



Aerosol chemical composition and light scattering during a winter season in Beijing



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HIGHLIGHTS

- Aerosol chemical and optical properties were compared in different pollution levels.
- Contributions of dominant chemical components to light scattering were quantified.
- Causes of heavy pollution events and related visibility degradation were explored.

ARTICLE INFO

Article history:

Received 23 December 2014

Received in revised form

13 March 2015

Accepted 19 March 2015

Available online 20 March 2015

Keywords:

PM_{2.5}

Aerosol size distribution

Hygroscopic growth

Biomass burning

Visibility degradation

ABSTRACT

To evaluate PM_{2.5} contributions to light scattering under different air pollution levels, PM_{2.5} and its major chemical components, PM₁₀, size-segregated water-soluble ions, and aerosol scattering coefficient (b_{sp}) under dry conditions were measured at an urban site in Beijing in January 2013 when heavy pollution events frequently occurred. Measurements were categorized into three pollution levels including heavy-polluted (Air Quality Index (AQI) ≥ 200), light-polluted ($200 > \text{AQI} \geq 100$) and clean periods (AQI < 100). The average PM_{2.5} mass concentration was 248 $\mu\text{g m}^{-3}$ during the heavy-polluted period, which was 2.4 and 5.6 times of those during the light-polluted (104 $\mu\text{g m}^{-3}$) and clean (44 $\mu\text{g m}^{-3}$) periods, respectively. The concentrations of SO_4^{2-} , NO_3^- and NH_4^+ increased much more than those of OC and EC during the heavy-polluted period compared with those during the light-polluted and clean periods. Good correlations between PM_{2.5} and b_{sp} were found ($R^2 > 0.95$) during the different pollution levels. The mass scattering efficiency (MSE) of PM_{2.5} was 4.9 $\text{m}^2 \text{g}^{-1}$ during the heavy-polluted period, which was higher than those during the light-polluted (4.3 $\text{m}^2 \text{g}^{-1}$) and clean periods (3.6 $\text{m}^2 \text{g}^{-1}$). To further evaluate the impact of individual chemical components of PM_{2.5} on light scattering, a multiple linear regression equation of measured b_{sp} against the mass concentration of $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , Organic Matter (OM), EC, Fine Soil (FS), Coarse Matter (CM) and Other chemical compounds were performed. $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 and OM were the dominant species contributing to b_{sp} under both dry and ambient conditions. OM contributed more to b_{sp} than the sum of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 did under the dry condition during all the pollution periods and this was also the case under the ambient condition during the light-polluted and clean periods. However, the total contributions of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 to b_{sp} under the ambient condition was 55%, much more than the 29% contribution from OM during the heavy-polluted period. High $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 concentrations and their hygroscopicity were the main reasons causing visibility degradation during the heavy-polluted period, and the effect can be enhanced under high RH conditions.

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1. Introduction

Fine particulate matter (PM_{2.5}) is a key group of air pollutants causing visibility degradation (Malm et al., 1994; Watson, 2002). Knowledge of contributions of individual chemical components of

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PM_{2.5} to light extinction – the sum of scattering and absorption, is critical in establishing control measures to alleviate visibility degradation. Sulfate, nitrate, OM and EC have been identified as dominant components of PM_{2.5} in urban areas worldwide (Bell et al., 2007; Chan and Yao, 2008; Hueglin et al., 2005; Lonati et al., 2005; Querol et al., 2001). These chemical compounds have also been reorganized as dominant contributors for visibility degradation (Hand and Malm, 2007; Lee et al., 2009; Malm et al., 2003). Aerosol hygroscopic properties are known to enhance aerosol scattering capability and thus are also important factors affecting visibility (Liu et al., 2008, 2011, 2012; Swietlicki et al., 2008). Earlier studies have shown that b_{sp} can be increased by ~1.6–2.7 times when RH increased from 40% to 80% (Liu et al., 2008; Xu et al., 2002; Tao et al., 2014a).

Beijing, the capital of China, is the largest city in North China Plain (NCP), which is one of the most polluted regions in China (Chan and Yao, 2008). Serious air pollution and visibility degradation frequently occurred in recent years in this city (Li et al., 2013; Lin et al., 2009; Liu et al., 2013; Zhang et al., 2010, 2013; Zhao et al., 2009). Many studies have been conducted recently aiming to understand aerosol physical, chemical and optical properties in Beijing (Bi et al., 2014; Boynard et al., 2014; Sun et al., 2014; Tian et al., 2014; Zhang et al., 2014, 2015). However, a quantified relationship between aerosol chemical components and visibility degradation is still lacking. It is not known if the relative contributions of dominant chemical components to light extinction and visibility degradation under heavy polluted conditions are different or not from the cases of less polluted conditions. Such knowledge has practical values in making pertinent control measures for alleviating visibility degradation.

