



## Impacts of aerosol chemical compositions on optical properties in urban Beijing, China



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### ABSTRACT

The optical properties of aerosols and their chemical composition, including water-soluble ions, organic carbon (OC), and elemental carbon (EC) in PM<sub>2.5</sub> and PM<sub>10</sub>, were measured from 26 May to 30 June of 2012 at an urban site in Beijing. The daily average concentrations of PM<sub>2.5</sub> and PM<sub>10</sub> were 103.2 and 159.6 μg/m<sup>3</sup>, respectively. On average, the OC and EC contributed 20.1% and 4.3%, respectively, to PM<sub>2.5</sub> and 16.3% and 3.9%, respectively, to PM<sub>10</sub>. Secondary ions (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup>) dominated the water-soluble ions and accounted for 57.9% and 62.6% of PM<sub>2.5</sub> and PM<sub>10</sub>, respectively. The wind dependence of PM<sub>2.5</sub>, OC, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup> implied that the pollution sources mainly came from south and southeast of Beijing during the summer. The monthly mean values of the scattering coefficient ( $\sigma_{sc}$ ) and absorption coefficient ( $\sigma_{ab}$ ) at 525 nm were 312.9 and 28.7 Mm<sup>-1</sup>, respectively, and the mean single-scattering albedo ( $\omega$ ) was 0.85. The wind dependence of  $\sigma_{sc}$  revealed that this value was mainly influenced by regional transport during the summer, and the relationship between  $\sigma_{ab}$  and wind indicated that a high  $\sigma_{ab}$  resulted from the joint effects of local emissions and regional transport. The reconstructed  $\sigma_{sc}$  that was derived from the revised IMPROVE equation agreed well with the observations. The contribution of different chemical species to  $\sigma_{sc}$  was investigated under different pollution levels, and it was found that secondary inorganic aerosols accounted for a large part of  $\sigma_{sc}$  during pollution episodes (35.7%), while organic matter was the main contributor to  $\sigma_{sc}$  under clean conditions (33.6%).

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### Introduction

Aerosols can directly disturb the radiation balance of the Earth by scattering and absorbing incoming light and can indirectly influence it by increasing the number of cloud condensation nuclei, which will increase cloud reflectivity and lifetime. As a result of the interference to the physical parameters caused by aerosol particles, the uncertainty in the direct aerosol radiative forcing is 0.5–1.0 W/m<sup>2</sup> (Loeb & Su, 2010). The single scattering albedo ( $\omega$ ) is the largest source of uncertainty in estimating the direct radiative forcing; it reflects the relative scattering capacity of aerosols, which depends on both the chemical components and the size dis-

tributions of aerosols. According to IPCC (Solomon et al., 2007), the uncertainties in the estimations of regional climate forcing lie mainly in calculating the optical properties of aerosols. Therefore, the precise measurement of the optical properties of aerosol and the closely related chemical compositions are urgently needed to evaluate the effect of aerosol particles on regional climate change and the energy budget of the Earth.

In situ observations of aerosol optical properties, such as the scattering coefficient ( $\sigma_{sc}$ ), absorption coefficient ( $\sigma_{ab}$ ), and  $\omega$ , have been widely conducted at both urban and rural sites in China. Garland et al. (2009) and Jung et al. (2009) conducted observations of the optical properties of aerosols at suburban and urban sites, respectively, in Beijing. While Yan (2007) and Yan et al. (2009) carried out experiments using filter-based and in situ ground instruments to measure aerosol optical properties in northern China. Meanwhile, Fan, Chen, Xia, Li, and Cribb (2010) and Xu et al.

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(2002) reported results from the Yangtze River Delta regions. The aerosol optical characteristics in the Pearl River Delta region were also analyzed (e.g., Andreae et al., 2008; Cheng et al., 2008; Garland et al., 2008). Due to the large spatial and temporal variation of the aerosol sources, their optical properties vary greatly. The optical properties of aerosols are considered to be related to their chemical compositions and particle size distributions (Bergin et al., 2001). To date, most studies have focused on analyzing the mass concentration, size distribution, and different chemical species in ambient air in China (Yan et al., 2012; Zhang, Cao, Lee, Shen, & Ho, 2007). As a recent example, Zhang et al. (2013) explored in detail the seasonal variation of the chemical species, including organic carbon (OC), elemental carbon (EC), ions, and elements of PM<sub>2.5</sub>. They also noted the potential sources of particulate matter in Beijing during different seasons. However, limited in situ measurements have been conducted in China on the relationship between the optical properties and chemical compositions (Li, Chen, Wang, Melluki, & Zhou, 2013; Tao et al., 2012, 2014).

Beijing, the capital of China, has been in the spotlight for its severe air pollution problems, which have posed, and might continue to pose, great threats to human health. According to a comprehensive evaluation index of urban–environment air quality in China, seven cities in the Hebei Province are among those highlighted as the most polluted cities (<http://www.zhb.gov.cn>). These cities are located to the south and east of Beijing, and, thus, may have a possible influence on the air quality and visibility in the capital city. It was reported that fine particles (PM<sub>2.5</sub>) are likely the major pollution source of the ambient air in Beijing (<http://www.bjepb.gov.cn/>). Measurements of the aerosol optical properties and chemical compositions were conducted by Li, Chen, Wang, Melluki, and Zhou (2013) during the summer of 2006 in Beijing. The results showed very serious air pollution in Beijing, and most of the particles were formed via secondary formation. However, the government had previously taken many actions to improve the air quality, including the promulgation of air pollution control measures for the period 2012–2020 and a ban on private car use inside Beijing's urban area for one business day per week (<http://www.bjtg.gov.cn/publish/portal0/tab62/info52267.htm>). Understanding the mechanisms of particle formation and the impact of chemical compositions on optical properties is very useful for the government in its attempts to improve air quality and visibility in China's megacities.

