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Variations of fine particle physiochemical properties during a heavy haze episode in the winter of Beijing

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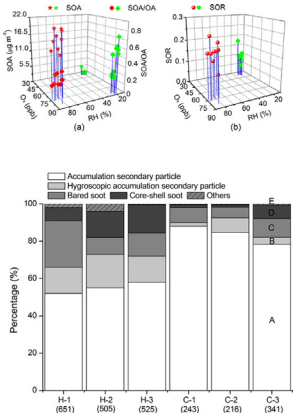
HIGHLIGHTS

- A process changing sharply from haze formation to dissipation was investigated.
- Both secondary formation and primary emission contributed significantly to the haze.
- Aged status of soot in the post-haze air was similar with heavy haze.
- Photochemical reactions in the post-haze induced the secondary formation of organics and sulfate.

GRAPHICAL ABSTRACT



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ABSTRACT

Chemical composition, morphology, size and mixture of fine particles were measured in a heavy haze and the post-haze air in Beijing in January 2012. With the occurrence of haze, the concentrations of gaseous and particulate pollutants including organics, sulfate, nitrate, and ammonium grew gradually. The hourly averaged $PM_{2.5}$ concentration increased from 118 μg m^{-3} to 402 μg m^{-3} within 12 h. In contrast, it was less than 10 μg m^{-3} in the post-haze air. Occupying approximately 46% in mass, organics were the major component of PM_1 in both the haze and post-haze air.

Analysis of individual particles in the size range of 0.2–1.1 μm revealed that secondary-like particles and soot particles were always the majority, and most soot particles had a core-shell structure. The number ratio of secondary-like particles to soot particles in accumulation mode in the haze air was about 2:1, and that in the post-haze air was 8:1. These results indicate both secondary particle formation and primary emission contributed substantially to the haze. The mode size of the haze particles was about 0.7 μm, and the mode size of the post-haze particles was 0.4 μm, indicating the remarkable growth of particles in haze. However, the ratios of the core size to shell size of core-shell structure soot particles in the haze were similar to those in the post-haze air, suggesting a quick aging of soot particles in either the haze air or the post-haze air.

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1. Introduction

Air pollution causes widespread haze and the concentrations of atmospheric particulate matter are reaching unprecedentedly high level in many cities in China (Guo et al., 2014; Huang et al., 2012a; Liu et al., 2014), and could increase by an order of magnitude during several days (Sun et al., 2014). Haze is a phenomenon of air pollution under stable weather conditions such as low wind speed and inversion thermodynamic structure, and can be formed due to heavy existing particulate and gaseous pollutants (Zheng et al., 2015; Yang et al., 2015). Haze alters the composition of airborne aerosols through aqueous reactions, and has significant effects on visibility, public health and even the global climate (Quan et al., 2015; Samset and Myhre, 2015; Samset et al., 2014).

Atmospheric aerosols in the heavy haze are mainly composed of high concentrations of soluble salts with hygroscopicity, such as sulfate and nitrate (Quan et al., 2015; Huang et al., 2014). During heavy haze, water soluble aerosols play an important role in the hygroscopic growth of particles, which will increase the light scattering of aerosol particles (Michel Flores et al., 2012; Healy et al., 2015). Humid and stagnant meteorological conditions can favor the modification of the atmospheric aerosol hygroscopicity and optical properties, as well as secondary formation (Guo et al., 2014; Yuan et al., 2015; Hu et al., 2015). Carbonaceous aerosol comprising about 40% of the particulate matter on average is also one of the key factors in the formation of haze (Szidat, 2009; Hou et al., 2011; Shi et al., 2015). The organic aerosol emitted from biomass burning, also led to regional haze in Beijing (Li et al., 2010) and Shanghai (Huang et al., 2012b). Guo et al. (2014) identified that the organics and sulfate were the main components of $PM_{2.5}$ in the haze. However, the formation mechanisms leading to severe haze episodes and rapid dispersion remain highly uncertain, and further research is required.

The morphology, mixing state and aging process of particles are necessary information for modeling climate effects of aerosols in the atmosphere (Pósfai and Buseck, 2010; Cappa et al., 2012; Li et al., 2016). The aging timescale of soot particles are different and varied from hours to weeks relying on the local environmental conditions and the characteristics of the fresh soot particles (Zhang et al., 2015; Fierce et al., 2015). Niu et al. (2011) indicated that the soot particles collected in less polluted air also aged quickly. Various shapes and mixing states of particles could lead to large uncertainties of their radiative forcing effect for climate modeling (Adachi et al., 2010). Severe haze pollution frequently appears in Beijing, especially during the winter. Although haze pollution has been a concern for decades, the comprehensive measurements, combining bulk chemical characteristics and morphologies of individual airborne particles deeply needed investigation. So, what is the aging process of soot particles like, how long is the timescale and what is the difference between haze and the clean episodes in winter in Beijing?