To shed some light on this topic, chemically-resolved aerosol data collected during a month with frequent heavy pollution events in Beijing were analyzed in this study. The whole data set was categorized into different PM_{2.5} pollution levels – heavy, light and clean, and the relationships between aerosol chemical composition and light scattering and contributions of individual chemical compounds to aerosol light scattering under dry and ambient conditions were investigated during different pollution levels.

2. Methodology

2.1. Site description

Measurements were conducted on the roof (20 m above ground) of an office building of the Chinese Research Academy of Environmental Sciences (CRAES) (116°24'E, 40°02'N) located near a residential area in the north part of Beijing (Fig. 1) and more than 2 km away north of the fifth-ring road. No major stationary air pollution sources were present within a circumference of 5 km of the site except mobile emissions. Thus, the site was considered to be representative of a typical urban environment in Beijing. More information about this station can be found in Gao et al. (2014) and Wang et al. (2010).

2.2. Continuous measurements of aerosol scattering coefficient and meteorological parameters

Aerosol scattering coefficient (b_{sp}) was measured using a single wavelength integrating nephelometer (Ecotech Pty Ltd, Australia, Model Aurora1000G) at the wavelength of 520 nm. The scattering intensities over angles from 7° to 170° were measured and integrated to yield b_{sp} . To obtain dry b_{sp} , RH of inflow air was controlled by a heated inlet to be less than 40% to minimize the influence of water vapor. The nephelometer was equipped with a conventional total suspended particulate (TSP) cyclone. The flow rate was set at

5 L min⁻¹. Zero calibration was performed once every day with particle-free air, and span check was done on weekly basis using particle-free HFC-R134a gas (Tao et al., 2014a). Total b_{sp} was corrected for Angular Nonidealities following the method described in Anderson and Ogren (1998).

Meteorological parameters, including wind speed (WS), wind direction (WD), relative humidity (RH), temperature (TEMP), solar radiation (SR) and precipitation (PR) were collected every 1 min. The meteorological instruments were mounted at 3 m above the roof of the station (20 m above ground) (Gao et al., 2014).

2.3. Aerosol sampling

During the sampling period, PM_{2.5} and PM₁₀ samples were collected for 23.5 h (from 09:00 a.m. to 08:30 a.m. of next day) by a four-channel sampler made by Tianhong Instrument Co. Ltd. of China (model: TH-16A, flow rate: 16.7 L/min for each channel). PM_{2.5} and PM₁₀ samples were collected on 47 mm Whatman quartz-fiber filter (QM/A, Whatman Inc., UK) and 47 mm Teflon filters (Whatman PTFE). Before sampling, the quartz filters were baked at 500 °C for at least 4 h to remove adsorbed organic vapors. A total of 24 sets PM_{2.5} and PM₁₀ samples was collected. Three field blanks were collected and used to account for any artifacts caused by gas absorption.

A nine stage Micro-Orifice Uniform Deposit Impactor (MOUDI model 100, MSP Corp, Shoreview, MN USA) was used to collect size-segregated aerosols. It had pre-impaction stage and nine regular stages with cut-point diameters of 18, 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32 and 0.18 μm. The flow impactor loaded with aluminum filters was operated at a flow rate of 30 L min⁻¹ for approximately 24 h to collect a set of size-segregated sample. Considering possible particle bounce at low RH conditions, only six out of the 25 sets of samples collected on January 13, 21, 23, 28, 29 and 30, respectively, when ambient RH >40% were used for further analysis. Such a choice was based on results obtained in a previous study which suggested that uncertainties in measurements due to particle bounce were smaller than 5% (Chen et al., 2011). Blanks followed the same procedures as sample collection except with pump turning on. Aerosol-loaded filter samples were stored in a freezer at -20 °C before being analyzed to prevent volatilization of particles.

2.4. Gravimetric weighing

Teflon filters were measured gravimetrically to obtain particle mass concentrations using a Sartorius MC5 electronic microbalance with a sensitivity of ±1 μg (Sartorius, Göttingen, Germany) after 24 h equilibration at 23 ± 1 °C with relative humidity at 40 ± 5%. Each filter was weighed at least three times before and after sampling. Differences among replicate weights were mostly less than 20 μg for each sample. Net mass was obtained by subtracting pre-weight from post-weight.

2.5. Chemical analysis

An area of 0.526 cm² punched from each quartz filter was analyzed for eight carbon fractions following the IMPROVE_A thermal/optical reflectance (TOR) protocol on a DRI model 2001 carbon analyzer (Atmoslytic, Inc., Calabasas, CA, USA) (Cao et al., 2003). Average field blanks OC and EC were subtracted from each sample filter.

An area of 2.0 cm² punched from each quartz filter was extracted in 2 mL of ultrapure water under ultrasonic agitation for 1 h. Extracts were filtered through a syringe filter (pore size 0.25 μm, PTFE, Whatman, USA) to remove insoluble materials. The

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