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# Characteristics of heavy aerosol pollution during the 2012–2013 winter in Beijing, China

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## HIGHLIGHTS

- Both aerosol concentrations and RH had strong effect for the occurrence of the haze events.
- The lower PBL height in haze events leads to an increase in the surface aerosol concentrations.
- During the heavy haze events, higher heterogeneous conversions from gas to particle phases of $NO_x$ and $SO_2$ was observed.

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## ABSTRACT

A comprehensive measurement was carried out to analyze the heavy haze events during 2012–2013 winter in Beijing. The measured variables include some important meteorological parameters, such wind directions, wind speeds, relative humidity (RH), planetary boundary layer (PBL), solar radiation, and visibility. The aerosol composition and concentrations (including particular matters ($PM_{2.5}$), nitrate ($NO_3$), sulfate ($SO_4$), ammonium ($NH_4$)) as well as their gas-phase precursors (including nitrogen oxides ($NO_x$) and sulfur dioxide ($SO_2$)) were analyzed during the period between Nov. 16, 2012 and Jan. 15, 2013. The results show that the hourly mean concentrations of $PM_{2.5}$ often exceeded 200 μg/m$^3$, with a maximum concentration of 600 μg/m$^3$ on Jan. 13, 2013. The relative humidity was increased during the haze events, indicating that both aerosol concentrations and RH had important effect on the reduction of visibility, causing the occurrence of the haze events. Because the wind speeds were generally low (less than 1 m/s) during the haze event, the vertical dispersion and the PBL heights were very important factors for causing the strong variability of aerosol concentrations. This study also finds that under the lower visibility condition, the conversion from the gas-phase of $NO_x$ and $SO_2$ to the particle phase of $NO_3$ and $SO_4$ were higher than the values under the higher visibility condition. Because the lower visibility condition was corresponding to the lower photochemical activity than the higher visibility condition, the higher conversion from gas phase to particle phase in the lower visibility condition indicated that there was important heterogeneous formation of $NO_3$ and $SO_4$ during the heavy haze events.



## 1. Introduction

Beijing is experiencing heavy air pollution in the past two decades, with particle matter (PM) being one of the top pollutants (Chan and Yao, 2008). PM, especially fine particles ($PM_{2.5}$; particle matter with the radius equal/less 2.5 μm) often exceed the new National Ambient Air Quality Standards of China (75 μg m$^{-3}$ for 24 h average) (Sun et al., 2013). Aerosol particles have a large impact on visibility by scattering (Charlson et al., 1987; Tegen et al., 2000) and absorbing (Ramanathan and Vogelmann, 1997; Jacobson, 2001) solar and infrared radiation. The hygroscopic growth of aerosol particles will further increase their effect on atmospheric visibility (Quan et al., 2011). Therefore, haze events (with visibility < 10 km) appear frequently in Beijing, especially under high relative humidity (RH). However, the air pollution control

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remains a great challenge due to the complex sources and evolution processes of aerosol particles, together with complicated aerosol-radiation-Planetary Boundary Layer (PBL) interactions.

In the last decade, extensive efforts have been made to characterize the sources, properties and processes of PM in Beijing. Recent studies indicate that a large mass fraction of ambient PM in Beijing is fine particles, of which carbonaceous particles, sulfate, nitrate and ammonium are the major components (Guinot et al., 2007; He et al., 2001; Yang et al., 2011). The secondary formation of coal/biomass burning products, crust, industrial and traffic emissions were the major sources of the fine aerosols in Beijing (Wang et al., 2005; Sun et al., 2010). The physical and chemical characteristics of aerosol particles affect directly their hygroscopic properties (Topping et al., 2005a,b). Liu et al. (2011) analyzed the hygroscopic growth factor at different RH for particles with dry diameters between 50 and 250 nm in North China Plain (NCP). Quan et al. (2011) calculated the visibility based on observed aerosol size distribution and their hygroscopic. Their results indicated that the calculated visibility with the hygroscopic growth of aerosol is consistent with measured visibility.

Moreover, the complicated aerosol-radiation-PBL interactions might further increase ground aerosol particles concentration and decrease visibility. The study of Quan et al. (2013) indicated that there might exist feedback between PBL height and aerosol loading. The enhancement of aerosols tends to depress the development of PBL by decreasing solar radiation, while the repressed structure of PBL will in turn weaken the diffusion of pollutants, leading to the heavy pollution. As a result, this possible positive feedback loop (more aerosols → lower PBL height → more aerosols) may induce an acceleration process for heavy ground pollution.

In this work, a comprehensive measurement was carried out in Beijing to understand the cause of haze events. The measured variables include some important meteorological parameters, such wind, RH, PBL, solar radiation, and visibility. The important aerosol composition and concentrations (including $PM_{2.5}$, $NO_3$, $SO_4$, $NH_4$, organic aerosol (OA), and chloride (Chl)) as well as their gas-phase precursors, including $NO_x$ and $SO_2$ were measured. The analysis focus on the following issues: (a) characteristics of PBL, $PM_{2.5}$, solar radiation, RH, wind in haze events; and (b) the gas to particle conversions under low photochemical conditions.