In this study, the optical properties, including  $\sigma_{sc}$ ,  $\sigma_{ab}$ , and  $\omega$ , were measured continuously for approximately a month at an urban site in Beijing during the summer of 2012. The diurnal variation and wind dependence pattern of the optical properties were recorded to estimate the characteristics of urban aerosols and their potential sources. In addition, the OC, EC, and ion concentrations in PM<sub>2.5</sub> and PM<sub>10</sub> were analyzed. The impacts of the chemical species on the optical properties were estimated according to the IMPROVE formula and correlated with the pollution levels. A long-term study of the physical and chemical properties of the aerosols will be carried out in the future to analyze the seasonal differences in the aerosol properties in Beijing.

## Experimental methods

### Observation site

An intensive observation campaign, including measurements of aerosol optical properties and particle filter sampling, was conducted in urban Beijing from 26 May to 30 June 2012. The sampling site was the Tower Division of the Institute of Atmospheric Physics, Chinese Academy of Sciences (Zhang, Shen, Cheng, Zhang, & Liu, 2010), which is located between the North Third and Fourth Ring

Roads of Beijing. It is surrounded mostly by residential areas. A busy road with heavy traffic during rush hours is approximately 150 m east of the site. Therefore, this campaign should be a good reflection of the typical characteristics of urban aerosols in Beijing. The sampling instruments were installed on the roof of a two-floor laboratory building, approximately 8 m above the ground.

### Filter sampling and chemical composition analysis

PM<sub>2.5</sub> and PM<sub>10</sub> samples were collected using two Mini-Volume samplers (Airmetrics, Oregon, USA) at a flow rate of 5 L/min with PM<sub>2.5</sub> and PM<sub>10</sub> inlets, respectively. The collection of the 24-h filter samples occurred at 09:00 LST. The clean filters were heated to 700 °C for three hours before sampling to remove any possible residual OC/EC. The masses of the filters before and after sampling were measured using an electronic microbalance with an accuracy of 1 μg (Sartorius, Göttingen, Germany) to determine the mass concentrations of the PM<sub>2.5</sub> and PM<sub>10</sub> in a constant temperature (25 °C) and humidity (40%) chamber. The sample filters were divided into four equal parts; one part was used for the OC/EC analyses using a carbon analyzer (Model 2001, DRI, USA) according to the protocol introduced by Chow et al. (1993, 2004), and the advantages and limitations of this instrument are described in detail in Cao et al. (2003). Another quarter of each filter was used to assess the concentrations of the major water-soluble ions, including three major anions (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and Cl<sup>-</sup>) and five major cations (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>), using a DX 500 ion chromatograph (Dionex Corp, Sunnyvale, CA). All of the water-soluble ions, OC, and EC concentrations were subtracted for the field blank.

### Scattering measurement and correction

$\sigma_{sc}$  was continuously measured by a Aurora-3000 integrating nephelometer (Ecotech, Australia) at three wavelengths (450, 525, and 635 nm). The nephelometer can measure  $\sigma_{sc}$  at less than 0.3 Mm<sup>-1</sup> (about one-tenth of the Rayleigh scattering of air) to greater than 2000 Mm<sup>-1</sup> at 525 nm. An LED light source is used in this instrument with a scattering integration angle from 10° to 170°. A correction for the light truncation was performed on the basis of Anderson and Ogren (1998) and Bond, Covert, and Müller (2009). The corrected  $\sigma_{sc}$  can be derived from the following formula:

$$\sigma_{sc} = C\sigma_{neph}, \quad (1)$$

where  $\sigma_{neph}$  is the raw scattering coefficient measured by the nephelometer and C is the correction factor for the truncation, which can be estimated according to Eq. (2):

$$C(\lambda) = a(\lambda) + b(\lambda)\alpha_{sc}, \quad (2)$$

where  $a(\lambda)$  and  $b(\lambda)$  are the fitting parameters at 450, 525, and 630 nm, as determined by Müller et al. (2009). The term  $\alpha_{sc}$  is the scattering Ångström exponent, which can be estimated from the uncorrected multi-wavelength  $\sigma_{sc}$  according to the following equation:

$$\alpha_{sc} = -\frac{\ln(\sigma_{\lambda_1}) - \ln(\sigma_{\lambda_2})}{\ln(\lambda_1) - \ln(\lambda_2)}. \quad (3)$$

$\alpha_{sc}$  was also utilized to estimate  $\sigma_{sc}$  at 520 nm from those at 525 nm.

Zero checks were performed automatically once a day, and full calibrations were necessary using both particle-free air and R22 gas (CHClF<sub>2</sub>) when the result of the span check showed a bias of more than 10%. The relative humidity (RH) is another factor that influences the amount of scattering by aerosol particles (Yan et al., 2009). To avoid the influence of RH on  $\sigma_{sc}$ , silica gel was installed before the inlet to lower the RH.

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