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Mixing state of ambient aerosols in Nanjing city by single particle mass spectrometry

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HIGHLIGHTS

- SPAMS was used to characterize over 1,989,725 single particles.
- K-rich particles accounted for 44.68% of the total hit particles.
- Different chemical components have distinct extinction effects.
- Proportion of EC particles at 0.65–1.4 μm was up to 25% on haze days.

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ABSTRACT

To investigate the mixing state and size-resolved aerosol in Nanjing, measurements were carried out for the period 14th January-1st February 2013 by using a Single Particle Aerosol Mass Spectrometer (SPAMS). A total of 10,864,766 particles were sized with vacuum aerodynamic diameter (d_{va}) in the range of 0.2–2.0 μm. Of which, 1,989,725 particles were successfully ionized. Aerosol particles employed for analyzing SPAMS data utilized 96% of the hit particles to identify 5 main particle groups. The particle classes include: K-rich particles (K-CN, K-Nitrate, K-Sulfate and K-Secondary), sodium particles, ammonium particles, carbon-rich particles (OC, EC and OCEC) and heavy-metal particles (Fe-Secondary, Pb-Nitrate, Cu-Mn-Secondary and V-Secondary). EC was the largest contributor with a fraction of 21.78%, followed by K-Secondary (17.87%), K-Nitrate (12.68%) and K-CN (11.25%). High particle level and high RH (relative humidity) are two important factors decreasing visibility in Nanjing. Different particle classes have distinct extinction effects. It anti-correlated well with visibility for the K-secondary, sodium, ammonium, EC, Fe-Secondary and K-Nitrate particles. The proportion of EC particles at 0.65–1.4 μm was up to 25% on haze days and was below 10% on clean days.

1. Introduction

Haze events are usually accompanied by sharp increases in air pollution, especially for aerosol concentrations, and have significant impacts on air quality, visibility and human health (Kunii et al., 2002; Okada et al., 2001). As one of the six largest city clusters in the world, the Yangtze River Delta (YRD) undergoes severe haze pollution due to the intensive emission of air pollutants (Cheng et al., 2013; Zhang et al., 2012b). Gao et al. (2011) identified a 2.4 km decrease of visual range per decade between 1981 and 2005. Related studies shown that the impaired visibility was mainly due to particulate matter pollution, especially $PM_{2.5}$ in YRD (Deng et al., 2011; Fu et al., 2008). Fu et al. (2008) observed a high ratio of $PM_{2.5}$/PM_{10} (61%) during the regional haze pollution in the YRD. Kang et al. (2013) shown that a high accumulation mode particle counts and high RH were the main reasons for visibility impairment during the haze event in Nanjing.

The characteristics of aerosol light extinction varied with their different chemical components. Many chemical species of aerosol have both high mass abundance and high extinction cross-section in the visible wavelength range (such as sulfate, nitrate, BC and organic matter) (Hand and Malm, 2007; Sloane, 1986). Hua et al. (2015) found sulfate, organic matter (OM) and nitrate of $PM_{2.5}$ had the highest impact on light extinction during heavy haze

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episode in YRD, constituting 30%, 28% and 19%, respectively. Tan et al. (2009) shown that the secondary species (OC, SO_4^{2-}, NO_3^- and NH_4^+) were the major chemical components and appeared to show a remarkably rapid increase from normal to haze days. Yu et al. (2010) indicated that the attenuation of light caused by carbonaceous aerosols was extremely important.

In addition, the aerosol concentration and their size distributions had great impacts on optical properties as well. Bullrich (1964) and Kang et al. (2013) observed that the scattering aerosols in the size range of 0.6–1.4 μm had significant extinction effects on visibility. Deng et al. (2008) found that small scattering aerosol particles (<1 μm in radius) have the largest contribution to the reduction of visibility (about 70%) in the Pearl River Delta. Sloane et al. (1991) showed that soot particles is much more efficient at absorbing light than the other constituents (sulfate, nitrate, organic) particles of the Denver brown cloud. Zhang et al. (2013) measured that OC, ECOC, V-ECOC and EC-Sulfate particles were generally increased during the haze episode in Guangzhou.

Knowledge on the mixing state of aerosol particles is a necessary prerequisite to accurately determine their contribution to visibility degradation, as well as to help gain an understanding on their roles in the regional climate (Zhang et al., 2013). Aerosol time-of-flight mass spectrometry (ATOFMS) provides continuous, real-time detection and characterization of single particles from polydisperse samples, supplying information on particle size and composition (Gross et al., 2000; Taiwo et al., 2014). Mixing state of individual particle is allowing insights into sources, atmospheric processing, optical and cloud properties of atmospheric aerosols (Murphy et al., 2006; Pratt et al., 2011; Zhang et al., 2013, 2014a). Moffet et al. (2008) observed high fractions of inorganic particles with internal mixtures of Pb, Zn, EC and Cl, representing up to 73% of the particles in the size of 0.2–3 μm. Yang et al. (2012) suggested that change in the mixing state played an important role in increasing aerosol light extinction during haze events in Shanghai. Zhang et al. (2012a) indicated that gas-to-particle partitioning of trimethylamine (TMA) in urban Guangzhou occurred preferentially during fog processing. It's reported that carbonaceous particles were commonly internally mixed with secondary species of ammonium, nitrate, and sulfate through atmospheric processes (Bi et al., 2011; Whiteaker et al., 2002; Zhang et al., 2015a).

