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Characteristics of atmospheric single particles during haze periods in a typical urban area of Beijing: A case study in October, 2014

Lang Liu[1], *Yanli Wang*[1], *Shiyong Du*[2], *Wenjie Zhang*[1], *Lujian Hou*[2], *Sverre Vedal*[1,3], *Bin Han*[1], *Wen Yang*[1], *Mindong Chen*[4], *Zhipeng Bai*[1,*]

1. *State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China. E-mail: liulang1991@foxmail.com*
2. *Environmental Protection Science Research Institute of Ji'nan, Ji'nan 250014, China*
3. *Department of Environmental and Occupational Health Sciences, University of Washington, Seattle, WA, USA*
4. *Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, Nanjing University of Information Science & Technology, Nanjing 210044, China*

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ABSTRACT

To investigate the composition and possible sources of particles, especially during heavy haze pollution, a single particle aerosol mass spectrometer (SPAMS) was deployed to measure the changes of single particle species and sizes during October of 2014, in Beijing. A total of 2,871,431 particles with both positive and negative spectra were collected and characterized in combination with the adaptive resonance theory neural network algorithm (ART-2a). Eight types of particles were classified: dust particles (dust, 8.1%), elemental carbon (EC, 29.0%), organic carbon (OC, 18.0%), EC and OC combined particles (ECOC, 9.5%), Na-K containing particles (NaK, 7.9%), K-containing particles (K, 21.8%), organic nitrogen and potassium containing particles (KCN, 2.3%), and metal-containing particles (metal, 3.6%). Three haze pollution events (P1, P2, P3) and one clean period (clean) were analyzed, based on the mass and number concentration of $PM_{2.5}$ and the back trajectory results from the hybrid single particle Lagrangian integrated trajectory model (Hysplit-4 model). Results showed that EC, OC and K were the major components of single particles during the three haze pollution periods, which showed clearly increased ratios compared with those in the clean period. Results from the mixing state of secondary species of different types of particles showed that sulfate and nitrate were more readily mixed with carbon-containing particles during haze pollution episodes than in clean periods.

Introduction

Due to the rapid economic and industrial development over the past few decades, coal consumption and the number of motor vehicles have increased significantly. These two major sources, as well as many other anthropogenic emissions, have made severe air pollution events more frequent (Sun et al., 2013; Guo et al., 2014; Zhang et al., 2014). In China, many of the industrial sources are located in the same region and emit atmospheric pollution together. Among 3 key industrial

* *Corresponding author*. E-mail: baizp@craes.org.cn (Zhipeng Bai).

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regions (the other two are the Yangtze River Delta and Pearl River Delta), the Beijing–Tianjin–Hebei region is of special concern because of the severe particulate matter (PM) pollution, which has profound ecological and human health effects (Sun et al., 2009, 2011). As the capital city of China with a dense population, increasing attention has been paid to the air pollution in Beijing (Lang et al., 2012; Zhao et al., 2013). In order to improve the air quality in Beijing, a series of control measures have been implemented: the energy source structure has been gradually changed by switching to clean fuels and low-sulfur coal, and a campaign has been conducted by the local government to relocate high-polluting industries (Zhang et al., 2010). However, air pollution control, especially particulate matter (PM), remains a big challenge.

Information on the chemical composition of particles is vital to tracing the sources of PM (Pastor et al., 2003), and there is a direct relationship between particle size and chemical composition (Thomas and Morawska, 2002). Many analytical methods have been developed to characterize the chemical and physical species, and atmospheric sources and sinks of particles. Traditional off-line measurement techniques generally need to collect samples on filters, which may cause the chemical species in samples to decay or degenerate during transport or storage. Therefore, high time-resolution analytical techniques were developed to characterize the variation of atmospheric particles and to capture sufficient variability in concentrations in order to isolate individual sources (Wood and Prather, 1998; Prather et al., 2008).

