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Characteristics of individual particles in the atmosphere of Guangzhou by single particle mass spectrometry

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ABSTRACT

Continuous ambient measurement of atmospheric aerosols was performed with a single particle aerosol mass spectrometer (SPAMS) in Guangzhou during summer of 2012. The aerosols mainly consisted of carbonaceous particles as major compositions in submicrometer range, including K-rich (29.8%), internally mixed organics and elemental carbon (ECOC, 13.5%), organic carbon-rich (OC, 18.5%), elemental carbon (EC, 12.3%) and high molecular OC (HMOC, 3.2%), and inorganic types (e.g., Na-rich Na-K, Fe-rich, V-rich, and Cu-rich) as major ones in supermicrometer range. Results show that carbonaceous particles were commonly internally mixed with sulfate and nitrate through atmospheric processing, in particular, with sulfate; inorganic types were dominantly internally mixed with nitrate rather than sulfate, indicative of different evolution processes for carbonaceous and inorganic particles in the atmosphere. It was observed that variations of these particle types were significantly influenced by air mass back trajectories (BTs). Under the influence of continental BTs, carbonaceous types were prevalent, while Na-K and Na-rich types considerably increased when the BTs originated from south marine regions. Number fraction of carbonaceous types exhibited obvious diurnal variation throughout the sampling period, which reflects their relatively stable emission and atmospheric processes. Two EC particle types LC-EC and NaK-EC showed different diurnal distributions, suggesting their different origins. The obtained information on the mixing state and the temporal variation of particle types is essential for developing an understanding on the origin and evolution processes of atmospheric aerosols.

1. Introduction

Atmospheric aerosols from anthropogenic and natural sources are the subject of enduring interest due to its effects on air quality, public health, and global climate change (Harrison and Yin, 2000; Pöschl, 2005; Watson, 2002). The impact of atmosphere aerosols on radiative forcing (Jacobson, 2001a,b; Kanakidou et al., 2005) and/or cloud condensation nuclei (CCN) (Sun and Ariya, 2006; Zhang et al., 2012) is highly dependent on their physical and chemical properties. Pearl River Delta (PRD) region faces increasing air pollution due to the rapid growing of population and the enhanced density of industrial activities (Chan and Yao, 2008). The air pollution problems have not only raised scientific interests, but also become a major concern of the government. Many measurements have shown that carbonaceous aerosols, sulfate and nitrate represent predominant fractions of fine particles, and significantly contribute to the regional haze formation in the PRD region (e.g., Andreae et al., 2008; Chan and Yao, 2008). Mixing state involving these compositions plays a substantially important role on the light extinction of ambient aerosols (Cheng et al., 2008; Yu

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et al., 2010). However, mixing state of atmospheric aerosols, relying on single particle measurement, remains poorly understood in the PRD region, since previous measurements were primarily based on bulk aerosol filter samples that represent average chemical compositions (Chan and Yao, 2008; Tan et al., 2009; Tao et al., 2012).

To improve the understanding of the evolution of individual particles with distinctly different properties, it is essential to collect the physical and chemical information of atmospheric particles at single particle level with high time resolution (Prather, 2009; Pratt and Prather, 2012). The recent emergence and development of single particle mass spectrometry technology has been significantly advancing ambient individual particle characterization (Pratt et al., 2009; Su et al., 2004). It has been utilized to characterize size and mixing state of both ambient and laboratory generated aerosols, greatly improving the understanding on the aging processes, source, and optical properties of atmospheric aerosols (Moffet and Prather, 2009; Spencer et al., 2008; Sullivan et al., 2007). In China, on-line single particle mass spectrometry has most recently been applied in the studies on physicochemical properties of individual particles and their potential influence on air quality (Chen et al., 2014; Yang et al., 2012), and the related researches have investigated the mixing state of carbonaceous particles in the atmosphere of the PRD region (Bi et al., 2011; Zhang et al., 2013). However, knowledge on the mixing state of atmospheric aerosols in the PRD region was still limited.