China experienced several severe haze episodes in January 2013. Although a lot studies have investigated these haze pollution from the perspectives of meteorology, chemistry and modeling (Sun et al., 2014; Wang et al., 2014a, 2014b; Zhang et al., 2015b), the mixing state, sources, size-resolved and evolution processes of aerosol particles during the January haze episodes in the YRD are not well known. In this paper, we present the real-time single particle analysis of aerosol in Nanjing using a Single Particle Aerosol Mass Spectrometer (SPAMS) in 14th January-1st February 2013, focusing on the mixing state and chemical composition of individual particles. We also analyzed the effects of different chemical species on visibility and the variation feature of different type particles during haze episode. The reasons for haze pollution in Nanjing were discussed as well.

2. Experimental methods

2.1. Sampling

The observation site was located on the meteorology building (32.21°N, 118.72°E) on the campus of Nanjing University of Information Science & Technology, which is 40 m above the ground. The information of the station and its' surroundings is shown in Fig. 1. The Nanjing Chemical Industry Area is located at approximately 3 km southeast of the observation site; besides, there are some iron and steel plants and cogeneration power plants in the range of 1 km from the site. This region represents a combination of traffic, urban, industry and croplands sources.

Single particles' chemical components, hourly of $PM_{2.5}$ and half-hourly of meteorological parameters (temperature, pressure, relative humidity, precipitation, wind speed and direction) were observed online using a Single Particle Aerosol Mass Spectrometer (SPAMS, Guangzhou Hexin Analytical Instrument Co., Ltd., China), the Thermo Scientific SHARP-5030 Continuous Particle Monitor (Thermo Fisher Scientific Inc., USA), with a CSI-CR1000 Measurement and Control System (Campbell Scientific, Inc., USA). Measurements were carried out continuously from 14th January to 1st February 2013.

2.2. SPAMS and data analysis

The particle detection method of SPAMS was described by Li et al. (2011). Aerosol particles are introduced into SPAMS using an aerodynamic lens; then focused and accelerated to specific velocities, which are determined by their flight time through two continuous diode Nd: YAG (neodymium: yttrium aluminum garnet) laser beams (532 nm) in the sizing region. The particle chemical composition is detected through the desorption/ionization process, using a 266 nm ultraviolet laser beam. Both positive and negative ion fragments generated are recorded with vacuum aerodynamic diameter (d_{va}) (Zhang et al., 2013). Particle size and mass calibrations for this instrument were carried out every three months using standard polystyrene latex particles (PSL) and metallic solution. http://www.sciencedirect.com/science/article/pii/S1674200114001680Li et al. (2011) and http://www.sciencedirect.com/science/article/pii/S1674200114001680Zhang et al. (2012a) provide further instrument details.

In this study, a total of 10,864,766 particles were observed, of which 1,989,725 particles with d_{va} in the size range of 0.2–2.0 μm were chemically analyzed with both positive and negative ion spectra. The first 1096 clusters dominated the initially generated clusters, representing more than 96% of all the ionized particles, and were manually merged to produce 13 final particle classes based on the spectral similarities.

Spectral peaks obtained for each single particle were subsequently analyzed using YAADA 2.1 (www.yaada.org), a MATLAB-based software tool kit for processing single-particle mass spectral data. The peaks identified in this paper corresponded to the most probable assignments for each specific mass-to-charge ratio (m/z). According to the SPAMS markers listed in Table S1 and the classification rules mentioned from Bi et al. (2011), Moffet et al. (2008), Taiwo et al. (2014), Yang et al. (2009, 2012) and Zhang et al. (2012a, 2013, 2014a, 2015a). An adaptive resonance theory based neural network algorithm (ART-2a) was applied to cluster individual particles into separate groups based on the presence and intensity of ion peaks in individual single-particle mass spectra (Song et al., 1999), with a vigilance factor of 0.75, learning rate of 0.05 and 20 iterations.

2.3. Air mass backward trajectories

24 h air mass backward trajectories for each day were simulated by the Hybrid Single-Particle Lagrangina Integrated Trajectory (HYSPLIT, http://www.arl.noaa.gov/HYSPLIT_info.php) model developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (ARL) and were calculated at 12:00 (LST, local time) at the height of 500 m (Fig 1). The National Weather Service's National Centers for Environmental Prediction (NCEP) Global Data Assimilation System (GDAS) archive was used for meteorological input data. The GDAS data with a horizontal