Single particle aerosol mass spectrometers (SPAMS) can provide continuous, real-time size-resolved information on the chemical composition and mixing state of single particles (Wood and Prather, 1998; Pastor et al., 2003; Li et al., 2014). Aerosol time-of-flight mass spectrometry (ATOFMS), one such instrument, has been utilized in a series of studies. Liu et al. (2003) used the instrument to detect the chemical composition of single particles in Atlanta, and classified particles into seven major classes. Lee et al. (2003) investigated nitrate and oxidized organic ions in single particles. Pastor et al. (2003) studied ambient single particles in Riverside, California by using an ATOFMS instrument to assess the temporal variation of different particle types. Manuel used ATOFMS to identify various indoor and outdoor sources in Athens (Dall'Osto et al., 2007). Prather et al. (2011) developed aircraft aerosol time-of-flight mass spectrometry (A-ATOFMS) and applied it in airborne smoke plume studies. In China, Yang and coworkers investigated the mixing state of oxalic acid, source apportionment of lead-containing particles and particulate nitrate formation in Shanghai by using ATOFMS (Wang et al., 2009; Yang et al., 2009; Zhang et al., 2009). SPAMS have been used to study the biomass burning particles, organic particles and the mixing state of secondary species in Guangzhou (Bi et al., 2011; Zhang et al., 2013), as well as the chemical variation of particles in Beijing (Li et al., 2014). However, the variability of single particles during heavy haze pollution events, or the mixing state of secondary species of different particle types in Beijing, has been little reported.

In this study, a single particle aerosol mass spectrometer (SPAMS 0515 Model, Hexin Analytical Instrument Co., Ltd., China) was deployed to measure the variation and size distribution in single particle species during different pollution events and a clean period in the Beijing urban area. Also, the different mass spectra signatures and possible sources of different particle types, as well as the mixing state of secondary species in particles, were assessed.

1. Methods

1.1. Sampling description

The single particle aerosol mass spectrometer (SPAMS 0515 Model, Hexin Analytical Instrument Co., Ltd., China) instrument was sited in a one-floor building in the Chinese Research Academy of Environmental Sciences (40.04°N, 116.42°E) located in the northern part of Beijing outside of the 5th Ring Road (Fig. 1), and operated continuously from 1st of October to 31st of October 2014. It employed a $PM_{2.5}$ cyclone inlet with the inlet of the ~4 m carbon sampling tube placed approximately 5 m above the ground.

The hourly mass concentration of $PM_{2.5}$ was obtained from the Olympic Sports Center Monitoring Station's data (http://www.pm2.5.in/). The meteorological data, including temperature, relative humidity (RH), wind speed, wind direction, and visibility, were obtained online (http://www.wunderground.com/).

1.2. Single particle aerosol mass spectrometer (SPAMS) and data analysis

SPAMS is designed to measure real-time particle size distribution and chemical composition; a detailed description has been published previously (Bi et al., 2011; Li et al., 2011; Zhang et al., 2013). Briefly, ambient particles were introduced through a ~100 μm metal orifice into the vacuum system of the instrument at a flow rate of 100 mL/min and then these polydispersed particles were focused onto a centerline by an aerodynamic lens. After leaving the aerodynamic lens, a single particle was introduced into the diameter sizing region. Two continuous 532 nm lasers were used to measure particle aerodynamic diameter based on the time-of-flight of a single particle (sized particle). Finally, the sized particle reached the laser desorption/ionization region, and positive and negative ions were produced by a 266 nm Nd:YAG (neodymium-doped yttrium aluminum garnet) laser (hit particle); ions were then analyzed by a bipolar mass spectrometer. The SPAMS recorded the single particle data on aerodynamic diameter and mass spectra. The data were analyzed using the Matlab (The MathWorks Inc., Natick, Massachusetts, USA) software toolkit. The particle mass spectra data were imported into Matlab software and then further classified by an adaptive resonance theory neural network algorithm (ART-2a). The ART-2a algorithm is used to identify groups of particles, and has been applied to single particle data analysis, including SPAMS and ATOFMS data sets (Phares et al., 2001; Pastor et al., 2003; Moffet et al., 2008; Bi et al., 2011; Zhang et al., 2013). The parameters of ART-2a analysis in this study included a learning rate of 0.05, a vigilance factor of 0.65, and a maximum of 20 iterations.