Particuology 20 (2015) 16–23

Contents lists available at ScienceDirect

Particuology

journal homepage: www.elsevier.com/locate/partic

Mixing state of individual carbonaceous particles during a severe haze episode in January 2013, Nanjing, China

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ARTICLE INFO

Article history:
Received 28 April 2014
Received in revised form 9 June 2014
Accepted 16 June 2014

Keywords:
Haze
Single particle
Mixing state
SPAMS
Carbonaceous particle
Secondary aerosols

ABSTRACT

Chemical composition, hourly counts, and sizes of atmospheric carbonaceous particles were measured to investigate their mixing state on clear and hazy days. 623,122 carbonaceous particles with sizes 0.2–2.0 μm was analyzed using a single-particle aerosol mass spectrometer from 1st to 17th January 2013. Particle types included biomass/biofuel burning particles (biomass), element carbon (EC-dominant) particles that were also mixed with biomass/biofuel burning species (EC-biomass) or secondary species (EC-secondary), organic carbon (OC), internally mixed OC and EC (OCEC), ammonium-containing (ammonium) and sodium-containing (sodium) particles. On clear days the top ranked carbonaceous particle types were biomass (48.2%), EC-biomass (15.7%), OCEC (11.1%), and sodium (9.6%), while on hazy days they were biomass (37.3%), EC-biomass (17.6%), EC-secondary (16.6%), and sodium (12.7%). The fractions of EC-secondary, ammonium (10%), and sodium particle types were elevated on hazy days. Numbers of EC-secondary particles were more than four times those on clear days (4.1%). Thus, carbonaceous particles mixed with ammonium, nitrate and sulfate during aging and transport, enhancing their light extinction effects and hygroscopic growth under high relative humidity on hazy days, further reducing visibility. Our real-time single-particle data showed that changes to mixing state had a significant impact on light extinction during haze events in Nanjing.

Introduction

Atmospheric aerosols play an important role in affecting visibility, human health, and global climate change (Bäumer et al., 2008; Langridge et al., 2012; Lohmann & Feichter, 2005). Carbonaceous aerosols, as one of the major aerosol components, constitute about 10–50% of the total aerosol mass concentration (Schauer et al., 2003). They are normally divided into two fractions: organic carbon (OC) with a strong scattering ability, and element carbon (EC) with a strong absorption ability (Ramanathan & Carmichael, 2008; Watson, 2002). OC is mainly emitted as primary organic carbon (POC), but also comprises secondary organic carbon (SOC) formed by photochemical reactions. EC usually originates from incomplete combustion of fossil fuel or wood (Cao et al., 2005; Szidat et al., 2009).

In urban areas, reduced visibility mostly results from excess particulate matter in the atmosphere from anthropogenic emission sources and gas-to-particle conversions. It is used as a visual indicator for ambient air quality (Liu et al., 2013; Watson, 2002). The Yangtze River Delta (YRD) is one of the fastest-growing economic regions in the world; hence, air pollution and haze are important environmental and meteorological issues in this region (Wang, Jiang, et al., 2012). Gao et al. (2011) reported that the number of hazy days has increased in last 30 years, while visibility has decreased at the rate of 2.41 km/decade. Observations also showed that carbonaceous aerosols represent a major fraction of the submicron aerosol particles (Chan & Yao, 2008; Yang et al., 2012; Zhang, Wang, et al., 2012), and that the attenuation of light caused by carbonaceous aerosols is extremely important in China (Cheng et al., 2011; Yang et al., 2005; Yu, Wu, Wu, & Yu, 2010). Research on the mixing state of carbonaceous particles is a prerequisite to determine their contribution to this reduced visibility, as well as to gain a better understanding of their role in regional climate change (Zhang et al., 2013). However, there are few studies on aerosol mixing state, owing to the limitations of observation methods.

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http://dx.doi.org/10.1016/j.partic.2014.06.013

In the recent years, online single-particle mass spectrometers have become effective tools to analyze almost all species of chemical components, and to provide size-resolved information on the chemical composition and mixing state of single particles in real time. Many researchers deployed single-particle aerosol mass spectrometry to analyze changes in aerosol composition and mixing state during haze or fog events (Bi et al., 2011; Dall'Osto, Harrison, Coe, & Williams, 2009; Li et al., 2014; Yang et al., 2012). Researches on chemical reaction mechanisms, source profiles of aerosols, and their interactions with climate have used the aerosol mass spectra, both in China and abroad. Using single particle aerosol time-of-flight mass spectrometry (ATOFMS), Gard et al. (1998) directly observed multiphase chemical reactions in haze on the south coast of California, revealing the basic reasons for this haze. Whiteaker, Suess, and Prather (2002) studied the effects of meteorological conditions on aerosol composition and mixing state. Bi et al. (2011) and Silva, Liu, Noble, and Prather (1999) obtained the size and chemical features of aerosols emitted from biomass burning in southern California. Cahill, Suski, Seinfeld, Zaveri, and Prather (2012) and Healy et al. (2012) discussed the source and mixing state of these aerosols.

