and foggy days in Beijing. The present study can provide useful information for establishing aerosol pollution control strategies.

1. Materials and methods

1.1. Sampling

The National Research Center for Environmental Analysis and Measurement (NERC) site is located on the campus of the National Research Center for Environmental Analysis and Measurement in northeast Beijing, as shown in Fig. 1.

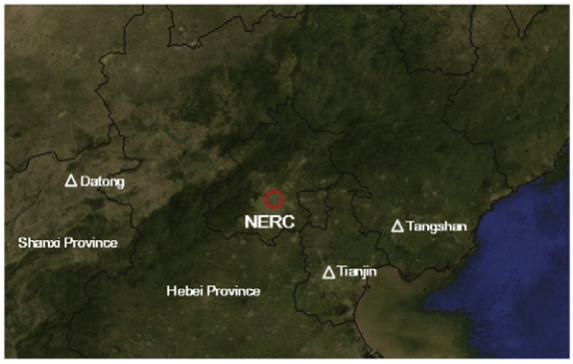

Fig. 1 – Location of National Research Center for Environmental Analysis and Measurement (NERC) site.

Instruments were installed about 40 m above ground on the office building roof of the National Research Center for Environmental Analysis and Measurement. Office and residential areas surround the NERC site, and the Fourth Ring Road, one of the roads with the heaviest traffic in northeast Beijing, is 50 m north of NERC station.

PM samples were collected with an eight-stage low pressure impactor (20–800, Thermo Fisher Scientific, USA) in spring (9–22 April, 2012), summer (3–16 August, 2012), autumn (13–26 October, 2012), and winter (14–27 January, 2013). A total of 504 PM samples and 56 blank samples were collected. Mixed cellulose ester filter substrates (41, Thermo Fisher Scientific, USA) were employed in all stages, and a flow rate of 28.3 L/min was used. The 50% cut-off diameters (D50) were 9.0, 5.8, 4.7, 3.3, 2.1, 1.1, 0.65, and 0.43 μm. The sampling time was 24 hr (from 8:00 am to 8:00 am of the following day). After sampling, the filters were individually placed into plastic bags and into a freezer at −20°C until transport and subsequent analysis.

1.2. Method

1.2.1. Ion analysis

Half of each sample and a blank were ultrasonically extracted using 25 mL of deionized water (deionized H_2O, 18.2 MΩ/cm resistivity). After passing each extracted sample through a microporous membrane (pore size = 0.45 μm, diameter = 25 mm, Pall, USA), three anions (SO_4^{2-}, NO_3^-, Cl^-) and five cations (NH_4^+, Ca^{2+}, Na^+, Mg^{2+}, K^+) were analyzed by ion chromatography (ICS-90, Dionex, USA). This system was outfitted with a separation column (Dionex AS14A for anions and CS12A for cations), a guard column (Dionex AG14A for anions and CG12A for cations), and a conductivity detector (DS5, Dionex, USA). A gradient weak base eluent (3.5 mmol/L Na_2CO_3; 1 mmol/L $NaHCO_3$) was used for anion detection, while a weak acid eluent (22 mmol/L methanesulfonic acid (MSA)) was used for cation detection. The detection limits for eight ions, calculated as three times the standard deviations of seven replicate blank samples, are all lower than 0.25 μg/m^3. Quality assurance was routinely conducted using standard reference materials (125052, Merck Co., USA). Data from blank samples was subtracted from the corresponding sample data after analysis (Zhang et al., 2011).

1.2.2. Meteorological data

An automatic weather station was placed 10 m away from the samplers. Meteorological parameters (Fig. 2), including air temperature, wind speed, air pressure, and relative humidity, were measured simultaneously. The average temperature was 18.0°C in spring, 26.7°C in summer, 12.1°C in autumn, and −3.1°C in winter. The average wind speed was 2.4 m/sec in spring, 1.5 m/sec in summer, and 1.4 m/sec in both autumn and winter. The average atmospheric pressure was 1005.6 hPa in spring, 1003.7 hPa in summer, 1014.3 hPa in autumn, and 1024.1 hPa in winter. The average relative humidity was 49.2% in spring, 72.2% in summer, 62.5% in autumn, and 64.2% in winter.

1.2.3. Trajectory cluster analysis

In order to evaluate and compare circulation patterns, two-day back-trajectories following 3D wind components were calculated