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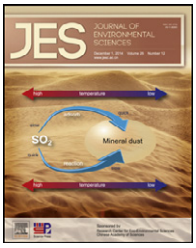

Characterization of aerosol optical properties, chemical composition and mixing states in the winter season in Shanghai, China

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ABSTRACT

Physical and chemical properties of ambient aerosols at the single particle level were studied in Shanghai from December 22 to 28, 2009. A Cavity-Ring-Down Aerosol Extinction Spectrometer (CRD-AES) and a nephelometer were deployed to measure aerosol light extinction and scattering properties, respectively. An Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) was used to detect single particle sizes and chemical composition. Seven particle types were detected. Air parcels arrived at the sampling site from the vicinity of Shanghai until mid-day of December 25, when they started to originate from North China. The aerosol extinction, scattering, and absorption coefficients all dropped sharply when this cold, clean air arrived. Aerosol particles changed from a highly aged type before this meteorological shift to a relatively fresh type afterwards. The aerosol optical properties were dependent on the wind direction. Aerosols with high extinction coefficient and scattering Ångström exponent (SAE) were observed when the wind blew from the west and northwest, indicating that they were predominantly fine particles. Nitrate and ammonium correlated most strongly with the change in aerosol optical properties. In the elemental carbon/organic carbon (ECOC) particle type, the diurnal trends of single scattering albedo (SSA) and elemental carbon (EC) signal intensity had a negative correlation. We also found a negative correlation ($r = -0.87$) between high mass-OC particle number fraction and the SSA in a relatively clean period, suggesting that particulate aromatic components might play an important role in light absorption in urban areas.

Introduction

Atmospheric aerosols have a “direct effect” on climate by scattering or absorbing solar radiation and an “indirect effect” by acting as cloud condensation and ice nuclei (Pöschl, 2005). The magnitude of these effects has still considerable uncertainties, especially the indirect effect (Forster et al., 2007; Schiermeier, 2010). In order to estimate the direct and indirect effect of

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aerosols, further understanding of aerosol optical properties is urgently needed.

The optical properties of aerosols govern their interaction with sunlight and are important parameters for estimating radiative forcing in modeling studies (Fischer et al., 2011). Studies have shown that aerosol optical properties are determined by particle size distribution, chemical components, and mixing state (Seinfeld and Pandis, 2006), with the latter being the most challenging to understand (Cappa et al., 2012; Huang et al., 2013). Different chemical species, especially soot and brown carbon (Lack and Cappa, 2010), can be mixed within a single particle (internal mixing) or across different particle types (external mixing); the exact mixing state changes aerosol optical properties and ultimately radiative forcing (Fuzzi et al., 2006; Ramanathan and Carmichael, 2008). Core–shell Mie theory has been widely used to calculate the theoretical aerosol optical properties (Jacobson, 2001). The coating shell on the cores often acts as a lens, enhancing the particle's absorbing and scattering ability, especially on black carbon cores (Lack and Cappa, 2010). However, field studies have shown that the theoretical model does not fit all cases (Cappa et al., 2012), and more work still needs to be done to investigate the influence of particle mixing state on aerosol optical properties.

Measurements of optical properties of aerosols along with mixing state within a single particle have been crucial in estimating aerosol radiative forcing (Pratt and Prather, 2010; McMeeking et al., 2011). Single particle mass spectrometers, such as the Aerosol Time-of-Flight Mass Spectrometer (ATOFMS), soot particle aerosol mass spectrometer (SP-AMS), and Single-Particle Soot Photometer (SP2), can provide information on the size-resolved chemical composition and internal mixing state of particles (Schwarz et al., 2006; Onasch et al., 2012; Pratt and Prather, 2012). Since SP-AMS and SP2 only measure material that is sufficiently light absorbing at 1064 nm (*i.e.*, soot particles, and only the non-refractory aerosol component with SP-AMS), the ATOFMS is preferred for full chemical measurements in regions where sea salt or mineral dust is an important contributor to the aerosol.

In different regions of China, the majority of studies have been focused on the effect of the chemical mass concentration, aerosol physical properties and water content on the optical properties (Che et al., 2009; Guo et al., 2009; Jung et al., 2009a; Yang et al., 2009b; Yu et al., 2009; Eck et al., 2010; Huang et al., 2010; Wang et al., 2010). Jung et al. (2009b) found that under polluted conditions in the urban area of Beijing, ammonium sulfate, ammonium nitrate, and organic carbon contributed to the increases of single scattering albedo. Yao et al. (2010) analyzed atmospheric light extinction properties and chemical speciation of fine particulates in Shenzhen and concluded that the organic matter in PM_1 contributed about 45% to the observed aerosol light extinction. Huang et al. (2011) measured black carbon (BC) mass loadings, size distributions and mixing state information in the Pearl River Delta region and estimated the potential contribution of BC mass to the radiative forcing. But studies of aerosol optical properties and their relationship with aerosol mixing state are very limited.