The mixing state of carbonaceous aerosols is influenced by various factors (e.g., local sources, atmospheric aging processes, and long-range transport). Qin, Pratt, Shields, Toner, and Prather (2012) and Zhang et al. (2013) reported that carbonaceous particles were dominantly mixed with nitrate and sulfate. Fu et al. (2012) observed four types of carbonaceous aerosols in Shanghai, and showed that most of the particles were coated with secondary organic aerosols. However, direct observations on the size-resolved mixing state of carbonaceous aerosols in the YRD region or in other parts of China are limited.

Serious particle matter (PM) levels resulted in long-term haze pollution in January 2013 in the YRD. The greatest instantaneous concentration of $PM_{2.5}$ reached 437 $\mu g/m^3$; while lowest visibility was only 0.04 km in Nanjing. In this study, we deployed real-time single-particle aerosol mass spectrometer (SPAMS) to measure and study the major types of carbonaceous particles, and to explore the variability of their number fraction as a function of vacuum aerodynamic diameter (d_{va}), aerosol mixing state, and particle acidity on hazy and clear days in the urban area of the YRD. We also discuss the effects of meteorological elements and $PM_{2.5}$ on these parameters.

Experimental methods

Sampling

Our observation site is located on the meteorology building (32.21° N, 118.72° E) at the campus of Nanjing University of Information Science & Technology, 40 m above ground. The Nanjing Chemical Industry Area is located approximately 3 km southeast of the observation site. In addition, there are iron and steel plants, as well as cogeneration power plants within 1 km of the site. Thus, local contributions to air particles are derived from traffic, urban, industry, and croplands sources.

Particle chemistry, $PM_{2.5}$, and meteorological parameters (wind speed/direction, temperature, pressure, relative humidity (RH), radiation, visibility and precipitation) were recorded online using a SPAMS (Guangzhou Hexin Analytical Instrument Co., Ltd., China), a Thermo Scientific FH 62 C14 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 January 1st to 17th, 2013.

SPAMS and data analysis

SPAMS provides size and spectral information for single particles with a temporal resolution higher than 30 min. Details of this instrument were reported by Li et al. (2011) and Zhang, Bi, et al. (2012). Aerosol particles are introduced into the SPAMS using an aerodynamic lens; particle diameter is calculated using two parallel laser beams at wavelength of 532 nm, while particle chemical composition is determined by desorption/ionization processes, using a strong 266 nm ultraviolet laser beam. Both positive and negative ion fragments are recorded with d_{va} (Zhang et al., 2013). In this study, approximately 623,122 carbonaceous particles with d_{va} between 0.2 and 2.0 μm were analyzed. Particle size and mass calibrations for this instrument were carried out every three months using standard polystyrene latex particles (PSL) and metallic solution. Li et al. (2011) and Zhang, Bi, et al. (2012) provide further instrument details. 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 correspond with the most probable assignments for each specific mass-to-charge ratio (m/z). We classified particles using the standards of Bi et al. (2011), Moffet, Foy, Molina, Molina, and Prather (2008), and Yang et al. (2009). 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 each single-particle mass spectra (Song, Hopke, Fergenson, & Prather, 1999). We used a vigilance factor of 0.80, learning rate of 0.05, and 20 iterations. A total of 4,560,405 particles were observed, of which 1,104,261 had size and spectral information, constituting 24.21% of the total number of particles.

Results and discussion

Meteorology, $PM_{2.5}$, carbon particles, and visibility

Nanjing has a typical north subtropical monsoon climate, controlled by the Siberian High in winter, with winds prevailing from the northeast. 30-Min-averaged levels of visibility, RH, $PM_{2.5}$, and the total carbonaceous particle count for January 1–17 are presented in Fig. 1. A strong cold air mass passed through Nanjing from 1st to 3rd January 2013; wind speed was large, with a maximum of 6.3 m/s and a mean of 2.8 m/s, and RH was relatively low, with a mean value of 51.4%, which was conducive to the dispersion of pollutants. Therefore, the average concentration of $PM_{2.5}$ was only 57.1 $\mu g/m^3$, which is relative low for east China; visibility was high, with a maximum of 18.5 km and a mean value of 10.2 km. Typically, mean visibility was below 10 km in January for the period 1981–2012 in the YRD region (Zhou, Gong, & Shi, 2014). During 4–16 January, flat westerlies dominated mid-eastern China, and pressure differences were equalized in the YRD; wind speed was low, with a mean of 1.7 m/s, while RH was high, with an average of 62.9%, which was unfavorable for the dispersion of pollutants. Thus, the $PM_{2.5}$ level was high, with an average value of 174.2 $\mu g/m^3$ and a maximum of 437 $\mu g/m^3$. The visibility was low, with an average value of 3.2 km and a minimum of 0.04 km. Hence, we selected 1–3 January to represent clear days, and 4–16 January to represent hazy days in this study.

Visibility had negative correlations with both RH ($R^2 = 0.47$) and $PM_{2.5}$ ($R^2 = 0.51$) levels, suggesting that high RH and $PM_{2.5}$ reduce visibility. Visibility also had negative correlations with both numbers of carbonaceous particles ($R^2 = 0.76$) and non-carbonaceous particles ($R^2 = 0.64$). Because the carbonaceous particles accounted for 56.4% of the total particles (1,104,261), we focused on