In this study, the chemical composition, morphology, size distribution, mixing state and aging status of fine particles were obtained during the process of sharp change from severe haze to post-haze air in the winter in Beijing, China. Through these analyses, the haze formation mechanism and probable sources of the fine particles were explained.

2. Instruments and measurements

2.1. Super site for online monitoring aerosol characteristics

The measurements were conducted at an urban site, PKU Urban Atmosphere Environment MonitoRing Station (PKUERS), on the sixth floor of an academic building (20 m a.g.l.) on the campus of Peking University (39.99°N, 116.31°E), which is located in the northwestern urban area of Beijing and outside of the fourth ring road (Wu et al., 2008). The measurement site operates as a supersite for comprehensive monitoring of air pollution, including $PM_{2.5}$ concentration, gaseous pollutants, as well as meteorological parameters. An Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) was deployed to measure non-refractory chemical components (organics, SO_4^{2-}, NO_3^-, NH_4^+, and Cl^-) of submicron aerosol particles (aerodynamic diameters less than 1 μm, PM_1) (Hu et al., 2013; Huang et al., 2012b). The multi-angle absorption photometer (MAAP) was used for aerosol black carbon (BC) measurement (Liu et al., 2013).

2.2. Samples of individual particles and morphological analysis

An extreme haze occurred on January 9th–10th, 2012. A three-stage cascade impactor was applied to collect particles on electron microscope Cu meshes, coated with carbon-sprayed Formvar film. The cut-off aerodynamic diameters of the sampler are about 1.1 μm and 0.2 μm for the first and second stages, respectively; besides, particles from 0.1–2.5 μm were routinely sampled. The collecting time for each sample was 2 min with the flow rate of 2.2 l min^{-1}. The sample collection was carried out on the roof of the measurement site. Three sets of samples were collected in the haze air, and three sets were collected in the post-haze air (Table 1). All the time points mentioned in this manuscript are Beijing standard time (BST), 8 h prior to GMT (Greenwich Mean Time).

Using a transmission electron microscope (TEM; FEI, Tecnai G2T20) and the attached energy dispersive X-ray spectrometer (EDX), samples collected on the second stage were analyzed at an accelerating voltage of 200 keV. The TEM images from the center to the margin on the mesh were randomly selected and photographed. The elemental composition of each particle in the photographs was quantified using the EDX. The X-ray accounts of a particle were collected from a square covering the particle and were integrated for 30 live seconds. The relative weight and atom ratios of elements with atom numbers larger than 5 was calculated from the accounts with ZAF calibration (Fukushima and Zhang, 2015). The equivalent diameter was determined by analyzing the particles on the image, which is defined as a diameter of a circle that has the same projection area as the measured particle (Niu et al., 2012).

3. Results and discussion

3.1. Evolution from haze to post-haze air

3.1.1. Meteorological conditions and air quality

In Beijing, the formation of heavy haze is closely related to the meteorology and air pollution (Guo et al., 2014; Zheng et al., 2015). The case study on January 10th, 2012 was performed in the weather condition of haze followed by a clean day. According to the records of the air pollution index (API) in Beijing, air pollution was serious on January 10th, especially in the southern part, and it was much cleaner in all districts on 11th (Fig. S1). The meteorological conditions and the concentrations of $PM_{2.5}$, SO_2, NO_2 and O_3 are illustrated in Fig. 1 and Table S1. The sample collection periods for single particle analysis are marked by six arrows on the X-axis. From 14:00 to 17:00 on January 9th, 2012, the wind direction was southwest and the wind speed was about 2.2 m s^{-1}. After 17:00, the wind speed decreased to 1.1 m s^{-1}, the atmospheric pressure kept at a lower level as about 1025 hPa, and the relative humidity (RH) increased from 50% to 75%. Under the unfavorable meteorological

Table 1
Sample collection list and the weather conditions.

Sample no.	Start (BST[a])	Stop	T (°C)	RH (%)	WS (m s^{-1})	WD	Weather
H-1	00:00	00:02	−2.1	45	0.5	SE	Haze
H-2	08:00	08:02	−4.5	88	1.0	NW	Haze
H-3	10:00	10:02	1.0	69	1.0	NW	Haze
C-1	12:00	12:02	2.8	22	4.5	NW	Clean
C-2	14:00	14:02	3.6	20	2.5	NW	Clean
C-3	20:00	20:02	−1.6	18	1.7	NW	Clean

[a] Beijing standard time (Greenwich Mean Time plus 8 h).