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Source apportionment of $PM_{2.5}$ light extinction in an urban atmosphere in China

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ABSTRACT

Haze in China is primarily caused by high pollution of atmospheric fine particulates ($PM_{2.5}$). However, the detailed source structures of $PM_{2.5}$ light extinction have not been well established, especially for the roles of various organic aerosols, which makes haze management lack specified targets. This study obtained the mass concentrations of the chemical compositions and the light extinction coefficients of fine particles in the winter in Dongguan, Guangdong Province, using high time resolution aerosol observation instruments. We combined the positive matrix factor (PMF) analysis model of organic aerosols and the multiple linear regression method to establish a quantitative relationship model between the main chemical components, in particular the different sources of organic aerosols and the extinction coefficients of fine particles with a high goodness of fit (R^2 = 0.953). The results show that the contribution rates of ammonium sulphate, ammonium nitrate, biomass burning organic aerosol (BBOA), secondary organic aerosol (SOA) and black carbon (BC) were 48.1%, 20.7%, 15.0%, 10.6%, and 5.6%, respectively. It can be seen that the contribution of the secondary aerosols is much higher than that of the primary aerosols (79.4% versus 20.6%) and are a major factor in the visibility decline. BBOA is found to have a high visibility destroying potential, with a high mass extinction coefficient, and was the largest contributor during some high pollution periods. A more detailed analysis indicates that the contribution of the enhanced absorption caused by BC mixing state was approximately 37.7% of the total particle absorption and should not be neglected.

Introduction

Visibility is an important indicator of the urban air quality, which depends on the extinction of the atmosphere. The atmospheric extinction effect includes the extinction of gases and particles, in which the extinction of particles, *i.e.*, the scattering and absorption of sunlight by the atmospheric particles, is the primary factor (Watson, 2002). The optical properties of particles depend on the particle size, morphology, chemical composition, mixed state and the hygroscopic properties of the particles (Meier et al., 2009; Ma et al., 2012; Liu et al., 2014; Cao et al., 2012). Therefore, the study of the

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physical and chemical properties of particulate matter is key to the quantitative study of solar radiation and particle environmental effects.

Early studies of the extinction of particulate matter have primarily focused on the relationship between the mass concentration of particles and the extinction coefficient and have found a significant positive correlation between the two (Chan et al., 1999; Wang et al., 2006); however, due to the complex chemical composition of particles and large differences in particle size, changes in the extinction coefficient cannot be well characterised by only the concentration of the particles. In addition, some studies have used the Mie model to simulate the mixed state of particulate matter (Cheng et al., 2008) to explore particle extinction properties; however, the Mie model, as a theoretical model, cannot quantitatively represent the impact of particles on the visibility in a satisfactory manner. Using the multiple regression analysis method, the United States IMPROVE project (Interagency Monitoring of Protected Visual Environments) constructed the IMPROVE formula to calculate the extinction coefficient with multiple chemical species mass concentrations and extinction efficiencies (Sisler and Malm, 2000). This formula has been widely used in related studies involving the extinction of particulate matter (Wang et al., 2016; Zhou et al., 2016; Yu et al., 2016). Note that the IMPROVE formula is primarily designed for the chemical compositions and optical properties of $PM_{2.5}$ and cannot be used for PM_1, which is more closely related to atmospheric extinction. In addition, most studies have calculated the extinction contribution of organic aerosols as a whole (Wang et al., 2016; Zhou et al., 2016; Yu et al., 2016); however, the physical and chemical properties of organic aerosols are very complex and the optical properties of different types of organic aerosols from different sources are very different. Therefore, it is necessary to explore the effect of different types of organic aerosols on atmospheric extinction.

Traditional filter-based sampling methods have a shading effect and a multiple scattering effect (Weingarten et al., 2003; Bond et al., 2006); in particular, the BC mass concentration and extinction coefficient is greatly influenced, which has a direct impact on the regression fit. In addition, off-line sampling has lower time resolution and its sample numbers and accuracy cannot satisfy our demands. In this study, we use high time resolution aerosol observation equipment to obtain *in situ* measurement data to establish the relationship between the chemical composition and extinction coefficient of atmospheric fine particles using the multiple linear regression method. In particular, the influence of different types of organic aerosols on the extinction of particulate matter is quantified and the influence of each component on the extinction coefficient is discussed to provide a scientific basis for haze management in China.

1. Material and method

1.1. Sampling site and period

The measurements were conducted in Dongguan City in the wintertime, from 11 December 2013, to 10 January 2014, during the polluted dry season in PRD with prevailing wind from the mainland (Huang et al., 2014). The Dongguan (DG) site is an urban site (23.0° N 113.7° E) in the middle of PRD with high urbanisation and industrialisation. The site was within a building beside a sports stadium located in the downtown area of Dongguan.

1.2. Instruments

The instruments were placed in a temperature-controlled room and the air was induced through a $PM_{2.5}$ cyclone inlet placed on the rooftop and then dried before entering the inlets of the instruments. A high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) (Aerodyne Research, MA, USA) was used to measure non-refractory species of PM_1, including the organic carbon, sulphate, nitrate, ammonium ions and chloride ions. A detailed description of the instrument is given by DeCarlo et al. (2006), and the calibration followed standard protocols (Jayne et al., 2000; Jimenez et al., 2003; Drewnick et al., 2005). Additional details concerning the HR-ToF-AMS operation can be found in He et al. (2011) and Huang et al. (2011).

A single particle soot photometer (SP2) (Droplet Measurement Technologies, CO, USA) was used to measure the black carbon (BC) mass concentration and size distribution. The technical details are described in Schwarz et al. (2006, 2008). The calibration of the SP2 was conducted with fullerene soot (Alpha Aesar, Inc., Ward Hill, MA) selected by size using a differential mobility analyser upstream of the SP2. Additional details concerning the SP2 operation are provided in Huang et al. (2012). The detection limit of the BC particles in this study was approximately 0.07 μg in volume equivalent diameter.

A three-wavelength Photo-acoustic Soot Spectrometer (PASS-3) (Droplet Measurement Technologies, CO, USA) was simultaneously used to obtain the light absorption b_{ap} and scattering b_{sp} coefficients at 532 nm. The principles and technical details of the PASS-3 are described by Arnott et al. (1999), and additional details concerning the calibration and operation can be found in Yuan et al. (2016). The aerosols were dried prior to the inlet; therefore, it is the dry aerosol extinction coefficients measured by this instrument that are later referred to.

A Nitrogen Oxide Analyser (EC9841) was used to measure the nitrogen dioxide, and the time resolution was set to 1 min. The absorption of solar visible wavelengths by nitrogen dioxide is the most significant for a gas; therefore, the gas absorption coefficient b_{ag} was calculated from the measured concentration of nitrogen dioxide. Because the concentration of gas in the atmosphere is relatively stable, the scattering effects of other gas molecules are generally constant, and generally the value of the atmospheric gas scattering coefficient b_{sg} is taken to be 13 Mm^{-1} (Cohen, 1975).

The atmospheric total extinction coefficient, b_{ext}, was obtained by summing the gas absorption coefficient b_{ag}, the gas scattering coefficient b_{sg}, the particle absorption coefficient b_{ap} and the particle scattering coefficient b_{sp}.

2. Results and discussion

2.1. Atmospheric extinction

Fig. 1 shows a time series of the atmospheric extinction in the Dongguan area during the campaign. The average extinction

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