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Light attenuation cross-section of black carbon in an urban atmosphere in northern China☆

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ABSTRACT

Fine particulate matter ($PM_{2.5}$) samples were collected over two years in Xi'an, China to investigate the relationships between the aerosol composition and the light absorption efficiency of black carbon (BC). Real-time light attenuation of BC at 880 nm was measured with an aethalometer. The mass concentrations and elemental carbon (EC) contents of $PM_{2.5}$ were obtained, and light attenuation cross-sections (σ_{ATN}) of $PM_{2.5}$ BC were derived. The mass of EC contributed ~5% to $PM_{2.5}$ on average. BC σ_{ATN} exhibited pronounced seasonal variability with values averaging 18.6, 24.2, 16.4, and 26.0 m^2/g for the spring, summer, autumn, and winter, respectively, while averaging 23.0 m^2/g overall. σ_{ATN} varied inversely with the ratios of EC/$PM_{2.5}$, EC/[SO_4^{2-}], and EC/[NO_3^-]. This study of the variability in σ_{ATN} illustrates the complexity of the interactions among the aerosol constituents in northern China and documents certain effects of the high EC, dust, sulfate and nitrate loadings on light attenuation.

Introduction

Aerosol species, including carbonaceous matter, dust, sulfate, and nitrate, are critically important to the radiative balance of the atmosphere (Crutzen & Andreae, 1990). Aerosols are major light absorbers in atmosphere due to their contents of light-absorbing substances, such as elemental carbon (EC) and hematite (α-Fe_2O_3). The absorption of solar radiation can lead to a warming effect similar to that caused by greenhouse gases, thereby possibly affecting the atmospheric stability over regional scales; these changes could alter the hydrological cycle and possibly cause other effects (Jacobson, 2001; Ramanathan et al., 2005).

The specific attenuation cross-section (σ_{ATN}) of BC is a critical parameter for light absorption calculations. This coefficient depends on the size distribution and fractal dimensions of BC, as well as its mixing state relative to other components. BC can exist in two mixing states: externally mixed with other particles or internally incorporated within other particles or as a core surrounded by a well-mixed shell (Haywood, Roberts, Slingo, Edwards, & Shine, 1997; Jacobson, 2000, 2001; Myhre, Stordal, Restad, & Isaksen, 1998). Obtaining accurate values for σ_{ATN} is currently challenging due to the effects of the mixing state and other factors (Arnott, Hamasha, Moosmüller, Sheridan, & Ogren, 2005; Weingartner et al., 2003). The literature values for σ_{ATN} vary over an order of magnitude, ranging from 5 to 55 m^2/g (Jeong, Hopke, Kim, & Lee, 2004; Liousse, Cachier, & Jennings, 1993). Because roughly one-fourth of the global BC emissions are believed to originate from China (Cooke, Liousse, Cachier, & Feichter, 1999), the high loading of BC in the

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atmosphere over China and its effect on the balance of solar radiation have serious implications for regional climatic change (Menon, Hansen, Nazarenko, & Luo, 2002).

Northern China often suffers from high loadings of air pollutants, particularly EC, dust, sulfate, and nitrate (Cao et al., 2007, 2009, 2012; Zhang et al., 2011); the interactions among these substances can alter their interactions with light, including the positive forcing from BC. However, no published data describing BC σ_{ATN} are available for $PM_{2.5}$ in China. Therefore, the purpose of this study is to characterize the σ_{ATN} at Xi'an, which is a large city in northwestern China and to investigate the relationships between various aerosol species. These results will help to evaluate σ_{ATN} and to understand the effects of urban aerosols on light attenuation in other regions of China.

Methods

Xi'an (34.2° N, 108.9° E), which is in Shaanxi Province, is the largest city in northwestern China and has a population of eight million. Xi'an also experiences the air pollution typical of many Chinese cities; high dust loadings (it is near Asian dust source regions) are often present with low relative humidity (RH). Elevated carbonaceous aerosol loadings contribute to the high PM levels (Cao, Wu, et al., 2005).

Samples of $PM_{2.5}$ were collected in Xi'an from 13 September 2003 to 31 August 2005 on the rooftop of a building ~10 m above ground at Institute of Earth Environment, Chinese Academy of Sciences, Xi'an. $PM_{2.5}$ samples were collected daily using MiniVol $PM_{2.5}$ Portable Air Sampler (Airmetrics Inc., 2095 Garden Ave. Suite 102 Eugene, OR 97403, U.S.A.) operating at 5 L/min (Cao et al., 2003; Cao, Wu, et al., 2005). The mass concentrations of $PM_{2.5}$ were determined gravimetrically using a Sartorius MC5 electronic microbalance (Sartorius, Gottingen, Germany) with a ±1 μg sensitivity. The EC contents were measured with a DRI-2001 carbon analyzer operated according to the IMPROVE thermal/optical reflectance (IMPROVE/TOR) protocol (Chow & Watson, 2002). The instrumental detection limit for the EC was 0.19 μg; this amount is equal to a mass concentration of 0.37 μg/m^3 under the experimental conditions used in this work. The quality assurance/quality control (QA/QC) procedures have been described in Cao et al. (2003).