The single particle studies have showed that there are many particle types with complex mixing state in the urban areas (e.g., Moffet et al., 2008a; Zhang et al., 2013). The physical and chemical properties (including density, shape, hygroscopicity, and refractive index) of these particle types are distinctly different from each other, influenced by various factors such as meteorological conditions and emission sources (e.g., Moffet and Prather, 2009; Zelenyuk et al., 2008). Therefore, it is expected that these particle types behave differently in the atmosphere and probably contribute differently to the environmental and climatic effect. In this study, a single particle aerosol mass spectrometer (SPAMS) was applied to characterize the physical and chemical properties of atmospheric aerosols with high time-resolution in Guangzhou, a megacity in the PRD region. We present three-week (1–21th August 2012) data on individual particles, including particle sizes and mass spectral characteristics. Located in a transitional zone of the East Asian monsoon system, Guangzhou experiences southwesterly summer monsoon, characterized by sea-land breezes during summer. High relative humidity (RH) and temperature (Temp) were frequently observed during this period. Coupled with meteorological conditions, the temporal profile, and size distribution of major particle types and also the influence of air mass on their mixing state were discussed.

2. Experiment set up

2.1. Sampling location and meteorological condition

Single particle measurements were carried out nearly continuously at Guangzhou Institute of Geochemistry (GIG), Chinese Academy of Sciences, during the summer (1–21th August) of 2012, using a SPAMS (Li et al., 2011) developed by Hexin Analytical Instrument Co., Ltd. (Guangzhou, China). Detail for the measurement site was described elsewhere (Bi et al., 2011). The sampling inlet was set up approximately 20 m above the ground level.

Temporal profiles (in 1 hour resolution) of local meteorological parameters, including solar radiation, Temp, RH, wind direction (WD) and wind speed (WS), and air quality parameters (i.e., NO_x, SO_2, O_3, PM_1) are shown in Fig. 1. Data for Temp, RH, WD, and WS was collected from Weather Underground (http://www.wunderground.com/), and the remaining parameters were provided by Guangdong Environmental Monitoring Center (http://www.gdemc.gov.cn/). The concentrations of NO_x, SO_2, and O_3 were measured by Model 42i ($NO–NO_2–NO_x$) Analyzer, Model 43i SO_2 Analyzer, and Model 49i O_3 Analyzer (Thermo Fisher Scientific Inc.), respectively. The concentrations of PM_1 and BC were continuously measured using a tapered element oscillating microbalance (TEOM 1405, Thermo Fisher Scientific Inc.) and a Multiangle Absorption Photometer (Model 5012, Thermo Fisher Scientific Inc.), respectively. Ambient Temp, RH, and WS during the field study varied between 23–38 °C, 37–100%, and 0–8 m/s, with average values of 30 °C, 77%, and 2 m/s, respectively. Temp, WS, and O_3 concentrations peaked at ~14:00 and reached their minimum at night, with RH showing an opposite trend. However, the concentration peaks for NO_x, SO_2, and PM_1 were often observed during the nighttime, due to the accumulation of pollutants under unfavorable meteorological conditions with lower WS and boundary layer depth.

2.1.1. Single particle acquisition and data analysis

Ambient aerosols were introduced from the sampling inlet to the SPAMS (Hexin Analytical Instrument Co., Ltd., Guangzhou, China), through a stainless steel tube (4 m). The particle detection method of SPAMS can be found elsewhere (Li et al., 2011). Briefly, particles are introduced into SPAMS through a critical orifice, then focused and accelerated to specific velocities that would be determined by two continuous diode Nd:YAG laser beams (532 nm) below in sizing region. Individual particle is then desorped/ionized by a pulsed laser (266 nm) triggered exactly based on the specific velocity. The positive and negative fragments generated are recorded with the recorded velocities. They were then converted to d_{va} using a calibration curve, created from the measured velocities of series of polystyrene latex spheres (Nanosphere Size Standards, Duke Scientific Corp., Palo Alto) with defined sizes.

Particle size and mass spectra information were imported into MATLAB (The MathWorks Inc.) and analyzed with YAADA (www.yaada.org), a MATLAB-based software toolkit for manipulating single particle mass spectral data set. We focus on the particles with vacuum aerodynamic diameter (d_{va}) ranging from 0.1 to 1.6 μm that were more effectively detected. The SPAMS collected approximately 750,000 individual particles with both positive and negative ion mass spectra. An adaptive resonance theory based neural network algorithm (ART-2a) is applied to cluster individual particles into separate groups based on the presence and intensity of ion peaks in single particle mass spectrum (Song et al., 1999), with a vigilance factor of 0.7, learning rate of 0.05, and 20 iterations. By merging similar clusters resulted from ART-2a, ten major particle types (16 if considering the subtypes) with distinct chemical patterns were obtained, representing ~92% of the population of the collected particles.