## 2. Methods and instruments

### 2.1. Sampling site

This observation was conducted from Nov. 16, 2012 to Jan. 15, 2013 at Baolian (BL) meteorological station, Chinese Meteorological Administration (CMA) (39°56′N, 116°17′E), which is located between the west 3rd and 4th highways in Beijing. The distance of the station from nearby major roads is about 400 m. The surrounding region of this site is mainly residential district, without large point sources of $PM_{2.5}$. In this measurement, atmospheric visibility, mass concentration of $PM_{2.5}$, chemical composition of $PM_1$ (particle matter with the radius equal/less 1.0 μm), gaseous pollutants ($SO_2$, $NO_x$, CO, $O_3$), PBL heights were observed simultaneously, together with meteorology variables of temperature, RH, pressure, wind speed, and wind direction.

### 2.2. Instruments and observation

The mass concentration of $PM_{2.5}$ was observed by a R&P model 1400a Tapered Element Oscillating Microbalance (TEOM, Thermo Scientific Co., USA) instrument, with a 2.5 mm cyclone inlet and an inlet humidity control system. A dedicated sampling line was used to obtain 5-min averaged fine particulate mass concentrations. This instrument was installed in an air-conditioned room and was operated with a hydrophobic filter material to reduce the humidity of the incoming sampled air. The sample stream was preheated before entering the mass transducer. Thus semi-volatiles and water were not measured. The filter loading percentage and flow rates of TEOM were checked once a week, and the filter was replaced when the filter loading percentage was greater than 30% (see also Zhao et al., 2009).

Chemical composition of $PM_1$ was measured by an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS). The details description of HR-ToF-AMS and its operation had been presented in many previous publications and reviewed by Drewnick et al. (2005). In the AMS, an aerodynamic lens was used to sample and focus ambient particles into a narrow beam that was transmitted to a heated surface (~600 °C), where particles were flashly vaporized. The resulting vapor molecules are ionized by 70 eV electron impaction (EI), and then the positive ions were analyzed by a ToF mass spectrometer. Because the aerodynamic lens has reduced transmission efficiencies for particles at sizes of approximately 1 μm and only non-refractory (NR) species (i.e., ammonium, sulfate, nitrate, chloride and organics) evaporate at the vaporizer temperature (~600 °C). As a result, the AMS measurements only represent non-refractory $PM_1$ (NR-$PM_1$). Particle size information was obtained by measuring particle velocity with a mechanical chopper wheel. The instrument provides 5 min averaged quantitative mass loading information on non-refractory components using a well characterized series of calibrations and error estimations (Jimenez et al., 2003; Allan et al., 2003, 2004), as well as species resolved size distributions. The HR-ToF-AMS calibration, e.g. inlet flow, ionization efficiency (IE) and particle sizing, was performed at the beginning, the middle and the end of the measurement period as the standard protocols recommend (Jayne et al., 2000; Jimenez et al., 2003; Drewnick et al., 2005).

A micro-pulse lidar (MPL-4B, Sigmaspace Co., USA) was employed to study the evolution of PBL. The PRF (pulse repetition frequency) of the MPL is 2500 Hz, with a wavelength of 532 nm of the laser beam. The peak value of the optical energy of laser beam is 8 μJ. The pulse duration was set to 100 ns, and the pulse interval was set to 200 ns, corresponding to a spatial resolution of 30 m. The PBL height is determined at the altitude where a sudden decrease in the scattering coefficient occurs (Boers and Eloranta, 1986; Brooks, 2003; Cohn and Angevine, 2000). The fundamental premise takes advantage of the large gradient in aerosol concentration that is generally evident between the boundary layer aerosols and those found in the free troposphere.

The concentrations of NO, $NO_2$, and $NO_x$ = (NO + $NO_2$) were measured with a chemiluminescent trace level analyzer (TEI; Model 42iTL). The analyzer has a detection limit of 0.025 ppbv. The concentrations of CO were measured by the Model 48iTL enhanced CO analyzer, using a gas filter correlation technology, with a detection limit of 0.04 ppmv. $SO_2$ was detected with a pulsed UV fluorescence analyzer (TEI; Model 43 i-TLE). The detection limit for this analyzer is 0.05 ppbv for 2-min integration with a precision of about 0.20 ppbv. $O_3$ was measured with a UV photometric analyzer (Model 49iTL, TEI Inc.), with a detectable limit of 0.05 ppbv.

Atmospheric visibility was observed by a PWD20 (Vaisala Co., Finland), with range of 10–20,000 m, and meteorology variables were observed by WXT-510 (Vaisala Co., Finland).

## 3. Result and analysis

### 3.1. General characteristics of the haze events

Fig. 1 shows the measured variations of visibility, $PM_{2.5}$, $PM_1$, PBL heights, RH, and wind speeds during the 2012–2013 winter (from Nov. 17, 2012 to Jan. 15, 2013). The results indicate that the visibility