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Light absorption of black carbon aerosol and its enhancement by mixing state in an urban atmosphere in South China

Zi-Juan Lan [a], Xiao-Feng Huang [a,*], Kuang-You Yu [b], Tian-Le Sun [a], Li-Wu Zeng [a], Min Hu [c]

[a] Key Laboratory for Urban Habitat Environmental Science and Technology, School of Environment and Energy, Peking University Shenzhen Graduate School, Shenzhen 518055, China
[b] Department of Atmospheric Sciences, School of Environmental Sciences and Engineering, Sun Yat-sen University, Guangzhou 510275, China
[c] State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China

HIGHLIGHTS

- Black carbon (BC) aerosol was characterized with advanced on-line instruments.
- The BC light absorption at 3 wavelengths was obtained using photoacoustic method.
- The enhancement of BC light absorption by mixing state is evaluated quantitatively.

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ABSTRACT

The effects of black carbon (BC) aerosol on climate warming have been the study focus in the recent decade, and the reduction of BC is now expected to have significant near-term climate change mitigation. Large uncertainties of BC optical properties, however, still exist and seriously restrict the ability to quantify BC's climate effects. In this study, advanced instrumentation (a three-wavelength photoacoustic soot spectrometer (PASS-3) and a single particle soot photometer (SP2)) were used to measure black carbon aerosol and analyze its optical properties in a mega-city in South China, Shenzhen, during the summer of 2011. The results indicated that the average BC mass concentration was 4.0 ± 3.1 μg m^{-3} during the campaign, accounting for ~11% of the total $PM_{2.5}$ mass concentration. The $PM_{2.5}$ light absorption at 405, 532 and 781 nm was 37.1 ± 28.1, 25.4 ± 19.0 and 17.6 ± 12.9 Mm^{-1}, respectively. The average absorption Angstrom exponent of $PM_{2.5}$ in visual spectrum ($AAE_{405-781\ nm}$) was 1.1 ± 0.1 during the campaign, indicating that the light absorbing carbon mainly came from vehicular emissions, with little contributions from biomass burning emissions. The mass absorption efficiency (MAE) of BC at 532 nm ranged from 5.0 to 8.5 $m^2\ g^{-1}$ during the campaign, with an average of 6.5 ± 0.5 $m^2\ g^{-1}$, and showed an obvious diurnal pattern with high values in the daytime. The average percentage of internally mixed BC was 24.3 ± 7.9% during the campaign, showing significant positive correlation relationship with the MAE of BC. More quantitative data analysis indicated that the internally mixed BC would amplify MAE by about 7% during the campaign, which stands in accordance with the new finding of a very recent *Science* magazine paper (Cappa et al., 2012) that the BC absorption enhancement due to internal mixing in the real atmosphere is relatively low, in apparent contrast to theoretical model predictions.

1. Introduction

Black carbon (BC) as the main light absorbing aerosol in the atmosphere has been the study focus in recent decade due to its strong positive forcing effect on climate change (Jacobson, 2001a; Ramanathan and Carmichael, 2008). The regional effect of BC light absorption is more significant, e.g. in Asia (Ramanathan et al., 2007a), Africa (Flanner et al., 2007), and Arctic (Quinn et al., 2007), because BC's life time in the atmosphere is shorter than other green house gases (about 1–4 weeks). As BC can also be transported to global areas, it also has great influence on global climate change (Ramanathan et al., 2007b). Ramanathan and Carmichael (2008) indicated that BC had been estimated to be the second contributor

* Corresponding author. Tel.: +86 755 26032532; fax: +86 755 26035332.
E-mail address: huangxf@pku.edu.cn (X.-F. Huang).

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to the climate change after CO_2. However, there are still many influencing factors on that estimation, e.g. uncertainties of emission sources (Bond et al., 2004), complicated optical properties of BC (Andreae and Gelencser, 2006), uncertainties of technical measurement (Arnott et al., 2005; Petzold et al., 2005; Coen et al., 2010). Therefore, large uncertainties still remain in determining the positive forcing effect of BC on global clime change. Further study on BC's optical properties with high-precision instruments is essential to quantifying the BC's effect on climate change.

Mass absorption efficiency (MAE) is one of the important optical properties of BC, and it is calculated based on the BC mass concentration and absorption (Bond and Bergstrom, 2006). BC mixing state is one main influencing factor for MAE. Models have estimated that BC radiative forcing can be increased by a factor of ~2 for internally versus externally mixed BC (Jacobson, 2001a; Chung and Seinfeld, 2005). On the other hand, some organic carbon had been found to significantly absorb light at UV or shorter wavelengths in the most recent studies, with strong spectral dependence (Chen and Bond, 2010; Kirchstetter et al., 2004; Lewis et al., 2008; Sandradewi et al., 2008; Schmid et al., 2006). Main sources for light absorbing organic carbon were from biofuel burning, e.g. coal (Bond, 2001) and biomass (Bergstrom et al., 2007). Kirchstetter et al. (2004) indicated that organic carbon contributed about 50% of the light absorption from biomass emission. Hence organic light absorption cannot be neglected because biomass is a major source of global carbon aerosols (Bond et al., 2007; Alexander et al., 2008).

