Atmospheric Environment 92 (2014) 162–170

Contents lists available at ScienceDirect

Atmospheric Environment

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

Variation of secondary coatings associated with elemental carbon by single particle analysis

Guohua Zhang [a], Xinhui Bi [a,*], Junjie He [b], Duohong Chen [c], Lo Yin Chan [a], Guangwu Xie [c], Xinming Wang [a], Guoying Sheng [a], Jiamo Fu [a], Zhen Zhou [b]

[a] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, PR China
[b] Department of Environmental Engineering, Jinan University, Guangzhou 510632, PR China
[c] State Environmental Protection Key Laboratory of Regional Air Quality Monitoring, Guangdong Environmental Monitoring Center, Guangzhou 510308, PR China

HIGHLIGHTS

- Secondary compositions associated with EC were observed with SPAMS in real time.
- EC-containing particles accounted for ~33% (21–50%), of total analyzed particles.
- EC was internally mixed with sulfate (97.4%), nitrate (89.5%), and ammonium (80%).
- Distinct diurnal cycle of the EC mixing state in condensation mode was observed.
- Photochemical aging may contribute to growth of smaller EC-containing particles.

ARTICLE INFO

Article history:
Received 8 December 2013
Received in revised form
3 April 2014
Accepted 10 April 2014
Available online 13 April 2014

Keywords:
Mixing state
Elemental carbon
Sulfate
Organics
Single particle
PRD

ABSTRACT

The mixing state of elemental carbon (EC) with secondary species has been highlighted as a major uncertainty in assessing its climate impact. However, the extent to which secondary coatings are present on EC and the underlying processes remained poorly understood in China, where there is a high loading of EC produced from extensive usage of fossil fuels and biomass. A single particle aerosol mass spectrometer (SPAMS) was applied to detect the chemical compositions associated with EC at the Guangdong Atmospheric Supersite, China. Efforts were made to track the variation of secondary coatings on EC. It is the first report on the direct observation of secondary compositions associated with EC with high time resolution in China. The hourly average number of EC-containing particles accounted for ~33% (21–50%) of total analyzed particles over the sampling period. EC was found to be extensively internally mixed with sulfate (97.4% in number), nitrate (89.5%), oxidized organics (69.6%), and/or ammonium (80%). The results also indicate that secondary processing on EC in condensation (0.2–0.5 μm) and droplet (0.7–1.1 μm) modes is different. Active photochemical formation of oxidized organics and ammonium sulfate during daytime, and formation of ammonium nitrate during nighttime led to a distinct diurnal circle of mixing state of EC in the condensation mode. However, the photochemical aging may have limited or negligible influence on the mixing state and growth of EC in the droplet mode. These findings improve the understanding of the evolution of physicochemical properties of EC, and may help to model its climate impact.

1. Introduction

Aerosols represent the largest uncertainty in estimating radiative forcing of atmospheric species, through strongly affecting the energy balance of the Earth by scattering and/or absorbing solar radiation (Pöschl, 2005), and influencing cloud formation (Jacobson, 2006). Generated exclusively by incomplete combustion of fossil fuel and biomass, elemental carbon (EC) represents a substantially important fraction of atmospheric aerosols (Chan and Yao, 2008) and imposes a strong positive forcing to the global climate. Recent studies suggested that EC may have a warming potential second only to CO_2 (e.g., Ramanathan and Carmichael, 2008).

* Corresponding author.
E-mail address: bixh@gig.ac.cn (X. Bi).

http://dx.doi.org/10.1016/j.atmosenv.2014.04.018
1352-2310/

Many studies have demonstrated that optical properties of EC are sensitive to their physical (e.g., size and morphology) and chemical (e.g., composition, mixing state) properties (Moffet and Prather, 2009). While freshly emitted EC may contain limited coating, atmospheric aging such as coagulation with other particles, condensation of vapors, and in-cloud processing could cause EC to internally mix with other chemical species (e.g., Moffet and Prather, 2009). Cappa et al. (2012) and Lan et al. (2013) had observed a limited enhancement due to the mixing state of ambient EC, however, other studies confirmed the enhancement effect of internally mixing under various conditions (Wei et al., 2013; Zhang et al., 2008). The internally mixing can result in enhanced absorption by nearly 2-fold and scattering capacity by approximately 10-fold at 80% relative humidity (RH) relative to fresh particles (Zhang et al., 2008).