Cavity ring down spectroscopy (CRDS) has recently been used for measuring aerosol extinction and absorption coefficients in field and laboratory studies (Butler et al., 2007; Dinar et al., 2008; Zhang et al., 2008; Khalizov et al., 2009; Xue et al., 2009; Li et al., 2011; Li et al., 2013). Compared with filter based techniques like the Aethalometer and the Particle Soot Absorption Photometer (Bond et al., 1999; Sheridan et al., 2005), CRDS offers rapid real-time measurement of absorption coefficients (Busch and Busch, 1999; Pettersson et al., 2004; Bulatov et al., 2006). Huang et al. (2013) employed ATOFMS and CRDS to study the evolution of aerosol chemical and optical properties during a period in Shanghai when pollution was highly present. They found that organic carbon coatings could dramatically change aerosol optical properties, suggesting that this combination of measurements is ideal for elucidating the impact of particle mixing states on aerosol optical properties.

In this study, a Cavity-Ring-Down Aerosol Extinction Spectrometer (CRD-AES) (Li et al., 2011) and a nephelometer were used in Shanghai from 22 to 28 December, 2009 for the measurements of extinction and scattering coefficients, respectively. Simultaneously, an ATOFMS was used to obtain both positive and negative mass spectra from individual particles, and thus provide information on aerosol mixing state (Murphy, 2007). Examining these measurements concurrently, the sources of particles and the aerosol optical properties as a function of particle size distribution, chemical composition and mixing states are investigated.

1. Experimental

Measurements were carried out in the laboratory building of the Department of Environmental Science and Engineering at Fudan University (31°17′47.14″N, 121°30′14.94″E) in Shanghai from December 22 to December 28, 2009 (24 hr per day). This site is near residential, traffic, and construction emissions sources and represents a typical urban area. Ambient air was drawn from a height of about 5.5 m above the ground through a half-inch diameter, six-meter long, stainless steel tube at a flow rate of 6.0 L/min. A scanning mobility particle sizer (SMPS, Model 3936, TSI, Minneapolis, Minnesota) was used to monitor the size distribution of particles in the range of 15–550 nm during this period (Appendix A Fig. S1). Hourly averaged concentrations of PM_{10} (Appendix A Fig. S2) and the meteorological data including temperature, relative humidity (RH), wind speed and direction were provided by the Shanghai Meteorological Bureau.

1.1. Single particle measurements

The ATOFMS (Model 3800, TSI, Minneapolis, Minnesota) has been described in detail elsewhere (Gard et al., 1997). Briefly, air is introduced into a vacuum region through an aerodynamic focusing lens (Model 3801-100, TSI, Minneapolis, Minnesota) whose optimum operating range is from 100 nm to 3 μm. Each particle is sized by measuring its flight time between two orthogonal continuous diode-pumped green lasers when accelerated to a terminal velocity that depends on its aerodynamic size. The time taken for a particle to move between the lasers is recorded by a logic circuit, which controls the firing of a pulsed ultraviolet laser (frequency-quadrupled Nd: YAG laser, 266 nm) to desorb/ionize chemical species from the particle. Both positive and negative ions generated from laser ablation are analyzed simultaneously. In this work, polystyrene latex spheres (Nanosphere Size Standards, Duke Scientific Corp., Palo Alto, California) from 0.22–2.00 μm diameter were generated via an atomizer (Model 3076, TSI, Minneapolis, Minnesota) to create monodisperse aerosols for size calibration. Ambient air passed through a dryer tube before entering the ATOFMS. No scaling was done to adjust the ATOFMS particle counts.

The mass spectra were converted to a list of peaks at each *m/z* by setting a minimum signal threshold of 30 arbitrary units above the baseline in the MS-Analyze software (TSI). The resulting peak lists were then imported into YAADA (version 2.11, www.yaada.org), a software toolkit for single particle data analysis written in the Matlab programming language (version R2010b). An adaptive resonance theory-based clustering method (ART-2a) (Bhave et al., 2001; Rebotier and Prather, 2007) was used to classify mass spectra with a vigilance factor of 0.85, a learning rate of 0.05 and 20 iterations. The resulting clusters were regrouped by hand