To quantitatively determine the optical properties of BC aerosol is still a challenge, especially in China where studies on light absorption spectral dependence, MAE characteristics, and the influence of mixing state are limited. Only general understanding of BC optical properties had been made. Cheng et al. (2011) had studied MAE of BC in Beijing using a thermal/optical carbon analyzer that also had fundamental analysis of organic carbon light absorption, but there were many uncertainties in the measurement method as indicated by the authors. In this paper, a one-month summer campaign to measure BC aerosols in Shenzhen was conducted with high-end *in situ* instruments in order to obtain high-precision data for i) BC pollution characteristics; ii) BC light absorption at different wavelengths; iii) BC internal mixing state and its influence on MAE.

2. Experimental methods

2.1. Sampling location

The measurement station in this study was located in the campus of Peking University Shenzhen Graduate School, with no significant pollution sources nearby. The campus is located in the western urban area of Shenzhen. Shenzhen (113.9° E, 22.6° N), a megacity in South China, is located in the subtropics along the southeast coast of China. It is in the southeast corner of the Pearl River Delta (PRD) region, neighboring Hong Kong to the south. The campaign took place between 25 August and 21 September 2011. The average temperature was 28.7 °C; relative humidity was 71.2%, with seldom rainfall during the sampling period.

2.2. Instrumentation

The instruments were placed in a temperature controlled laboratory on the fourth floor of a building in the campus. The sample flow was dried by silicon drier and with a $PM_{2.5}$ Cyclone inlet placed above the rooftop. A three-wavelength Photoacoustic Soot Spectrometer (PASS-3) (Droplet Measurement Technologies, CO, USA) was used to measure the aerosol light absorption and scattering coefficients simultaneously. PASS-3 is capable of on-line measuring *in situ* aerosol light absorption and scattering at 405, 532, and 781 nm directly, with a high time resolution of up to 2 s. The principles and technical details of PASS have been described previously by Arnott et al. (1999). The calibration of PASS-3 in this study was performed following the standard procedures provided by the operational manual. Firstly, the laser power for each wavelength was calibrated by a laser power meter; secondly, the absorption of NO_2 at 532 nm was utilized to produce acoustic signals to calibrate the microphone and polystyrene latex (PSL) spheres (220 nm) were used to calibrate the scattering signal detectors, all resulting in a good linear regression coefficient (R^2) of >0.99 for the calibration curve. The detection limits of aerosol light absorption at the three wavelengths were all measured to be <3 Mm^{-1}.

A Single Particle Soot Photometer (SP2) (Droplet Measurement Technologies, CO, USA) was used to measure black carbon, and its technical details have been described elsewhere (Schwarz et al., 2006, 2008). The calibration of the SP2 was conducted with fullerene soot (Alpha Aesar, Inc., Ward Hill, MA), which were size-selected by introducing a differential mobility analyzer (DMA) upstream of the SP2. The BC particle detection limit in this study was about 0.07 μm in VED. The mixing state of BC, i.e., internally mixed versus externally mixed with other aerosol materials, was also identified by SP2 with the method described in Schwarz et al. (2008). More details about the SP2 operation can be found in our previous publication (Huang et al., 2012). A TEOM 1405 $PM_{2.5}$ monitor (Thermo, USA) was deployed simultaneously to obtain the real-time $PM_{2.5}$ mass concentrations. All the on-line measurement data were processed for 1-h averages for the later data analysis and discussion.

2.3. Optical properties calculation

2.3.1. Absorption Angstrom exponent

The variation of absorption with wavelength is characterized by the absorption Angstrom exponent (AAE), defined as:

$$\mathrm{AAE} = -\left(\frac{\ln(B_{\mathrm{abs}-\lambda_1}/B_{\mathrm{abs}-\lambda_2})}{\ln(\lambda_1/\lambda_2)}\right) \quad (1)$$

where B_{abs} is the observed absorption measured by PASS-3. An AAE = 1 corresponds to λ^{-1} dependence of absorption. It is thought that brown carbon (i.e., light absorbing organic carbon) shows strong deviations from the λ^{-1} relationship. Therefore it has been assumed that the observation of an AAE larger than 1 is an indication of absorption by brown carbon (or dust if present (Yang et al., 2009)).

2.3.2. Mass absorption efficiency

Mass absorption efficiency (MAE), a parameter characterizing the optical properties of BC serves as one convenient proxy for the relationship between radiative transfer and the aerosol mass represented in models.

$$\mathrm{MAE} = \frac{B_{\mathrm{abs}}}{\mathrm{BC}} \quad (2)$$

where B_{abs} is the light absorption measured by PASS-3, Mm^{-1}; BC is the BC mass concentration measured by SP2, μg m^{-3}.

3. Results and discussion

3.1. BC mass concentration and light absorption coefficient

The time series of BC concentration and its related optical properties with 1-h time resolution during the campaign are shown in Fig. 1. The average mass concentration of $PM_{2.5}$ was 38.5 ± 17.5 μg m^{-3} during the campaign. The average BC mass