The mixing state of individual EC particles is very complex and constantly changing in the atmosphere. Advances in on-line instrumentation have provided a direct measurement of size-resolved mixing state, and thus this could help to track the evolution of chemical compositions and their influence on the optical properties of aerosols with high time resolution. Volatility Tandem Differential Mobility Analyzer (VTDMA) and Single Particle Soot Photometer (SP2) can obtain the information on mixing state of refractory black carbon (rBC), in addition to mass quantification (Schwarz et al., 2006). Through the application of VTDMA, Cheng et al. (2009) observed significantly enhanced light scattering and absorption capacity of rBC due to the secondary processing of rBC in a polluted region of China. With a SP2, the rBC in the Pearl River Delta (PRD) region of China was also frequently found to be internally mixed with non-refractory materials (Huang et al., 2011, 2012). However, these measurements are based on the thermo or optical methods and thus they do not provide any chemical information. Single particle mass spectrometry (SPMS) can provides the details of chemical composition measurements for single particles, including EC (e.g., Cahill et al., 2012; Pratt and Prather, 2012 and references therein; Zauscher et al., 2013). For example, Moffet and Prather (2009) observed a rapid coating process of organic carbon (OC) and sulfate on the EC core and assessed the related absorption enhancement in the polluted atmosphere of the Mexico city. Healy et al. (2012) found that the mixing state of EC-containing particles showed dependency on vacuum aerodynamic diameter (d_{va}), with smaller particles ($d_{va} \leq 0.4$ μm) mainly externally mixed and larger particles ($d_{va} > 0.4$ μm) mainly internally mixed, influenced by sources and transport. Cahill et al. (2012) showed that majority of soot is internally mixed and temporally varied. The term EC is used herein, instead of BC or soot since the SPMS uses mass spectrometry as method of detection, rather than light absorption. The definitions of EC and BC have been discussed in details elsewhere (Bond and Bergstrom, 2006).

Previous studies demonstrated an important role of EC in atmospheric light extinction in the PRD region (e.g., Yu et al., 2010). However, the aerosol measurements of EC in China reported so far have been primarily based on bulk techniques (Wu et al., 2012) that could not provide sufficient information on compositions of EC-containing particles, including the coating materials at single particle level. The details of coating materials and their influence on the physicochemical properties of EC are still very limited in China. Additionally, the mechanisms governing transformation of EC from being externally to internally mixed are also unclear. In this study, both d_{va} and chemical compositions of ambient aerosols with high-time resolution in the PRD region, China were analyzed by a Single Particle Aerosol Mass Spectrometer (SPAMS) in order to improve the understanding on atmospheric aging processes of EC. EC-containing particles analyzed by SPAMS were in the size range of 0.2–1.2 μm, which is consistent with the dominant fraction of EC mass in the atmosphere of the PRD region (Huang et al., 2011, 2012). Variations of the most abundant secondary species (i.e., sulfate, organics, ammonium, and nitrate) associated with EC as a function of d_{va}, and also their diurnal trends are discussed.

2. Methods

2.1. Sampling site and ambient observation

Ambient measurements were conducted at Guangdong Atmospheric Supersite (22.73N, 112.93E), a suburban site of Heshan city in the PRD region, surrounded mainly by farm land (Fig. S1 in Supplementary material (SM)). The site is located on a hill with an elevation of 60 m, approximately 80 and 50 km downwind site to Guangzhou and Foshan, respectively, and both cities are densely industrial areas. A sampling inlet was set up on a building at approximately 15 m above the ground level. Continuous SPAMS measurements lasted approximately for 10 days, from 21st November to 1st December 2010. The details of single particle detection method can be found in the SM.

2.2. Data analysis procedure

A total of approximately 1,500,000 particles, with d_{va} in the size range of 0.2–1.2 μm, were chemically analyzed with both positive and negative ion spectra. Particles sizes and mass spectra were imported into MATLAB (The Mathworks Inc.) and further analyzed with YAADA (www.yaada.org), a MATLAB-based software toolkit for processing single-particle mass spectra. Single particles clustering was performed with adaptive resonance theory based neural network algorithm (ART-2a) (Song et al., 1999), based on the presence and intensities of ion peaks in individual mass spectra. Parameters applied in the algorithm were set as 0.7 (vigilance factor), 0.05 (learning rate), and 20 (iterations). The first 400 hundred of all clusters (2182) generated by ART-2a, accounting for ~95% of all analyzed particles, were further manually combined into 11 single particle types.

3. Results and discussion

3.1. Meteorological conditions and pollution level

Fig. 1 shows real-time (in 1 h resolution) meteorological data, including ambient temperature (Temp), RH and wind speed (WS), and concentrations of gaseous pollutants (SO_2, NO_x, and O_3), BC and $PM_{2.5}$. Ambient Temp and RH during the field study generally varied between 12 and 26 °C and 45–95%, with an average of 19 °C and 69%, respectively. BC, CO, and $PM_{2.5}$ similarly exhibited pronounced diurnal variation, with two major peaks during morning (8:00–10:00, local time) and night hours (19:00–23:00). The concentrations of BC and $PM_{2.5}$ varied in the ranges of 2.9–13.8 and 23.5–145.2 μg m^{-3}, with mean values of 8.2 and 74.6 μg m^{-3}, respectively. Their diurnal trend was likely associated with variations of traffic emission, wind speed and boundary layer. Relatively strong wind and higher boundary layer diffused the pollutions and eventually led to lower pollution levels during the daytime, however, light wind enhanced pollution in a thinner boundary layer after sunset (Fan et al., 2008, 2011). The meteorological conditions during the nighttime facilitated the accumulation of pollutants, with frequently observed high level of $PM_{2.5}$ (>75 μg m^{-3}). According to back-trajectory analysis (more details can be found in the SM), air masses from northeastern continental areas dominated over the sampling period. Many short and circled back trajectories