The light attenuation was recorded at 5-min intervals using an aethalometer (Model AE-16, Magee Scientific) with a $PM_{2.5}$ inlet and a flow rate of 4 L/min. This instrument collects particles on a quartz fiber tape and measures the light attenuation caused by the sampled particles. The attenuation (ATN, in Mm^{-1}), which is measured at 880 nm, was determined based on the following equation:

$$\mathrm{ATN} = 100 \ln\left(\frac{I}{I_0}\right). \quad (1)$$

In this equation, I and I_0 are the transmitted light intensities for the loaded filter and the blank, respectively. The factor of 100 is used for numerical convenience. The measured light attenuation can be converted into BC concentrations [BC], as follows:

$$[\mathrm{BC}] = \frac{\mathrm{ATN}}{\sigma_{ATN}}, \quad (2)$$

where σ_{ATN} is the specific attenuation cross-section of the particle-laden filter (m^2/g). We note that the light-attenuation measurements made through the filters used by the aethalometers can be influenced by several factors unrelated to BC mass (Weingartner et al., 2003). In this work, the manufacturer's default value (16.6 m^2/g) for σ_{ATN} was used to calculate the BC concentrations. In addition, 206,600 individual 5-min BC concentrations were used to calculate the daily averages of the total BC. Due to instrument failures, the data were missing from May to June 2004 and for several other shorter periods (one or two days) (Table 1). In this instance, the EC was obtained by using the IMPROVE/TOR protocol, while BC refers to what was measured by the aethalometer. Previous studies have reported the differences between EC and BC (Andrea & Gelencsér, 2006).

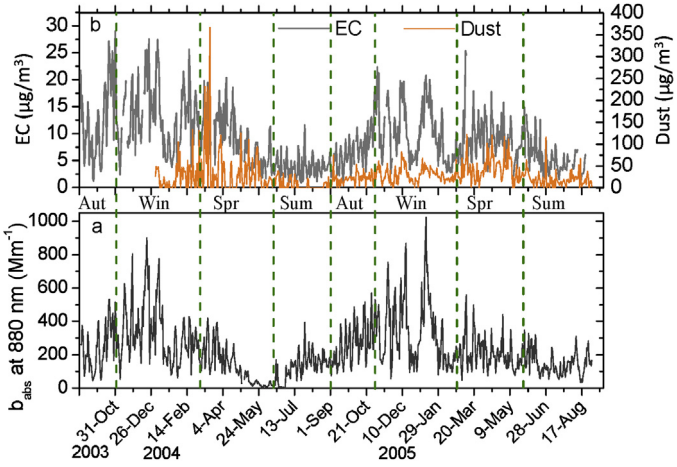

Fig. 1. Time series for (a) aerosol light absorption coefficient (b_{abs}) at 880 nm, and (b) concentrations of dust and EC.

The mineral dust loadings were estimated from the Fe concentrations, which were determined through a proton-induced X-ray emission (PIXE) technique while assuming that the Fe constituted 4% of mineral dust content (Zhang et al., 2003). The PIXE analyses were performed using the 2.5 MeV protons with a 50 nA beam current, which was produced by 2 × 1.7 MV tandem accelerator at Beijing Normal University (GIC4117, General Ionex Corp.). The PIXE trace element data were corrected for the background by using blank filters, specifically, filters brought to the field and installed in the samplers but through which no air was pumped.

A Dionex-600 Ion Chromatograph (Dionex Inc., Sunnyvale, CA, USA) was used to determine the contents of both the cations and the anions in the aqueous extracts of the air filters. The instrument was equipped with an IonPacCS12A column (20 mM methanesulfonic acid as the eluent) to analyze the cations, while an IonPac AS14A column (8 mM Na_2CO_3/1 mM $NaHCO_3$ as the eluent) was used to analyze the anions. The minimum detection limits were as follows: 0.001 μg/mL for Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}; 0.008 μg/mL for Cl^-, 0.025 μg/mL for NO_3^-; 0.027 μg/mL for SO_4^{2-}. Standard reference materials produced by the National Research Center for Certified Reference Materials (Beijing, China) were analyzed for quality control and quality assurance purposes. All of the reported ion concentrations were corrected using the field blanks. The experimental uncertainties were ±0.04 for NO_3^- and SO_4^{2-}, ±0.03 for Ca^{2+}, ±0.02 for Cl^-, ±0.01 for NH_4^+, K^+ and Mg^{2+}, and ±0.004 for Na^+.

Results and discussion

Aerosol light absorption

The aerosol light absorption coefficient (b_{abs}) at 880 nm showed relatively low values in summer and high values in winter that ranged from 15.0 to 1025.0 Mm^{-1} and averaged 241 Mm^{-1} over the entire sampling period (Fig. 1(a)). The seasonally averaged values were 184.0, 142.8, 248.0, 329.0 Mm^{-1} for the spring (March, April, and May), summer (June, July, and August), autumn (September and October) and winter (November, December, January, and February), respectively. The present results were higher than the